

“What we know is a drop, what we don’t know is an ocean”

Sir Isaac Newton



**Silesian University
of Technology**



POLITECNICO
MILANO 1863

DOCTORAL DISSERTATION

in the discipline: Chemical Engineering

*prepared under the Joint Doctoral Degree (Cotutelle) agreement between
Silesian University of Technology and Politecnico di Milano*

Department of Chemical Organic Technology and Petrochemistry,
Silesian University of Technology, Gliwice, Poland

Department of Chemistry, Materials and Chemical Engineering “Giulio
Natta”, Politecnico di Milano, Milan, Italy

Carbon nanotubes as advanced catalysts and supports in oxidation processes

Author: Shakir Ul Azam

Supervisor: Prof. Dr. Beata Orlńska (Silesian University of Technology)

Supervisor: Prof. Dr. Carlo Punta (Politecnico di Milano)

September 2026
Gliwice (Poland), Milan (Italy)

Acknowledgement

My doctoral journey has been one of the most transformative experiences of my life, shaping me not only as a scientist and professional but also as a person. I am sincerely grateful to all those who supported and guided me along the way.

First and foremost, I owe my deepest gratitude to my parents (Inayat Ullah Khan and Bibi Hanifa), whose unwavering belief in the value of education remained steadfast despite financial challenges. Their sacrifices, patience, and unwavering support have provided the foundation for my academic journey and have been a constant source of strength, without which this achievement would not have been possible.

I am sincerely grateful to my supervisors, Prof. Beata Orlńska (Poland) and Prof. Carlo Punta (Italy), for their invaluable guidance, continuous support, and constructive feedback throughout my doctoral studies. Their expertise and encouragement have been essential in shaping the quality and direction of this research.

I am truly appreciative of my research team at the Department of Organic Chemical Technology and Petrochemistry at Silesian University of Technology (Poland) for their invaluable support and collaborative environment. Especially, I would like to thank Dr. Kamil Peckh, Dr. Dawid Lisicki, Dr. Agata Wawoczny, Dr. Adam Marek, Dr. Dymitr Czechowicz, Dr. Tomasz Piotrowski, and Ms. Iwona Szmidt for their assistance, insightful discussions, and encouragement throughout this journey. I also sincerely appreciate the support I received during my research stay at the Organic Synthesis, Catalysis, and Materials Laboratory (OSCM Lab) of the Department of Chemistry, Materials, and Chemical Engineering “G. Natta” at the Politecnico di Milano (Italy), especially from my colleague Arianna de Santis.

I gratefully acknowledge the Silesian University of Technology for supporting my joint doctorate and providing the funding necessary to pursue my research. The opportunities and resources offered have been essential to my academic growth. I am sincerely thankful to everyone who contributed to my academic and personal development; your support and belief in me have been instrumental in reaching this milestone.

Abstract

Selective liquid-phase oxidation of hydrocarbons with oxygen is industrially crucial, yet achieving high conversion and selectivity remains challenging. These processes require activation of strong C-H bonds via radical-chain pathways, demanding strict control of overoxidation, hydroperoxide management, and safe oxidant transfer into the liquid-phase reaction medium. Beyond the inherent advantage of air or molecular oxygen as a green, abundant, and atom-economical oxidant, sustainable implementation demands recyclable catalytic systems that minimize or eliminate solvent use and waste generation, while avoiding toxic or scarce components. To support Sustainable Development Goal 12 (responsible consumption and production) and to translate the “3R” concept (reduce, reuse, and recycle) into practical green-chemistry strategies, this dissertation developed reusable catalytic systems based on multi-walled carbon nanotubes (MWCNTs) for the solvent-free, liquid-phase oxidation of hydrocarbons using oxygen. All reactions were performed employing ethylbenzene (EB) as a model hydrocarbon, molecular oxygen as a green oxidant, and under mild conditions (80 °C, 0.1 MPa, 6 h). The catalytic activities of pristine MWCNTs and metal-modified MWCNTs were evaluated in the absence and presence of *N*-hydroxyphthalimide (NHPI) as a cocatalyst. NHPI is an economical and efficient organocatalyst, but is limited by poor solubility in apolar hydrocarbons and difficulty in recovery and recycling. To address these limitations, thin-film ionic liquid (IL) catalytic systems were developed based on pristine and functionalized MWCNTs to stabilize NHPI, tune interfacial polarity, and enhance oxygen solubility and transport. Moreover, NHPI was covalently grafted onto various grades of MWCNTs to enhance NHPI stability and recyclability. The recyclability and reusability of all catalytic systems developed in this dissertation were thoroughly investigated.

Transition metals modified MWCNTs were developed using Cu(II), Co(II), and Mn(II) salts, yielding three types of catalysts identified as metal-rich MWCNT composites, metal-modified MWCNTs, and metal-functionalized MWCNTs. These materials were developed to systematically evaluate the influence of metal loading and dispersion on CNT-supported catalysts in NHPI-mediated EB oxidation. The metal-rich MWCNT composites were prepared via oxidative pretreatment, followed by metal precursor incorporation and calcination, yielding high metal loadings (619, 667, and 706 g·kg⁻¹ for Mn, Cu, and Co, respectively, for the 6 h samples) with metal nanoparticles distributed on both the external surfaces and within the CNT channels. These composite catalysts achieved up to a fourfold

increase in EB conversion relative to pristine MWCNTs under similar reaction conditions (0.025 g catalyst, 1 mol% NHPI), with enhanced selectivity towards acetophenone (AcPO). Specifically, EB conversion increased from 6.3% for pristine MWCNTs to 24.4% (Cu-MWCNT@14h), 20.8% (Cu-MWCNT@6h), 18.0% (Co-MWCNT@6h), and 21.1% (Mn-MWCNT@6h). However, varying catalyst loading provided minimal additional benefits. For instance, at 0.0125 g and 0.0375 g Cu-MWCNT@6h with 1 mol% NHPI displayed 19.3% and 21.1% EB conversion, respectively, indicating that high metal content alone does not govern performance.

To probe this effect, metal-modified MWCNTs with low metal loadings (0.70, 1.09, and 3.85% for Co, Mn, and Cu, respectively) were evaluated. These catalysts exhibited reduced yet consistent activity. At 0.0375 g, Cu-MWCNTs exhibited comparable EB conversion (19.3%) to their metal-rich counterpart under similar reaction conditions.

In contrast, under similar reaction conditions (0.025 g, 1 mol% NHPI), Cu(II) functionalized industrial-grade carboxylated MWCNTs (IGMWCNT-COO-Cu, 1.25% Cu) demonstrated the highest activity, achieving 26.3% EB conversion with 60.7% AcPO selectivity. Control experiments with pristine and carboxylated MWCNTs favored the formation of 1-phenylethyl hydroperoxide (PEHP), highlighting the crucial role of Cu(II) sites. These sites facilitate both the generation of phthalimide-*N*-oxyl (PINO) radicals and the selective decomposition of PEHP into AcPO.

All the MWCNT-based catalysts exhibited stable catalytic activity, with minor fluctuations attributed to metal leaching and catalyst loss during recycling. Overall, catalytic performance is governed by controlled metal incorporation rather than excessive loading in NHPI-mediated EB oxidation. The enhanced activity observed across all transition-metal-modified MWCNTs could be attributed to a synergistic interaction with NHPI, in which the metal species promote PINO radical generation and accelerate PEHP decomposition, while NHPI facilitates PEHP formation, thereby collectively enhancing the overall oxidation rate.

Based on the Cu(II) functionalized IGMWCNTs, a novel SCILL-SILP hybrid catalytic system was developed by coating a thin layer of IL ([emim][O₂SO₃]) containing NHPI onto IGMWCNT-COO-Cu, integrating SCILL (solid catalyst with an IL layer) and SILP (supported IL phase) concepts in a single interfacial catalyst design. The resultant SCILL-SILP system displayed ~27% EB conversion with augmented AcPO selectivity (~77%); however, recyclability tests (supported by TGA and FTIR) revealed progressive activity loss

due to partial leaching of the mixture of IL and NHPI during the reaction (as oxygenated products increased the medium polarity) as well as during the catalyst recovery. On the other hand, coating IGMWCNT-COO-Cu with the IL ([emim][OcOSO₃]) to produce the SCILL system displayed reduced activity. This reduction in activity could be attributed to the coverage of Cu(II)/CNT active sites by the high viscosity of the IL, which hindered radical formation and suppressed oxidation. However, in the presence of a radical initiator, the positive effect of the coated IL was observed, increasing the EB conversion from 6.8% for IGMWCNT-COO-Cu (without NHPI) to 14.1% (SCILL system with 1:1 w/w IL/IGMWCNT-COO-Cu) with enhanced selectivity towards AcPO (72.9%).

To mitigate leaching and to improve the stability of the hybrid catalytic system, a series of ILs, particularly [bmim]-based ILs, was thoroughly investigated to develop SILP and SCILL-SILP systems. SILP systems were prepared by depositing an NHPI-dissolved IL layer onto pristine MWCNTs, whereas SCILL-SILP hybrid catalytic systems were obtained by coating the same NHPI-dissolved IL onto Cu(II) functionalized MWCNTs (MWCNT-COO-Cu). All the produced [bmim]-based SILP systems were more active than pristine MWCNTs or the MWCNTs and NHPI combination, reflecting a synergistic interaction among MWCNTs, IL, and NHPI that promotes PINO radical formation and PEHP (1-phenylethyl hydroperoxide) decomposition. Among them, the [bmim][Cl] based system exhibited the highest EB conversion (12.2%), while maintaining elevated AcPO selectivity (84.1%), consistent with halide-assisted NHPI activation (PINO formation) and accelerated PEHP decomposition.

SCILL-SILP systems are generally less active than the MWCNT-COO-Cu support because the viscous IL layer partially covers the active Cu(II) sites, imposing mass-transfer limitations. Nevertheless, they consistently delivered enhanced AcPO selectivity over their SILP analogs, supporting a robust cage- or confinement-selectivity mechanism in the IL thin film, combined with Cu(II)-mediated hydroperoxide decomposition pathways. Among them, the [bmim][NTf₂]-based SCILL-SILP system demonstrated the highest EB conversion (22.6%), attributed to its comparatively low viscosity and higher oxygen solubility. In the produced hybrid catalytic systems, catalyst stability emerged as a critical design factor: increasing cation lipophilicity could raise initial activity but often reduced recyclability due to IL leaching as the medium became more polar. Nonetheless, [bmim][OcOSO₃] based systems offered superior film retention and overall robustness under solvent-free aerobic oxidation conditions.

At the same time, to address leaching issues related to NHPI in the SILP and SCILL-SILP systems and the recyclability challenges associated with homogeneous NHPI, the study transitioned to covalent grafting of NHPI onto MWCNTs. NHPI was grafted onto commercial amine-functionalized MWCNTs (~0.45% and ~7%) via trimellitic anhydride chloride (TAC) mediated amidation and subsequently converted to NHPI using hydroxylamine hydrochloride. The NHPI was additionally grafted onto IGMWCT-COOH through an EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) and NHS (*N*-hydroxysuccinimide) coupling strategy. The carboxyl groups were extended with a 1,8-diaminooctane spacer, then coupled to a trityl-protected 4-carboxy-NHPI, followed by deprotection to regenerate the active NHPI moiety. In solvent-free aerobic oxidation of EB, the NHPI-grafted MWCNTs increased PEHP selectivity compared with the precursor supports, and in the presence of a trace amount of CuCl₂, exhibited higher EB conversion with higher AcPO selectivity. Interestingly, replacing CuCl₂ with Cu(II) functionalized IGMWCNTs preserved activity and selectivity in a fully heterogeneous configuration. The NHPI-grafted catalysts were consistently recyclable, demonstrating that covalent anchoring effectively eliminates the key limitations in recyclability and stability of homogeneous NHPI and IL-based thin films while retaining the advantage of NHPI-mediated hydrogen atom transfer (HAT) chemistry.

Streszczenie

Selektywne utlenianie węglowodorów w fazie ciekłej z wykorzystaniem tlenu ma kluczowe znaczenie przemysłowe, jednak osiągnięcie wysokiej konwersji i selektywności wciąż pozostaje wyzwaniem. Procesy te wymagają rozerwania silnych wiązań C–H poprzez mechanizm łańcuchowy rodnikowy, ścisłej kontroli niepożądanych reakcji następczego utleniania oraz ograniczania ryzyka wynikającego z obecności wodoronadtlenków i czynnika utleniającego. Oprócz zalet powietrza i tlenu jako ekologicznych, powszechnie dostępnych i efektywnych utleniaczy, zrównoważone wdrożenie procesów z ich udziałem wymaga opracowania możliwych do odzysku i zawrotu stabilnych układów katalitycznych, przy równoczesnym ograniczeniu ilości rozpuszczalników oraz odpadów i unikaniu toksycznych lub rzadkich chemikaliów. Zgodnie z 12. Celem Zrównoważonego Rozwoju ONZ: Odpowiedzialna konsumpcja i produkcja oraz koncepcją “3R” (reduce, reuse, recycle), w niniejszej rozprawie opracowano układy katalityczne możliwe do kilkukrotnego zastosowania oparte na wielościennych nanorurkach węglowych (MWCNTs) do bezrozpuszczalnikowego utleniania węglowodorów tlenem w fazie ciekłej. Wszystkie reakcje prowadzono w łagodnych warunkach (80 °C, 0,1 MPa, 6 h) z wykorzystaniem etylobenzenu (EB) jako modelowego węglowodoru i tlenu jako zielonego utleniacza. Aktywność katalityczną MWCNTs oraz modyfikowanych metalami MWCNTs określano wobec dodatku *N*-hydroksyftalimidu (NHPI). NHPI jest ekonomicznym i efektywnym organokatalizatorem, jednak jego zastosowanie ogranicza niska rozpuszczalność w apolarnych węglowodorach oraz trudności związane z jego odzyskiem i zawrotem. W celu przezwyciężenia tych ograniczeń opracowano układy katalityczne oparte na MWCNTs oraz modyfikowanych metalami MWCNTs pokrytych cienką warstwą cieczy jonowej (IL) zawierającą rozpuszczony NHPI. IL może wpływać na polarność układu, stabilność i dostępność NHPI oraz transport tlenu. Ponadto otrzymano układy, w których NHPI kowalencyjnie związano z różnymi rodzajami MWCNTs w celu zwiększenia efektywności procesu oraz odzysku katalizatora. Możliwość ponownego wykorzystania wszystkich opracowanych układów katalitycznych została zbadana.

MWCNTs modyfikowane metalami przejściowymi otrzymano z wykorzystaniem soli Cu(II), Co(II) i Mn(II). Stosując różne metody wprowadzania metali do MWCNTs uzyskano trzy rodzaje materiałów różniących się zawartością metalu oraz sposobem jego związania ze stałym nośnikiem, które nazwano: kompozyty MWCNT (bogate w metal), MWCNT modyfikowane metalami (z mniejszą zawartością metalu) oraz MWCNT

funkcjonalizowane metalami (metal immobilizowany poprzez wiązanie jonowe). Materiały te opracowano w celu systematycznej oceny wpływu zawartości, dyspersji i rodzaju immobilizacji metalu na utlenianie EB z udziałem NHPI.

Kompozyty MWCNTs bogate w metal przygotowano poprzez wstępne utlenianie kwasem azotowym, następnie wprowadzenie prekursora metalu i kalcynację, uzyskując wysoką zawartość metalu (619, 667 i 706 g·kg⁻¹) rozmieszczonego zarówno na powierzchniach zewnętrznych, jak i wewnątrz kanałów MWCNTs. Użycie kompozytów pozwoliło na nawet czterokrotny wzrost konwersji EB w porównaniu z niemodyfikowanymi MWCNTs (0,025 g katalizatora, 1 mol% NHPI), tj. z 6,3% do 24,4% (Cu-MWCNT@14h), 20,8% (Cu-MWCNT@6h), 18,0% (Co-MWCNT@6h) oraz 21,1% (Mn-MWCNT@6h), przy zwiększonej selektywności do acetofenonu (AcPO). Zmiana ilości zastosowanego w reakcji katalizatora przyniosła jednak niewielkie korzyści. Przykładowo, wobec 0,0125 g i 0,0375 g Cu-MWCNT@6h i 1 mol% NHPI uzyskano odpowiednio 19,3% i 21,1% konwersji EB, co wskazuje, że wysoka zawartość metalu nie determinuje wysokiej konwersji.

Podjęto więc próby zastosowania MWCNTs modyfikowane znacznie mniejszą ilością metalu, tj.: 0,70, 1,09 i 3,85% odpowiednio Co, Mn i Cu, które wykazały często niższą, lecz stabilną w kolejnych zawrotach aktywność. Przykładowo, stosując 0,0375 g MWCNTs modyfikowanych Cu uzyskano konwersję EB 19,3%, porównywalną do otrzymanej wobec odpowiednika - kompozytu bogatego w metal.

Najwyższą aktywność w analogicznych warunkach (0,025 g katalizatora, 1 mol% NHPI) wykazały przemysłowe karboksylowane MWCNTs funkcjonalizowane solą Cu(II) (IGMWCNT-COO-Cu, 1,25% Cu). Wobec nich uzyskano konwersję EB 26,3% i selektywność do AcPO 60,7%. W eksperymentach kontrolnych z niemodyfikowanymi karboksylowanymi MWCNTs uzyskano jako główne produkty wodoronadtlenek 1-fenyletylowy (PEHP) i alkohol 1-fenyletylowy (PEA), co wskazuje na kluczową rolę centrów Cu(II) w selektywnym rozkładzie PEHP do AcPO. Wszystkie otrzymane układy oparte o MWCNTs i metale przejściowe wykazywały stabilną aktywność w kolejnych zawrotach, a niewielkie zmiany przypisano wymywaniu metalu. Stwierdzono, że aktywność badanych układów jest determinowana przez kontrolowaną inkorporację metalu, a nie jego nadmierną ilością. Ich aktywność wynika z synergii z NHPI, gdzie metal sprzyja generacji rodników PINO i rozkładowi PEHP, natomiast NHPI ułatwia powstawanie PEHP.

Na bazie IGMWCNT-COO-Cu opracowano hybrydowy układ SCILL-SILP poprzez naniesienie na jego powierzchnię cienkiej warstwy cieczy jonowej ([emim][OcOSO₃]) zawierającej rozpuszczony NHPI. W ten sposób połączono koncepcję SCILL (*solid catalyst with IL layer*) oraz SILP (*supported IL layer*). Wobec tego układu uzyskano konwersję EB ~27% oraz selektywność do AcPO ~77%, jednak podczas zawrotu (TGA, FTIR) obserwowano stopniowy spadek aktywności układu w kolejnych cyklach wskutek częściowego wymywania IL z NHPI między innymi spowodowanego wzrostem polarności układu w trakcie reakcji utleniania. Równocześnie stwierdzono, że jeśli powierzchnię IGMWCNT-COO-Cu pokryto cieczą jonową bez dodatku NHPI (SCILL) to aktywność układu była niższa niż prekursora prawdopodobnie z powodu ograniczenia dostępności centrów metalicznych przez wysokiej lepkości IL. Dodatek inicjatora azowego pozwolił na wzrost konwersji EB wobec z 6.8% (IGMWCNT-COO-Cu bez NHPI) do 14,1 (SCILL: 1:1 w/w IL/IGMWCNT-COO-Cu) dla selektywności do AcPO 72.9%.

W celu ograniczenia wymywania IL zbadano wpływ szeregu cieczy jonowych, opartych głównie na kationie [bmim] na aktywność i stabilność układów SILP i SCILL-SILP. Układy SILP otrzymano poprzez naniesienie warstwy IL z rozpuszczonym NHPI na MWCNTs, a SCILL-SILP wykorzystując MWCNT-COO-Cu jako nośnik. Stwierdzono, że wprowadzenie warstwy IL z NHPI ma korzystny wpływ na konwersję EB wskazując na synergistyczne oddziaływanie MWCNTs, IL i NHPI promujące generowanie PINO i rozkład wodoronadtlenku PEHP. Najwyższą konwersję EB (około 12%) uzyskano stosując [bmim][Cl] (selektywności do AcPO około 84%). Natomiast pokrycie MWCNT-COO-Cu warstwą IL z NHPI o wysokiej lepkości spowodowały spadek konwersji EB, jako efekt ograniczenia dostępu do aktywnych centrów Cu(II). Równocześnie selektywność do AcPO była wyższa niż wobec analogów typu SILP, co przypisuje się efektowi klatki rozpuszczalnika (*cage effect*) w połączeniu z rozkładem wodoronadtlenku katalizowanym przez Cu(II). Najwyższą konwersję EB uzyskano wobec układu SCILL-SILP złożonego z [bmim][NTf₂] (22,6%), co związane jest z niższą lepkością i większą rozpuszczalnością tlenu w stosunku do pozostałych badanych ILs. Stwierdzono, że wzrost lipofilowości kationu w zastosowanej IL mimo, że wpływa na wzrost konwersji w pierwszym cyklu to jednak w kolejnych cyklach obserwowano znaczny spadek aktywności w wyniku intensywniejszego wymywania. Spośród badanych układów najwyższą stabilność wykazał układ z udziałem [bmim][OcOSO₃].

W celu ograniczenia wymywania NHPI z układów SILP i SCILL-SILP podjęto badania nad jego kowalencyjnym zakotwiczeniem na MWCNTs. NHPI związane z handlowymi aminofunkcjonalizowanymi MWCNTs (~0,45% i ~7%) poprzez reakcję z chlorkiem bezwodnika trimelitowego, a następnie z chlorowodorkiem hydroksyloaminy. W kolejnej metodzie wykorzystano IGMWCNT-COOH oraz reakcję sprzęgania stosując EDC (3-(3-dimetyloaminopropyl)-1-etylokarbodiimid i NHS (*N*-hydroksysukcynoimid). W reakcji grup karboksylowych 1,8-diaminooktanem wprowadzono grupę łączącą (*spacer*), a w kolejnym etapie tak aminofunkcjonalizowany nośnik poddano reakcji z 4-karboksy-NHPI, w którym uprzednio zabezpieczono grupę -NOH w reakcji z chlorkiem trytylu. W reakcji utleniania EB bez dodatku rozpuszczalnika otrzymany NHPI szczepiony na MWCNTs wpływał na wzrost selektywności do PEHP, a w obecności CuCl₂ na wzrost selektywności do AcPO w porównaniu do wyjściowych materiałów węglowych. Zastąpienie CuCl₂ przez IGMWCNTs sfunkcjonalizowane Cu(II) pozwala na zachowanie konwersji i selektywności do AcPO wobec w pełni heterogenicznego układu. Otrzymany NHPI szczepiony na MWCNTs wykazywał możliwość wielokrotnego użycia, potwierdzając skuteczność strategii kowalencyjnego zakotwiczenia NHPI z zachowaniem korzyści wynikających z mechanizmu transferu atomu wodoru (HAT) z jego udziałem.

Riassunto

L'ossidazione selettiva in soluzione liquida degli idrocarburi in presenza di ossigeno riveste un'importanza cruciale a livello industriale. Tuttavia, il raggiungimento di elevati valori di conversione e selettività rimane una sfida significativa. Tali processi richiedono l'attivazione di legami C–H forti attraverso meccanismi a catena radicalica, il che implica un controllo rigoroso della sovra-ossidazione, una gestione degli idroperossidi che si formano e una diffusione efficace e controllata dell'ossidante nel mezzo di reazione liquido. Oltre al vantaggio intrinseco dell'aria o dell'ossigeno molecolare come ossidanti verdi, abbondanti ed economicamente efficienti in termini atomici, un'implementazione sostenibile richiede sistemi catalitici riciclabili in grado di minimizzare o eliminare l'uso di solventi e la generazione di rifiuti, evitando al contempo reattivi tossici o di difficile reperibilità. Al fine di supportare l'Obiettivo di Sviluppo Sostenibile 12 (consumo e produzione responsabili) e di tradurre il concetto delle “3R” (ridurre, riutilizzare e riciclare) in strategie pratiche di chimica verde, questa tesi ha sviluppato sistemi catalitici riciclabili basati su nanotubi di carbonio a parete multipla (MWCNTs) per l'ossidazione aerobica in fase liquida, priva di solvente, degli idrocarburi. Tutte le reazioni sono state condotte utilizzando etilbenzene (EB) come idrocarburo modello, ossigeno molecolare come ossidante verde e in condizioni blande (80 °C, 0,1 MPa, 6 h). Le attività catalitiche dei MWCNTs non modificati e dei MWCNTs modificati con metalli sono state valutate sia in assenza sia in presenza di *N*-idrossiftalimide (NHPI) come co-catalizzatore. NHPI è un organo-catalizzatore economico ed efficiente, ma il suo utilizzo è limitato dalla scarsa solubilità negli idrocarburi apolari e dalla difficoltà di recupero e riciclo. Per superare tali limitazioni, sono stati sviluppati sistemi catalitici a film sottile di liquidi ionici (IL), basati su MWCNTs non modificati e funzionalizzati, al fine di stabilizzare NHPI, modulare la polarità interfacciale e migliorare la solubilità e il trasporto dell'ossigeno. Inoltre, NHPI è stato ancorato covalentemente su diverse tipologie di MWCNTs per migliorarne la stabilità e la riciclabilità. La riciclabilità e il riutilizzo di tutti i sistemi catalitici sviluppati in questa tesi sono stati oggetto di un'analisi approfondita.

MWCNTs modificati con metalli di transizione sono stati preparati utilizzando sali di Cu(II), Co(II) e Mn(II), ottenendo tre tipologie di catalizzatori: compositi MWCNTs ricchi in metallo, MWCNTs modificati con metallo e MWCNTs funzionalizzati con metallo. Questi materiali sono stati progettati per valutare sistematicamente l'influenza del contenuto e della dispersione del metallo sui catalizzatori supportati su MWCNTs nell'ossidazione dell'EB

mediata da NHPI. I compositi MWCNTs ricchi in metallo sono stati preparati mediante pretrattamento ossidativo, seguito dall'incorporazione del precursore metallico e calcinazione, ottenendo elevati carichi metallici (619, 667 e 706 g·kg⁻¹ rispettivamente per Mn, Cu e Co nei campioni a 6 h) con nanoparticelle metalliche distribuite sia sulle superfici esterne sia all'interno dei canali dei MWCNTs. Questi catalizzatori hanno consentito un aumento fino a quattro volte della conversione dell'EB rispetto ai MWCNT non modificati nelle stesse condizioni di reazione (0,025 g di catalizzatore, 1 mol% NHPI), con una selettività aumentata verso l'acetofenone (AcPO). In particolare, la conversione dell'EB è aumentata dal 6,3% per i MWCNTs non modificati al 24,4% (Cu-MWCNT@14h), 20,8% (Cu-MWCNT@6h), 18,0% (Co-MWCNT@6h) e 21,1% (Mn-MWCNT@6h). Tuttavia, la variazione della quantità di catalizzatore ha fornito benefici aggiuntivi limitati; ad esempio, con 0,0125 g e 0,0375 g di Cu-MWCNT@6h in presenza di 1 mol% NHPI si sono ottenute conversioni dell'EB rispettivamente del 19,3% e 21,1%, indicando come un maggiore contenuto di metallo da solo non governi le prestazioni ossidative.

Per approfondire questo aspetto, sono stati studiati MWCNTs modificati con metallo a basso contenuto metallico (0,70, 1,09 e 3,85% rispettivamente per Co, Mn e Cu). Questi catalizzatori hanno mostrato un'attività inferiore ma costante. A 0,0375 g, i Cu-MWCNT hanno mostrato una conversione dell'EB comparabile (19,3%) a quella dei corrispondenti materiali ricchi in metallo nelle stesse condizioni. Al contrario, nelle stesse condizioni (0,025 g, 1 mol% NHPI), i MWCNT carbossilati di grado industriale funzionalizzati con Cu(II) (IGMWCNT-COO-Cu, 1,25% Cu) hanno mostrato la massima attività, raggiungendo una conversione dell'EB del 26,3% con una selettività verso AcPO del 60,7%. Gli esperimenti di controllo con MWCNT non modificati e carbossilati hanno portato alla formazione di 1-feniletil idroperossido (PEHP), evidenziando il ruolo cruciale dei siti Cu(II). Questi siti facilitano sia la generazione dei radicali ftalimide-*N*-ossilici (PINO) sia la decomposizione selettiva del PEHP in AcPO. Tutti i catalizzatori hanno mostrato una buona stabilità, con lievi variazioni attribuite al dilavamento del metallo e alla perdita di catalizzatore durante il riciclo. Complessivamente, le prestazioni catalitiche sono governate da un'incorporazione controllata del metallo piuttosto che da un carico eccessivo. La migliore attività osservata per tutti i MWCNTs modificati con metalli di transizione può essere attribuita a un'interazione sinergica con NHPI, in cui le specie metalliche promuovono la generazione dei radicali PINO e accelerano la decomposizione del PEHP,

mentre NHPI facilita la formazione del PEHP, migliorando complessivamente la velocità di ossidazione.

Sulla base dei risultati conseguiti con IGMWCNTs funzionalizzati con Cu(II), è stato sviluppato un sistema catalitico ibrido SCILL-SILP mediante deposizione di un sottile strato di liquido ionico ([emim][OcOSO₃]) contenente NHPI su IGMWCNT-COO-Cu, integrando i concetti di SCILL (catalizzatore solido con strato di IL) e SILP (fase di IL supportata) in un'unica architettura interfacciale. Il sistema risultante ha mostrato una conversione dell'EB di circa il ~27% con una selettività aumentata verso AcPO (~77%); tuttavia, i test di riciclabilità (supportati da TGA e FTIR) hanno evidenziato una perdita progressiva di attività dovuta al parziale dilavamento della miscela IL/NHPI durante la reazione (a causa dell'aumento della polarità del mezzo per la formazione di prodotti ossigenati) e durante il recupero del catalizzatore. Al contrario, il rivestimento di IGMWCNT-COO-Cu con il solo liquido ionico ([emim][OcOSO₃]) per ottenere il sistema SCILL ha mostrato una riduzione dell'attività, attribuibile alla copertura dei siti attivi Cu(II)/CNT da parte dell'elevata viscosità dell'IL, che ostacola la formazione dei radicali e sopprime l'ossidazione. Tuttavia, in presenza di un iniziatore radicalico, si è osservato un effetto positivo dell'IL, con un aumento della conversione dell'EB dal 6,8% (IGMWCNT-COO-Cu senza NHPI) al 14,1% (sistema SCILL con rapporto 1:1 p/p IL/IGMWCNT-COO-Cu), accompagnato da una maggiore selettività verso AcPO (72,9%).

Per mitigare il fenomeno del dilavamento e migliorare la stabilità del sistema catalitico ibrido, è stata studiata una serie di liquidi ionici, in particolare quelli a base di [bmim], per lo sviluppo di sistemi SILP e SCILL-SILP. I sistemi SILP sono stati preparati depositando uno strato di IL contenente NHPI su MWCNTs non modificati, mentre i sistemi ibridi SCILL-SILP sono stati ottenuti rivestendo lo stesso IL contenente NHPI su MWCNTs funzionalizzati con Cu(II) (MWCNT-COO-Cu). Tutti i sistemi SILP basati su [bmim] hanno mostrato un'attività superiore rispetto ai MWCNTs non modificati o alla combinazione MWCNT+NHPI, indicando un'interazione sinergica tra MWCNTs, IL e NHPI che favorisce la formazione dei radicali PINO e la decomposizione del PEHP. Tra questi, il sistema basato su [bmim][Cl] ha mostrato la più alta conversione dell'EB (~12%), mantenendo un'elevata selettività verso AcPO (~84%), coerente con l'attivazione di NHPI assistita da alogenuri e con la decomposizione accelerata del PEHP.

I sistemi SCILL-SILP risultano generalmente meno attivi rispetto al supporto MWCNT-COO-Cu, poiché lo strato viscoso di IL copre parzialmente i siti attivi Cu(II), limitando

trasferimento di massa. Tuttavia, essi mostrano sistematicamente una maggiore selettività verso AcPO rispetto agli analoghi SILP, supportando un meccanismo di selettività da confinamento (“cage effect”) nello strato sottile di IL, combinato con percorsi di decomposizione degli idroperossidi mediati da Cu(II). Tra questi, il sistema SCILL-SILP basato su [bmim][NTf₂] ha mostrato la più alta conversione dell’EB (22,6%), attribuita alla sua viscosità relativamente bassa e alla maggiore solubilità dell’ossigeno. Nei sistemi catalitici ibridi sviluppati, la stabilità del catalizzatore emerge come fattore critico: un aumento della lipofilicità del catione può incrementare l’attività iniziale, ma spesso riduce la riciclabilità a causa del dilavamento dell’IL con l’aumento della polarità del mezzo. Tuttavia, i sistemi basati su [bmim][OcOSO₃] hanno mostrato una migliore ritenzione del film e una maggiore robustezza complessiva in condizioni di ossidazione aerobica senza solvente.

Parallelamente, per risolvere i problemi di dilavamento di NHPI nei sistemi SILP e SCILL-SILP e le difficoltà di riciclabilità associate a NHPI omogeneo, lo studio si è orientato verso il grafting covalente di NHPI su MWCNTs. NHPI è stato ancorato su MWCNTs funzionalizzati con gruppi amminici (~0,45% e ~7%) mediante amidazione mediata da cloruro di anidride trimellitica (TAC) e successiva conversione a NHPI mediante cloridrato di idrossilammina. Inoltre, NHPI è stato graftato su IGMWCNT-COOH mediante una strategia di accoppiamento EDC/NHS. I gruppi carbossilici sono stati funzionalizzati con 1,8-diaminooottano, al fine di introdurre unità amminiche distanziate dalla superficie del MWCNT. I gruppi amminici così inseriti sono poi stati fatti reagire con 4-carbossi-NHPI protetta con tritile, e in seguito si è proceduto de-protezione per rigenerare il gruppo NHPI attivo. Nell’ossidazione aerobica senza solvente dell’EB, i MWCNTs graftati con NHPI hanno aumentato la selettività verso PEHP rispetto ai supporti precursori e, in presenza di tracce di CuCl₂, hanno mostrato una maggiore conversione dell’EB con una maggiore selettività verso AcPO. È interessante notare che la sostituzione di CuCl₂ omogeneo con IGMWCNTs funzionalizzati con Cu(II) ha mantenuto attività e selettività in una configurazione completamente eterogenea. I catalizzatori graftati con NHPI hanno mostrato una buona riciclabilità, dimostrando che l’ancoraggio covalente elimina efficacemente le principali limitazioni in termini di stabilità e riutilizzo associate a NHPI omogeneo e ai sistemi a film di IL, preservando al contempo i vantaggi della chimica di trasferimento di atomo di idrogeno (HAT) mediata da NHPI.

Contents

Acknowledgement.....	iii
Abstract	iv
Streszczenie	viii
Riassunto	xii
List of Abbreviations	xix
1. Introduction	1
2. Background and State of the Art	3
2.1 Liquid Phase Oxidation of Hydrocarbons Using Dioxygen.....	3
2.1.1 Significance of liquid-phase oxidation of hydrocarbons.....	4
2.1.2 Mechanism of the liquid-phase oxidation of hydrocarbons	6
2.1.3 Transition metals as catalysts for liquid-phase oxidation.....	9
2.2 Carbon Nanotubes, Organocatalysts, and Ionic Liquids-Based Oxidation Systems	10
2.2.1 CNT-based catalysts for liquid-phase oxidation of hydrocarbons	10
2.2.2 NHPI as a catalyst for liquid-phase oxidation of hydrocarbons.....	33
2.3 Development of SILP, SCILL, and SCILL-SILP systems	50
3. Aims, Objectives, and Scope of the Doctoral Dissertation	53
4. Experimental Section	55
4.1 Materials.....	55
4.2 Preparation of Metal-Rich MWCNT Composites.....	55
4.3 Preparation of Metal-Modified MWCNTs	56
4.4 Preparation of Cu(II) Functionalized MWCNTs.....	57
4.5 Preparation of SILP, SCILL, and SCILL-SILP Systems.....	57
4.6 NHPI Grafting onto MWCNT-NH ₂	59
4.7 NHPI Grafting onto Carboxylated MWCNTs.....	60
4.8 EB Oxidation.....	63

4.9	Analytical Methods	65
5.	Results and Discussion.....	69
5.1	Transition Metals Modified MWCNTs	69
5.1.1	Metal-rich MWCNT composites.....	70
5.1.2	Metal-modified MWCNTs	80
5.1.3	Metal-functionalized carboxylated MWCNTs	88
5.1.4	Summary	98
5.2	SCILL and SCILL-SILP Hybrid Catalytic System Based on IGMWCNT-COO-Cu and [emim][OcOSO ₃].....	100
5.2.1	Catalyst preparation and characterization	102
5.2.2	Catalytic activities of SCILL and SCILL-SILP hybrid catalytic system	107
5.2.3	Recyclability of the SCILL-SILP hybrid catalytic system.....	110
5.2.4	Summary	113
5.3	SILP and SCILL-SILP Hybrid Catalytic Systems Based on MWCNTs, MWCNT-COO-Cu and Various ILs.....	115
5.3.1	Catalyst preparation and characterization	116
5.3.2	Catalytic activities of the SILP systems	120
5.3.3	Catalytic activities of SCILL-SILP hybrid systems	125
5.3.4	Recyclability of SILP systems.....	130
5.3.5	Recyclability of SCILL-SILP hybrid catalytic systems	134
5.3.6	Summary	138
5.4	NHPI Grafting onto MWCNTs	140
5.4.1	Introduction	140
5.4.2	NHPI grafting onto commercial MWCNT-NH ₂	141
5.4.3	Catalytic activity of MWCNT-NHPI	142
5.4.4	Recyclability of NHPI-grafted MWCNTs.....	147
5.4.5	NHPI grafting onto IGMWCNT-COOH	149

5.4.6	Catalytic activity of the IGMWCNT-NHPI	153
5.4.7	Recyclability of IGMWCNT-NHPI	156
5.4.8	Summary	158
6.	Summary and Conclusion of the Study.....	159
	References	165
	Appendices: Supplementary Data	203
	Scientific Achievements	208

List of Abbreviations

Abbreviation	Definition	Abbreviation	Definition
A	Cyclohexanol	AA	Adipic acid
AcOH	Acetic acid	AcPO	Acetophenone
AIBN	Azobisisobutyronitrile	ATR-FTIR	Attenuated total reflectance Fourier transform infrared spectroscopy
BA	Benzaldehyde	BAL	Benzyl alcohol
BDE	Bond dissociation energy	BP	2-Benzyl-2-propanol
BzA	Benzoic acid	CHHP	Cyclohexyl hydroperoxide
CNTs	Carbon nanotubes	Co-MWCNT@6h	Cobalt-rich MWCNTs (acid treatment time: 6 h)
Co-MWCNTs	Cobalt-modified MWCNTs	Cu-MWCNT@14h	Copper-rich MWCNTs (acid treatment time: 14 h)
Cu-MWCNT@6h	Copper-rich MWCNTs (acid treatment time: 6 h)	Cu-MWCNTs	Copper-modified MWCNTs
CUHP	Cumene hydroperoxide	CVD	Chemical vapor deposition
Cy-diol	1,2-Cyclohexanediol	Cy-HP	Cyclohexenyl hydroperoxide
Cy-ol	2-Cyclohexen-1-ol	Cy-one	2-Cyclohexen-1-one
DADCAQ	1,4-diamino-2,3-dichloroanthraquinone	DDAB	Didecyldimethylammonium bromide
DDDAB	Didodecyldimethyl ammonium bromide	DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetry	EB	Ethylbenzene
EDC	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide	EDS	Energy-dispersive X-ray spectroscopy
E-factor	Environmental factor	Ep-Cy	Epoxy cyclohexane
FID	Flame ionization detector	GC	Gas chromatography
HAT	Hydrogen atom transfer	HHA	Hydroxyhexanoic acid
ICP-MS	Inductively coupled plasma mass spectrometry	ICP-OES	Inductively coupled plasma optical emission spectroscopy
IGMWCNT-COO-Cu	Cu(II)-functionalized industrial-grade carboxylated MWCNTs	IGMWCNT-COOH	Industrial-grade carboxylated multi-walled carbon nanotubes
IGMWCNT-NHPI	NHPI-grafted industrial-grade MWCNTs	IL	Ionic liquid
ILs	Ionic liquids	K	Cyclohexanone
MeCN	Acetonitrile	Mn-MWCNT@6h	Manganese-rich MWCNTs (acid treatment time: 6 h)
Mn-MWCNTs	Manganese-modified MWCNTs	MWCNT-COO-Cu	Cu(II)-functionalized carboxylated multi-walled carbon nanotubes

MWCNT-COOH	Carboxylated multi-walled carbon nanotubes	MWCNT-NHPI-1	NHPI-grafted MWCNTs (~0.45% amine-functionalized precursor)
MWCNT-NHPI-2	NHPI-grafted MWCNTs (~7% amine-functionalized precursor)	MWCNTs	Multi-walled carbon nanotubes
N-CNTs	Nitrogen-doped carbon nanotubes	NAPI	<i>N</i> -Acetoxypthalimide
NDHPI	<i>N,N'</i> -Dihydroxypyromellitimide	NHNI	<i>N</i> -Hydroxynaphthalimide
NHPI	<i>N</i> -Hydroxypthalimide	NHS	<i>N</i> -Hydroxysuccinimide
NHTPPI	<i>N</i> -Hydroxy-3,4,5,6-tetraphenylphthalimide	NMPI	<i>N</i> -Methoxypthalimide
OD	Outer diameter	P-CNTs	Phosphorus-doped carbon nanotubes
PEA	1-Phenylethanol	PEHP	1-Phenylethyl hydroperoxide
PINO	Phthalimide <i>N</i> -oxyl radical	PP	2-Phenyl-2-propanol
PPE	Personal protective equipment	SCILL	Solid catalyst with an ionic-liquid layer
SEM	Scanning electron microscopy	SILP	Supported ionic liquid phase
SWCNTs	Single-walled carbon nanotubes	TBHP	tert-Butyl hydroperoxide
TEM	Transmission electron microscopy	TEMPO	2,2,6,6-Tetramethylpiperidine 1-oxyl
TGA	Thermogravimetric analysis	THICA	<i>N,N',N''</i> -Trihydroxyisocyanuric acid
TOF	Turnover frequency	TON	Turnover number
V-HP	Verbenyl hydroperoxide	V-ol	Verbenol
V-one	Verbenone	XPS	X-ray photoelectron spectroscopy
[bmim][BF ₄]	1-Butyl-3-methylimidazolium tetrafluoroborate	[bmim][Br]	1-Butyl-3-methylimidazolium bromide
[bmim][Cl]	1-Butyl-3-methylimidazolium chloride	[bmim][NTf ₂]	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[bmim][OcOSO ₃]	1-Butyl-3-methylimidazolium octyl sulfate	[bmim][PF ₆]	1-Butyl-3-methylimidazolium hexafluorophosphate
[C ₁₀ mim][Cl]	1-Decyl-3-methylimidazolium chloride	[emim][NTf ₂]	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[emim][OcOSO ₃]	1-Ethyl-3-methylimidazolium octyl sulfate	[omim][Cl]	1-Octyl-3-methylimidazolium chloride
α -p-O	α -Pinene oxide		

1. Introduction

Liquid-phase oxidation of hydrocarbons using molecular oxygen is a key process for converting hydrocarbons into value-added intermediates. However, achieving high process efficiency remains challenging due to the strength of C–H bonds in hydrocarbons. The chemistry requires the activation of C–H bonds in radical-chain pathways. In practice, this activation must be performed while limiting overoxidation, controlling the formation and decomposition of intermediate hydroperoxides, and ensuring reliable, safe transfer of the oxygen into the liquid phase. From a sustainability perspective, the increasing attention on air or molecular oxygen goes beyond their abundance and high atom economy. A sustainable, greener oxidation process often depends on a catalytic system that reduces or even eliminates solvent use, limits waste generation, avoids the use of toxic or scarce reagents, and enables stable recycling without loss of activity.

In this context, catalyst design is crucial for achieving sustainable oxidation processes. Transition-metal compounds have been widely employed as catalysts in these processes; however, issues related to toxicity and recyclability remain their main drawbacks. In contrast, carbon nanotubes (CNTs) can function both as catalysts and as catalyst supports, offering chemically resilient structures with high specific surface areas and tunable surfaces that enable the immobilization and grafting of active species. Similarly, *N*-hydroxyphthalimide (NHPI) has emerged as an efficient, low-toxic, and economical organocatalyst capable to promote hydrocarbons oxidation by activating C–H bonds via hydrogen-atom transfer (HAT). Its catalytic activity arises from in situ generation of the phthalimide *N*-oxyl (PINO) radical, a highly effective hydrogen abstractor. Nonetheless, limited solubility in apolar hydrocarbons, PINO deactivation at elevated temperatures, and challenges in efficient catalyst recovery and recycling impose practical constraints on its broader application.

Ionic liquids (ILs) can further enable process intensification by providing non-volatile, composition-tunable media that dissolve and stabilize catalytically active species while modulating catalytic activity. They can also tune polarity and influence gas-liquid mass transfer. In addition, they can retain active species as an immobilized thin layer, which may simplify separation and reduce solvent-derived waste. The integration of pristine and/or modified CNTs with NHPI and ILs in hybrid catalytic design could integrate their

remarkable properties and produce a synergistic effect. CNTs and/or modified CNTs provide a robust support for immobilization, while NHPI (via PINO radical) drives HAT-mediated C–H activation. The IL offers a tunable, non-volatile medium that can stabilize and influence the catalytically active species while operating as a thin supported film rather than a bulk phase. Consequently, these systems could enhance O₂ utilization by alleviating mass-transfer constraints, retain NHPI within the immobilized IL layer to facilitate recovery and recycling, and reduce solvent-related waste under aerobic liquid-phase oxidation conditions.

2. Background and State of the Art

2.1 Liquid Phase Oxidation of Hydrocarbons Using Dioxygen

Liquid-phase oxidation of hydrocarbons with oxygen is a key route to oxygenated compounds, supplying a wide range of high-value intermediates and end products for the petrochemical and pharmaceutical industries [1–3]. These transformations proceed via a free-radical chain mechanism consisting of initiation, propagation, and termination steps [3–5]. A characteristic feature of liquid-phase hydrocarbons oxidation is the formation of the primary hydroperoxide products, which subsequently can be converted into a broad spectrum of oxygenated products, including carbonyl compounds, alcohols, carboxylic acids, esters, etc. [1,6]. Because these oxygenated products are generally more reactive than the parent hydrocarbons, they are inclined towards undergoing further oxidation, often with a rate exceeding that of the parent hydrocarbons. Consequently, suppressing over-oxidation and maintaining high selectivity towards the desired product remain persistent challenges.

From an industrial perspective, air or molecular oxygen is a lucrative oxidant choice because it is abundant, economical, environmentally benign, and offers high atom economy. On the other hand, the direct oxidation of hydrocarbons with molecular oxygen or air is challenging. In addition to the high bond dissociation energies (BDEs) and low polarity of C–H bonds, ground-state dioxygen exists as a triplet, whereas most hydrocarbons are singlets, so direct oxidation is spin-forbidden as per the Wigner spin-conservation rule [7]. Consequently, catalysts are essential for liquid-phase aerobic oxidations under mild conditions. Various types of homogeneous [1,8–10] and heterogeneous [11,12] catalysts have been employed in these processes.

The term catalysis was coined by Berzelius in 1835, and Ostwald later described it in 1894 as “Catalysis is the acceleration of a slow chemical process by the presence of a foreign material” [13]. In general, catalysis refers to an increase in reaction rate brought about by an added substance (the catalyst). Although the catalyst participates in the reaction steps, it is regenerated and is therefore not consumed overall [14]. In the present context, catalysts are commonly classified as homogeneous (same phase) or heterogeneous (solid catalyst in liquid systems).

2.1.1 Significance of liquid-phase oxidation of hydrocarbons

The key industrial processes that employ liquid-phase oxidation of hydrocarbons are summarized in Table 2.1, which compiles the corresponding operating conditions, feedstock, target products, and their downstream applications. *p*-xylene is directly oxidized to purified terephthalic acid (TA) in the Amoco (Mid-Century) process, supplying the key feedstock for polyethylene terephthalate (PET). In contrast, BASF/DuPont processes convert *p*-xylene to dimethyl terephthalate (DMT) for the same value chain. In the Hock process, cumene (CU) is oxidized to cumene hydroperoxide (CUHP) using air as an oxidant. The produced CUHP is subsequently acid-cleaved to produce phenol and acetone. Similarly, the oxidation of toluene produces benzoic acid (BzA), an important intermediate widely used in the manufacture of esters, salts, and other derivatives, while the oxidation of cyclohexane produces a mixture of cyclohexanol and cyclohexanone (commonly known as KA oil), which serves as the precursor for ϵ -caprolactam and adipic acid in nylon production.

In the oxirane or indirect oxidation route to propylene oxide (PO), a carrier hydrocarbon is first selectively oxidized to a hydroperoxide, typically, isobutane to *tert*-butyl hydroperoxide (TBHP) or ethylbenzene (EB) to ethylbenzene hydroperoxide (PEHP). These hydroperoxides subsequently transfer their peroxidic oxygen to propylene, producing PO while being reduced to *tert*-butyl alcohol (TBA) and 1-phenylethanol (PEA), respectively. The economics of coproduct largely govern the overall process design: in the isobutane-based route, TBA can be directly marketed as a high-octane fuel additive or dehydrated to isobutene for downstream methyl *tert*-butyl ether (MTBE) synthesis, whereas in the EB-based route, PEA is readily dehydrated to styrene, linking PO production with the styrene monomer industry.

Despite their industrial relevance, liquid-phase oxidations of hydrocarbons are among the most severe and technically challenging operations due to the intrinsic inertness of C-H bonds, low O₂ solubility, high exothermicity/over-oxidation risks, and safety limitations [5,15]. Consequently, these processes are executed under severe reaction conditions (elevated temperature and pressure) to meet kinetic and selectivity targets. The oxidation of *p*-xylene to produce TA employs the Amoco process, which operates at 190-205 °C and 1.5-3.0 MPa in AcOH (90-95%) using a mixed Co-Mn-Br catalyst and air as the oxygen source. Similarly, cyclohexane oxidation to KA oil requires 125-165 °C and 0.8-1.5 MPa. It is worth noting that the oxidation of CU and EB to their respective hydroperoxides proceeds without

transition-metal catalysts. Air is used as the oxidant, while a small amount of initiator initiates the radical chain reaction. CU is oxidized to CUHP at 130-140 °C and approximately 0.5 MPa, whereas EB is converted to PEHP (oxirane route) at 120-140 °C and about 3.5 MPa. A notable exception is the Dow process for EB oxidation, which operates at 110-120 °C and 0.2-0.3 MPa and employs cobalt salts as catalysts.

It can be observed that in most of the oxidation processes, conversions are relatively low while selectivity toward the target compounds remain high. The Amoco process for the oxidation of *p*-xylene to TA, and of toluene to BzA, represents an exception among large-scale liquid-phase oxidations, achieving both high conversion and selectivity. This distinction arises from the nature of the desired product: in most oxidation systems, the target molecule is an intermediate oxidation product, whereas in the Amoco process, it represents the final oxidation state of the substrate. When the desired product is a reactive intermediate such as KA oil, CHP, PEHP, or TBHP, over-oxidation is a major concern. To maintain selectivity, such reactions are therefore operated at low per-pass conversion, with extensive recycling of unreacted feed to achieve the desired overall yield.

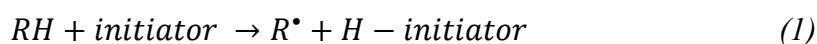
Another industrially relevant process is the production of acetophenone (AcPO), which is mainly a coproduct of the Hock process for phenol. It yields in the CU oxidation stage via the decomposition of CUHP [16]. It can also be produced commercially by the liquid-phase oxidation of EB with dioxygen in the presence of cobalt or manganese catalysts. This reaction is typically performed in the range of 130-150 °C, and the conversion of EB is around 25% [17].

Air has been employed in industrial oxidation processes because it is abundant, inexpensive, and safer than pure dioxygen. The N₂ dilution reduces flammability risk and provides thermal ballast for temperature control. Nonetheless, the lower O₂ partial pressure limits gas-liquid mass transfer, often requiring higher gas rates, larger contactors, or off-gas recycle, thereby increasing capital and operating costs. Oxygen-enriched feeds can improve oxygen uptake and reduce off-gas volume, but they demand stricter safety management. Thus, the choice of industrial oxidants is ultimately based on a balance among safety, cost, and process efficiency [18,19].

2.1.2 Mechanism of the liquid-phase oxidation of hydrocarbons

Liquid-phase oxidation of hydrocarbons (RH) proceeds via a free-radical chain reaction mechanism involving initiation, propagation, and termination steps. During initiation, radical species are generated from the hydrocarbon substrate by an external initiator (reaction 1) or formed by hydroperoxide decomposition (reactions 2-4). In the propagation stage, carbon-centered radicals react rapidly with dioxygen to form peroxy radicals (reaction 5), which subsequently abstract hydrogen atoms from the hydrocarbon, yielding hydroperoxides and regenerating carbon-centered radicals (reaction 6). Termination occurs through radical recombination reactions that quench the chain process. These mechanistic steps are commonly represented by reactions (1) - (9), where Q=O indicates the ketone formed [3,20,21].

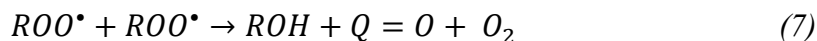
Initiation:



Propagation:

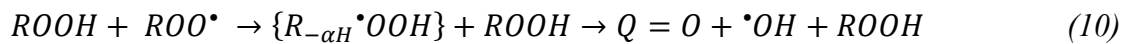


Termination:

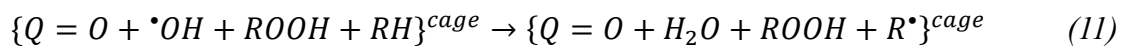


In liquid-phase autoxidation, the primary oxidation product is the hydroperoxide (ROOH), which plays a central role in sustaining the radical chain mechanism. Under reaction conditions, hydroperoxides may undergo thermal and/or catalytic decomposition to generate alkoxy (RO[•]) and peroxy (ROO[•]) radicals, thereby accelerating chain propagation.

Hermans et al. showed that the classical autoxidation mechanism is inconsistent with experimental observations for both cyclohexane and EB, especially regarding the unexpectedly high ketone/alcohol product ratios [21]. They postulated that during the autoxidation, the peroxy radicals abstract not only H-atoms from the substrate (reaction 6) but, respectively, 55 and 10 times faster, the α -H atom of the formed hydroperoxide (reaction 10). The resulting α -hydroperoxyalkyl radicals $R_{-\alpha H}\cdot OOH$ decomposes to a ketone ($Q = O$) and $\cdot OH$ radical. This reaction is identified as the main ketone source.



The formed $\cdot OH$ radical rapidly abstracted the H-atom from RH in the solvent cage (reaction 11).



Besides the out-of-cage diffusion (reaction 12), the subsequent cage reaction (reaction 13) as the source of ROH was proposed.

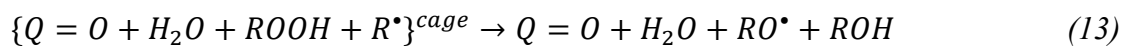
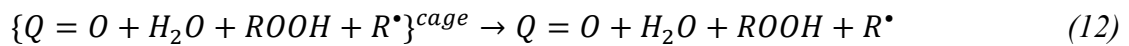


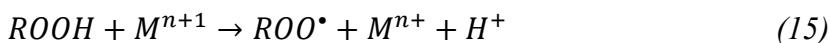
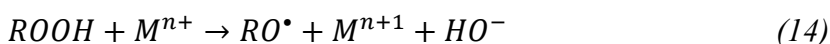
Table 2.1. Overview of major industrial liquid-phase hydrocarbon oxidations: feedstocks, products, catalysts, and operating conditions [4,22].

Product	Capacity (10 ⁶ t.y. ⁻¹ ; year) [Ref.]	Hydrocarbon feed (liquid)	Gas	Oxidation step / desired product	Industrial process/route	T (°C)	P (MPa)	Medium	Catalyst/ initiator	Conv. (%)	Sel. (%)	Main application(s)
TA	96.84 (2026) [23]	<i>p</i> -Xylene	Air	<i>p</i> -Xylene to TA	Amoco (Mid-Century process)	190-205	1.5-3.0	AcOH (90- 95%)	MC catalyst	95	>90	PET (fiber, film, resin)
DMT	~0.74 (2026) [24]	<i>p</i> -Xylene + monomethyl ester of PTA	Air + MeOH	One-step to DMT	DuPont one-step process	100-200	0.5-2.0	<i>p</i> - Xylene + reaction products	-	-	90	PET (fiber, film, resin)
Phenol	12 (2024) [25]	CU	Air	CU to CUHP to phenol	Hock process (BP, Kellogg, etc.)	130-140	0.5	-	CUHP initiator	30	93- 95	Phenol
BzA	0.63 (2026) [26]	Toluene	Air	Toluene to BzA	DSM, Dow	110-120	0.2-0.3	-	Co acetate	-	90	Phenol and salts/esters of benzoic acid
		Toluene	Air	Toluene to BzA	Amoco	165	0.9	-	MC catalyst	99	96	
ϵ - Caprola ctam	6.5 (2023) [27]	Cyclohexane	Air	Cyclohexane to KA oil	BASF, Bayer, DuPont, DSM, Stamicarbon Scientific Des.	125-165	0.8-1.5	-	Co and Mn salts	5-8	80- 85	Nylon-6 (Perlon)
Adipic acid	4.4 (2023) [28]	Cyclohexane	Air	Cyclohexane to KA oil	BASF, Bayer, DuPont, Stamicarbon Scientific Des.	-	-	-	-	-	-	Nylon-6,6
		<i>iso</i> -Butane	Air	<i>iso</i> -Butane to TBHP	Oxirane process	120-140	3.5	-	Initiator	25	60	Propylene glycol, polyols, styrene
PO	11.2 (2020) [29]	EB	Air	EB to PEHP	Oxirane process	120-140	3.5	-	Initiator	15- 17	87	Styrene
		EB	Air	EB to PEHP	Dow route	110-120	0.2-0.3	-	Co salts	-	90	

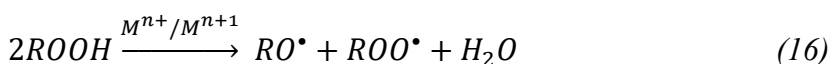
Reported production capacities for the listed products, compiled from recent sources and independent of the production routes discussed here.

2.1.3 Transition metals as catalysts for liquid-phase oxidation

Transition-metal salts such as Cu(I)/Cu(II), Co(II)/Co(III), Mn(II)/Mn(III), and Fe(II)/Fe(III) are widely employed as catalysts in hydrocarbon oxidation reactions. Their catalytic performance depends on several factors, including the identity and redox potential of the metal ion, the nature of the substrate, and the composition of the reaction medium. Nevertheless, their primary catalytic function is associated with the promotion of hydroperoxide decomposition via redox cycling, as represented by reactions (14) and (15) [1,20].



Net Reaction:



Through these catalytic cycles, hydroperoxides are rapidly converted into alkoxy and peroxy radicals, sustaining the radical chain mechanism and enhancing the overall oxidation rate. However, the increased concentration of reactive radical species also promotes secondary oxidation pathways, leading to the formation of alcohols, ketones, and aldehydes at the expense of hydroperoxide selectivity. In particular, aldehydes formed during oxidation are readily further oxidized to the corresponding carboxylic acids. Consequently, when hydroperoxides are the desired products, such reactions are typically conducted in the absence of metal catalysts, relying instead on controlled autoxidation to suppress excessive hydroperoxide decomposition.

On the other hand, transition-metal salts and complexes [3,20] are easy to introduce into the reaction medium but difficult to recover effectively after use. Their separation often results in product contamination, catalyst loss, and increased waste-handling requirements. These drawbacks become even more pronounced in the presence of halide promoters, which exacerbate corrosion, solvent degradation, and metal leaching [4,30,31].

Organic solvents are often employed to facilitate oxygen transfer and stabilize the catalyst, but they introduce toxicity, flammability, and VOC-emission risks while demanding energy-intensive recovery [32]. Solvent losses also elevate the environmental impact expressed by

the E-factor. For bulk chemicals, the E-factor is typically $< 1-5$ for $10^4 - 10^6$ tonnes of product, whereas for fine chemicals it ranges from $5- >50$ for $10^2 - 10^4$ tonnes [32–35].

2.2 Carbon Nanotubes, Organocatalysts, and Ionic Liquids-Based Oxidation Systems

The growing emphasis on sustainable oxidation technologies has reshaped research in hydrocarbon oxidation catalysis, with a focus on processes that balance operational safety, environmental compatibility, and high catalytic efficiency under relatively mild conditions. In this context, three classes of materials, i.e., carbon nanotubes (CNTs), organocatalysts such as NHPI, and ionic liquids (ILs), have gained tremendous attention. Each possesses unique physicochemical properties that can be harnessed to address persistent challenges in oxidation chemistry, including radical generation, improved oxygen utilization, and stabilization of active species within robust catalytic environments.

2.2.1 CNT-based catalysts for liquid-phase oxidation of hydrocarbons

With advances in nanostructured catalyst design, carbon materials, particularly CNTs, have attracted considerable research attention as advanced catalysts and catalyst supports. Their distinct physicochemical properties, for instance, high surface area, remarkable mechanical and thermal stability, enhanced electrical conductivity, corrosion resistance, and the opportunity of functionalization and/or modification, make them highly versatile in catalytic applications [36–40]. Since their discovery by Sumio Iijima in 1991 via the arc-discharge method [41], CNTs have become an important class of nanomaterials with applications including catalysis, energy storage, and environmental science. CNTs are tubular nanostructures made up of sp^2 -hybridized carbon atoms arranged in a graphene-like network. They are classified into single-walled carbon nanotubes (SWCNTs), formed by rolling a single graphene sheet, and multi-walled carbon nanotubes (MWCNTs), which consist of several concentric graphene tubes (Figure 2.1) [42,43]. Although both SWCNTs and MWCNTs are composed of sp^2 -hybridized carbon atoms, they exhibit distinct physical properties (Table 2.2), arising from differences in the number of graphene layers, diameter, and surface area.

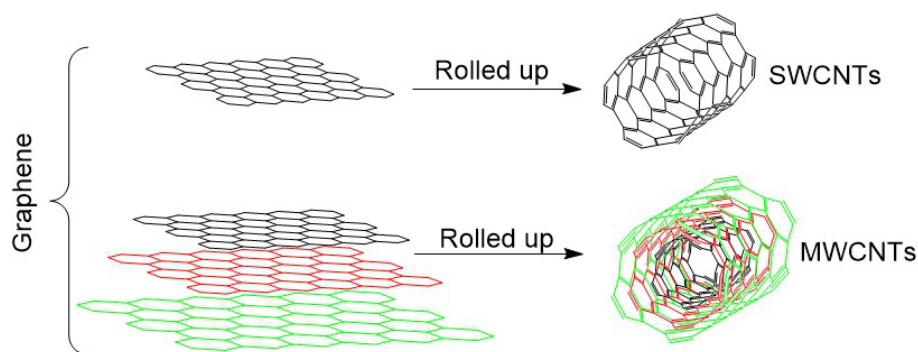


Figure 2.1. Schematic illustration of the formation of SWCNTs and MWCNTs from graphene sheets. Redrawn from Ref. [40].

Table 2.2. Comparison of the physical properties of SWCNTs and MWCNTs [44].

Property	SWCNTs	MWCNTs
Diameter (nm)	1-2	5–100
Length (nm)	100-1000	15,000
Elastic modulus (GPa)	1000-3000	300–1000
Thermal conductivity at 300 K ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	3000-6000	2000–3000
Band gap (eV)	0-0.5	2.9–3.7
Density ($\text{kg} \cdot \text{m}^{-3}$)	2600	1600
Specific heat C_p ($\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$)	425	796
Melting point ($^{\circ}\text{C}$)	3527	3527
Tensile strength (GPa)	22.2 ± 2.2	11–63

CNTs, both pristine and functionalized, have been extensively investigated as catalysts and catalyst supports in a wide spectrum of reactions, including wet air oxidation [45–48], oxidative dehydrogenation [49–51], decomposition (such as methane and ammonia) [52–55], Friedel-Crafts [56,57], Fischer-Tropsch [58–60], dehydrogenation [61,62], and oxidation of alcohols [63–66] and hydrocarbons [67–71]. Collectively, these studies demonstrate that CNTs are not merely inert supports; rather, they can act as metal-free catalysts, attributed to their exceptional electronic and structural properties.

The inherent tubular morphology and delocalized π -electron network of CNTs facilitate efficient electron transfer and promote uniform dispersion of the active sites, making them a promising material for catalytic oxidation reactions. In addition to serving as robust catalyst supports, CNTs can also display intrinsic catalytic activity, acting as metal-free catalysts in the oxidation of hydrocarbons [40]. Thanks to their enhanced electrical

conductivity, which efficiently promotes electron transfer between active sites and reactant molecules.

In the aerobic oxidation of hydrocarbons under the liquid phase, the catalytic activity of sp^2 -hybridized carbons, such as CNTs, originates from their capability to foster the decomposition of the intermediate hydroperoxides [72]. The delocalized π -electron network on the graphene sheets of CNTs facilitates π - π interactions, accelerating the decomposition of intermediate hydroperoxides into reactive radicals and thereby improving overall catalytic performance [67,73]. Consequently, efficient electron transfer across the graphene layers of CNTs is a key contributing factor to their catalytic performance in these processes. The electrical conductivity of CNTs can be further augmented via heteroatom doping [74,75] or modification with metals and metal oxides [40]. Such modifications alter the electronic structure, enhance electron mobility, and create additional active sites, thereby improving catalytic performance.

EB is commonly employed as a model alkyl aromatic hydrocarbon to investigate catalytic performance and to gain mechanistic insight into oxidation pathways, particularly over CNT-based catalysts. Under liquid-phase aerobic conditions using dioxygen as the oxidant, EB oxidation over CNTs yields PEHP, 1-phenylethyl alcohol (PEA), AcPO, benzaldehyde (BA), and BzA, as shown in Figure 2.2.

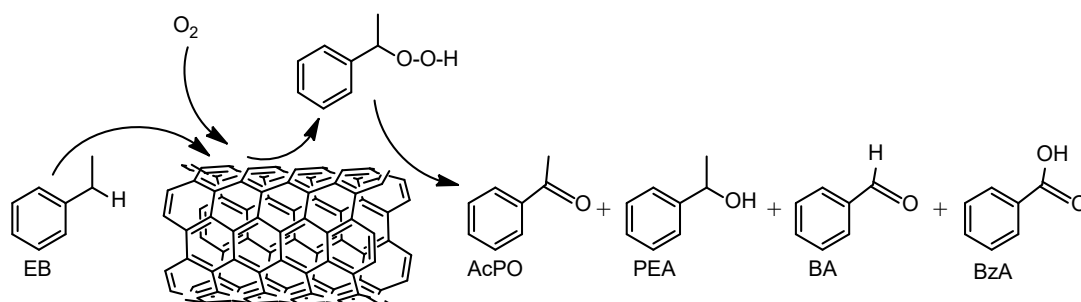


Figure 2.2. EB oxidation products. Redrawn from Ref. [67].

A plausible reaction mechanism, based on the previous investigations, is illustrated in Figure 2.3. In this mechanism, EB is initially adsorbed onto the surface of CNTs, where π - π interactions between the aromatic ring of EB and the graphitic framework of CNTs facilitate activation by weakening the α -C-H bond in EB. Subsequently, a nearby oxygen molecule abstracts the activated hydrogen atom, generating a phenylethyl radical (PE) and a hydroperoxyl radical (HOO $\cdot$) [67].

Despite general agreement on the radical nature of the process, the precise role of oxygen activation remains debated. Some studies suggest that oxygen participates predominantly in its molecular form (O_2) [67,76,77], whereas others propose partial electron transfer from CNTs to oxygen, producing superoxide radical anion ($\cdot O_2^-$) [78,79]. In the presented mechanism, dioxygen is considered to react with the PE to form the corresponding 1-phenylethylperoxyl radical (PEPO).

The PEPO subsequently abstracts a hydrogen atom from the α -H bond of EB, producing PEHP and regenerating PE. In this process, PEHP serves as the crucial intermediate and the principal species responsible for sustaining chain propagation during EB oxidation [67]. As described by Lin et al. [78] and illustrated in Figure 2.3, this sequence constitutes a cyclic process in which the generated PE radical reacts with O_2 to produce PEPO, thereby continuing the cycle.

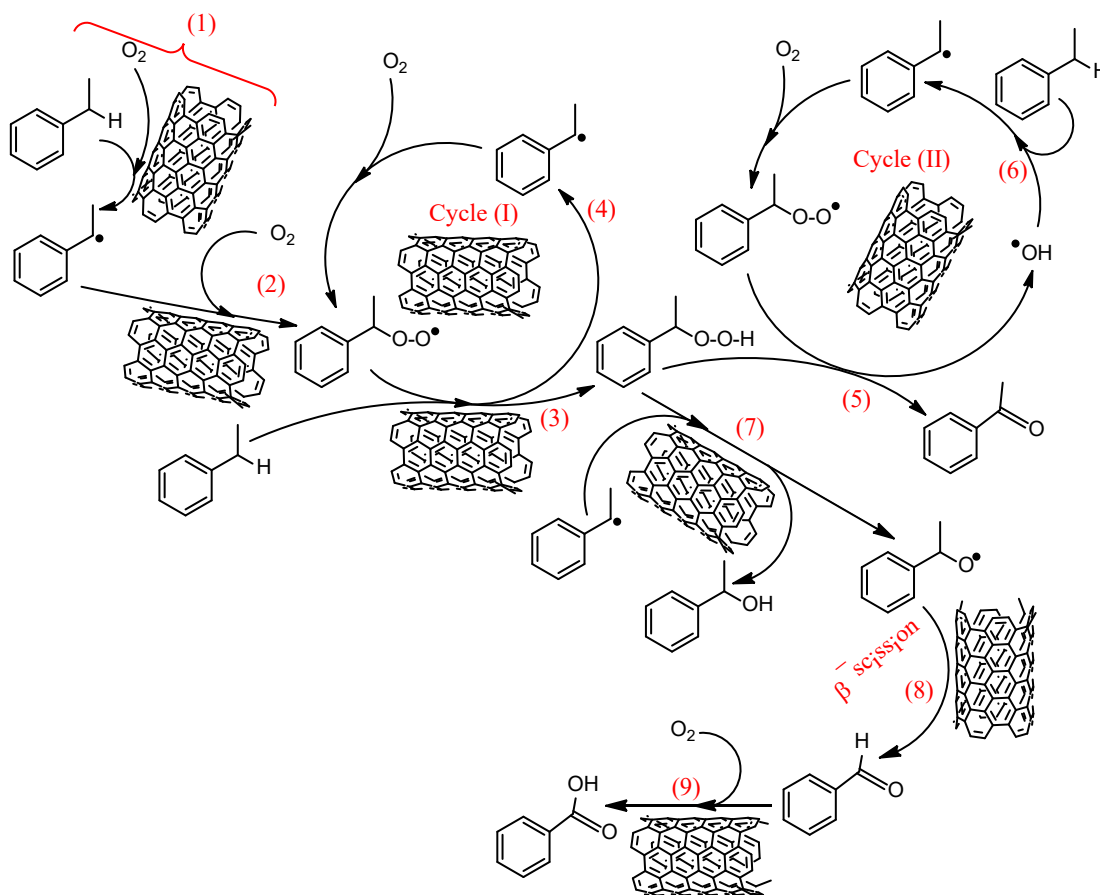


Figure 2.3. Plausible aerobic oxidation mechanism of EB. Redrawn from Ref. [67,78].

On the other hand, Luo et al. [67] proposed that PEPO predominantly abstracts the relatively weakly bound α -H atom from PEHP rather than from EB, owing to the higher reactivity of

the C-H bond adjacent to the -OOH group compared with the secondary benzylic C-H bond in EB. Simultaneously, PEHP promptly decomposes on the CNTs surface, yielding AcPO via the generation of hydroxyl radicals ($\cdot\text{OH}$). The $\cdot\text{OH}$ generated in this step readily abstracts the α -H atom from neighboring EB molecules, yielding a new PE radical. These radicals subsequently react with O_2 to form PEPO. The resulting PEPO radical rapidly engages with nearby PEHP, promoting its conversion to AcPO while regenerating $\cdot\text{OH}$ radicals, thereby sustaining the radical chain cycle. In a parallel pathway, PEHP can react with PE radicals, yielding PEA together with the corresponding 1-phenylethyloxy radical (PEO). Subsequent β -C-C bond scission of the PEO produces BA, which may further undergo oxidation in the presence of O_2 to produce BzA [21].

2.2.1.1 *Pristine CNTs as metal-free catalysts*

Pristine CNTs, both SWCNTs and MWCNTs, have demonstrated activity, selectivity, and stability as metal-free catalysts for liquid-phase hydrocarbon oxidation reactions. Their catalytic performance is closely related to their ability to propagate free-radical chain reactions and facilitate electron transfer at the solid-liquid interface, thereby enhancing the utilization of reactive intermediates, improving overall reaction efficiency, and enabling the selective formation of ketones and alcohols [80]. In this context, sp^2 carbons, such as graphene and CNTs, outperform sp^3 carbons (e.g., diamond), primarily due to their ability to promote the decomposition of intermediate peroxides during the oxidation reactions [81].

The delocalized π -electrons of CNTs facilitate π - π interactions with peroxides and radical intermediates, which accelerate peroxide decomposition into reactive radicals [73]. Such behavior has been observed by Luo et al. [67], who reported efficient metal-free liquid-phase aerobic oxidation of EB to AcPO over CNTs, achieving 38.2% conversion with 60.9% selectivity. It is noteworthy that the catalytic performance was comparable to that of metal-based systems, and the CNTs retained their activity and structural integrity over six consecutive cycles. Similar trends were observed in the low-temperature aerobic oxidation of cumene (CU) using commercial-grade CNTs [68], where a conversion of 24.1% and a selectivity of 88.4% toward cumene hydroperoxide (CUHP) were achieved. Recycling studies confirmed the catalyst's stability, with consistent conversion and selectivity across multiple cycles. A comparative evaluation of pristine CNTs with functionalized CNTs and metal-based catalysts is summarized in Table 2.3.

2.2.1.2 Heteroatom-doped CNTs

The surface chemistry of CNTs plays a key role in hydrocarbon oxidation reactions, as their electrical properties can be effectively tuned through heteroatom doping, including oxygen, nitrogen, phosphorus, sulfur, or boron. Such doping modifies the electronic structure of CNTs, thereby altering their catalytic behavior [80,82–84]. In particular, nitrogen doping enhances interactions between radical intermediates and surface carbon atoms, promoting electron transfer and accelerating the decomposition of peroxide intermediates, ultimately leading to an enhanced catalytic activity [69,85,86]. Gao et al. demonstrated that nitrogen incorporated into sp^2 -hybridized carbon does not directly activate the reactant but instead increases the reactivity of adjacent carbon sites through electronic modification. Additionally, a higher concentration of graphitic nitrogen was revealed to further improve the catalytic performance [87].

The superior performance of MWCNTs and nitrogen-doped CNTs (N-CNTs) to catalyze the aerobic oxidation of cyclohexane in the liquid phase is reported by Yu et al. [73]. CNTs synthesized by chemical vapor deposition (CVD) exhibited high activity without post-treatment, reducing catalyst preparation costs, and achieved 34.3% cyclohexane conversion with 52.4% selectivity toward adipic acid. Nitrogen doping, introduced via CVD with aniline, increased pyridinic nitrogen content and surface area, thereby enhancing catalytic performance. Under identical conditions, N-CNTs displayed higher activity and selectivity (45.3% conversion and 59.7% adipic acid selectivity) compared to pristine CNTs, outperforming metal-based catalysts even at a lower temperature (125 °C). The N-CNTs also exhibited remarkable recyclability over five consecutive cycles.

Cao et al. [69] investigated nitrogen (N)-, phosphorus (P)-, and boron (B)-doped CNTs as a catalyst for the liquid-phase aerobic oxidation of cyclohexane. All the CNTs were produced by CVD using xylene as the carbon source. Aniline- NH_3 , triphenylphosphine, and triethyl borate were utilized as precursors for N, P, and B, respectively. While both the N-CNTs and P-CNTs exhibited significant catalytic activity, the B-doped CNTs were inactive. The maximum mass-normalized activity was attained for N-CNT ($761 \text{ mmol g}^{-2} \cdot \text{h}^{-1}$), whereas the maximum surface area-normalized activity was achieved for P-CNTs ($28 \text{ mmol m}^{-2} \cdot \text{h}^{-1}$). It was observed that the specific activity of N- and P-doped CNTs enhanced exponentially with decreasing work function, emphasizing the critical role of surface electron transfer in cyclohexane oxidation. In several cases, their catalytic activities surpassed those of metal-based catalysts. Further corroborating these results, Yang et al. [79] employed in situ

electron paramagnetic resonance (EPR) spectroscopy to directly probe radical-CNT interaction during the cyclohexane oxidation, confirming the formation of $\text{C}_6\text{H}_{11}^\bullet$, $\text{C}_6\text{H}_{11}\text{OO}^\bullet$, and $\text{O}_2^\bullet$ radicals. The results revealed that N-doped MWCNTs generated a higher amount of active radicals at the early stages of the reaction than pristine MWCNTs, providing direct mechanistic evidence for the superior catalytic performance of N-doped MWCNTs.

CNTs and N-CNTs have been investigated as metal-free catalysts for the liquid-phase aerobic oxidation of cyclohexene (80 °C, 1 MPa, 4 h). N-CNTs synthesized by CVD exhibited superior performance, achieving 59% conversion and a mass-normalized activity of $620.1 \text{ mm g}^{-1} \cdot \text{h}^{-1}$. The cyclohexene conversion rate per gram of catalyst over N-CNTs was nearly six times higher than that of pristine CNTs and was comparable to state-of-the-art metal catalysts. This enhanced activity was attributed to the improved ability of N-CNTs to promote radical chain propagation, while recyclability tests confirmed their stability and reusability [86].

Liao et al. examined pristine CNTs and N-CNTs as metal-free catalysts for the liquid-phase aerobic oxidation of cumene (80 °C, 0.101 MPa, and 8 h). N-CNTs augmented the cumene hydroperoxide decomposition, resulting in higher cumene conversion and enhanced selectivity toward AcPO and 2-benzyl-2-propanol. Under identical reaction conditions, N-CNTs with 3.33 atom% of nitrogen achieved a conversion of 74.7%, approximately 4.6 times higher than that of pristine CNTs (16.1%). The catalytic activity of N-CNTs increased with nitrogen content up to this optimal loading, beyond which a decline was observed. The enhanced performance was attributed to nitrogen-induced modification of the CNTs' surface electronic structure, which finely tuned reactivity and selectivity. In addition, N-CNTs retained their activity over four consecutive cycles, demonstrating good recyclability [77]. Mu et al. [88] conducted a detailed kinetic analysis of cumene aerobic oxidation over CNTs and N-CNTs. Their radical-based kinetic model showed that N-doping accelerates all elementary steps, particularly hydroperoxide decomposition into $\text{RO}^\bullet$ and $\text{HO}^\bullet$ radicals, thereby increasing the oxidation rate. Enhanced interactions between O_2 , intermediate radicals, and the catalyst surface resulted in higher yields of ketones and alcohols, with alcohol formation favored over N-CNTs compared to CNTs.

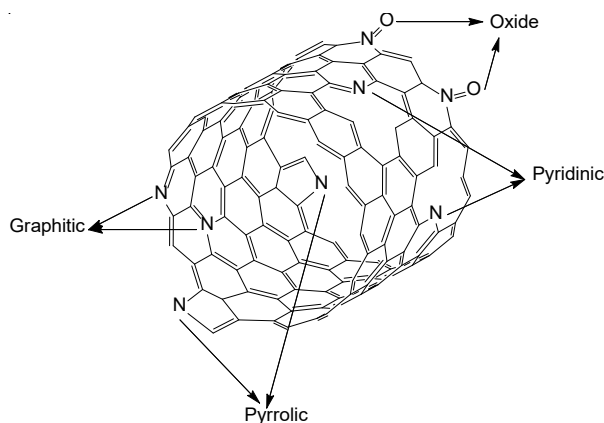


Figure 2.4. Schematic representation of nitrogen bonding configurations in N-doped CNTs. Redrawn from Ref. [40].

Su et al. [89] investigated the effect of N-CNTs loading on the aerobic oxidation of EB (155 °C, 1.5 MPa, 4 h). The catalytic activity increased at low N-CNT dosages but declined at higher loadings. Mechanistic analysis supported by DFT calculations indicated that N doping hinders α -H abstraction from EB, suppressing the initial radical propagation step and thereby reducing the overall activity. To overcome this limitation, TBHP was introduced as a co-oxidant to bypass the initiation stage. The combination of O₂ and TBHP, with an optimal N-CNT loading, resulted in a maximum EB conversion of 46% and 72% selectivity towards AcPO. Nonetheless, the authors noted that further studies are required to elucidate the role of N-CNTs in EB oxidation fully.

Nitrogen atoms incorporated into carbon frameworks can adopt distinct bonding configurations, including pyrrolic N, pyridinic N, graphitic N, and N-oxides species [90–92], as illustrated in Figure 2.4. Identifying the catalytically active N species is therefore essential for understanding the reaction mechanism on N-doped carbon materials. For instance, graphitic N sites have been shown to promote aerobic oxidation of benzyl alcohol under mild conditions [93], while pyridinic N sites are particularly effective for cathodic oxygen reduction in acidic media [94]. Fu et al. [71] examined the catalytic performance of N-CNTs in the oxidation of styrene using TBHP as an oxidant. The catalytic activity increased with N content up to 3.51%, beyond which a decline was observed. At an N content of 7.51%, the catalyst exhibited the lowest activity, performing even worse than the sample containing 0.98% N. They found that the oxidation reaction was enhanced when the N content in the N-CNTs was below 3.51%. However, at higher N content, activity decreased. Surprisingly, the catalytic activity was even worse when the N content increased to 7.51%, compared to the 0.98% N content in the CNTs. DFT calculations revealed distinct

roles of N species: graphitic N acted as the primary active site for styrene oxidation, while pyrrolic N preferentially facilitated the generation of reactive oxygen species (HOO[•]). Extending the heteroatom-doped CNTs catalysis to olefin oxidation, Cao et al. reported that the N-CNTs exhibited superior catalytic activity in the epoxidation of α -pinene utilizing molecular oxygen, achieving 54.4% conversion, almost 2.2 times higher than pristine CNTs. The N-CNTs displayed remarkable stability, retaining both conversion and product selectivity over five consecutive reaction cycles [95]. A thorough comparison of heteroatom-doped CNTs with metal-based catalysts has been provided in Table 2.3.

Table 2.3. Comparison of the catalytic performance of CNTs, heteroatom-doped CNTs, and metal-based catalysts for the liquid-phase oxidation of hydrocarbons with molecular oxygen as an oxidant.

Entry	Catalyst	BET (m ² ·g ⁻¹)	T (°C)	P (MPa)	t (h)	Substrate conversion (%)	Product selectivity (%)						Ref.
							EB	AcPO	PEA	PEHP	BA	BzA	
1 ^a	CNTs	138	155	1.5	4	38.2	60.9	9.8	2.3	7.5	19.5		
2 ^a	CoAc(Co(OAc) ₂ ·4H ₂ O	-	155	1.5	4	5.5	43.1	42.8	1.5	12.6	-		[67]
3 ^b	CoAc(Co(OAc) ₂ ·4H ₂ O	-	155	1.5	4	40.7	77.5	8.7	0.1	4.5	9.2		
4 ^a	CNTs	178	155	1.5	4	22	25	12	41	-	-		[89]
5 ^a	N-CNTs	133	155	1.5	4	23	45	13	30	-	-		
6	MnOx/HTS	-	150	0.6	1	37.1	68.6	20.4	3.5	3.4	-		[96]
7	Mn-N-C@SiO ₂	310.9	120	0.8	5	15.7	73.6	19	-	7.4	-		[97]
8	Co(OAc) ₂	-	120	1	6	9.2	27.5	12.9	78.6	-	-		
9	Co ₃ O ₄	-	120	1	6	7.1	43.7	9.5	46.9	-	-		[98]
10	Co/SBA-15	-	150	1	9	70.1	83.7	4.1	0.1	-	12.1		
11	MnMCM	-	110	1	6	34	88	-	-	-	-		[99]
12	CrMCM-141	-	95	1	24	66	90	-	-	-	-		[100]
							Cyclohexane	K	A	CHHP	AA	HHH	
13 ^c	N-CNTs	49.3	125	1.5	2.5	6.7	25.6	31.7	2.5	31.1	14.8		[69]
14 ^c	P-CNTs	4	125	1.5	5	10.2	22	23.4	3.9	31.3	11.7		
15 ^c	B-CNTs	53.9	125	1.5	2.5	2.8	25.1	32.9	7.2	13.4	13.9		
16 ^c	CNTs	127.8	125	1.5	8	34.3	40.4 ^d		-	52.4	-		[73]
17 ^c	N-CNTs	155.1	125	1.5	8	45.3	26.7 ^d		-	59.7	-		
18	Au/ZSM5	421	150	1	3	15	68	24	-	-	-		[101]
19	Co ²⁺	-	150	1.2-1.5	0.77	4	17	48	17	-	-		
20	Au/SBA-15	-	150	1.2-1.5	1.53	4	28	43	7	-	-		[102]
21	Au/Al ₂ O ₃	-	150	1.2-1.5	1.92	4	18	42	19	-	-		

22	Au/TiO ₂	-	150	1.2-1.5	2	4	20	45	15	-	-	
						Cyclohexene	Cy-one	Cy-ol	Cy-HP	Ep-Cy	Cy-diol	
23 ^a	CNTs	127.8	80	1	4	21	8.1	7.1	62.9	2.2	1.2	[86]
24 ^a	N-CNTs	155.1	80	1	4	59	41.1	11.2	27.3	5.9	0.18	
25	Au/La-OMS	-	80	0.4	24	48	44.4	40.3	-	2.5	-	[103]
26	Au/Al ₂ O ₃	258	150	1.5	3	12	32.1	52.6	-	-	-	[104]
27	Co-MCM-41	-	70	0.1	7	~100	15.5	20.1	-	-	-	[105]
28	Cobalt resinate	-	70	0.1	7	94.5	44.4	40.2	-	-	-	
29	Au-graphene	186.1	60	0.1	24	55.5	7.24	30.2	-	0.7	61.6	[106]
30	CrMCM-41	1150	60	0.1	24	52.2	71.2	11.2	14.2	3.4	-	[107]
						CU	AcPO	BP	CUHP	-	-	
31	CNTs	85.3	80	0.1	8	24.1	1.6	10	88.4	-	-	
32	CuO	-	80	0.1	8	38.5	5.7	21.1	73.2	-	-	[68]
33	CuO	-	80	0.1	8	31.6	2.7	14.2	83.1	-	-	
34	CNTs	20.9	80	0.1	8	16.1	1.6	8.4	90	-	-	
35	NCNTs-0.31 ^c	35.1	80	0.1	8	30.7	5.1	23.9	71	-	-	
36	NCNTs-2.21 ^c	48.9	80	0.1	8	53.9	27.1	57.2	15.7	-	-	[77]
37	NCNTs-3.33 ^c	72.6	80	0.1	8	74.7	40.8	56.1	3.1	-	-	
38	NCNTs-4.36 ^c	52.4	80	0.1	8	72.1	40.5	56.2	3.3	-	-	
39	Co-BTC	-	90	0.4	7	49	-	-	69	-	-	
40	Co5Ni-BTC	-	90	0.4	7	30	-	-	91	-	-	[108]
						α-pinene	V-one	V-ol	V-HP	α-p-O	-	
41 ^a	CNTs	127.8	80	1.5	4	24.6	7.9	6.1	37.9	33.8	-	[95]
42 ^a	NCNTs	155.1	80	1.5	4	54.5	14.1	17.5	15.3	37.8	-	
43	Co(III)-HMS	1071	80	0.1	24	34.2	22	16	-	34	-	[109]
44	MnAlPO-36	-	50	3	8	59	-	-	-	91	-	[110]
45	Co-POM/MIL-101	2050	50	0.1	2	45	27	29	-	-	-	[111]

^a CH₃CN or ^b CH₃COOH or ^c C₃H₆O was used as a solvents; ^d KA oil (Mixture of cyclohexanone and cyclohexanol); ^e (N/N+C) atom%.

2.2.1.3 Oxygenated CNTs

The surface structure of CNTs plays a crucial role in governing their catalytic activity in the oxidation reactions. Introducing oxygen-containing functional groups, such as carboxyl, phenol, carbonyl (ketone), lactone, ether, and anhydride species onto the surface of CNTs (Figure 2.5) significantly influences their activity. Recent studies have shown that oxygen-functionalized CNTs can exhibit appreciable activity in the oxidative dehydrogenation of light alkanes [112,113] and EB [114,115]. In particular, ketonic ($\text{C}=\text{O}$) and hydroxyl/quinone-type functional groups have been proposed as catalytically active sites in the oxidative dehydrogenation reaction [116,117].

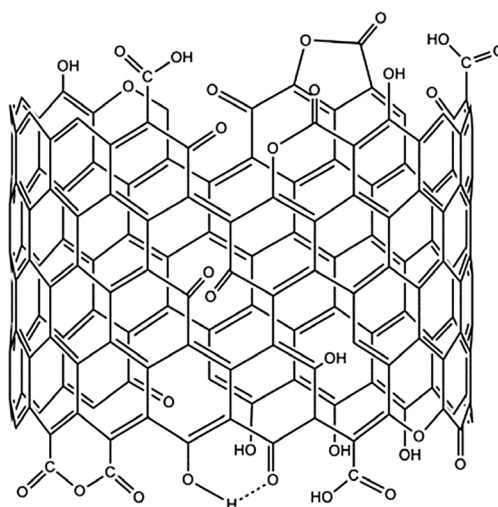


Figure 2.5. Diagrammatic representation of surface-oxidized CNTs with possible functional groups containing oxygen. Reproduced from Ref. [36] with permission from the Royal Society of Chemistry.

Conversely, liquid-phase hydrocarbon oxidation reactions involve a more intricate radical-mediated mechanism compared to dehydrogenation reactions. Consequently, the precise role of oxygen-containing functional groups in CNT-catalyzed liquid-phase oxidation remains equivocal. Yu et al. demonstrated that the introduction of oxygen-containing functional groups and surface defects on CNTs negatively affects catalytic activity in the liquid-phase aerobic oxidation of cyclohexane, owing to electron localization induced by surface oxygen functionalities, which weakens the delocalized π -electrons of CNTs and suppresses π - π interactions with radicals [73]. Consistent with these findings, subsequent studies reported that oxygenated CNTs adversely affect catalytic performance in the liquid-phase aerobic oxidation of EB to AcPO [67], CU to CUHP [68], and cyclohexene to the corresponding ketones and alcohols [86].

Chi et al. investigated the influence of oxygenated and surface-defected CNTs on the aerobic oxidation of CU. Their results demonstrated that oxidized CNTs inhibit CU oxidation, with the deactivation primarily arising from the surface oxygen functionalities. These functional groups act as radical scavengers, capturing reactive radicals and thereby suppressing the propagation of the free-radical chain mechanism responsible for oxidation. In contrast, surface defects alone exhibited only a minor influence on catalytic activity [118]. Additional factors that further constrain the effectiveness of oxygenated CNTs in the liquid-phase aerobic oxidation of hydrocarbons are: (i) the introduction of surface oxygen functionalities significantly modifies the wettability of CNTs, increasing their polarity and hydrophilicity, consequently limiting effective interactions with nonpolar hydrocarbons [119,120]. (ii) These surface functional groups can introduce diffusion resistance, reducing the accessibility and effective affinity of CNT surfaces towards organic molecules [120,121]. Table 2.4 summarizes the catalytic performance of oxygenated CNTs in the liquid-phase aerobic oxidation of various hydrocarbons. The data indicate that increasing the surface concentration of oxygen-containing functional groups leads to a progressive decline in catalytic activity. In contrast, thermal annealing of oxidized CNTs can remove these oxygen functionalities and repair the surface defects, thereby restoring the catalytic performance.

Table 2.4. Influence of oxygen-containing functional groups on the catalytic performance of CNTs in liquid-phase aerobic oxidation of hydrocarbons.

Entry	Catalyst	Solvent	BET (m ² ·g ⁻¹)	T (°C)	P (MPa)	t (h)	Surface oxygen- containing functional groups			Substrate conversion (%)	Product selectivity (%)					Ref.
							-OH	-C=O	-COOH		EB	AcPO	PEA	PEHP	BA	BzA
1	CNTs -HNO ₃ -5 ^a	CH ₃ CN	159	155	1.5	4	9.6 ^c	5.9 ^c	4.1 ^c	30.5	53.4	15.9	25.4	8.6	16.6	[67]
2	CNTs-HNO ₃ -9 ^a	CH ₃ CN	165	155	1.5	4	8.7 ^c	5.1 ^c	4.6 ^c	25.7	42.1	26.5	10.2	12.8	8.4	
3	CNTs-HNO ₃ -15 ^a	CH ₃ CN	209	155	1.5	4	9.7 ^c	6.9 ^c	7.2 ^c	6.7	30.6	26.3	23.2	19.9	0.0	
4	CNTs-HNO ₃ -15 ^a -600 ^b	CH ₃ CN	259	155	1.5	4	-	-	-	14.6	36.1	28.3	17.7	14.0	3.9	
5	CNTs-HNO ₃ -15 ^a -900 ^b	CH ₃ CN	229	155	1.5	4	-	-	-	17.7	49.6	18.7	13.4	9.4	8.9	
											Cyclohexane	A	K	-	-	AA
6	CNTs-HNO ₃ -0 ^a	C ₃ H ₆ O	127.8	125	1.5	8	0.30 ^d	0.18 ^d	0.12 ^d	34.3	40.4 ^e	-	-	-	52.4	[73]
7	CNTs-HNO ₃ -0.5 ^a	C ₃ H ₆ O	130.8	125	1.5	8	0.52 ^d	0.72 ^d	0.33 ^d	32.6	33.1 ^e	-	-	-	48.5	
8	CNTs-HNO ₃ -4 ^a	C ₃ H ₆ O	136	125	1.5	8	0.66 ^d	1.10 ^d	0.55 ^d	23.8	36.9 ^e	-	-	-	47.5	
9	CNTs-HNO ₃ -8 ^a	C ₃ H ₆ O	149.4	125	1.5	8	0.59 ^d	1.13 ^d	0.97 ^d	15.8	39.2 ^e	-	-	-	46.7	
10	CNTs-HNO ₃ -8 ^a -900 ^b	C ₃ H ₆ O	-	125	1.5	8	-	-	-	22.4	32.6 ^e	-	-	-	55.5	
11	CNTs-HNO ₃ -8 ^a -1100 ^b	C ₃ H ₆ O	-	125	1.5	8	-	-	-	25.8	33.5 ^e	-	-	-	47.7	

										Cyclohexene	Cy-one	Cy-ol	Cy-HP	Ep-Cy	Cy-diol
12	N-CNTs-HNO ₃ -0 ^a	CH ₃ CN	88.3	80	1	4	0.26 ^d	0.19 ^d	0.10 ^d	59.0	41.1	11.2	27.3	5.9	1.3
13	N-CNTs-HNO ₃ -0.5 ^a	CH ₃ CN	153.9	80	1	4	0.47 ^d	0.69 ^d	0.34 ^d	52.6	31.6	9	31.1	5.0	0.7
14	N-CNTs-HNO ₃ -4 ^a	CH ₃ CN	176.8	80	1	4	0.73 ^d	1.15 ^d	0.65 ^d	44.9	32.1	8.1	45.5	4.8	1.5
15	N-CNTs-HNO ₃ -7 ^a	CH ₃ CN	179.7	80	1	4	0.74 ^d	1.22 ^d	1.03 ^d	35.6	30	7.8	43.1	4.6	1.5
16	N-CNTs-HNO ₃ -7 ^a -900 ^b	CH ₃ CN	207.1	80	1	4	-	-	-	52.1	34.2	7.3	36.2	6.1	1.6
17	N-CNTs-HNO ₃ -7 ^a -1100 ^b	CH ₃ CN	248.7	80	1	4	-	-	-	55.6	36.8	6.6	37.8	5.8	1.6
										CU	-	-	CUHP	-	-
18	CNTs-HNO ₃ -2 ^a	-	104.2	80	0.1	8	4.3 ^c	7.3 ^c	4.9 ^c	1.2	-	-	91.1	-	-
19	CNTs-HNO ₃ -4 ^a	-	116	80	0.1	8	13.3 ^c	5.9 ^c	5.2 ^c	0.8	-	-	90.2	-	-
20	CNTs-HNO ₃ -2 ^a -600 ^b	-	122.3	80	0.1	8	-	-	-	13.1	-	-	88.0	-	-
21	CNTs-HNO ₃ -2 ^a -900 ^b	-	141.5	80	0.1	8	-	-	-	21.6	-	-	86.0	-	-
										α -pinene	V-one	V-ol	V-HP	α -p-O	-
22	N-CNTs-HNO ₃ -0 ^a -60 ^b	CH ₃ CN	88.3	80	1.5	4	0.26 ^c	0.19 ^c	0.10 ^c	54.5	14.2	17.5	15.3	37.8	-
23	N-CNTs-HNO ₃ -7 ^a -60 ^b	CH ₃ CN	179.7	80	1.5	4	0.74 ^c	1.22 ^c	1.03 ^c	51.0	17.1	13.8	16.4	40.6	-
24	N-CNTs-HNO ₃ -7 ^a -900 ^b	CH ₃ CN	207.1	80	1.5	4	-	-	-	61.4	18.7	13.4	15.9	41.1	-

[86]

[68]

[95]

^a Reflux time (h) in HNO₃. ^b Annealing temperature (°C) of oxygenated CNTs. ^c Data collected using XPS analysis (%). ^d Data collected using Boehm titration (mmol g⁻¹). ^e KA oil (Mixture of cyclohexanone and cyclohexanol).

2.2.1.4 Metal-modified CNTs

In liquid-phase hydrocarbon oxidations, catalytic performance is largely influenced by surface electron-transfer processes on solid catalysts [69,122]. Taking these considerations into account, the activity of CNTs can be further enhanced by promoting surface electron transfer via the incorporation of metals, such as Fe, Co, Mn, etc. [123–125]. A wide range of metal-based compounds have further been explored, including metallic salts of Cu(II), Co(II), Mn(II) [126], metal oxides (e.g., Mn_3O_4 [127], MnO_2 [128]), as well as metal complexes including Pt- and Pd-based pincer complexes [129], Mn (III) porphyrins [130]. These compounds can be integrated with CNTs via covalent or noncovalent interactions.

These metals and metal-based compounds are known to promote the decomposition of intermediate hydroperoxides into the corresponding alcohols and ketones, thereby enhancing activity during these processes [131–135]. Moreover, several studies have reported a substantial enhancement in catalytic activity when metal nanoparticles are encapsulated or confined within CNT channels (Figure 2.6) [136,137], or through bonding to the carbon via metal-nitrogen-carbon (M-N-C) [125,138,139]. These configurations promote strong metal-support interactions, giving rise to a synergistic effect between the metal species and the CNTs [78,139].

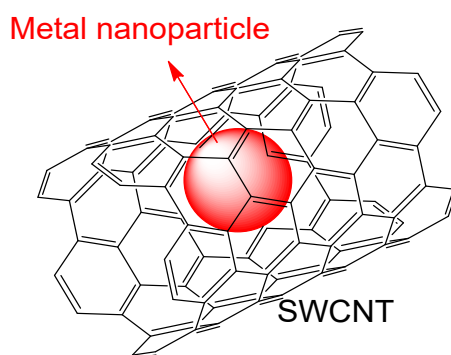


Figure 2.6. Schematic of a metal nanoparticle encapsulated/confined in a SWCNT.

The concentric graphene walls of CNTs form nanoscale channels with diameters spanning from sub-nanometer dimensions to several tens of nanometers, creating a highly confined environment for catalytic processes and nanocatalyst stabilization [140]. Such nanoscale confinement has been widely recognized as advantageous for catalytic applications, including hydrocarbon oxidation reactions, where metal nanoparticles confined within CNT channels often exhibit superior activity [141]. This improvement can be attributed to confinement of metal within CNTs, which improves metal-CNT interactions via curvature-

induced distortion of the graphene walls' sp^2 hybridization. This deviation from planarity drives a redistribution of π -electron density from the concave inner surface toward the convex outer surface, generating an electron-deficient interior and an electron-enriched exterior without changing the external surface area [136]. Accordingly, studies have revealed that increased electron mobility in CNTs has increased their catalytic activity [73].

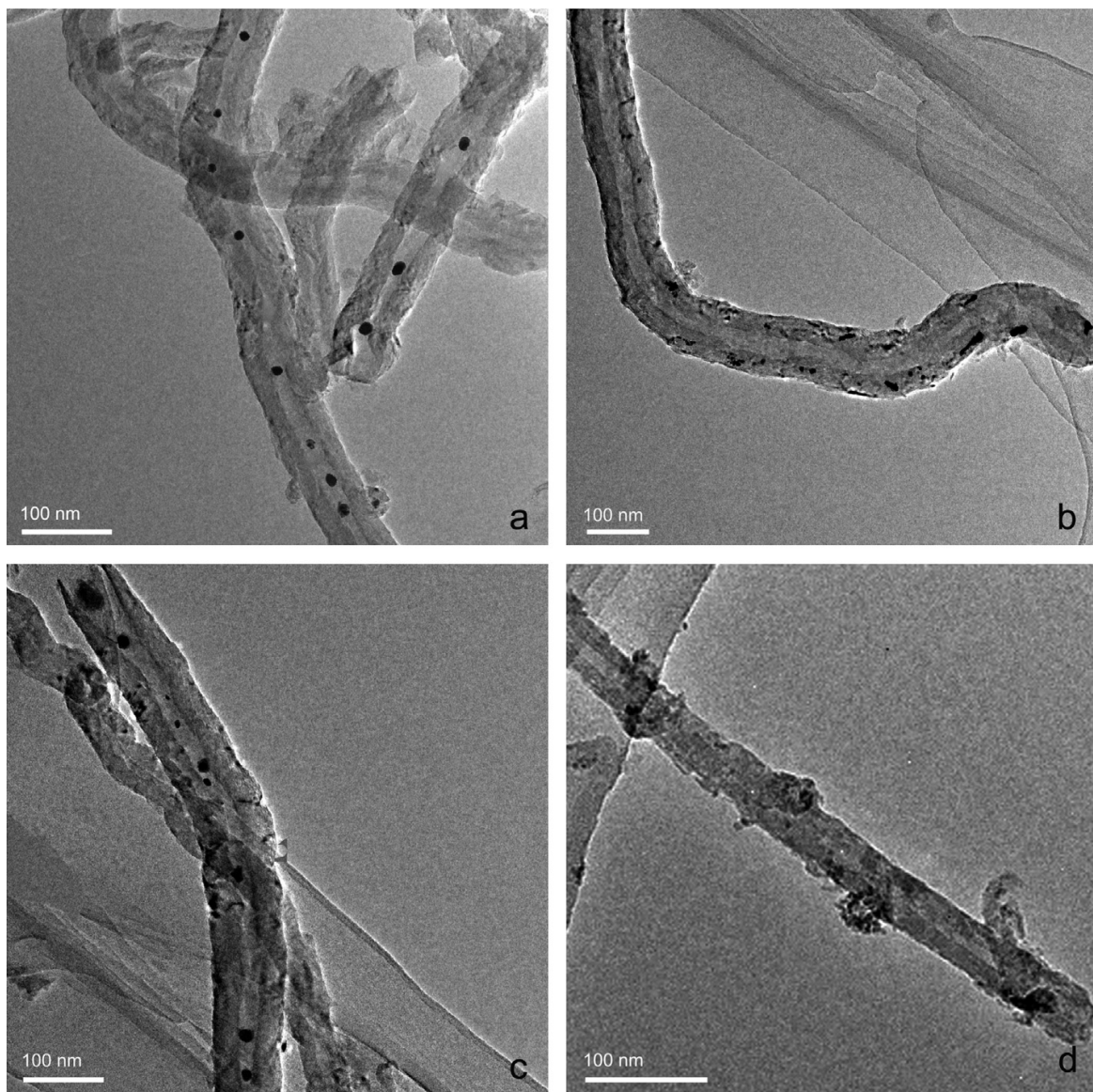


Figure 2.7. TEM images of (a) Co@CNTs (in), (b) Co@CNTs (out), (c) recycle of Co@CNTs (in), and (d) recycle of Co@CNTs (out) [142]. By permission from Elsevier, copyright 2014.

Employing this confinement strategy, Yang et al. [122] examined the activity of Fe nanowires confined within CNTs for the aerobic oxidation of cyclohexane. The Fe CNTs displayed remarkable performance, with maximum activity at an Fe loading of 19 wt.%;

higher loadings induced surface defects that hindered electron transfer and reduced activity. The catalytic activity increased exponentially with decreasing work function. Additionally, the confined Fe nanowires exhibited high magnetic saturation, allowing facile catalyst separation, while the recyclability test showed stable performance without activity loss. Similarly, Luo et al. [124] also demonstrated the effectiveness of Fe nanowire-filled CNTs in the aerobic oxidation of EB to AcPO. The enhanced activity arises from improved electron transfer enabled by nanowire confinement within the CNTs. Optimal performance was observed at ~17 wt.% Fe, while higher Fe loading (~22 wt.%) reduced the activity, which could be due to defect formation and/or an increased work function that hinders charge transfer. Fe@CNTs also facilitated the decomposition of PEHP to AcPO and could be easily magnetically recovered and reused for 6 cycles without noticeable loss of activity.

Researchers have shown that encapsulated metal nanoparticles within CNTs can promote the decomposition of the intermediate hydroperoxide into the corresponding products, thereby significantly enhancing catalytic performance by enabling more efficient electron transfer from the metal nanoparticles to the CNT [123]. This enhanced electron transport could increase the local electron density at the CNT surface and lower the effective work function [128,130], thereby promoting hydroperoxide decomposition via π - π interactions with the graphene layers, ultimately improving overall catalytic performance.

Shi et al. investigated CNT-confined Co nanoparticles as nanoreactors for styrene epoxidation employing molecular oxygen and compared their performance with Co nanoparticles deposited on the external CNT surface (Figure 2.7). The Co@CNT(in) exhibited dramatic catalytic performance, achieving >99% styrene conversion with 93% epoxide selectivity within one hour, corresponding to a product yield of 93%. In contrast, the Co@CNT(out) afforded only ~50% yield under identical conditions. Additionally, the nanoreactors were readily recovered employing an external magnet and reused for up to 3 cycles without any significant loss of activity [142].

Cobalt encapsulated within graphitic N-doped CNT (Co@CGNs, Figure 2.8) has shown elevated catalytic performance in the solvent-free selective aerobic oxidation of EB to AcPO, achieving 68.1% EB conversion with 93.2% selectivity towards AcPO. The catalyst also demonstrated broad applicability in the oxidation of various arylalkanes, with enhanced performance attributed to the synergistic interaction between metallic Co- and N-doped CNTs [78]. Similarly, Xiang et al. reported that nitrogen doping further enhances the activity of Co-encapsulated CNTs, delivering 78.3% EB conversion with 93.8% AcPO selectivity.

Their results revealed that the nitrogen source plays a key role in promoting the growth of bamboo-shaped CNTs, while Co-N_x in Co@NCNTs-X served as the active sites due to the synergistic interaction between pyridinic N and metallic Co [143]. The resulting Co-N_x coordination stabilizes Co nanoparticles, suppressing agglomeration and ensuring uniform dispersion. This metal-nitrogen interaction also modifies the spin, charge, and π -electron densities of adjacent carbon atoms, generating additional active sites and facilitating the adsorption and desorption of intermediates, thereby enhancing overall catalytic activity [144–147].

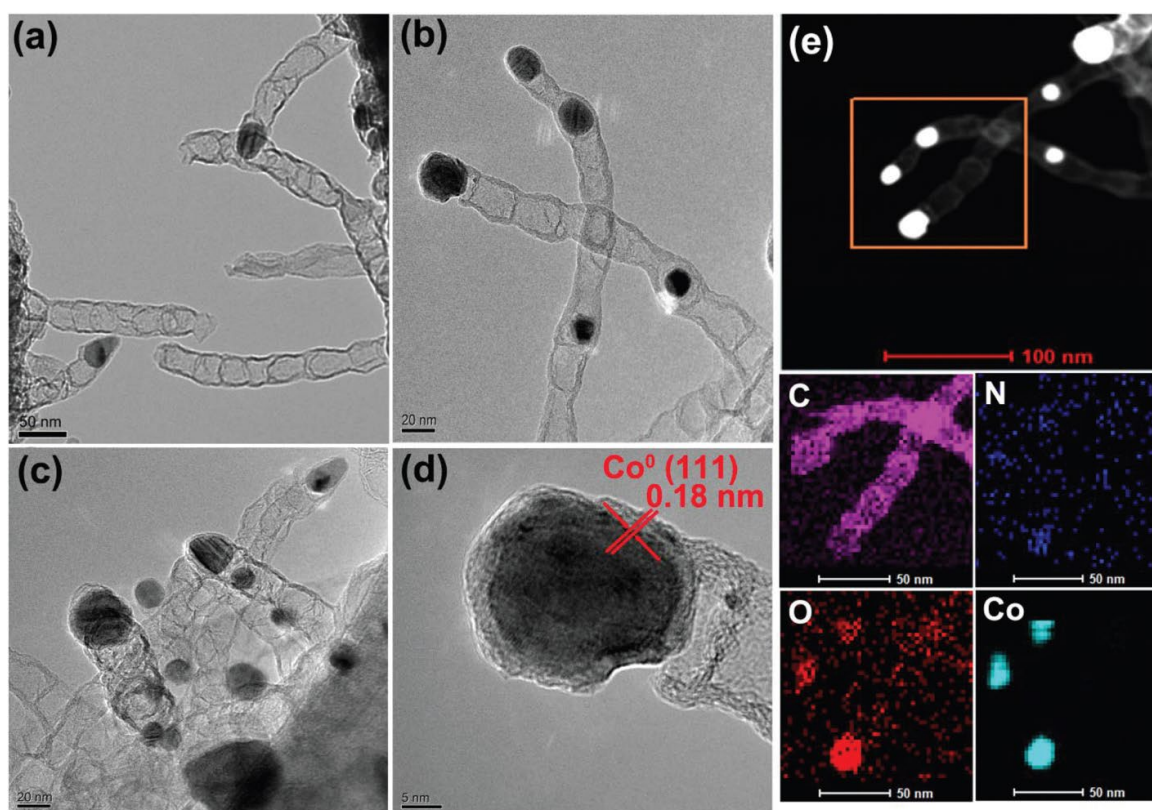


Figure 2.8. HRTEM (a-d), HAADF image, and elemental mappings (e) of cobalt-encapsulated CGNs. Reproduced from Ref. [78] with permission from the Royal Society of Chemistry.

The reaction mechanism of EB oxidation over CNTs and Co-confined CNTs (Co@CNTs) was elucidated through empirical studies and kinetic modeling. Co@CNTs demonstrated higher activity than pristine CNTs due to superior interfacial charge transfer, with homolytic cleavage of PEHP identified as the rate-determining step in AcPO formation. Kinetic simulations confirmed AcPO as the dominant product, as its addition has little effect on the reaction rate. In contrast, PEA could have suppressed oxidation by quenching RO[•] radicals, thereby inhibiting PEHP decomposition and reducing the overall catalytic efficiency [76].

This behavior is consistent with the known radical-quenching effect of alcohols in aerobic hydrocarbon oxidation systems [148–151].

Peckh et al. [126] evaluated carboxylated MWCNTs functionalized with Co(II), Cu(II), and Mn(II) salts for the aerobic oxidation of EB under solvent-free conditions using NHPI as a cocatalyst. Among the tested systems, Cu(II) functionalized MWCNTs displayed the highest activity, achieving 27% EB conversion with 66% selectivity towards AcPO, outperforming Co(II)- and Mn(II)-based catalysts. In a related study, Chen et al. developed a Co@N/Co-CNT catalyst for the solvent-free aerobic oxidation of toluene to BzA, consisting of encapsulated Co nanoparticles and atomically dispersed CoN₄ sites embedded within N-doped CNTs. The catalyst achieved 33.5% toluene conversion with 91.6% selectivity towards BzA, operating without a radical initiator, with CoN₄ moieties identified as the primary active sites [152]. Building on the concept of metal immobilization on CNTs, Machado et al. reported Pt and Pd complexes covalently immobilized on superparamagnetic, amine-functionalized SWCNTs for cyclohexane oxidation. The Pd-based system exhibited better performance, achieving 22.86% conversion and 3.3% selectivity under solvent-free aerobic conditions [129].

Transition metal oxides such as MnO₂ [128], Fe₂O₃, Cr₂O₃ [135], and Mn₃O₄ [153,154] have been widely explored for liquid-phase oxidation reactions, owing to their variable valence states and redox flexibility. In addition, manganese carbonate (MnCO₃) [155] has been investigated in a related oxidation system. Feng et al. supported Mn₃O₄ on CNTs and demonstrated enhanced solvent-free oxidation of toluene using dioxygen, achieving 24.6% conversion with 90.5% selectivity towards BzA and BA. The catalyst exhibited higher activity than either Mn₃O₄ or CNTs alone and showed good stability and recyclability [127]. Similarly, Deng et al. reported MnO₂ supported on CNTs as a catalyst for aerobic CU oxidation. The catalyst displayed 73.44% CU conversion with a 59.06% selectivity towards 2-phenyl-2-propanol (PP), significantly higher than either component alone. DFT analysis confirmed that CNT-supported MnO₂ promotes hydroperoxide decomposition through synergistic metal oxide-CNT interactions [156]. Although oxygen-containing functional groups on CNTs may localize electrons and diminish intrinsic activity [73,86,118], strong synergistic interactions between TMOs and CNTs could have compensated for these effects and improved catalytic performance. A thorough comparison of metal-modified and/or functionalized CNTs with pristine CNTs and other metal-based catalysts is presented in Table 2.5.

Table 2.5. Comparison of the catalytic activities of CNTs with those of metal-functionalized CNTs in the liquid phase oxidation of hydrocarbons using dioxygen as an oxidant.

Entry	Catalyst	Metal Content (wt.%)	BET (m ² g ⁻¹)	T (°C)	P (MPa)	t (h)	Substrate conversion (%)	Product selectivity (%)					Ref.
							Cyclohexane	K	A	CHHP	AA	-	
1 ^a	CNTs	5.3	34.8	125	1.5	8	19.1	17.7	24.6	-	46.3	-	[122]
2 ^a	Fe-filled CNTs	12.3	34.9	125	1.5	8	25.2	11	19.3	-	58.6	-	
3 ^a	Fe-filled CNTs	19	32.7	125	1.5	8	36.7	9.9	19.1	-	60.5	-	
4 ^a	Fe-filled CNTs	19.7	26.9	125	1.5	8	14.7	17.1	21.3	-	49.1	-	
5	SWCNTs	-	-	150	1	6	11.63	82.54 ^c		-	-	-	
6	SWCNTs/Pd	-	-	150	1	6	22.86	93.27 ^c		-	-	-	[129]
7	SWCNTs/Pt	-	-	150	1	6	20.70	95.17 ^c		-	-	-	
							EB	AcPO	PEA	PEHP	BA	BzA	
8	CNTs	0	145.6	150	2	3	13.3	14.7	16.6	67.8	-	-	
9	Co@C/CNTs	10	156.19	150	2	3	51.7	79.6	14.8	0.5	-	-	
10	Co@C/SiO ₂	-	26.73	150	2	3	14.7	26.2	12.7	60.2	-	-	[123]
11	Co@C/Al ₂ O ₃	-	124.79	150	2	3	11.3	19.0	13.4	66.8	-	-	
12	Co@C/AC	-	278.01	150	2	3	11.5	18.8	23.4	56.8	-	-	
13 ^b	Fe@CNTs	12.8	30.1	155	1.5	3	31.8	59.8	5.4	0.8	11.8	22.7	
14 ^b	Fe@CNTs	17.3	25.9	155	1.5	3	36.8	60.2	5.9	0.6	12.2	21.1	[124]
15 ^b	Fe@CNTs	21.8	18.5	155	1.5	3	25.2	53.5	11.2	5.9	12.9	16.5	
16 ^b	Fe@CNTs (6 th cycle)	16.9	-	155	1.5	3	36.7	59.5	7.8	0.2	9.8	22.7	
17	Co	-	-	120	0.8	5	22.3	80.9	17	-	2.1	-	[78]
18	CNTs	-		120	0.8	5	12.7	87.4	12	-	0.6	-	

19	Co@N-CNTs	-	232	120	0.8	5	68.1	93.2	6.8	-	-	-	
20	Fe/CNTs	-	-	120	0.8	5	16.2	72.8	24.8	-	2.4	-	
21	Ni/CNTs	-	-	120	0.8	5	12.4	83	17	-	-	-	
22	Co/C	-	-	120	0.8	5	49.7	84.7	14.8	-	0.5	-	
23	Co@N-CNTs		220	120	0.8	5	65.9	92.2	-	-	-	-	[143]
24	MWCNT-COOH	-	-	80	0.1	6	6	65	17	-	18	-	
25	MWCNT-COO-Co	-	-	80	0.1	6	18	69	30	-	1	-	
26	MWCNT-COO-Cu	-	-	80	0.1	6	27	66	28	-	6	-	[126]
27	MWCNT-COO-Mn	-	-	80	0.1	6	13	66	27	-	7	-	
							Toluene	-	BAL	-	BA	BzA	
33	Co@N/Co-CNTs	-	419	140	3	15	28	-	0.2	-	9.8	90	
34	Co@N/Co-CNTs	-	419	140	3	24	33.5	-	-	-	-	91.6	[152]
35	CNTs	-	341	90	15 ^d	12	0.65	-	41.56	-	58.44	-	
36	Mn ₃ O ₄	-	-	90	15 ^d	12	3.54	-	40.47	-	58.51	-	[127]
37	Mn ₃ O ₄ /CNTs	-	269	90	15 ^d	12	24.63	-	43.51	-	46.98	-	
							CU	AcPO	PP	CUHP	-	-	
38	CNTs	-	166.59	80	25 ^d	7	26.8	2.32	17.68	80	-	-	
39	MnO ₂ /CNTs	-	222.29	80	25 ^d	7	73.44	30.63	59.06	10.3	-	-	
40	MnO ₂ /CNTs (5 th cycle)	-	-	80	25 ^d	7	62.55	6.58	39.62	53.79	-	-	[156]

^a C₃H₆O or ^b CH₃CN was used as a solvent; ^c KA oil (Mixture of cyclohexanone and cyclohexanol). ^d Oxygen flow rate in cm³·min⁻¹.

2.2.1.5 Influence of CNT purity

Conventional CNT synthesis typically produces randomly oriented, closed-ended structures and requires high temperature ($>700\text{ }^{\circ}\text{C}$), which often introduces residual metallic impurities that can significantly influence catalytic efficiency [157]. These impurities originate from the metal catalysts used during synthesis and must therefore be carefully assessed and minimized. Zeynalov et al. [70] demonstrated the role of CNT impurities in liquid-phase aerobic hydrocarbon oxidation using MWCNTs synthesized by thermal pyrolysis of cyclohexane. Kinetic analysis of CU oxidation showed that residual metallic species embedded in the CNT structure, originating from synthesis catalysts and typically present as acid-resistant metal carbides, significantly promote oxidation activity. These metal-containing impurities enable parallel reaction pathways involving both CNT surfaces and metal sites, including metal-assisted hydroperoxide decomposition. As a result, branched radical chain processes are established, suppressing radical trapping by the CNTs and leading to an autocatalytic oxidation regime.

Liquid-phase aerobic oxidation of hydrocarbons is highly sensitive to even trace contaminants, which can either suppress radical formation by acting as a radical scavenger or, conversely, promote oxidation by accelerating key reaction steps. For instance, the presence of a small amount of zinc salts (ZnCl_2 and ZnBr_2) completely inhibited CNT-catalyzed aerobic oxidation of CU ($80\text{ }^{\circ}\text{C}$, 8 h). Mechanistic studies suggested that Zn^{2+} might suppress oxidation via two pathways: first, by strongly coordinating reactive oxygen species generated on the CNT surface, thereby increasing the activation barrier; and second, by interacting with alkyl and peroxy radicals ($\text{RO}^{\bullet}$ and $\text{ROO}^{\bullet}$), which disrupts free-radical chain propagation [158].

In contrast, CU oxidation under similar conditions ($80\text{ }^{\circ}\text{C}$, 8 h) was significantly accelerated by introducing trace amounts of $\text{Cu}(\text{OAc})_2$ (1 ppm relative to CNTs) in the presence of CNTs and molecular oxygen [159]. The CU conversion increased from 38.5% to 54.2%, while alcohol selectivity rose from 25.1% to 44.7%, indicating that even minute quantities of Cu species can significantly influence CNT activity and product distribution. This promotional effect was attributed to residual chloride species adsorbed on the CNT surface during HCl washing, a common pretreatment step. Under reaction conditions, these surface-bound Cl species interact

with $\text{Cu}(\text{OAc})_2$ to form Cu-Cl species, which facilitate hydroperoxide decomposition and consequently enhance catalytic performance.

Given the pronounced sensitivity of CNT-catalyzed aerobic oxidation to trace contaminants and surface chemistry, the choice of CNT purification protocol is of paramount importance. Although several purification strategies have been proposed, acid treatment remains the most widely adopted method [160–162]. This approach typically involves oxidation with concentrated acids, such as HNO_3 or mixed HNO_3 - H_2SO_4 systems. However, acid treatment is often accompanied by undesirable structural modifications, including opening of CNT ends, shortening of nanotubes, disruption of the graphitic frameworks, and the introduction of oxygen-containing functional groups (-OH, -COOH, and -C=O) on the CNT surface [163]. As discussed above, these oxygen functionalities adversely affect catalytic performance in liquid-phase aerobic hydrocarbon oxidation by altering surface electronic properties and suppressing efficient radical-mediated reaction pathways.

2.2.2 NHPI as a catalyst for liquid-phase oxidation of hydrocarbons

NHPI has emerged as an efficient organocatalyst for free-radical-mediated organic transformations, particularly in liquid-phase aerobic oxidation of hydrocarbons, while mitigating many drawbacks associated with conventional metal-based systems [22,164–171]. Grochowski and co-workers first recognized the catalytic potential of NHPI in 1977, who demonstrated its ability to accelerate the reaction between diethyl azodicarboxylate (DEAD) and ethers [172]. Although the uncatalyzed reaction proceeded at elevated temperatures, the presence of NHPI significantly shortened the reaction time, confirming its catalytic effect. The authors proposed that NHPI generated a reactive N-oxyl species, later identified as the phthalimide-N-oxyl (PINO) radical, which initiated hydrogen abstraction from the ether substrate, thereby propagating a radical chain mechanism. The radical nature of the process was supported by inhibition experiments using radical scavengers such as hydroquinone and tetrachloro-*p*-benzoquinone. Subsequent studies by Masui and co-workers in 1983 established NHPI as an effective electrochemical mediator for the oxidation of secondary alcohols to ketones [173]. Later, in 1995, Ishii and colleagues pioneered the use of NHPI under non-electrochemical conditions, demonstrating its remarkable catalytic efficiency in the oxidation of alkanes and alcohols with molecular oxygen [174]. Since then, NHPI has become a

cornerstone in aerobic oxidation chemistry and other C-H functionalization reactions [22,164–171].

NHPI is a relatively inexpensive and non-toxic compound [175,176]. It is the precursor to the hydrogen-abstracting species known as the PINO radical, which can effectively abstract hydrogen atoms, approximately 2 to 20 times faster compared to peroxy radicals in hydrocarbon oxidation reactions [22]. The reaction mechanism associated with NHPI-catalyzed reactions has been extensively investigated [165,166,171,177–181] and is illustrated in Figure 2.9 using the aerobic oxidation of hydrocarbons as a representative example. The crucial step in initiating these reactions is the homolytic dissociation of the NO-H bond in NHPI, leading to the formation of the PINO radical, an excellent hydrogen-atom abstractor in the HAT processes. Various compounds, for instance, transition metal salts, peroxides, azo compounds, quinones, and enzymes, have been applied to generate the PINO radical from NHPI [166,169,170]. The produced PINO radical abstracts a hydrogen atom from the hydrocarbon substrate, producing the carbon-centered radical and restoring NHPI. The carbon-centered radical then reacts with nearby diffused oxygen to produce a peroxy radical, and this peroxy radical can abstract a hydrogen atom from NHPI, taking advantage of NHPI's effectiveness as an impressive hydrogen donor, thereby regenerating PINO and yielding hydroperoxides while allowing the cycle to continue.

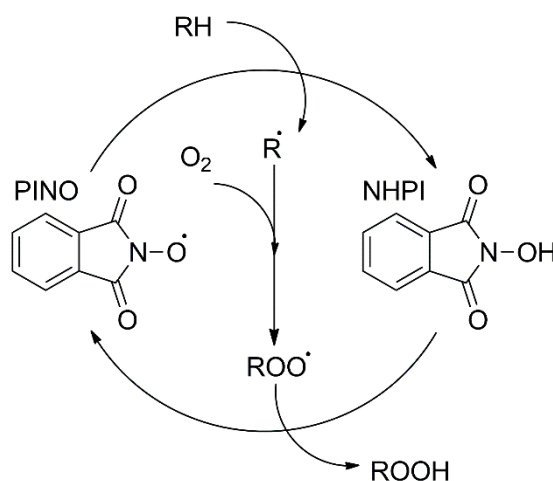


Figure 2.9. NHPI-catalyzed oxidation mechanism. Redrawn from ref. [182].

The activity of NHPI and its descendant PINO radical is associated with the O-H bond dissociation energy (BDE) of NHPI, which is approximately $88.1 \text{ kcal} \cdot \text{mol}^{-1}$ [182]. This value

is comparable to the O-H BDE of hydroperoxides. Consequently, the enhanced reactivity of the PINO radical relative to peroxy radicals can be attributed to a more favorable polar effect during hydrogen atom abstraction by the nitroxyl radical [183]. Additionally, NHPI acts as an efficient hydrogen donor, thanks to the relatively high rate constant for HAT ($k_{NHPI} = 7.2 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$) [182]. This property facilitates sustained chain propagation by intercepting peroxy radicals before termination, subsequently augmenting the performance of the HAT process. Despite these favorable kinetics and mechanistic features, NHPI-catalyzed reactions also suffer from several practical limitations, including (i) poor solubility in apolar or weakly polar hydrocarbons, (ii) the absence of efficient strategies for its recovery and recyclability, and (iii) the limited thermal stability of both NHPI and its corresponding PINO radical at temperatures above 80 °C.

In light of these constraints, NHPI-catalyzed hydrocarbon oxidation reactions are commonly conducted in polar solvents, such as acetonitrile (MeCN), acetic acid (AcOH), and benzonitrile (PhCN), to overcome the inherently poor solubility of NHPI in nonpolar hydrocarbons [184–187]. Nonetheless, the use of solvents that are hydrogen-bond acceptors, such as acetic acid and acetonitrile, forms complexes with NHPI, which subsequently reduces the catalytic performance [182,188]. Conversely, it has been demonstrated that only tiny amounts of MeCN can promote the autoxidation process in apolar media by disrupting hydrogen-bond-driven self-aggregation of NHPI-type catalysts, thereby releasing the catalytically active monomeric species and favoring the HAT step. This indicates that, beyond mere solubility, the aggregation state of the catalyst is a crucial factor governing HAT efficiency under homogenous, low-polarity conditions [189]. Nevertheless, reliance on polar solvents constrains the practical implementation of NHPI-based catalysts in industrial oxidation processes [190]. Consequently, from both economic and environmental perspectives, considerable efforts have been made to conduct NHPI-catalyzed oxidation reactions under solvent-free conditions by enhancing NHPI's solubility in nonpolar and/or weakly polar hydrocarbons. These strategies generally fall into three categories: i) structural modification of the NHPI framework to increase lipophilicity, ii) formation of solubilizing micelles or higher-order aggregates, and iii) incorporation of suitable additives into the reaction system.

2.2.2.1 NHPI and NHPI-derived organocatalysts

Ishii and colleagues disclosed for the first time the use of NHPI as a catalyst under non-electrochemical conditions for the aerobic oxidation of a wide range of organic compounds [174]. They subsequently explored its remarkable catalytic activity, together with metal salts, in the aerobic oxidation of various hydrocarbons [191–193]. The use of metal salts significantly enhanced the catalytic performance of NHPI by promoting the generation of the active PINO radical from NHPI. Furthermore, the metallic salts also act as a catalyst for the decomposition reaction of the intermediate hydroperoxides. For instance, the aerobic oxidation of toluene conducted employing NHPI (10 mol%) and $\text{Co}(\text{OAc})_2$ (0.5 mol%) in AcOH at room temperature and pressure yields 81% BzA and 2% BA [192]. On the other hand, NHPI-catalyzed oxidations of alkylbenzenes and hydroaromatic compounds with molecular oxygen have yielded hydroperoxides at higher yields [194].

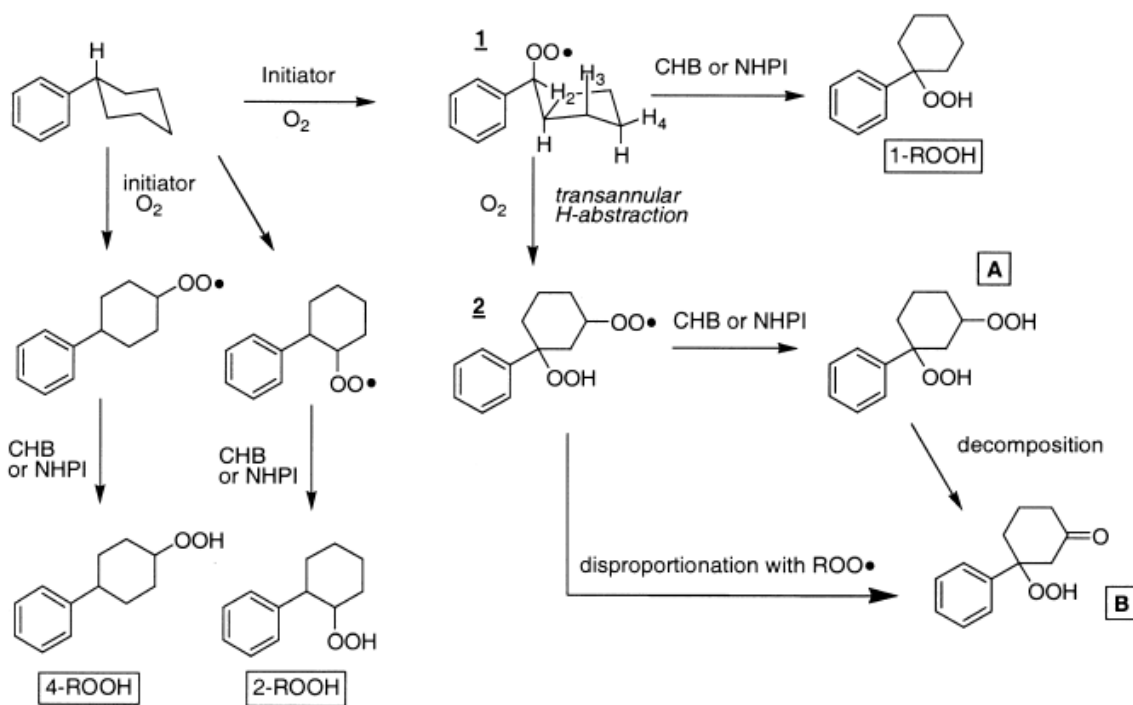


Figure 2.10. Oxidation products of cyclohexylbenzene [195]. By permission from Elsevier, copyright 2002.

Sheldon et al. [195] demonstrated that NHPI-catalyzed oxidation can achieve elevated hydroperoxide selectivity using appropriate organic hydroperoxide initiators. In a solvent-free system, the aerobic oxidation of cyclohexylbenzene (100 °C, 0.1 MPa O_2 , 8 h) to

cyclohexylbenzene-1-hydroperoxide (CHBHP) achieved 32% conversion with 98% selectivity employing 0.5 mol% NHPI and 2 mol% CHBHP. Higher NHPI loading provided no additional benefit; this may be due to its limited solubility. The remarkable selectivity was attributed to site-selective hydrogen abstraction at the 1-position via a transannular mechanism (Figure 2.10). On the other hand, the azo initiator showed significantly lower activity and selectivity, whereas CHBHP maintained high selectivity even at elevated temperatures.

In the corresponding study, the solvent-free oxidation of CU and EB was investigated using a combined NHPI/alkyl hydroperoxide [196]. For CU oxidation, the conversion increased from 27% to 37% as the NHPI loading increased from 0% to 0.5%. Additionally, the selectivity towards CUHP also increased from 84% to 94% (3 mmol of CUHP, 100 °C, 10 bar, 100 cm³/min flow rate of 8% O₂, 5.5 - 6 h). Similarly, the autoxidation of EB (115 °C, 1 atm O₂, 8 h) was significantly enhanced when NHPI (1 mol%) was used as a catalyst, with PEHP (0.1 mol%) as an initiator; a maximum conversion of 12% was achieved for EB, with an 89% selectivity towards PEHP. The lower conversion observed for EB compared to CU was attributed to differences in C-H bond reactivity, as EB undergoes oxidation at a secondary C-H position, whereas CU is oxidized at a more reactive tertiary C-H position.

Koshel et al. [197] reported that NHPI and its 3- and 4-methyl-substituted derivatives significantly enhance the solvent-free liquid-phase oxidation of CU at 110-130 °C, achieving 40-50% conversion within 2-2.5 h while maintaining elevated hydroperoxide selectivity (~90%). In a subsequent study on solvent-free CU oxidation, Koshel and colleagues [198] employed NHPI (2.7 wt.%) at 120 °C for 1 h. They observed that increasing the oxygen pressure from 0.0170 MPa (air) to 0.1013 MPa (pure O₂) enhanced the rate of AIBN-initiated oxidation by a factor of 1.6. In contrast, the addition of NHPI led to a 3.7-fold rate enhancement under comparable conditions.

Sapunov et al. [199] examined the solvent-free liquid-phase oxidation of *p*-cymene employing NHPI, investigating the reaction mechanism and kinetics in the range of 80-120 °C. NHPI significantly improved the selectivity for hydroperoxide (95%) at a *p*-cymene conversion of 25-30%. Kinetic modeling confirmed the effectiveness of NHPI, which originates from the formation and efficient regeneration of the PINO radical, which prolongs radical chain propagation and results in higher reaction rates and higher hydroperoxide selectivity compared

with metal-based catalysts. Extending their mechanistic study, Sapunov et al. [200] further investigated the solvent-free liquid-phase aerobic oxidation of CU using NHPI. Their findings revealed that higher NHPI concentration and elevated temperatures increase CU conversion while maintaining elevated hydroperoxide selectivity, with approximately 34.4% CUHP remaining after 30 min, even at 120-130 °C, indicating limited CUHP decomposition. Kinetic modeling showed that NHPI governs chain initiation by generating a steady-state concentration of PINO radicals through interaction with oxygen, with the initiation rate primarily controlled by the reaction between PINO radicals and the hydrocarbon to form alkyl and peroxy radicals. Consistent with these findings, Frolov et al. [201] investigated the aerobic oxidation of *p*-tert-butylcumene using NHPI and developed a kinetic model that effectively described the time-dependent evolution of reaction components. Their analysis confirmed that NHPI promotes the conversion of peroxy radicals into intermediates, thereby suppressing quadratic chain termination and reducing side-product formation, while simultaneously enhancing the overall oxidation rate.

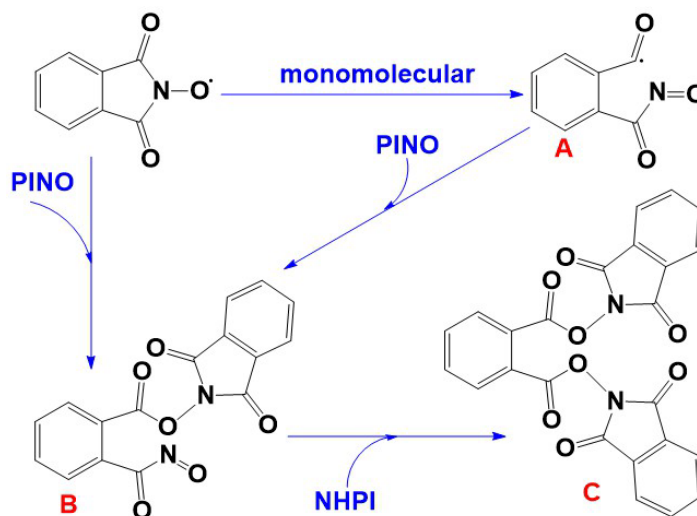


Figure 2.11. Self-decomposition route of PINO radical. Redrawn from ref. [180].

On the contrary, several studies have reported the deactivation of the PINO radical, especially at higher reaction temperatures (>80 °C), which has remained one of the main drawbacks in these free-radical processes. These studies revealed the self-decomposition of PINO radicals in two possible ways, monomolecular and bimolecular [178,182,202–205]. In monomolecular decomposition, as shown in Figure 2.11, the cleavage of one of the carbonyl-nitrogen bonds

leads to the formation of compound A, while in the bimolecular decomposition, the reaction between two PINO radicals and/or compound A and a PINO radical leads to the formation of compound B. Compound B may also be trapped by another NHPI, which acts as a nucleophile towards the nitrosyl group of B, producing the byproduct C.

The H-abstraction capability of the PINO radical is the key parameter defining the activity of NHPI, which is directly related to the BDE of the O-H bond. This BDE can be systematically tailored via structural modifications, including the introduction of electron-withdrawing substituents, heteroaromatic rings, multiple *N*-hydroxy groups, enlarged lactam rings, or the removal of the fused phenyl ring. Inspired by the pioneering work of Ishii and colleagues, Wentzel et al. [206] investigated the NHPI/Co(II) as a catalytic system for low-temperature benzylic oxidation employing dioxygen. They also examined the influence of substituents on the aromatic ring of NHPI in the oxidation of EB. Their results revealed that electron-withdrawing groups enhanced oxidation rates and favored AcPO production, while electron-donating groups suppressed oxidation rates and shifted selectivity toward PEA production. In light of these observations, Sheldon and colleagues [207] employed *N*-hydroxysaccharin (NHS), in which one carbonyl group of NHPI is replaced by a strong electron-withdrawing sulfonyl (SO₂) group, for the aerobic oxidation of large-ring cycloalkanes in the presence of Co(acac)₃. This modification delivers remarkable catalytic performance compared to NHPI, highlighting the promising role of increased electron-withdrawing ability. In parallel, Ishii and colleagues [208] explored *N,N',N''*-trihydroxyisocyanuric acid (THICA) as an NHPI analog and demonstrated its superior performance with (Co(OAc)₂) in the aerobic oxidation of alkylbenzenes, including toluene and its electron-deficient derivatives, compared to NHPI. Employing THICA with *p*-xylene also yielded TA with yields exceeding 95%. *AB initio* calculations revealed O-H BDEs of 88.1 and 91.6 kcal mol⁻¹ for the O-H bond in NHPI and THICA, respectively, indicating higher temperatures required to generate the active *N*-oxyl radical from THICA. This higher BDE describes the lack of catalytic activity observed for THICA at room temperature. Consistent with the preceding studies, Annunziatini et al. [209] demonstrated that aryl-substituted NHPIs bearing electron-withdrawing groups enhance BA oxidation by increasing the O-H BDE and strengthening polar effects in the HAT step. Hammett analysis revealed increasingly negative ρ values with increasing electron-withdrawing strength, supporting a HAT mechanism involving a charge-transfer complex between X-PINO and BA.

In an effort to enhance NHPI activity under mild aerobic oxidation conditions, Nechab and colleagues [210] developed a new type of NHPI catalyst, *N*-hydroxy-3,4,5,6-tetraphenylphthalimide (NHTPPI). When applied at low loading (1 mol%) with CuCl (5 mol%), NHTPPI efficiently catalyzed the aerobic oxidation of benzylic substrates under mild conditions (35 °C, 0.1 MPa). Among a series of NHPI derivatives bearing OMe, Cl, and NO₂ substituents, NHTPPI exhibited the highest activity, realizing 80% yield in the oxidation of indane. Later, Kusch investigated NHPI and various structurally modified NHPI, including NHTPPI, 4-carboxy-NHPI, 3-nitro-NHPI, *N*-hydroxynaphthalimide (NHNI), *N,N*-dihydroxypyromellitimide (NDHPI), *N*-methoxyphthalimide (NMPI), and *N*-acetoxyphthalimide (NAPI), in the oxidation of CU using CuCl or CuBr as cocatalysts. Among these systems, NHTPPI/CuBr exhibited elevated activity, which was attributed to the improved charge transfer in the H-atom abstraction transition state of the corresponding *N*-oxyl radical, the auspicious role of bromide anions in the catalytic cycle, and the reduced specific solvation of NHTPPI in chlorobenzene as the reaction solvent [211].

Electron-withdrawing modification of NHPI-based and/or type catalysts improves aerobic oxidation of hydrocarbons under mild conditions. Following the earlier reports, Zhang et al. [212] developed a series of aryl-tetrahalogenated NHPI and 1,4-diamino-2,3-dichloroanthraquinone (DADCAQ) as efficient metal-free catalysts, with tetrachloro-NHPI/DADCAQ system demonstrating elevated conversion for EB (82.3%) with enhanced selectivity towards AcPO (86.9%). Consistent with these findings, Wang et al. [213] reported that the NDHPI/DADCAQ system outperformed the NHPI/DADCAQ system in EB oxidation even at half the NHPI loading, confirming that the incorporation of strong electron-withdrawing functionalities enhances H-atom abstraction efficiency. These experimental trends are well supported by theoretical studies demonstrating that electron-withdrawing substituents increase the O-H BDE of NHPI derivatives, consequently lowering hydrogen abstraction barriers by PINO-type radicals when sufficient radical concentrations are present [214]. Oxidation of primary C-H bonds with NHPI is particularly challenging because their BDEs exceed that of the O-H bond in NHPI [22]; increasing the O-H BDE can be fruitful in such cases. This could be translated and linked to the work of Ishii and colleagues, who found better catalytic activity of NDHPI than NHPI or NHNI in the aerobic oxidation of ethane to AcOH, achieving up to 9.5 turnovers in acetonitrile and 15.3 in propionic acid [215]. Subsequent reports further confirmed

that NDHPI has a higher BDE than NHPI. Later reported data found that NDHPI has a higher O-H BDE than NHPI, providing a mechanistic basis for its enhanced activity [214,216].

While many studies indicate that increasing the electron-withdrawing character of NHPI derivatives enhances hydrogen abstraction, this trend is not universal. Novikova et al. [216] reported that, in CU oxidation conducted in acetonitrile, NHPI derivatives bearing stronger electron-withdrawing functional groups exhibited lower activity. The oxidation rate followed the order 4-tert-BuNHPI > NHPI > 4-carb-NHPI > NDHPI > NAPI, indicating that in this system, a lower O-H BDE correlated with higher catalytic performance.

Structural modification of NHPI to enhance lipophilicity represents an effective strategy to improve the catalytic activity under solvent-free conditions by increasing its solubility in nonpolar and/or weakly polar hydrocarbons. Thanks to Ishii et al, who developed lipophilic NHPI derivatives to catalyze hydrocarbon oxidations under solvent-free conditions [217]. Utilizing trimellitic anhydride as the precursor, a series of 4-alkyl-oxycarbonyl NHPI 1a-d (Figure 2.12) was synthesized and evaluated in the aerobic oxidation of alkanes, including cyclohexane (100 °C, 1 MPa, 14 h). The catalytic activity increased with alkyl chain length, attributed to enhanced lipophilicity and improved catalyst solubility in the reaction medium.

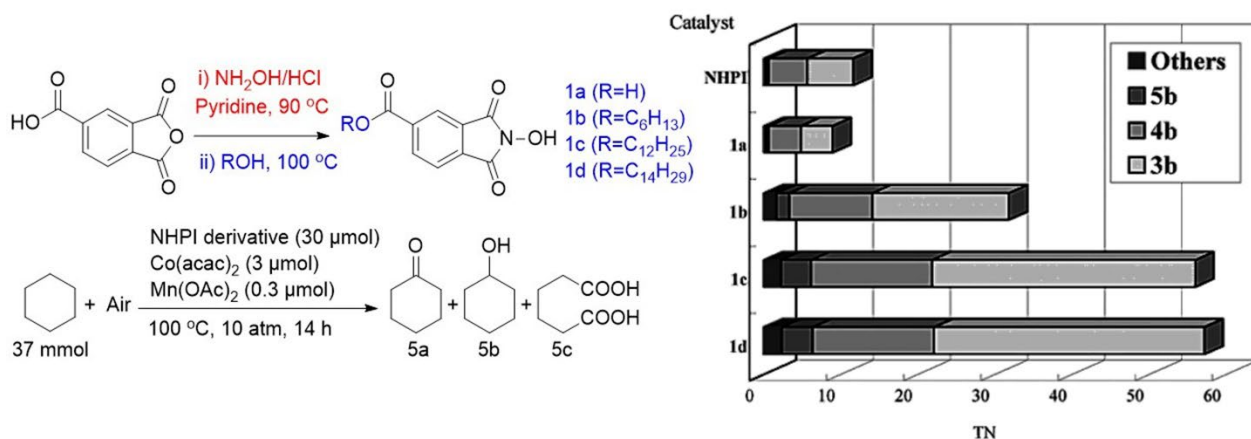


Figure 2.12. Lipophilic NHPI derivatives and their activity in cyclohexane oxidation. Adapted with permission from ref. [217]. Copyright 2001 American Chemical Society.

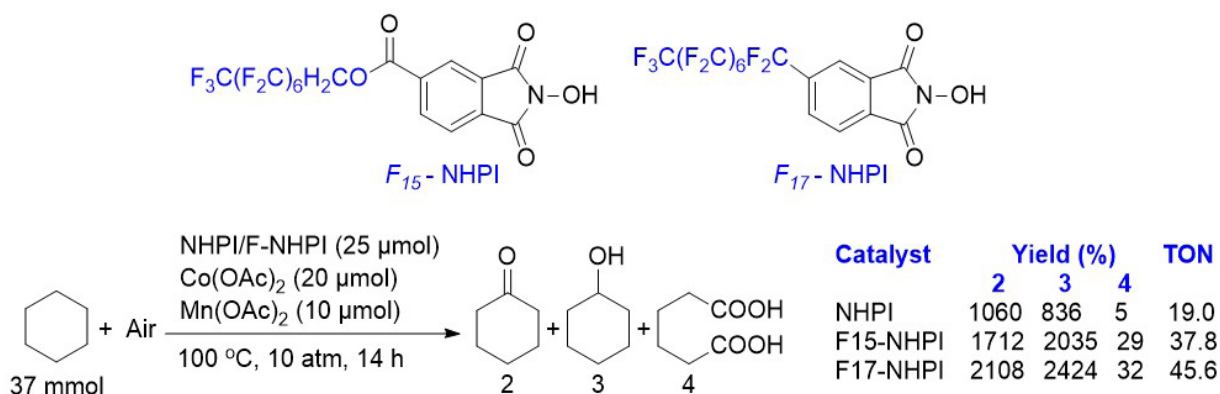


Figure 2.13. Lipophilic derivatives of NHPI, F15- and F17-NHPI, and their catalytic activities in cyclohexane oxidation. Adapted with permission. [218] Copyright 2008, Wiley-VCH GmbH.

To further enhance the lipophilicity and solubility in nonpolar hydrocarbons, Ishii et al. [218] synthesized two fluorinated NHPI derivatives, F₁₅-NHPI and F₁₇-NHPI (Figure 2.13). Both catalysts were evaluated in the solvent-free aerobic oxidation of cyclohexane and exhibited higher activity compared to pristine NHPI. The total turnover number increased with increasing fluoroalkyl chain length; consequently, F17-NHPI displayed the highest activity. The improved activity of both catalysts was primarily attributed to their better solubility in hydrocarbons. Additionally, the electron-withdrawing nature of the fluoroalkyl substituents could have contributed to the enhanced catalytic performance by increasing the hydrogen-abstraction efficiency of the corresponding *N*-oxyl radicals, consistent with previous reports on electron-withdrawing substituted NHPIs [206,209].

The lipophilic NHPI derivatives developed by Ishii and colleagues require relatively harsh reaction conditions for cyclohexane oxidation, which complicates selectivity control. Moreover, these derivatives may be less suitable for the selective hydroperoxidation of alkylaromatic hydrocarbons, limiting their industrial applicability. It has been observed that the presence of carboxylic groups increases the N-O-H BDE [209], thereby reducing the hydrogen donor efficiency of Ishii's catalysts. Additionally, ester functionalities may compromise catalyst stability under oxidative conditions, hindering catalyst recovery.

To address these limitations, Punta and colleagues [219] synthesized a new lipophilic derivative of NHPI, designed to preserve the inherent hydrogen-donor capability of pristine NHPI while enabling aerobic oxidation under milder conditions (70 °C). The catalyst, synthesized from a

commercially available bisphenol A-derived precursor (Figure 2.14), exhibited an O-H BDE ($88.0 \text{ kcal} \cdot \text{mol}^{-1}$) comparable to pristine NHPI ($88.1 \text{ kcal} \cdot \text{mol}^{-1}$). Consequently, it efficiently catalyzed the oxidation of CU, EB, and cyclohexylbenzene to the corresponding hydroperoxides at 70°C using a significantly reduced amount of cosolvent. The catalytic activity was comparable to that of the pristine NHPI and higher than that of Ishii's catalysts. Moreover, when propionaldehyde was replaced with AIBN, the obtained activity was even higher than that of pristine NHPI.

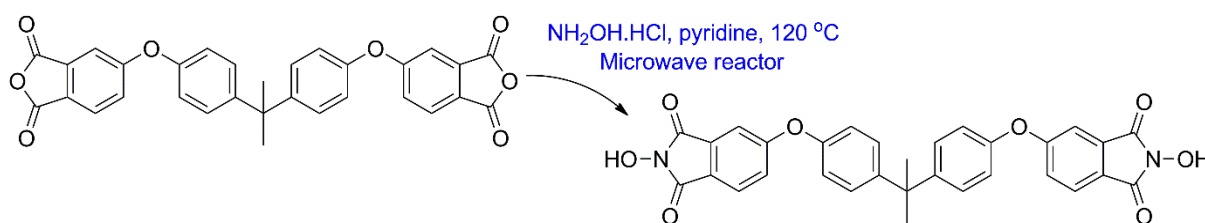


Figure 2.14. Synthesis of lipophilic NHPI derivative. Reproduced with permission. [219]

Copyright 2014, Wiley-VCH GmbH.

In the later work, Kasperczyk et al. [220] synthesized a series of lipophilic NHPI derivatives bearing 4-hexyloxycarbonyl-, 4-dodecyloxycarbonyl-, and 4-hexadecyloxycarbonyl-substituents utilizing trimellitic anhydride chloride as a precursor (Figure 2.15). These catalysts were evaluated for the aerobic, solvent-free oxidation of CU. However, as the reaction time proceeded, the accumulation of more polar hydroperoxide products increased the solubility of pristine NHPI, resulting in comparable final conversions.

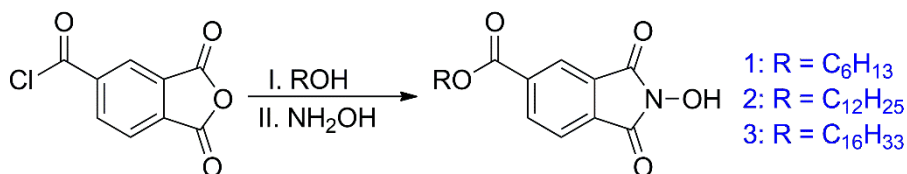


Figure 2.15. Synthesis of lipophilic NHPI derivatives. Adapted from ref. [220].

Punta and colleagues [189] in the subsequent study developed a new class of lipophilic NHPI catalysts (Figure 2.16) and evaluated their performance in the solvent-free aerobic oxidation of CU. Solubility tests in neat CU revealed that selected derivatives (d and e) achieved complete dissolution at low temperatures ($28\text{--}29^\circ\text{C}$ and $47\text{--}50^\circ\text{C}$, respectively), significantly outperforming pristine NHPI and Ishii's catalysts. Consequently, these systems exhibited

augmented activity, selectivity, and stability in the oxidation of CU under mild conditions (45 °C, 0.1 MPa), highlighting the advantages of rational lipophilic catalyst design.

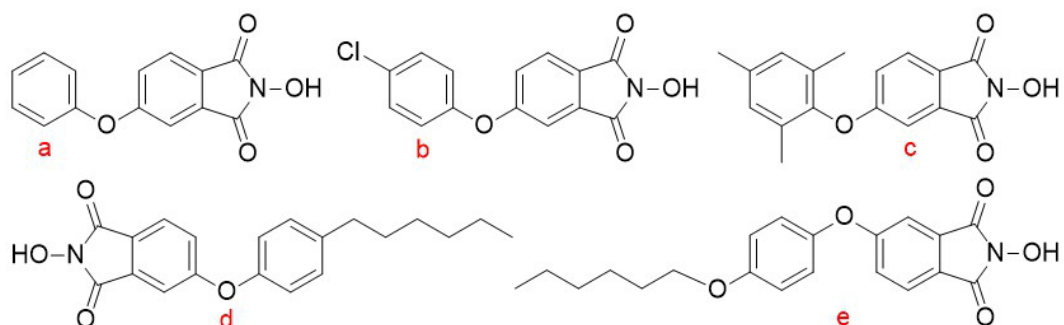


Figure 2.16. Lipophilic NHPI derivatives. Redrawn with permission. [189] Copyright 2017, Wiley-VCH GmbH.

Recently, Kaneiwa et al. [221] developed four lipophilic *N*-hydroxyimides derived from NHPI (Figure 2.17), *N*-hydroxysuccinimide (NHSI), *N*-hydroxynaphthalimide (NHNI), and *N*-hydroxyglutarimide (NHGI). Their solubilities in toluene and cyclohexane were higher than those of pristine NHPI, tetrachloro-NHPI, and the lipophilic derivatives developed by Ishii and colleagues. According to the DFT calculations, the >NO-H relative BDEs of 1-4 to NHPI were -0.5, 3.2, 5.2, and 6.5 kcal·mol⁻¹, respectively. Catalysts 1 and 4 were more stable compared to pristine NHPI as determined by UV-Vis spectroscopy. Furthermore, the solvent-free aerobic oxidation of cyclohexane at 120 °C had the highest TONs of 61 and 64 for catalysts 1 and 4, respectively. Additionally, their improved solubilities enabled efficient solvent-free oxidation even at lower temperatures, achieving TONs of up to 39 at 90 °C and 10 at 60 °C.

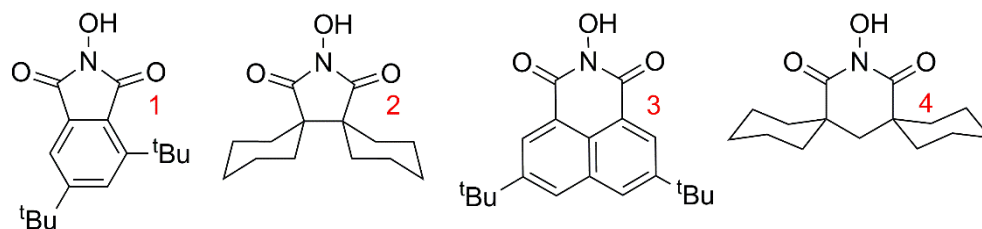


Figure 2.17. Lipophilic *N*-hydroxyimides. Adapted with permission. [221] Copyright 2022, Wiley-VCH GmbH.

2.2.2.2 Solubilizing micelles and higher aggregates

To address the solubility and stability challenges associated with NHPI-based systems, Sasson and colleagues [222] developed a dual-function phase transfer catalyst (PTC) comprising NHPI, Co(II) salts, and lipophilic quaternary ammonium salts (quats). These salts simultaneously solubilize NHPI and extract the Co(II) salts into the organic phase while stabilizing NHPI under the oxidation conditions. The catalytic systems were employed in the solvent-free autoxidation of methylbenzenes under mild conditions. Remarkable performance was achieved with long alkyl chains in lipophilic quaternary ammonium salts such as didecyldimethylammonium bromide (DDAB) and didodecyldimethyl ammonium bromide (DDDAB). For instance, complete conversion of *p*-*tert*-butyltoluene (PTBT) was achieved with an NHPI (1 mol %), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1 mol %), and DDAB (0.5 mol %) system at 90 °C for 12 h under continuous O_2 flow ($100 \text{ cm}^3/\text{min}$). Extending the same protocol to toluene, *o*-, *m*-, and *p*-xylene, mesitylene, and halogenated toluene derivatives (*o*-, *m*-, and *p*-chloro- or -bromo), all of which were oxidized with high conversion (>95%) and selectivity (>99%) to the corresponding benzoic acid derivatives. The exceptional performance was attributed to the self-assembly of these salts into giant multilamellar vesicles (MLVs).



Figure 2.18. Light microscope image of reverse MLVs. Reproduced with permission. [223]

Copyright 2016, Wiley-VCH GmbH.

In a related study, Sasson and colleagues [223] further investigated the solvent-free aerobic oxidation of alkylbenzene catalyzed by Co/NHPI under phase transfer conditions (PTC). The effect of catalyst composition, concentration, temperature, oxygen pressure, and reaction kinetics was thoroughly investigated. The ternary Co/DDAB/NHPI system demonstrated

exceptional catalytic performance, good recyclability, and no formation of hazardous byproducts. In this system, DDAB facilitates the transfer of both NHPI and the Co salt into the organic phase via hydrogen-bonding interactions and protects NHPI from thermal degradation by forming reverse MLVs, as confirmed by a light microscope (Figure 2.18).

2.2.2.3 Additive-assisted solubilization of NHPI

In this context, ILs have emerged as an attractive additive to enhance the solubility of NHPI in nonpolar reaction media. ILs were initially introduced as the greener alternative to conventional organic solvents [224–228]. ILs are organic salts with melting points near room temperature, typically less than 100 °C, and have incredible properties such as low volatility, high polarity, chemical and thermal stability, and tunable functionality [224–226,229]. The first generation of room-temperature ILs (RTILs), based on 1-alkyl-3-methylimidazolium salts, was reported by Wilkes et al. [230] in 1982 as tetrachloroaluminate systems. Nonetheless, these early ILs were limited by their sensitivity to air and moisture. The subsequent substitution of moisture-sensitive anions with more stable ones, such as tetrafluoroborate in 1992, led to the development of air- and water-stable second-generation ILs [231]. These advances greatly broadened their horizons as reaction media for a wide range of organic transformations. Entering the new millennium, Davis introduced the concept of task-specific ILs (TSILs), or third-generation ILs [232], which can be chemically modified to perform specific catalytic, separative, or electrochemical tasks.

As research progressed, ILs spurred substantial scientific interest owing to their negligible vapor pressure, excellent thermal and chemical stability, non-flammability, broad electrochemical window, and tunable polarity. Key properties such as viscosity, hydrophobicity, acidity, and solvation capability can be precisely adjusted by varying the cation-anion combination, making ILs highly versatile materials in green and sustainable chemistry. Consequently, they have been widely explored across various applications [233,234].

Several researchers have reported the use of ILs as a green solvent in the process of hydrocarbon oxidation reactions [30,235–241]. In fact, the positive impact of imidazolium cation-based ILs on electron-transfer reactions has been reported, showing that they enhance aerobic oxidation by accelerating electron transfer from metal complexes to molecular oxygen. This effect is

attributed to the stabilization of oxygen radical anions by coordination with the acidic C2-H of imidazolium-based ILs, a stabilization that is not achievable with conventional solvents [242].

Wang and colleagues [241] explored the catalytic activity of NHPI in IL for aerobic oxidation reactions. Their finding revealed that both NHPI and its ionic derivative, 3-pyridinylmethyl-NHPI (Py-NHPI), were catalytically more active in IL ([bmim][PF₆]) than in the conventional solvents for the oxidation of *N*-alkylamides to imides. More interestingly, the Py-NHPI acted as a better catalyst than NHPI in the aerobic oxidation of benzylic substrates in [bmim][PF₆]. In the corresponding study, Koguchi and Kitazume [243] developed an IL-supported NHPI complex and employed it in the oxidation and nitration reactions in IL ([bmim][PF₆]). The developed catalytic system was recoverable and reusable, compared to NHPI in ILs. Lu et al. investigated the remarkable performance of PEG-1000-based di-cationic IL as a solvent in the NHPI-catalyzed aerobic oxidation of alkylaromatics [244]. Recently, the aerobic oxidation of alkylaromatic hydrocarbons to hydroperoxides, catalyzed by *N*-hydroxyimides including NHPI in several ILs, such as 1-alkyl-3-methylimidazolium cations with ethyl, butyl, hexyl, or octyl substituents and anions such as [BF₄], [PF₆], [NTf₂], [CF₃SO₃], [O₂OSO₃], and [CH₃OSO₃] as the green solvents, has been reported [245].

Despite replacing conventional organic solvents with ILs, it is insufficient to realize them on an industrial scale from an economic and process perspective. To tackle this issue, ILs have also been used in a catalytic amount in various hydrocarbon oxidation processes [30,240,246–248]. On the other hand, only a few researchers have employed NHPI in combination with ILs as a novel catalytic system for hydrocarbon oxidations. For instance, Mahmood et al. [249] employed a cobalt/NHPI catalytic system along with imidazolium-based ILs as additives for the solvent-free aerobic oxidation of hydrocarbons. Their findings revealed that these amphipathic ILs self-assemble at the interface between organic hydrocarbons and the aqueous catalyst phase (Co/NHPI), forming a solution of reversed multilamellar vesicles that facilitate catalysis, and that activity depends not only on the microdomains but also on the structure of the employed IL. Thus, an optimal water content in the ILs was essential to maximize reactivity. Additionally, the interfacial boundary between the aqueous and organic phases formed by C2-alkylated imidazolium ILs, such as [bdmim]SbF₆ and [C₁₂dmim]SbF₆, not only produces more stable ternary aggregates (hydrocarbons/IL/H₂O) but also facilitates faster diffusion and higher concentration of O₂. This, in turn, enhances the reactivity of the protocol for hydrocarbon

oxidation. The presence of micelles and/or higher aggregates within ILs and/or IL-containing multicomponent systems has already been reported [250–256].

Recently, small amounts of various imidazolium-based ILs were employed as additives to the NHPI/Co(II) catalytic system for the solvent-free aerobic oxidation of EB (Figure 2.19) [257]. An exceptional catalytic activity with 35% conversion (80 °C, 0.1 MPa O₂, 6 h) was obtained when the IL with lipophilic anion, [bmim][O₂SO₃] (1 mol%) along with NHPI (1 mol%) and Co(OAc)₂ (0.1 mol%) were employed, and the obtained catalytic activity is almost 4.3 times more than the conversion obtained for the system containing only NHPI and Co(II). The positive effect of the IL was not attributed to polar interactions; rather, the key role of [bmim][O₂SO₃] was in enhancing the solubilization of NHPI in the apolar medium. This was demonstrated by conducting reactions in the presence of more lipophilic NHPI derivatives developed by Ishii et al. [217] and Petroselli et al. [219]. In these cases, the positive effect of the ILs decreased significantly, likely because the lipophilic NHPI derivatives are inherently more soluble in apolar media compared to NHPI, rendering the solubilization effect of ILs negligible. On the other hand, a recent study identified the critical role of hydrogen bonding between the –NO–H bond in NHPI and the anion in halide ILs during the hydrocarbon oxidation reactions (Figure 2.20) [258]. This interaction significantly enhanced the reaction rate by facilitating the formation of the PINO radical from NHPI, a related, though mechanistically distinct, activation effect was reported for tiny amounts of MeCN, which disrupt hydrogen-bond-driven self-aggregation of NHPI in apolar media, thereby freeing the catalytically active monomer for HAT [189]. During the EB oxidation under solvent conditions (PhCN), the interaction between the anion in halide ILs ([Rmim][X] and [R₄N][X]) and NHPI decreased in the order [Cl]>[Br]>[I]. This interaction weakened the N–O–H bond in NHPI, thereby promoting the formation of the PINO radical. In solvent-free EB oxidation reactions, the catalytic activity was influenced by the solubility of the ILs, NHPI, and Co(II). The highest catalytic activity was observed with the lipophilic IL [C₁₀mim][Cl], attributed to its ability to enhance the solubility of NHPI and Co(II) in the nonpolar medium. Furthermore, the high activity of [C₁₀mim][Cl] may be linked to the formation of reverse micelles, which acted as catalytic microreactors, accelerating the reaction rate.

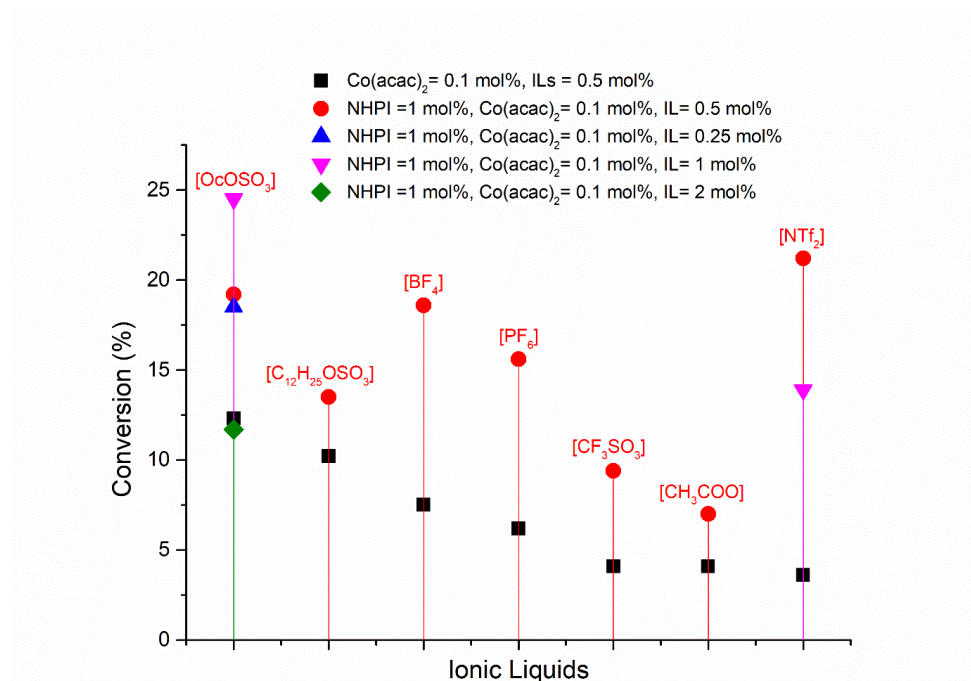


Figure 2.19. EB conversion in the solvent-free aerobic oxidation using [bmim]-based ILs as additives to the NHPI/Co(II) catalytic system. Reaction Conditions: EB: 2 cm³, 0.1 MPa O₂, 80 °C, 6 h, 1200 rpm. Data taken from ref. [257].

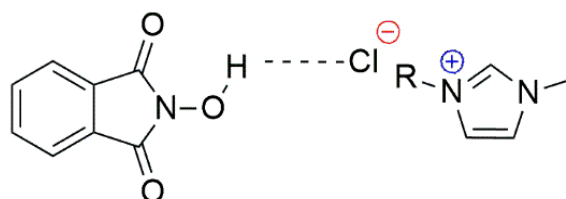


Figure 2.20. Interaction between NHPI and [bmim][Cl]. Adapted with permission. [258]

Copyright 2021, Wiley-VCH GmbH.

Ding et al. [259] recently ported a synergistic catalytic effect of NHPI and [bmim][Br] in solvent-, metal-, and initiator-free oxidation of CU using molecular oxygen as the oxidant. Under optimized conditions (0.03 mmol of NHPI, 0.03 mmol of [bmim][Br], 90 °C, 0.1 MPa O₂, and 6 h), the combined catalytic system enhanced the oxidation rate by 33.3% compared to the individual components. Mechanistic study revealed that this synergy originates from two key contributions: (i) facilitated generation of PINO radical from NHPI via H-atom abstraction promoted by the bromide anion of [bmim][Br], and (ii) efficient decomposition of CUHP by [bmim][Br], leading to the formation of carbene-Br and cumyloxy free radicals (RO[•]), which

subsequently drive CU oxidation towards the key products. The interaction between NHPI and [bmim][Br] was further elucidated by projected density of states (PDOS) analysis, which showed overlap between the H 1s states and Br p-states near the HOMO level, indicating a strong H and Br interaction that facilitates H-atom abstraction and PINO radical formation (Figure 2.21). In a related study, Chen et al. [248] revealed that [bmim][Br] enhances the initiation step in the oxidation of CU by promoting the formation of cumyl radicals. Additionally, the hydrogen in the imidazolium cations of the IL actively participated in the decomposition of CUHP, generating free radicals, thereby accelerating the reaction rate.

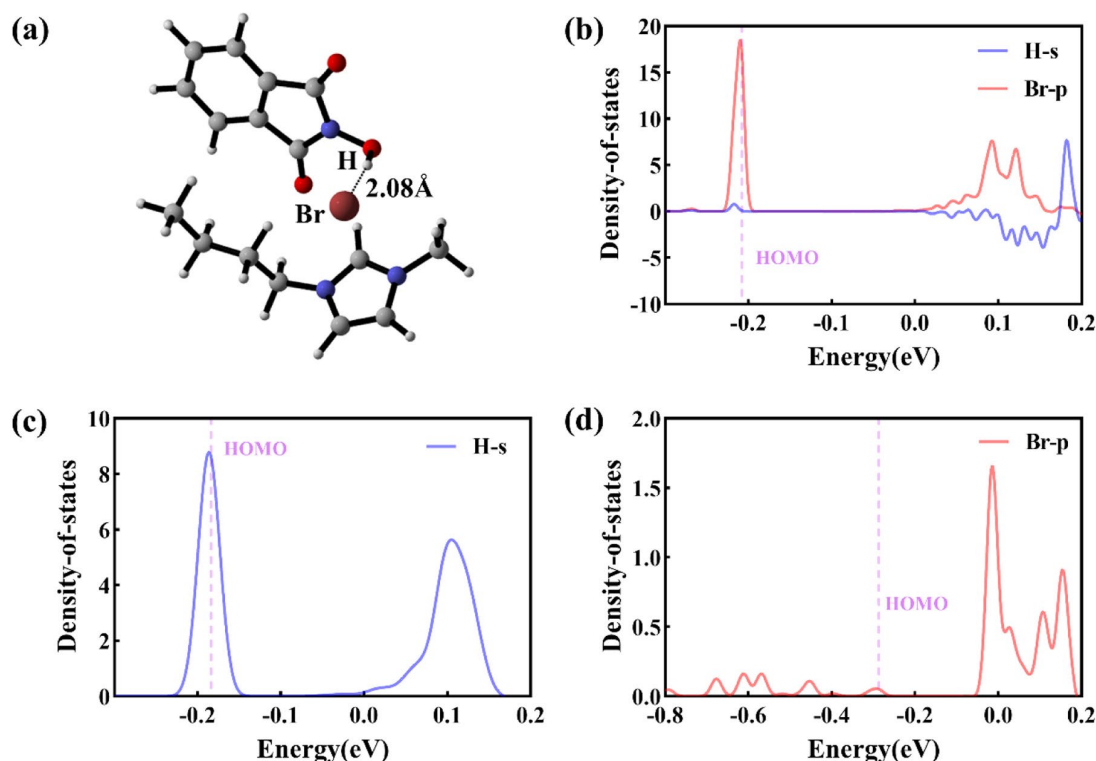


Figure 2.21. (a) Chemical adsorption state of NHPI with BmimBr, (b) PDOS analysis of H and Br orbitals of adsorption state of NHPI with BmimBr, (c) PDOS analysis of H orbital of NHPI, and (d) PDOS analysis of Br orbital of BmimBr [259]. By permission from Elsevier, copyright 2024.

2.3 Development of SILP, SCILL, and SCILL-SILP Systems

Despite the advantages of ILs in catalytic oxidation processes, their application as liquid-IL biphasic catalytic systems, where IL can serve either as a catalytically active phase or as a reaction medium for transition-metal catalysts, forming a catalytically active ionic solution, is

limited by several drawbacks. These include catalyst leaching due to reagent polarity, deactivation in the presence of moisture or impurities, and reduced reaction rates resulting from the high viscosity of ILs, which limits efficient mass transfer. Additionally, the requirement for substantial amounts of ILs increases operational costs and further exacerbates mass-transfer limitations, ultimately diminishing overall catalytic efficiency [260].

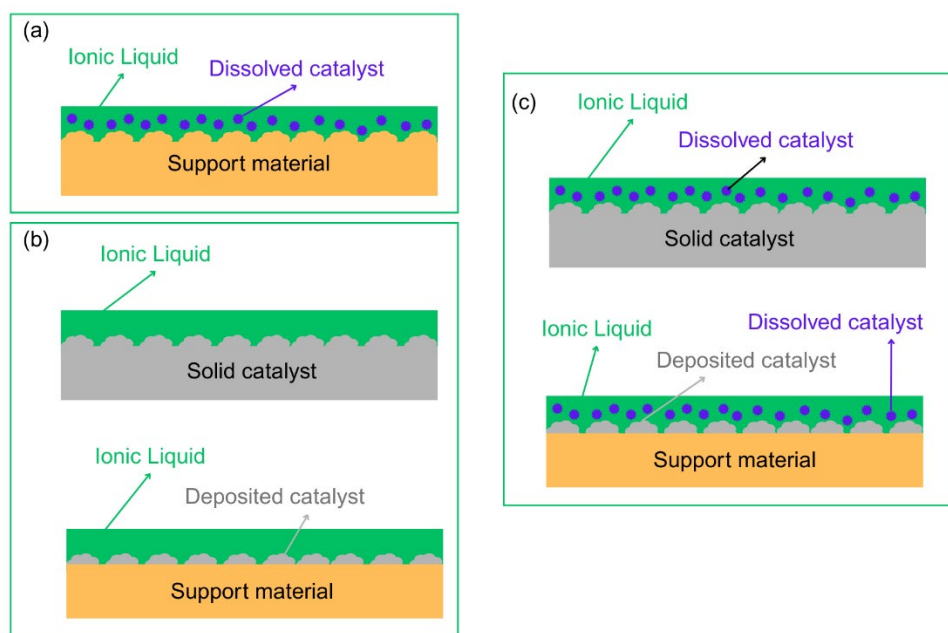


Figure 2.22. Schematic illustration of the (a) SILP, (b) SCILL, and (c) SCILL-SILP system.

To overcome these limitations, researchers developed the concept of IL thin-film catalysis, in which a thin IL layer is applied to shorten diffusion paths and improve mass transfer [261]. The concept of a Supported Ionic Liquid Phase (SILP), illustrated in Figure 2.22 (a), involves a thin film of IL containing a dissolved catalyst that is immobilized and/or coated onto a solid support. This strategy, as proposed by Mehnert et al. [262,263] and Riisager et al. [264,265], provides an effective means of heterogenizing IL-based homogeneous catalysts. Following this approach, known as the Solid Catalyst with Ionic Liquid Layer (SCILL), shown in Figure 2.22 (b), involves coating a thin IL layer directly onto a solid catalyst or a catalyst deposited onto a support [266,267]. Both the SILP and SCILL concepts integrate the advantages of homogeneous catalysis, for instance, high activity and selectivity, with those of heterogeneous catalysis, including facile catalyst recovery and recyclability. On the other hand, the SCILL and SILP concepts can be integrated, as illustrated in Figure 2.22 (c), to produce a SCILL-SILP

hybrid system. In such a configuration, an IL containing the dissolved catalyst can be immobilized and/or coated as a thin layer on a solid heterogeneous catalyst. The solid support could be a solid catalyst itself or a catalyst deposited on an inert support.

Over the past few years, researchers have investigated the application of SCILL systems in various catalytic processes, for example, hydrogenations [266,268,269], oxidation reactions of alcohols [270,271], and hydrocarbons [272,273]. Dobras et al. [272] studied the catalytic activity of NHPI grafted onto silica gel (SiOCO-NHPI) through an ester bond and subsequently coated with different ILs containing dissolved CoCl_2 ($\text{SiOCO-NHPI}@\text{CoCl}_2@\text{IL}$) for the aerobic oxidation of EB under solvent-free conditions. The results revealed that the SCILL systems enhanced EB conversion, particularly the $[\text{bmim}][\text{OcOSO}_3]$ based system, which achieved 12.1% EB conversion. The recyclability test revealed that the $[\text{bmim}]$ cation-based SCILL system, containing $[\text{OcOSO}_3]$ and $[\text{CF}_3\text{SO}_3]$ anions, displayed a drop in conversion after the fourth cycle, whereas the conversion of the $[\text{bmim}][\text{Cl}]$ -based SCILL system dropped after the third cycle, which was due to the leaching of the mixture of IL and CoCl_2 from the solid support surface. In the corresponding study, Talik et al. [273] examined the solvent-free aerobic oxidation of EB employing a SCILL/SILP system, composed of NHPI immobilized on a polystyrene support via an ester bond, coated with a thin IL layer of 1-ethyl-3-methylimidazolium octylsulfate ($[\text{emim}][\text{OcOSO}_3]$) containing CoCl_2 ($\text{PS-NHPI}@\text{CoCl}_2@[\text{emim}][\text{OcOSO}_3]$). The SCILL/SILP systems demonstrated enhanced selectivity towards AcPO and were recycled multiple times without any substantial loss of catalytic performance.

3. Aims, Objectives, and Scope of the Doctoral Dissertation

This doctoral dissertation aims to develop selective, recyclable, heterogeneous catalytic systems for the solvent-free liquid-phase oxidation of alkylaromatic hydrocarbons using oxygen as a green oxidant. The key strategy is to utilize CNTs as both catalytically active materials and robust supports.

Herein, the surface of MWCNTs is tailored via transition-metal incorporation to obtain metal-modified and metal-functionalized MWCNTs. The pristine and metal-functionalized MWCNTs are then rationally integrated with NHPI and ILs to develop interface-engineered hybrid catalytic systems. In particular, NHPI is confined within a thin immobilized IL layer on MWCNTs and on functionalized MWCNT-based supports in SILP and novel integrated SCILL-SILP hybrid catalytic configurations.

In parallel, covalent grafting of NHPI onto MWCNTs is investigated as an alternative heterogenization technique to improve NHPI recyclability.

The catalytic performance of the obtained MWCNT-based systems is evaluated using EB as a model hydrocarbon under mild, solvent-free conditions (80 °C, 0.1 MPa, 6 h). The systems are systematically assessed in terms of EB conversion, product selectivity, catalyst stability, and recyclability.

To realize the aims of this dissertation, the following major objectives have been defined:

1. To investigate the intrinsic catalytic performance of CNTs, including pristine, metal-modified, and/or functionalized CNTs, in aerobic oxidations.
2. To elucidate the synergistic role of NHPI and CNTs, including functionalized and/or metal-modified CNTs, in promoting hydroperoxide formation and decomposition during aerobic oxidation.
3. To develop SILP and SCILL catalytic systems by coating NHPI-dissolved ILs and ILs onto CNT-based supports, respectively, and to evaluate their catalytic performance.
4. To design and evaluate integrated, novel SCILL-SILP hybrid catalytic systems by coating NHPI-dissolved ILs onto metal-functionalized CNTs catalysts and to investigate their catalytic performance.

5. To explore covalent grafting strategies for NHPI immobilization on CNTs as an approach to enhance catalyst stability and reusability, and to systematically evaluate the resulting catalytic performance.
6. To comprehensively characterize the developed catalytic systems using advanced physicochemical characterization techniques, and to evaluate their catalytic activity, product distribution and selectivity, as well as catalyst stability and recyclability, under solvent-free liquid-phase aerobic oxidation conditions.

The aforementioned research objectives form the foundation of this doctoral study and delineate its scope. While the present work focuses on CNT-based hybrid catalytic systems for the solvent-free aerobic oxidation, the concept, methodologies, and insights developed herein are not limited to the specific systems investigated. The strategies of CNT functionalization and metal modifications, interfacial engineering, and hybrid catalytic system design explored in this dissertation may be extended to other materials to enable their functionalization and modification, as well as the development of advanced hybrid catalytic systems. Furthermore, the catalytic systems developed in this dissertation may be adapted and applied to other oxidation reactions and to a broader range of catalytic transformations. Consequently, the outcomes of this research provide a foundation for broader applications beyond the specific catalyst designs and reactions examined, offering transferable insights for future developments in sustainable catalytic process design.

4. Experimental Section

4.1 Materials

EB (99.8%; Acros Organics) was purified by H₂SO₄ washing, followed by vacuum distillation. MWCNTs (95+ wt.% purity, 20-40 nm OD, and 1-2 μ m L), MWCNT-COOH (95+ wt.% purity, 8-15 nm OD, and 10-50 μ m L), and amine-functionalized MWCNTs ($\sim$ 0.45% -NH₂, 95+ wt.% purity, 8-15 nm OD, 50 μ m L, and 233 m² · g⁻¹ SSA), were obtained from IoLiTec Ionic Liquids Technologies GmbH (Heilbronn, Germany). IGMWCNT-COOH (90 wt.% purity, 20-40 nm OD, 5-10 nm ID, 10-30 μ m L, 110 m² · g⁻¹ SSA) and amine-functionalized MWCNTs ($\sim$ 7 $\pm$ 1.5% -NH₂, 13-18 nm, 1-12 μ m L) were purchased from Cheap Tubes, Grafton, VT, USA. Copper chloride dihydrate (CuCl₂ · 2H₂O), dichloromethane (CH₂Cl₂), *N,N*-dimethylformamide (DMF), and tetrahydrofuran (THF) were acquired from POCH, Poland. Ammonia solution (25%), acetone (99%), ethanol (99.8%), methanol (99.8%), and pyridine (99%) were obtained from Chempur, Poland. NHPI, copper(II) nitrate trihydrate (Cu(NO₃)₂ · 3H₂O), cobalt(II) nitrate hexahydrate (Co(NO₃)₂ · 6H₂O), manganese(II) nitrate tetrahydrate (Mn(NO₃)₂ · 4H₂O), trimellitic anhydride chloride (TAC), triethylamine (Et₃N), hydroxylamine hydrochloride (NH₂OH · HCl), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC · HCl), *N*-hydroxysuccinimide (NHS), 1,8-diaminooctane, trimellitic anhydride (TA), trifluoroacetic acid ($\geq$ 99.0%), trityl chloride (TrCl) and nylon membrane filters (pore size 0.22 μ m and diameter 47 mm), were purchased from Sigma-Aldrich, Steinheim, DE, USA. ILs: [bmim][Cl], [bmim][Br], [bmim][O₂SO₃], [bmim][PF₆], [bmim][BF₄], [bmim][NTf₂], [emim][NTf₂], [emim][O₂SO₃], [omim][Cl], and [C₁₀mim][Cl] were commercial materials and were dried under vacuum before use (50 °C, 0.01 MPa).

4.2 Preparation of Metal-Rich MWCNT Composites

The metal-rich MWCNT composites were prepared using a modified method originally developed for Co encapsulation [142]. Specifically, Cu-MWCNT composites were prepared as follows: 1 g of MWCNTs was refluxed for 14 h in 50 cm³ of nitric acid (68%) at 140 °C on a hot plate with stirring. The MWCNTs were then filtered (using PTFE membranes) and washed several times with distilled water until the pH reached 7. The washed MWCNTs were then dried

at 80 °C for 3 h, followed by additional vacuum drying for 24 h (the recovered CNTs weighed 0.5485 g). The dried MWCNTs were added to 50 cm³ of 5 wt.% Cu(NO₃)₂ · 3H₂O solution. The mixture was sonicated in an ultrasonic bath for 1 h, followed by stirring for 24 h at room temperature. The solvent was then evaporated using a rotary vacuum evaporator. The metal-rich MWCNT composite was ground into a fine powder and calcinated at 355 °C in a muffle furnace for 5 h in an inert atmosphere. The black solid obtained, denoted as Cu-MWCNT@14h, was further washed with methanol and acetone and dried before being employed in the oxidation reactions.

An analogous procedure was again employed to prepare metal-rich MWCNT composites containing Cu, Co, and Mn nanoparticles using Cu(NO₃)₂ · 3H₂O, Co(NO₃)₂ · 6H₂O, and Mn(NO₃)₂ · 4H₂O. However, the acid treatment time of MWCNTs was reduced to 6 hours, and the resultant metal-rich MWCNT composites were termed Cu-MWCNT@6h, Co-MWCNT@6h, and Mn-MWCNT@6h, respectively. The prepared catalysts were characterized using TEM (Thermo Fisher Scientific TecnaiG2) and ICP-OES. The recyclability and reusability of the metal-rich MWCNT composites were evaluated by recovering the catalysts from the reaction mixture via filtration, thoroughly washing with methanol and acetone, and reusing them in subsequent cycles.

4.3 Preparation of Metal-Modified MWCNTs

MWCNTs were modified with Cu, Co, and Mn salts following the modified method described in Section 4.2. According to the modified procedure, 1 g of MWCNTs was refluxed for 6 hours in 50 cm³ of nitric acid (68%) at 140 °C on a hot plate with continuous stirring. After cooling, the MWCNTs were recovered by filtration using PTFE membranes and thoroughly washed with deionized water until the pH reached 7. The washed MWCNTs were then dried at 60 °C for 24 h, followed by additional drying under reduced vacuum at 60 °C for 3 h. Equal amounts of the dried MWCNTs (~0.3 g) were added separately to 10 cm³ of 1 M aqueous solutions of Cu(NO₃)₂ · 3H₂O, Co(NO₃)₂ · 6H₂O, and Mn(NO₃)₂ · 4H₂O, respectively. The suspensions were sonicated in an ultrasonic bath for 1 h, followed by stirring for 24 h at room temperature. The MWCNTs from each salt solution were separated employing filtration and flash-washed with fresh deionized water. The MWCNTs were subsequently dried at 60 °C under reduced pressure

employing a vacuum pump. The dried MWCNTs containing the respective metal salts were then calcined at 355 °C for 5 h under an inert atmosphere and at atmospheric pressure. The resulting metal-modified MWCNTs were represented as Cu-MWCNTs, Co-MWCNTs, and Mn-MWCNTs. The produced metal-modified MWCNTs were characterized using SEM/EDS and ICP-MS. The recyclability and reusability of the metal-modified MWCNTs were evaluated by recovering the catalysts from the reaction mixture via filtration, thoroughly washing with methanol and acetone, and reusing them in subsequent cycles.

4.4 Preparation of Cu(II) Functionalized MWCNTs

IGMWCNT-COO-Cu or MWCNT-COO-Cu were prepared following a modified protocol reported in [126,274]. 1 g of carboxylated MWCNTs was dispersed in 40 cm³ of 10% aqueous solution of ammonia and treated by employing bath ultrasonication for 3 h. The solid was subsequently recovered by filtration, washed thoroughly with deionized water, and dried at 90 °C for 3 h, yielding approximately 1 g of the corresponding ammonium carboxylate form (MWCNT-COO-NH₄). Subsequently, 0.2 g of MWCNT-COO-NH₄ was suspended in 25 cm³ of ethanol, followed by the addition of 5 cm³ of a 0.3 M CuCl₂·2H₂O solution. The resulting suspension was sonicated for 1.5 h, after which the solid was filtered, thoroughly washed with ethanol, and dried at 90 °C for 3 h to afford approximately 0.2 g of MWCNT-COO-Cu. The recyclability and reusability of the catalyst were evaluated by recovering the solid catalyst from the reaction mixture via filtration, washing it with ethanol, and subsequently employing it in the successive oxidation cycle. The synthesized catalysts were characterized using SEM (Phenom Pro desktop SEM), TEM, and EDS (Thermo Fisher Scientific Titan³ G2 S/TEM 60-300, FEI), FTIR (Thermo Scientific Nicolet 6700), ICP-MS (NexION 300D, Perkin-Elmer), N₂ physisorption (Micromeritics ASAP 2020 Plus system), and TGA (Mettler Toledo TGA851e thermobalance, Greifensee, Switzerland).

4.5 Preparation of SILP, SCILL, and SCILL-SILP Systems

The preparation of the hybrid catalytic systems was adapted from the previous works [272,273], employing the solvent evaporation technique with a minor modification involving the introduction of an ultrasonication step before stirring. The SILP systems were prepared by immobilizing a mixture of the selected IL and NHPI onto pristine MWCNTs. In a typical

preparation, 0.025 g of the IL and 0.027 g of NHPI were combined with 0.025 g of MWCNTs in 5 cm³ of acetone. The resulting suspension was ultrasonicated for 30 min and subsequently stirred at 1200 rpm for 3 h at room temperature to ensure homogeneous dispersion. Acetone was then evaporated under reduced pressure employing a rotary evaporator, while maintaining the bath temperature at 60 °C and gradually reducing the pressure from 600 to 300 mbar.

The SCILL systems were produced employing the same procedure, by coating the IL (0.0125, 0.025, or 0.0375 g) directly onto 0.025 g of Cu(II)-functionalized industrial-grade MWCNTs (IGMWCNT-COO-Cu). The SCILL-SILP hybrid catalytic systems were produced using an identical protocol to SILP, except that MWCNTs were replaced with IGMWCNT-COO-Cu or MWCNT-CO-Cu. The synthesis of the hybrid catalytic systems is schematically illustrated in Figure 4.1.

The recyclability and reusability of the hybrid catalytic systems were evaluated by recovering the catalysts from the reaction mixture via filtration. The recovered catalysts were washed with fresh EB and/or hexane and dried under vacuum in a desiccator for 12 h, after which they were reused in subsequent oxidation reactions.

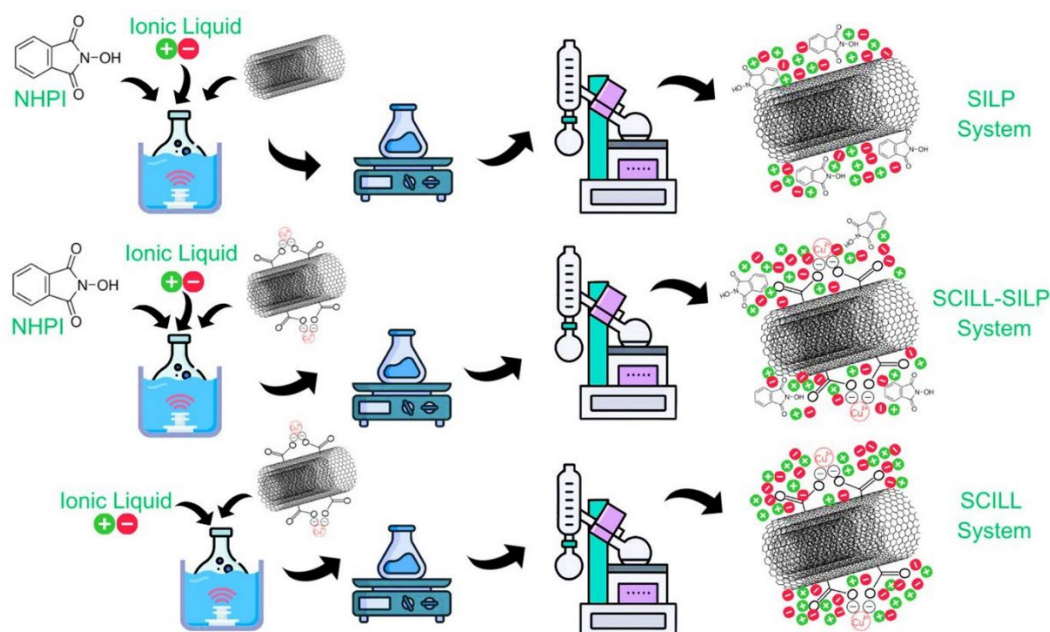


Figure 4.1. Schematic illustration of the synthesis of hybrid catalytic systems.

The [emim][OcOSO₃]-based SCILL-SILP system, obtained by using an IGMWCNT-COO-Cu supported catalyst, was characterized using SEM (Phenom Pro desktop SEM), TEM, and EDS

(Thermo Fisher Scientific Titan³ G2 S/TEM 60-300, FEI), FTIR (Thermo Scientific Nicolet 6700), ICP-MS (NexION 300D, Perkin-Elmer), N₂ physisorption (Micromeritics ASAP 2020 Plus system), and TGA (Mettler Toledo TGA851e thermobalance, Greifensee, Switzerland). While the latter [bmim][OcOSO₃]-based SILP and SCILL-SILP systems were characterized using TEM (Thermo Fisher Scientific TecnaiG2 F20 X-TWIN/FEI), ATR-FTIR (PerkinElmer Spectrum Two spectrometer equipped with a diamond ATR), and TGA/DTG analyses (TGA/DSC STAR system analyzer from Mettler Toledo).

4.6 NHPI Grafting onto MWCNT-NH₂

The grafting of NHPI onto commercially available amine-functionalized MWCNTs (amine functionalization degree of ~0.45% and ~7%) was adopted from a previously reported procedure [275], in which NHPI was grafted onto (aminomethyl) polystyrene via amide bond formation. The respective amine-functionalized MWCNTs (MWCNT-NH₂ with either ~0.45% or ~7% surface amine functional groups) were dispersed in 25 cm³ of dichloromethane (CH₂Cl₂) and sonicated for 10 min to deagglomerate the CNTs and obtain homogeneous suspensions. The amounts of all the reagents used are summarized in Table 4.1. The resulting suspensions were subsequently cooled to 0 °C, after which trimellitic anhydride chloride (TAC) was added. Triethylamine (Et₃N) was then introduced in five portions over 1 h while maintaining the temperature at 0 °C. The reaction mixture was stirred for an additional 3 h at 0 °C and then at room temperature for 24 h.

The product was isolated by filtration and subsequently washed with CH₂Cl₂, *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), and CH₂Cl₂ (25 cm³ each), to remove the unreacted and residual reagents. The resulting TAC-grafted CNTs were dried under vacuum and transferred to 40 cm³ of a pyridine:1,2-dichloroethane mixture (3:1, v/v), followed by the addition of hydroxylamine hydrochloride (NH₂OH·HCl). The mixture was stirred at 75 °C for 24 h, then cooled to room temperature. The product was recovered by filtration and thoroughly washed with deionized H₂O (2 × 25 cm³ at 50 °C), MeOH (2 × 25 cm³), DMF, DMF: H₂O (1:1, 2 × 25 cm³), DMF (2 × 25 cm³), THF (3 × 25 cm³), CH₂Cl₂ (2 × 25 cm³), and EtOH (2 × 25 cm³). The purified product was finally dried under vacuum for 24 h. The grafting procedure is illustrated in Figure 4.2. FTIR (iS50 ATR-FTIR) and DSC (Linseis L63) analyses were

performed to characterize TA immobilization and NHPI grafting, respectively, onto amine-functionalized MWCNTs.

Table 4.1. Amounts of reagents used for NHPI grafting onto amine-functionalized MWCNTs.

MWCNT-NH ₂		TAC		Et ₃ N			NH ₂ OH·HCl	
(mmol NH ₂ /g)	(g)	(mmol)	(g)	(mmol)	(g)	(cm ³)	(mmol)	(g)
0.3	1.0	1.4	0.3	28.0	2.8	3.9	1.5	0.1
4.4	1.0	21.8	4.6	28.0	2.8	3.9	22	1.5

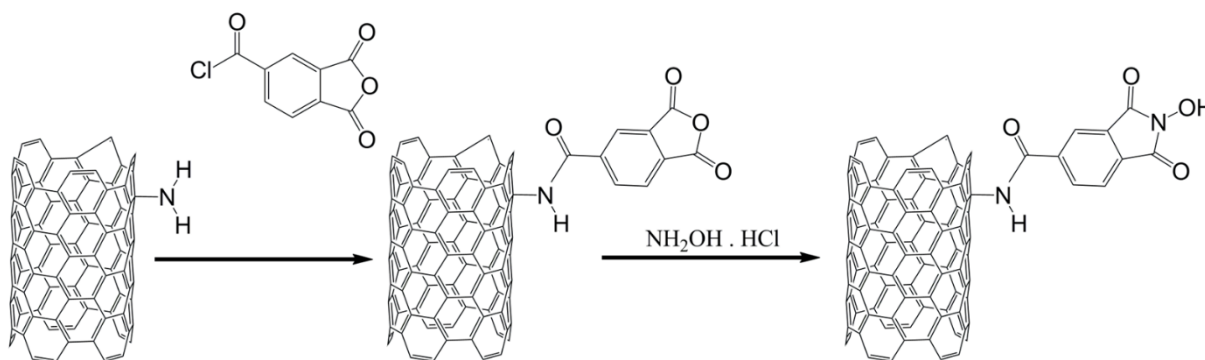


Figure 4.2. NHPI grafting onto amine-functionalized MWCNTs.

4.7 NHPI Grafting onto Carboxylated MWCNTs

The NHPI grafting onto IGMWCNT-COOH was performed employing the following stepwise synthesis procedure:

Step 1. Amine functionalization of the IGMWCNT-COOH

The amine functionalization of carboxylate IGMWCNTs (IGMWCNT-COOH) was adapted from the procedure reported by Rusconi et al. [276], who employed this method for rhodamine grafting onto cellulose nanofibers. IGMWCNT-COOH (1000 mg; -COOH content 0.3332 mmol/1000 mg), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, 8.33 mmol, ~1597 mg), and *N*-hydroxysuccinimide (NHS, 2.899 mmol, ~333.43 mg) were dispersed in 50 cm³ of deionized water (beaker A). This mixture was vigorously stirred for 30 min at 0 °C using an ice bath to activate the carboxyl groups. In parallel, 1,8-diaminooctane was employed in an amount corresponding to two equivalents with respect to the surface carboxyl groups of IGMWCNT-

COOH ($2 \times 0.3332 \text{ mmol} = 0.6664 \text{ mmol}$, $\sim 96.2 \text{ mg}$) and mixed with $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (380 mg) in 50 cm^3 of deionized water (beaker B). The mixture in beaker A was then transferred to beaker B, and the resulting mixture was stirred continuously at ambient temperature for 48 h. Upon completion, the solid product was collected by vacuum filtration using a Büchner funnel and subsequently washed with deionized water ($3 \times 10 \text{ cm}^3$), 0.1 M NaOH ($3 \times 10 \text{ cm}^3$), 0.1 M HCl ($3 \times 10 \text{ cm}^3$), and acetone ($3 \times 10 \text{ cm}^3$) to remove unreacted species and residual reagents. The final material was dried in an oven at 60°C for 3 h. A schematic representation of the synthetic route is provided in Figure 4.3. The produced amine-functionalized IGMWCNTs and the precursor were characterized using elemental analysis (Costech ECS 4010 elemental analyzer), FTIR (iS50 ATR-FTIR), and TGA/DTG (TA instruments SDT Q600).

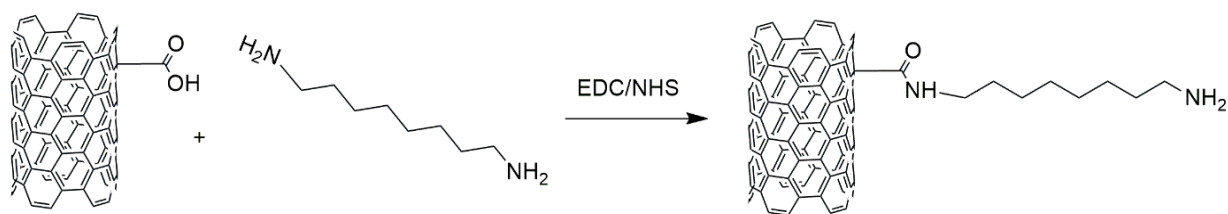


Figure 4.3. Amine functionalization of IGMWCNT-COOH.

Step 2. Synthesis of 4-carboxy-NHPI

4-Carboxy-NHPI was synthesized following the substrate ratio reported by Ishii et al. [217], with modifications that the reaction was carried out in a microwave reactor at a different temperature and reaction time. Hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) and trimellitic anhydride (TA) were combined in a molar ratio of 1.1:1 and dissolved in 30 cm^3 of pyridine. The resulting mixture was refluxed at 120°C for 2 h under vigorous stirring in a microwave reactor operating at high power. After completion of the reaction, pyridine was removed under reduced pressure. The obtained product was washed with ice-cold acidic water (1 M HCl), followed by ice-cold deionized water, then collected by filtration and dried under vacuum. A schematic illustration of the synthesis is presented in Figure 4.4, and the ^1H NMR spectrum of the obtained product is provided in Figure A2. (Appendices).

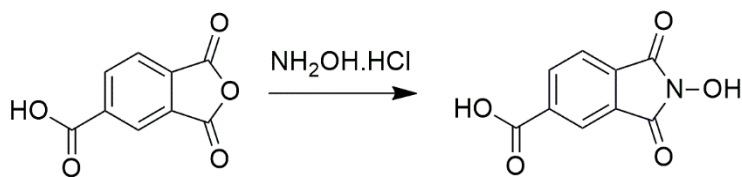


Figure 4.4. Synthesis of 4-carboxy-NHPI.

Step 3. Protection of the -NO-H group in 4-carboxy-NHPI

The protection procedure of the NO-H group in 4-carboxy-NHPI was adopted from the previous work with appropriate modifications [277]. An amount of 4-carboxy-NHPI corresponding to 2.5 equivalents with respect to the amine-functionalized CNTs (amine loading 0.3332 mmol/1000 mg) was dissolved in 25 cm³ of acetonitrile. To this solution, *N,N*-diisopropylethylamine (DIEA), in an amount equivalent to 2 equivalents relative to 4-carboxy NHPI, was added dropwise under continuous stirring. In a separate flask, trityl chloride (TrCl), corresponding to 1.2 equivalents with respect to the N-OH groups of 4-carboxy NHPI, was dissolved in 25 cm³ of acetonitrile and then slowly added to the first solution. The resulting reaction mixture was refluxed at 70 °C for 15 h with thorough stirring. After completion, the solvent was removed under reduced pressure using a rotary vacuum evaporator. The product was extracted with ethyl acetate and deionized water; the crude organic phase was separated, and the solvent was evaporated under reduced pressure. ¹H NMR analysis (400 MHz, DMSO-d₆) confirmed the successful introduction of the protecting group (Figure A3, Appendices). The scheme has been illustrated in Figure 4.5.

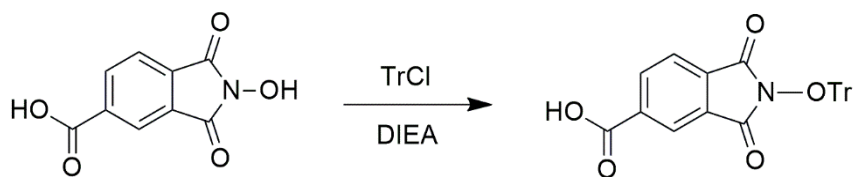


Figure 4.5. Protection of 4-carboxy-NHPI.

Step 4. Grafting the 4-carboxy-NHPI on amine-functionalized CNTs and removing the protection

The amine-functionalized CNTs (IGMWCNT-CO-NH-NH₂) (1000 mg, 0.3332 mmol of -NH₂) and Na₂CO₃·H₂O (380 mg) were mixed in 50 cm³ of deionized water in beaker A. In another beaker B, the protected 4-carboxy-NHPI, EDC·HCl (20.825 mmol, ~3992.15 mg), and NHS

(7.25 mmol, ~834 mg) were dissolved in 50 cm³ of deionized water and rigorously stirred employing a magnetic stirrer for 30 min at 0 °C using an ice bath. The solution was then added slowly to beaker A and stirred at room temperature for 48 h. The solid was then separated using a Büchner funnel and washed thoroughly with deionized water, then acetone. The recovered material was additionally washed with ethyl acetate to extract all the impurities and dried in an oven at 60 °C for 3 h.

Deprotection of the trityl group using a 10:1 mixture of dichloromethane (CH₂Cl₂): trifluoroacetic acid (TFA) completes the grafting procedure. The protected NHPI-grafted CNTs were first sonicated in the solution for 10 min and then stirred at room temperature for 25 min. The product was separated using filtration and washed again with CH₂Cl₂ and acetone. The filtrate was concentrated under reduced pressure employing a rotary evaporator, yielding a solid residue. ¹H NMR analysis of the solid residue confirmed the presence of the trityl group, most probably in the form of trityl trifluoroacetate (Figure A4, Appendices), thereby unequivocally demonstrating the successful grafting procedure. The scheme has been presented in Figure 4.6. FTIR analysis (iS50 ATR-FTIR) was performed for the protected NHPI-grafted IGMWCNTs and the final NHPI-grafted IGMWCNTs product.

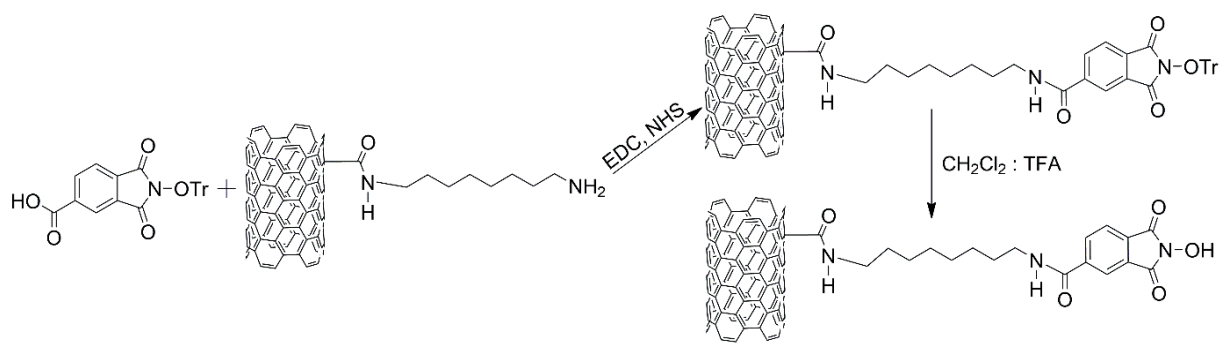


Figure 4.6. Grafting of NHPI onto amine-functionalized IGMWCNTs.

4.8 EB Oxidation

The oxidation reactions were performed employing a gasometric apparatus [220]. The required amounts of substrate (EB), catalysts, and initiator were added to a 10 cm³ two-neck flask. Subsequently, the flasks were connected to a burette. The reaction mixtures were then purged and filled with oxygen at atmospheric pressure and maintained at 80 °C under rigorous stirring (> 1000 rpm) for the selected reaction time. The volume of oxygen consumed (cm³) during the

oxidation reactions was measured from the burette, and the corresponding moles of oxygen (n_{O_2}) were determined with the following equation:

$$n_{O_2} = \frac{V_{O_2} \times 273.15 \times P}{101325 \times 22415 \times T} \text{ (mol)}$$

Where, V_{O_2} represents the volume of oxygen consumed (cm^3), while P and T denote the atmospheric pressure (Pa) and room temperature (K), respectively. The percentage conversion of EB was subsequently calculated using the following equation:

$$\alpha = \frac{n_{O_2}}{n} \times 100 \text{ (\%)}$$

Where n is the moles (mol) of EB used.

The product analyses were performed employing iodometric and gas chromatography (GC) analyses. The quantity of PEHP produced was determined by iodometric analysis [278]. A sample of approximately 0.2 g was withdrawn from the reaction mixture into a flask immediately after the completion of the predetermined reaction time. To this, 20 cm^3 of glacial acetic acid was introduced, and the flask was purged with carbon dioxide to eliminate air. Following the addition of 2 g of sodium iodide, the flask was sealed and kept in a dark place for 30 min to allow iodine formation. Subsequently, 20 cm^3 of deionized water was introduced, and the mixture was titrated with 0.1 M standard sodium thiosulfate solution, employing a Brand Digital II burette. The moles of PEHP (n_{PEHP}) and then its selectivity (S_{PEHP}) were then determined using the following equations:

$$PEHP = 0.0069 \times \left[\frac{V - V'}{m} \right] \text{ (\%)}$$

Where m is the mass of the sample, and V and V' are the volumes of sodium thiosulfate solution used for the sample titration and blank titrations, respectively.

$$n_{PEHP} = \left[\frac{PEHP(\%)}{100} \right] \times \left[\frac{m_{total}}{MW_{PEHP}} \right] \text{ (mol)}$$

Where m_{total} is the mass of the reaction mixture at the beginning of the reaction, and MW_{PEHP} is the molecular weight of PEHP. The selectivity of the PEHP was then calculated using the following equation.

$$S_{PEHP} = \frac{n_{PEHP}}{n_{O_2}} \times 100 (\%)$$

On the other hand, PEHP is an unstable compound and can readily decompose into PEA and/or AcPO. Consequently, PEHP was reduced to PEA using triethyl phosphite ((EtO)₃P) before GC analysis. The utilized (EtO)₃P is oxidized to triethyl phosphate (EtO)₃PO; therefore, the quantity of PEA measured by GC analysis is equal to the sum of the PEA produced during the reaction and the decomposed PEHP. The selectivity of PEA can be calculated by simply subtracting the selectivity of the PEHP determined using iodometric analysis from the selectivity of PEA determined from GC analysis.

4.9 Analytical Methods

Gas Chromatography (GC)

Gas chromatographic analyses were performed using a Shimadzu GC-2010 Plus (Shimadzu Corporation, Kyoto, Japan) equipped with a flame ionization detector (FID) and a ZB-5HT capillary column (29.5 m × 0.25 mm i.d.). A representative chromatogram is shown in Figure 4.7. Samples were injected in split mode (1:100) with an injection volume of 0.5 mm³, using acetonitrile as the solvent, and *p*-methoxytoluene as an internal standard. The injector and detector temperatures were maintained at 280 °C and 320 °C, respectively. The carrier gas was operated at a constant linear velocity of 40 cm/s. The oven temperature program was initiated at 120 °C (held for 2.4 min), followed by a ramp to 300 °C and a final hold of 6 min. PEA, AcPO, BA, and BzA were determined using GC analysis.

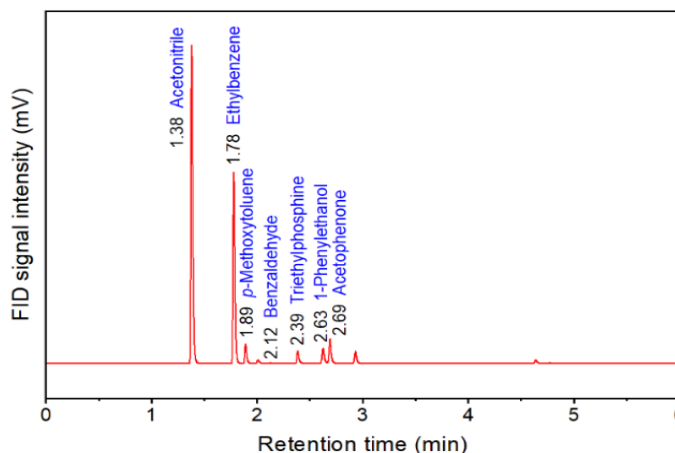


Figure 4.7. Example of a GC chromatogram obtained from the analysis of the reaction mixture.

Scanning Electron Microscopy (SEM)

The morphologies of the synthesized catalysts were examined by SEM employing a Phenom Pro desktop SEM equipped with an energy-dispersive X-ray spectroscopy (EDS) detector at 15 kV.

Transmission Electron Microscopy (TEM)

TEM analyses were carried out employing two different instruments to analyze various samples:

- (i) Thermo Fisher Scientific Titan³ G2 S/TEM 60-300 (FEI), equipped with a ChemiSTEM EDS detector, was employed for high-resolution imaging and elemental analysis. The microscope was operated at an accelerating voltage of 80kV.
- (ii) Thermo Fisher Scientific TecnaiG2 F20 X-TWIN/FEI was employed for high-resolution imaging to analyze the morphology and structural features.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

The metal content of the samples was determined using inductively coupled plasma mass spectrometry (ICP-MS) NexION 300D (Perkin-Elmer).

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

The metal content of the samples was determined by ICP-OES analysis, employing a Thermo Scientific iCAP 7400 Duo spectrometer equipped with a TELEDYNE CETAC ASX-560 autosampler.

Textural Properties (N₂ Adsorption-Desorption Analysis)

The textural properties of the catalysts were investigated by nitrogen adsorption-desorption isotherms using a Micromeritics ASAP 2020 Plus system. The specific area was calculated using Brunauer-Emmett-Teller (BET) and Langmuir models. The micropore surface area was determined by the t-plot method. At the same time, the pore size distribution was evaluated using the N₂ density functional theory (DFT) model method, as well as the Barrett-Joyner-Halenda (BJH) method applied to the adsorption and desorption branches of the isotherms.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analyses were performed employing various spectrometers and measurement configurations, based on samples, as outlined below:

- (i) FTIR spectra were recorded employing a Thermo Scientific Nicolet 6700 spectrometer. Solid samples were finely ground with KBr and pressed into pellets before the analysis. Spectra were acquired at a resolution of 4 cm^{-1} with 32 accumulations over the wavenumber range from 4000 to 400 cm^{-1} . The IL [emim][OcOSO₃] was analyzed on the same instrument using an ATR Smart Orbit accessory.
- (ii) FTIR spectra were acquired using a PerkinElmer Spectrum Two spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory. Spectra were acquired over 4000 - 400 cm^{-1} at a resolution of 4 cm^{-1} , averaging 4 scans per measurement.
- (iii) FTIR spectra were recorded employing an iS50 ATR-FTIR spectrophotometer from Thermo Fischer Scientific. Solid samples were finely ground with KBr and pressed into pellets before the analysis. Spectra were acquired at a resolution of 4 cm^{-1} with 32 accumulations over the wavenumber range from 4000 to 400 cm^{-1} .

Thermogravimetric and Differential Scanning Calorimetry Analyses (TGA/DSC)

TGA/DSC analyses were performed to assess the thermal stability of the prepared catalysts, detect the presence of NHPI and IL in recycled hybrid catalyst samples, and confirm the successful grafting of a long-chain amine spacer and NHPI. The following equipment was used for the analysis:

- (i) Mettler Toledo TGA851e thermobalance (Greifensee, Switzerland)
- (ii) TGA/DSC STAR system analyzer from Mettler Toledo (Temperature range was from 25 - $800\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under N_2 atmosphere)
- (iii) PerkinElmer thermal analyzer (Temperature range was from 30 - $900\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under N_2 atmosphere)
- (iv) TA instruments SDT Q600 (Temperature range was from 30 - $900\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under air atmosphere)

- (v) Linseis L63 DSC (Temperature range was from 0-300 °C with heating rate of 5 °C · min⁻¹ under N₂ atmosphere (20 cm³ · min⁻¹))

Elemental Analysis

The elemental composition of the samples was determined by CHNS analysis using a Costech ECS 4010 elemental analyzer, which simultaneously quantifies carbon, hydrogen, nitrogen, and sulfur. Each sample was analyzed in triplicate, and the reported values represent the average of three independent measurements. The corresponding standard deviations reflect the reproducibility of the analyses.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The ¹H-NMR spectra were recorded using an Agilent-MR spectrometer (400 MHz). The samples were dissolved in dimethyl sulfoxide-d₆, with tetramethylsilane as the internal resonance shift standard.

5. Results and Discussion

5.1 Transition Metals Modified MWCNTs

The catalytic activity of pristine CNTs in the liquid-phase oxidation of hydrocarbons is attributed to the efficient electron transfer in the graphene sheets, which arises from the delocalized π -electrons of the sp^2 hybridized graphitic units of CNTs [67,73]. It has been demonstrated that these materials facilitate the decomposition of primary hydroperoxide products into the corresponding alcohols and/or ketones via π - π interactions between the aromatic rings and the graphitic surfaces of the CNTs, thereby enhancing the oxidation reaction rate [67,68,80]. The incorporation of transition metals (e.g., Fe, Co, Mn), via covalent and noncovalent approaches, further enhances catalytic activity by increasing the rate of hydroperoxide decomposition [123–127,129,130]. It is well established that transition metal compounds promote the decomposition of primary hydroperoxides into the corresponding alcohols and ketones during the liquid-phase oxidation of hydrocarbons [131–135].

It is also postulated that metal-support interactions are particularly significant in configurations where metal nanoparticles are confined within CNT channels [136,137]. The intrinsic tubular structure of CNTs provides nanoscale confinement, stabilizing active species and enhancing catalytic performance [140,141]. This confinement induces curvature-driven distortion of the sp^2 carbon framework, resulting in redistribution of π -electron density, which ultimately enhances the electron mobility and catalytic activity [136,279].

Based on the literature, herein, MWCNTs and carboxylated MWCNTs (MWCNT-COOH) were modified with transition metal salts of Cu(II), Co(II), and Mn(II) using modified protocols derived from previously reported methods. Three types of catalysts were obtained to enhance the oxidation rate and are distinguished as follows:

1. Metal-rich MWCNT composites
2. Metal-modified MWCNTs
3. Metal-functionalized carboxylated MWCNTs.

This study aims to obtain transition metals modified MWCNTs that may accelerate the oxidation of hydrocarbons in the liquid phase by, among others, facilitating the decomposition

of the primary product PEHP into the corresponding AcPO and/or PEA under solvent-free conditions using molecular oxygen as the oxidant. These metal-modified MWCNTs are hypothesized to interact also synergistically with NHPI, possibly promoting the generation of the PINO radical while concurrently enhancing oxidation rate. The hypothesized synergistic effect between the metal-modified MWCNTs and NHPI is presented in Figure 5.1.

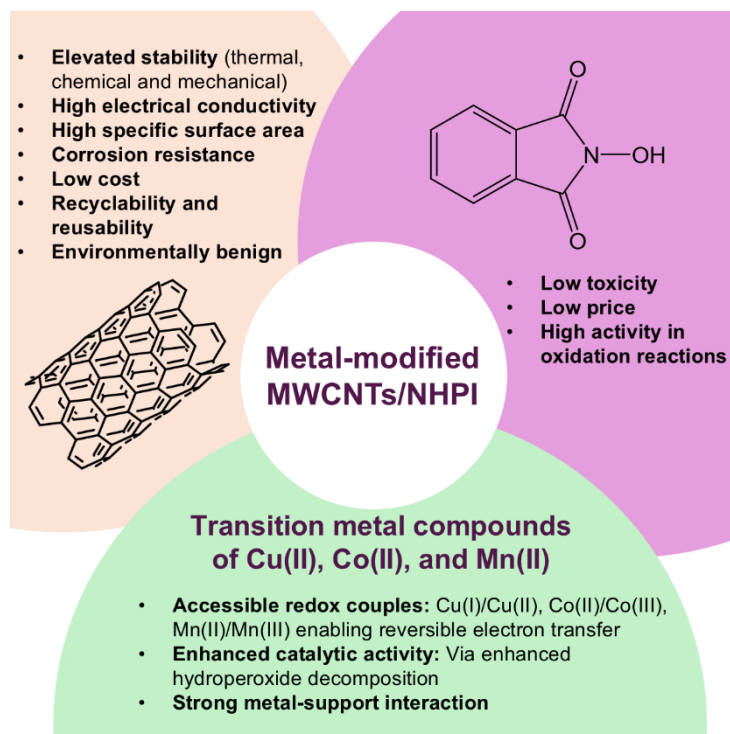


Figure 5.1. Synergistic effect between metal-modified MWCNTs and NHPI.

5.1.1 Metal-rich MWCNT composites

Metal-rich MWCNT composites were prepared using a previously reported method [142], and their catalytic activity was evaluated in the liquid-phase oxidation of hydrocarbons. The materials were prepared using MWCNTs as supports, while Cu(II), Co(II), and Mn(II) nitrate salts served as the metal precursors for the respective composites. The primary objective was to incorporate the catalytically active metal species onto and/or into the CNT framework, thereby combining their known catalytic influence on these processes with potential synergistic interactions with π -conjugated CNT structure. This design was intended to enhance catalytic efficiency under metal-rich conditions in the presence of NHPI under solvent-free conditions.

5.1.1.1 *Metal-rich MWCNT composites preparation and characterizations*

The procedure for the preparation of metal-rich MWCNT composites was adapted from the Co-encapsulation method reported by Shi et al. for styrene epoxidation [142]. In the reported protocol, CNTs were treated with concentrated HNO_3 (140 °C, 14 h) to produce open-ended and shortened structures, followed by impregnation with 50 wt.% aqueous $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution under ultrasonication (1 h) and stirring for 24 h. Controlled solvent evaporation enabled capillary-driven incorporation of Co species into the channels of the CNTs. The resulting paste-like mixture was then dried under vacuum (60 °C, 10 h) and calcinated at 350 °C for 5 h to obtain the Co/CNTs catalyst. The authors reported a cobalt content of ~4.3% determined by ICP.

In the present study, this approach was extended to prepare Cu-, Co-, and Mn-rich MWCNT composites. The oxidative treatment step was employed to introduce surface defects, open tube ends, and shorten the nanotubes, thereby facilitating both surface anchoring and internal encapsulation of metal species. However, treatment at 140 °C for 14 h using concentrated HNO_3 resulted in substantial mass loss (~50%), indicating significant oxidative degradation of the MWCNTs frameworks. Probably, prolonged oxidation at elevated temperatures progressively disrupted the graphitic framework, leading to severe structural damage and, in extreme cases, to transformation into highly disordered (amorphous-like) carbon.

Despite this, the obtained MWCNTs were utilized to prepare Cu-rich MWCNTs composite (Cu-MWCNT@14h) using a 5 wt.% precursor solution (50 cm³). To minimize the structural degradation, the acid treatment time was subsequently reduced to 6 h. Under these conditions, the majority of the MWCNTs mass was preserved, and the materials were used for the preparation of Cu-MWCNT@6h, Co-MWCNT@6h, and Mn-MWCNT@6h composites. ICP-OES analysis revealed high metal concentrations of 619, 667, and 706 g · kg⁻¹ for Mn, Cu, and Co, respectively.

The morphologies of pristine and metal-rich MWCNT composites were examined using TEM. The TEM images were acquired at various magnifications and are presented in Figure 5.2. The TEM images of pristine MWCNTs, shown in Figure 5.2 (a), demonstrated smooth, defect-free structures with outer diameters (OD) ranging from 20 to 40 nm. In contrast, the TEM images of Cu-, Co-, and Mn-MWCNT composites (Figure 5.2 (b), (c), and (d), respectively)

demonstrated a high loading of metal nanoparticles, present as dispersed particles distributed over the nanotube surfaces and within the nanotube bundles, while localized agglomerates were observed on the surfaces. The acid treatment not only opened the CNT ends but also generated surface defects, such as cracks, vacancies, and exposed edges, which served as anchoring sites for the nanoparticles during the catalyst preparation process (Figure 5.3).

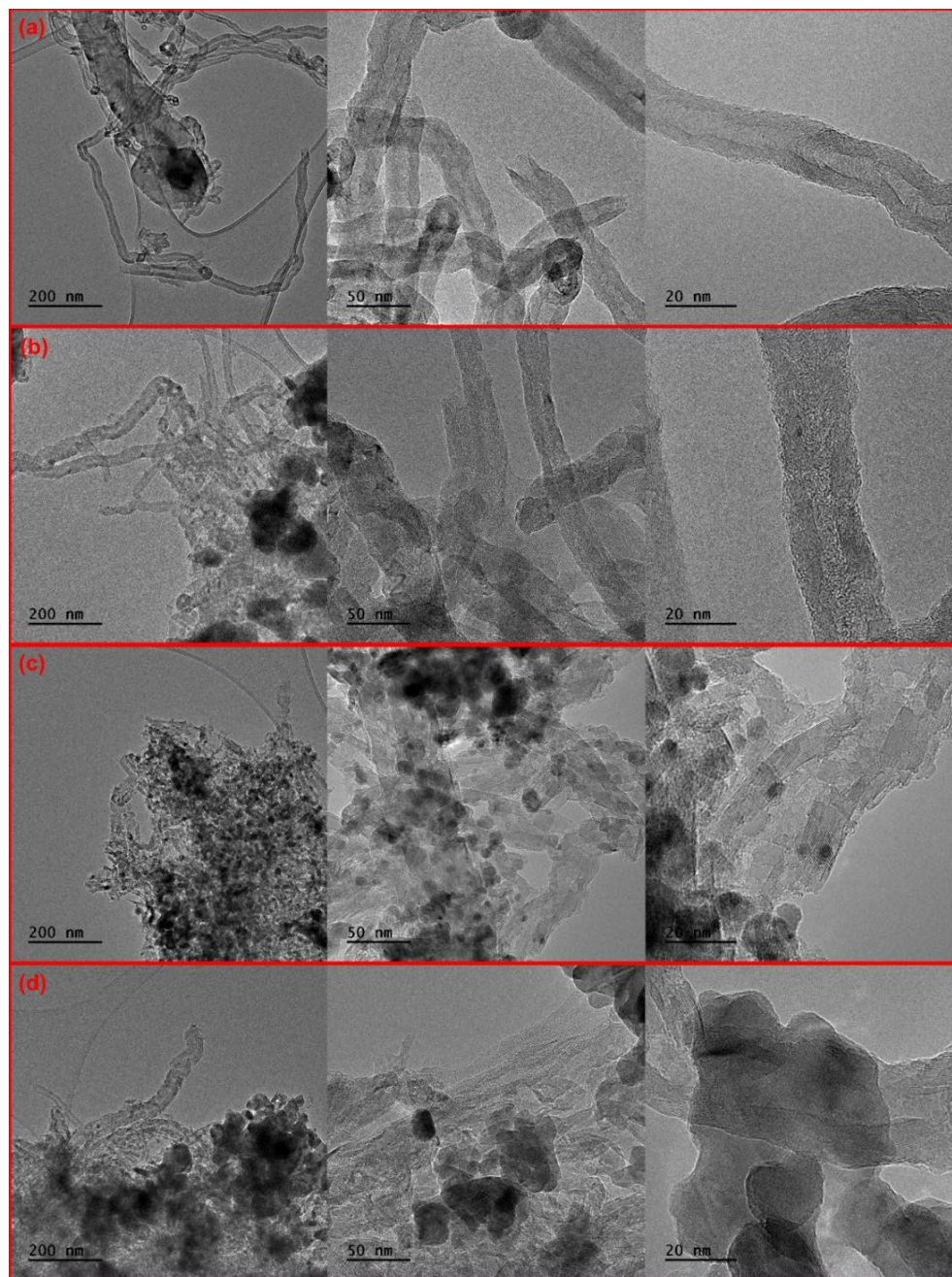


Figure 5.2. TEM images of the fresh samples of (a) MWCNTs, (b) Cu-MWCNT@6h, (c) Co-MWCNT@6h, and (d) Mn-MWCNT@6h.

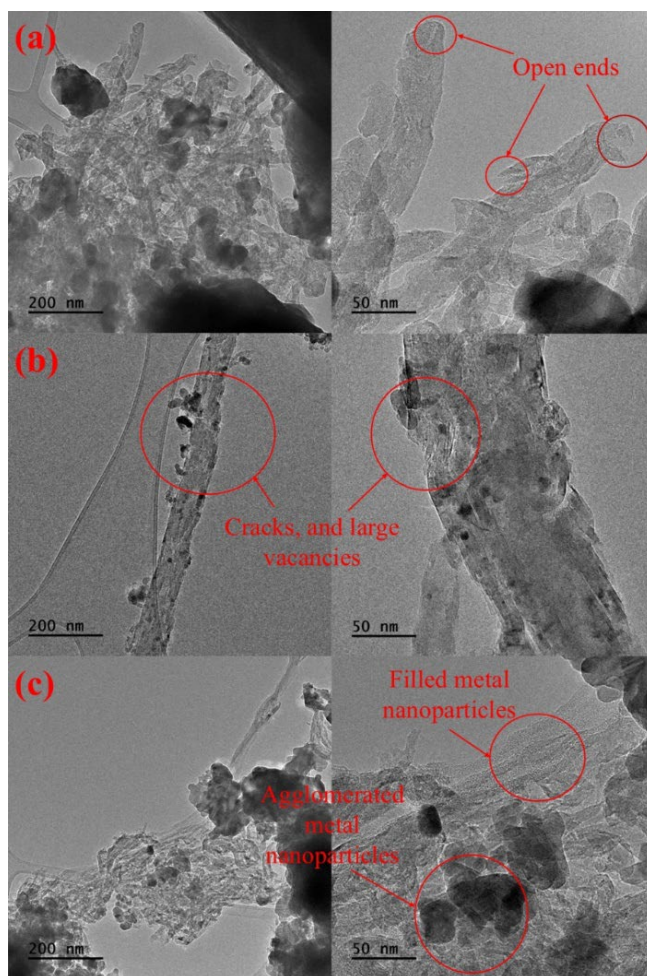


Figure 5.3. TEM Images of the metal-rich MWCNT composites for (a) Cu-, (b) Co-, and (c) Mn-MWCNT@6h.

5.1.1.2 Catalytic activity of the metal-rich MWCNT composites

The influence of metal-rich MWCNT composites in combination with NHPI on solvent-free oxidation of EB with dioxygen was investigated. The obtained results are presented in Table 5.1. For comparison, the performance of MWCNTs was also evaluated.

Table 5.1. Effect of metal-rich MWCNT composites, in combination with NHPI, on the solvent-free oxidation of EB with oxygen.

Entry	Catalyst	Metal loading (g. kg ⁻¹)	Con. (%)	Sel. (%)				mmol of EB converted / mmol of metal
				PEHP	PEA	AcPO	BA	
1	-	-	6.4	73.2	21.1	5.7	-	-
2	MWCNTs	-	6.3	91.2	4.9	3.9	-	-
3	Cu-MWCNT@14h	-	25.4	23.9	2.0	73.3	0.8	-
4	Cu-MWCNT@6h	667	20.8	21.2	1.7	76.2	0.9	12.9
5	Co-MWCNT@6h	706	18.0	39.6	3.7	55.8	0.9	9.8
6	Mn-MWCNT@6h	619	21.1	29.8	4.1	64.9	1.2	12.3

Reaction conditions: EB:16.33 mmol; catalyst: 0.025 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

It can be observed that the incorporation of Cu, Co, and Mn into MWCNTs (entries 3-6) enhanced the catalytic activity compared to pristine MWCNTs (entry 2). Under the same conditions, the EB conversion achieved with metal-rich MWCNT composites is 3-4 times higher than that of pristine MWCNTs. For Mn- and Cu-rich composites, a similar EB conversion (~21%) was obtained, slightly higher than that for Co-rich MWCNTs (entries 4-6). The results also demonstrated that metal incorporation significantly alters the product distribution, leading to a decrease in PEHP selectivity and a shift toward AcPO. The highest AcPO selectivity (76.2%) was observed for Cu-MWCNT@6h. The PEHP selectivity decreases in the opposite order to the metal loading (mmol per 0.025 g catalyst), which follows Co (0.30 mmol) > Mn (0.28 mmol) > Cu (0.26 mmol). Probably, the catalytic activity of the obtained composites is not governed only by metal type and loading but is also influenced by additional factors such as metal dispersion, accessibility of active sites, metal-support interactions, and the form of the incorporated metal. The catalytic activity could also be attributed to improved electron-transfer processes at the surface of the metal-rich MWCNT composites, which facilitates interaction between radical species, PEHP, and the CNT framework. This, in turn, promotes the decomposition of the primary PEHP product into AcPO. Probably, the metal-rich

MWCNT composites also promote PINO generation from NHPI, thereby facilitating PEHP formation and accelerating the reaction rate.

It can also be observed that the acid treatment time also affects the activity of the metal-rich MWCNT composites. The EB conversion obtained after 6 h of reaction in the presence of Cu-MWCNT@14h is higher than that obtained by using the material treated for 6 h, i.e., Cu-MWCNT@6h. This enhancement can be attributed to the increased structural distortion and shortening of the CNTs, which likely leads to a higher specific surface area compared with the sample treated for 6 h. However, this improvement is accompanied by a drawback, as prolonged acid treatment results in a partial loss of the initially used CNTs material during the preparation process.

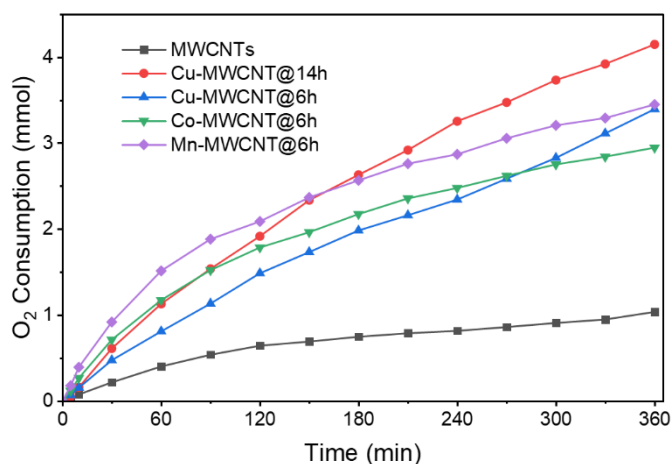


Figure 5.4. Oxygen consumption vs. time of EB oxidation reaction in the presence of metal-rich MWCNT-based catalysts. Reaction conditions: EB:16.33 mmol; catalyst: 0.025 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

The course of the studied reactions, i.e., the amount of oxygen consumed versus reaction time, is presented in Figure 5.4. At the initial stage of reactions, the rate of O₂ consumption over metal-rich MWCNT-based catalysts is significantly higher compared to that over pristine MWCNTs and increases in the following order: Co < Cu < Mn. However, the O₂ consumption rates decrease gradually as the reaction proceeds, faster for Co- and Mn-rich composites. The Cu-MWCNT@16h shows the highest overall O₂ consumption rate.

The effect of catalyst loading on the oxidation reaction was also investigated. Catalyst amounts of 0.0125, 0.025, and 0.0375 g were employed. Increasing the catalyst loading slightly

enhanced the O₂ consumption rate for the metal-rich MWCNT composite-based catalysts (Figure 5.5). The O₂ consumption rate for Cu-MWCNT@6h increased gradually with time across all the catalyst loadings (Figure 5.5 (a)). However, the O₂ consumption profiles for Co- and Mn-MWCNT@6h (Figure 5.5 (b) and (c), respectively) show an initial rapid increase, followed by a gradual decrease in the reaction rate over the course of the reaction at all loadings. Similarly, Table 5.2 shows that the EB conversion only slightly increased with higher catalyst loadings. Simultaneously, the selectivity towards PEHP decreased. Nonetheless, all metal-rich MWCNT composite catalysts displayed high activity, promoting EB oxidation while selectively decomposing the PEHP towards AcPO.

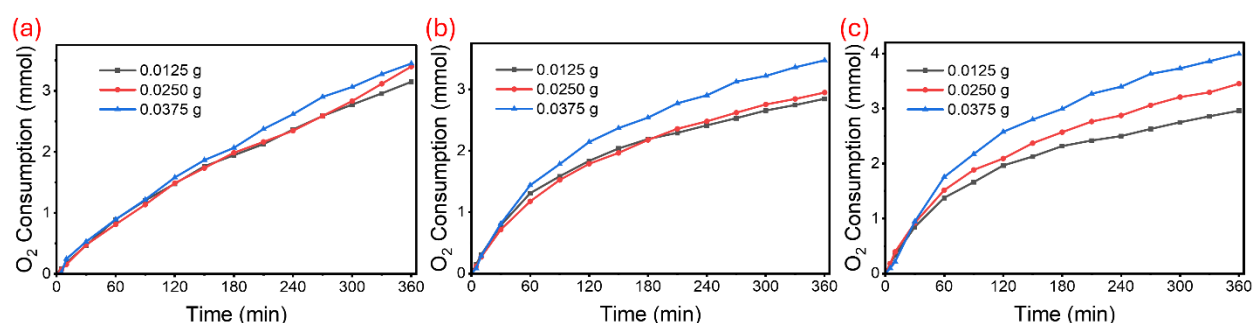


Figure 5.5. Oxygen consumption vs. time of EB oxidation reaction in the presence of metal-rich MWCNT composites-based catalysts: (a) Cu-MWCNTs, (b) Co-MWCNTs, and (c) Mn-MWCNTs, at various loadings. Reaction conditions: EB:16.33 mmol; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

Table 5.2. Effect of metal-rich MWCNT composites loading on the solvent-free oxidation of EB with oxygen.

Entry	Catalyst	Catalyst (g)	Con. (%)	Sel. (%)				mmol of EB converted / mmol of metal
				PEHP	PEA	AcPO	BA	
1	Cu-MWCNT@6h	0.0125	19.3	44.0	13.4	42.0	0.6	24.0
2	Cu-MWCNT@6h	0.0250	20.8	21.2	1.7	76.2	0.9	12.9
3	Cu-MWCNT@6h	0.0375	21.1	26.6	5.3	67.1	1.0	8.7
4	Co-MWCNT@6h	0.0125	17.5	53.9	6.0	39.6	0.5	19.1
5	Co-MWCNT@6h	0.0250	18.0	39.6	3.7	55.8	0.9	9.8
6	Co-MWCNT@6h	0.0375	21.3	37.3	5.6	55.9	1.2	7.7
7	Mn-MWCNT@6h	0.0125	18.1	48.8	3.8	46.6	0.8	21.0
8	Mn-MWCNT@6h	0.0250	21.1	29.8	4.1	64.9	1.2	12.3
9	Mn-MWCNT@6h	0.0375	24.4	24.3	7.4	66.7	1.6	9.4

Reaction conditions: EB:16.33 mmol; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

5.1.1.3 Recyclability of metal-rich MWCNT composites

The recyclability and reusability of all the metal-rich MWCNT composites were thoroughly examined, and the results are presented in Table 5.3 and Figure 5.6. During the recyclability test, the catalyst was separated from the reaction mixture after the completion of the reaction, thoroughly washed with methanol and acetone, dried, and reused in subsequent cycles. Complete recovery of the catalyst proved difficult, as a portion was lost due to adherence to the flask and filter papers and/or membranes during the washing process. To thoroughly compare the catalytic activity in the corresponding cycles, the amount of EB, NHPI, and AIBN used was taken in relation to the weight of the recovered catalyst. Nonetheless, catalyst recovery will be higher in large-scale reactions.

Table 5.3. Recyclability of Cu-, Co-, and Mn-MWCNT composites.

Entry	Cycle	Catalyst	Con. (%)	Sel. (%)			
				PEHP	PEA	AcPO	BA
1	0	Cu-MWCNT@14h	25.4	23.9	2.0	73.3	0.8
2	1	Cu-MWCNT@14h	23.1	31.0	7.0	61.4	0.6
3	2	Cu-MWCNT@14h	23.9	24.8	8.8	65.8	0.6
4	3	Cu-MWCNT@14h	22.6	46.2	5.3	48.0	0.5
5	0	Cu-MWCNT@6h	20.8	21.2	1.7	76.2	0.9
6	1	Cu-MWCNT@6h	20.9	38.0	8.1	53.4	0.5
7	2	Cu-MWCNT@6h	17.6	33.5	2.0	62.7	1.8
8	0	Co-MWCNT@6h	18.0	39.6	3.7	55.8	0.9
9	1	Co-MWCNT@6h	18.7	48.9	8.4	42.2	0.5
10	2	Co-MWCNT@6h	20.1	39.6	3.7	55.8	0.9
11	0	Mn-MWCNT@6h	21.1	29.8	4.1	64.9	1.2
12	1	Mn-MWCNT@6h	19.2	45.6	4.2	49.7	0.5
13	2	Mn-MWCNT@6h	17.6	39.9	1.7	56.8	1.6

Reaction conditions: EB: 16.33 mmol; catalyst: 0.025 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; P: MPa; 6 h. For cycle *i*, the EB, NHPI, and AIBN amounts were adjusted according to the mass of recovered catalyst.

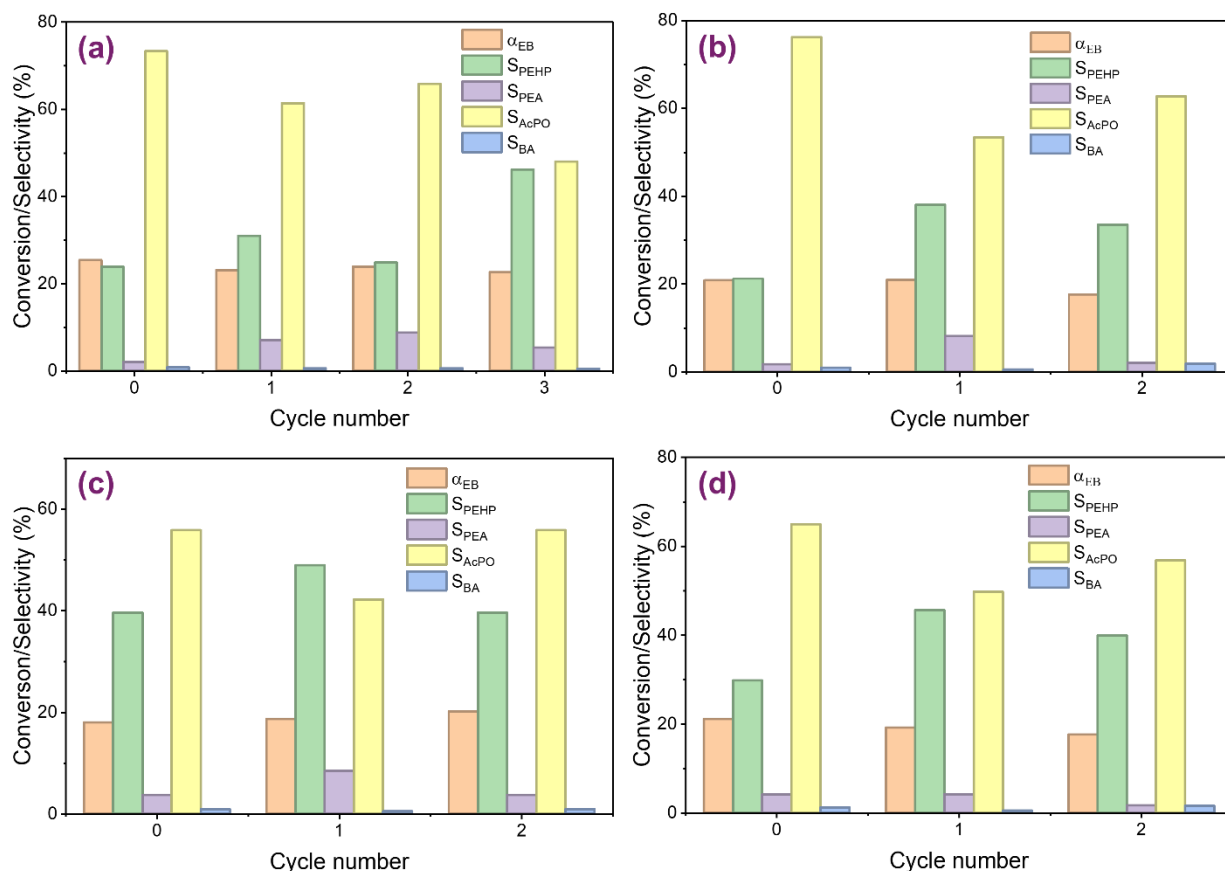


Figure 5.6. Recyclability of (a) Cu-MWCNT@14h, (b) Cu-MWCNT@6h, (c) Co-MWCNT@6h, and (d) Mn-MWCNT@6h. Reaction conditions: EB: 16.33 mmol; metal-rich MWCNT composite: 0.025 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. For cycle i , the EB, NHPI, and AIBN amounts were adjusted according to the mass of recovered catalyst.

The conversion of EB decreased slightly in the subsequent cycles in the presence of recovered metal-rich MWCNT. Simultaneously, the selectivity of PEHP increased, and the selectivity of AcPO decreased, especially in the third cycle. Probably, this was an effect of partial loss of the active catalyst during the successive recycling process and leaching of the metal agglomerates, which was confirmed by ICP-OES analysis (Table 5.4). The slight fluctuations in EB conversion and product distribution in subsequent cycles could also be attributed to differences in the proportion of the recovered catalysts and the corresponding amounts of EB and NHPI used.

Table 5.4. Metal content in the fresh and recycled catalysts.

Catalyst	Fresh	Recycled	Metal loss (%)
	Metal content ($\text{g} \cdot \text{kg}^{-1}$)	Metal content ($\text{g} \cdot \text{kg}^{-1}$)	
Cu-MWCNT@6h	667	594	10.95
Co-MWCNT@6h	706	648	8.22
Mn-MWCNT@6h	619	504	18.85

5.1.2 Metal-modified MWCNTs

The metal-modified MWCNTs were prepared following a similar approach to that for metal-rich MWCNT composites, with appropriate modifications leading to lower metal loading. The produced metal-modified MWCNTs were evaluated under similar conditions in the solvent-free liquid-phase oxidation of EB using molecular oxygen as a green oxidant. The recyclability of the resultant metal-modified MWCNTs was also tested in the solvent-free oxidation reaction.

5.1.2.1 Metal-modified MWCNTs preparation and characterization

The metal-modified MWCNTs were produced by refining the procedure for metal-rich MWCNT composites. The key differences were that 1 M solutions of the metal precursors were used (in place of 5% solutions) and, after the metal impregnation step, the precursor solutions were separated, and the MWCNTs were briefly washed to remove part of metal species from the surface, thereby promoting better metal dispersion. The metal-impregnated MWCNTs were then dried under vacuum and subsequently calcinated under an inert atmosphere to obtain metal-modified MWCNTs. This modified protocol led to a more controlled incorporation of metal species and is expected to favor improved dispersion of the active metal species across the MWCNT framework.

It can be reasonably assumed that the pristine MWCNTs employed, being identical to those used for the preparation of the metal-rich MWCNT composite and subjected to the same oxidative acid treatment conditions, exhibit comparable structural morphology, as shown in Figure 5.1 and Figure 5.2. The observed morphology is characterized by open ends and/or

shortened nanotubes with surface defects such as cracks and vacancies that host the metal nanoparticles.

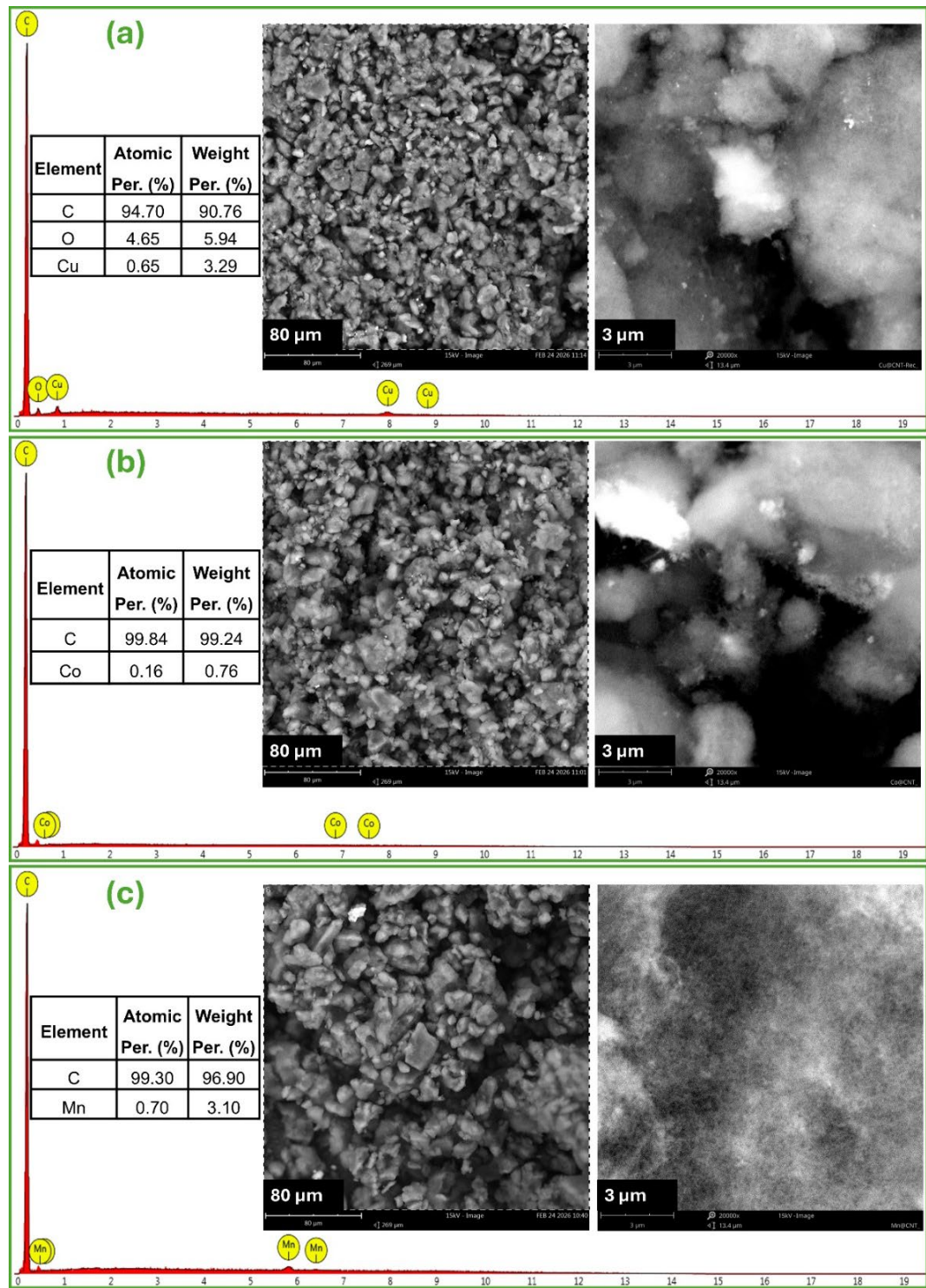


Figure 5.7. SEM images and EDS analyses of the metal-modified MWCNTs: (a) Cu-MWCNTs, (b) Co-MWCNTs, and (c) Mn-MWCNTs.

SEM and EDS analyses were performed on the metal-modified MWCNTs, and the results are presented in Figure 5.7. The SEM images do not provide sufficient resolution to clearly reveal morphological alterations at the nanoscale. Images obtained at lower magnifications indicate the presence of agglomerates; however, images at higher magnifications lack sharpness, which may be attributed to the limitations of the instrument as well as the intrinsic properties of the material. EDS analysis confirmed the presence of metals in the modified materials, with metal contents of 0.76, 3.10, and 3.29% for Co, Mn, and Cu, respectively. In the case of the Cu-modified sample, the presence of oxygen was also detected, which may indicate the presence of an oxidized form of this metal. Since EDS is not a suitable method for the quantitative determination of light elements (such as carbon and oxygen), the obtained quantitative determinations should be considered as approximate. ICP-MS analysis was also performed to accurately quantify the metal content, which was determined to be 0.70, 1.09, and 3.85% for Co, Mn, and Cu, respectively, in the fresh samples.

5.1.2.2 Catalytic activity of metal-modified MWCNTs

The effects of metal-modified MWCNTs on solvent-free aerobic oxidation of EB, in the absence and presence of NHPI as a cocatalyst, are presented in Table 5.5. For comparison, reaction data for the blank experiment (entry 1), NHPI (entry 2), and MWCNTs (with/without NHPI, entries 3-4) were also acquired under identical conditions. It can be observed that, under similar reaction conditions, both the blank experiment and the NHPI-containing system selectively promoted the formation of PEHP, although the presence of NHPI slightly enhanced the EB conversion. In contrast, when the reaction was performed in the presence of pristine MWCNTs without NHPI (entry 3), the product distribution shifted toward PEA. This behavior can be attributed to the capability of MWCNTs to promote the decomposition of PEHP into the corresponding alcohol. Upon introducing NHPI as a cocatalyst alongside MWCNTs (entry 4), selectivity shifted back toward PEHP, consistent with NHPI's well-established role in favoring hydroperoxide formation in the absence of metal-based catalysts. Similarly, when the acid-treated MWCNTs were employed in the oxidation reaction with NHPI (entry 5), the EB conversion decreased drastically to 2.4%, with elevated selectivity towards PEHP. This could be attributed to the oxygen-containing functional groups introduced during acid treatment. The high density of these oxygenated functional groups on the MWNCTs negatively affects the

catalytic activity in the liquid-phase aerobic oxidation of hydrocarbons, as discussed in detail in Section 2.2 (2.2.1.3).

Table 5.5. Effect of metal-modified MWCNTs on the solvent-free oxidation of EB with oxygen.

Entry	Catalyst	Catalyst (g)	Con. (%)	Sel. (%)				mmol of EB converted / mmol of metal
				PEHP	PEA	AcPO	BA	
1 ^a	-	-	4.1	84.5	4.6	10.9	-	-
2	-	-	6.4	73.2	21.1	5.7	-	-
3 ^a	MWCNTs	0.025	5.2	43.8	51.3	4.9	-	-
4	MWCNTs	0.025	6.3	91.2	4.9	3.9	-	-
5 ^b	MWCNTs	0.025	2.4	76	9.8	14.2	-	-
6 ^a	Cu-MWCNTs	0.025	7.0	3.3	2.0	93.9	0.8	75.5
7 ^a	Co-MWCNTs	0.025	6.6	21.6	28.8	47.4	2.2	363.0
8 ^a	Mn-MWCNTs	0.025	5.5	31.9	1.8	61.7	4.6	181.1
9	Cu-MWCNTs	0.025	15.3	32.4	9.4	56	2.2	165.0
10	Co-MWCNTs	0.025	10.8	54.3	16.9	25	3.8	594.0
11	Mn-MWCNTs	0.025	11.7	37.9	17.2	40.3	4.6	385.3
12	Cu-MWCNTs	0.0375	19.3	22.3	9.3	66.2	2.2	138.7
13	Co-MWCNTs	0.0375	12.5	50.3	13.5	31.4	4.8	458.3
14	Mn-MWCNTs	0.0375	13.2	33	14.3	47.5	5.2	289.8
15	Cu-MWCNTs	0.050	21.8	5.7	8.3	83.7	2.3	117.5
16	Co-MWCNTs	0.050	14.8	7.3	13.3	78.3	1.1	407.0
17	Mn-MWCNTs	0.050	13.8	16.8	36.2	41.2	5.8	227.2

Reaction conditions: EB: 16.33 mmol; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. ^a without NHPI. ^b acid-treated (140 °C for 6 h)

The incorporation of Cu, Co, and Mn into MWCNTs (entries 6-8) in the absence of NHPI shifted selectivity towards AcPO, with slight enhancement in EB oxidation compared to pristine MWCNTs. On the other hand, when the NHPI was used as a cocatalyst, the activity of the metal-modified MWCNTs was enhanced significantly, with reduced selectivity towards PEHP (entries 9-11) in comparison with the MWCNTs/NHPI system. The highest EB conversion was achieved when Cu-modified MWCNTs (Cu-MWCNTs) and NHPI were applied, followed by Mn-MWCNTs and Co-MWCNTs. The order is in accordance with the amount of metal loading.

The catalytic activity of metal-modified CNTs can be attributed to several synergistic effects. First, the incorporated transition metals are known to accelerate the decomposition of hydroperoxides into corresponding ketones and alcohols [22,131,273]. Additionally, a beneficial effect on the PINO radical generation from NHPI is also plausible. Furthermore, this could also be attributed to improved electron transfer at the CNT surface after the incorporation of metals. Such effects have been previously reported for the metal-CNT system with a comparable configuration [78,143].

It can be observed that the product distribution is strongly dependent upon the type of incorporated metal; for instance, Cu-MWCNTs demonstrated higher selectivity towards AcPO, whereas Co-MWCNTs retained comparatively higher selectivity towards PEHP and/or PEA. The redox potential of the transition metal ions employed follows the order: Co(III)/Co(II) (1.82 V) > Mn(III)/Mn(II) (1.51 V) > Cu(II)/Cu(I) (0.16 V) [258]. Based on these differences in redox potential, it has been reported that cobalt and manganese ions can both reduce and oxidize hydroperoxides to alkoxyl and peroxy radicals, whereas copper ions predominantly reduce hydroperoxides to alkoxyl radicals. For instance, in the oxidation of cumene, the type of metal salt employed was found to influence the molar ratio of ketones to alcohols in the oxidation products; this ratio was higher in the presence of Cu(II) ions and lower in the presence of cobalt ions, and increased in the order acetylacetonate < acetate < chloride [280]. Similarly, in the oxidation of 1-methoxy-4-(1-methylethyl)benzene, higher ketone selectivity was achieved in the presence of copper salts [131]. The higher AcPO selectivity observed in the presence of Cu-MWCNTs in the present study may therefore be a consequence of this effect.

The reaction profiles (Figure 5.8) show that in the presence of metal-modified MWCNT catalysts, the rate of O₂ consumption was significantly higher compared to that for pristine

MWCNTs under the same reaction conditions, demonstrating the enhanced catalytic activity of these materials in the solvent-free oxidation of EB. The highest O₂ consumption rate was initially observed for Co-MWCNTs, however, it decreased over time. A similar trend was observed for Mn-MWCNTs, where the O₂ consumption rate also declined as the reaction proceeded. In contrast, for Cu-MWCNTs, the O₂ consumption rate increased gradually with reaction time.

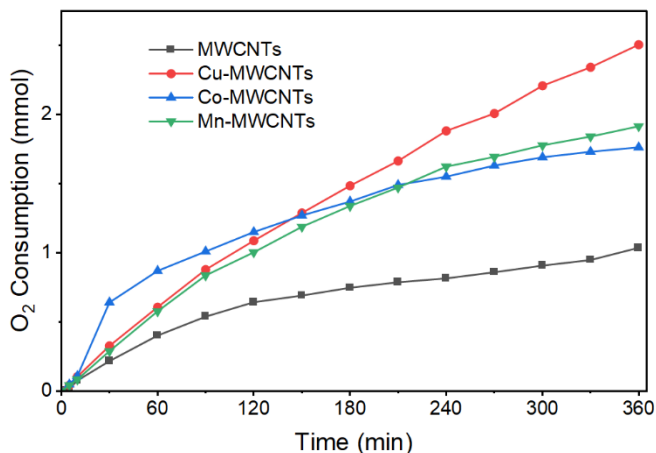


Figure 5.8. Oxygen consumption vs. time of EB oxidation reaction in the presence of metal-modified MWCNT-based catalysts. Reaction conditions: EB:16.33 mmol; catalyst: 0.025 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

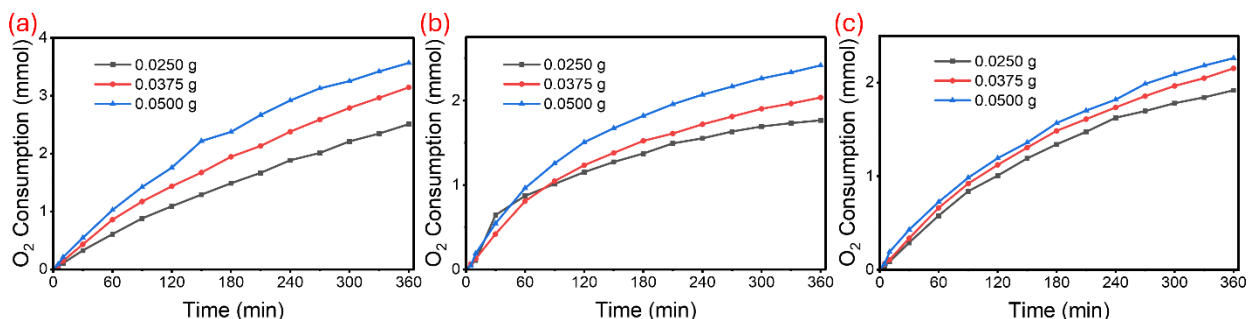


Figure 5.9. Oxygen consumption vs. time of EB oxidation reaction in the presence of metal-modified MWCNT-based catalysts: (a) Cu-MWCNTs, (b) Co-MWCNTs, and (c) Mn-MWCNTs, at various loadings. Reaction conditions: EB:16.33 mmol; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

The influence of catalyst amount on the oxidation reactions in the presence of NHPI as a cocatalyst was also investigated. Catalyst amounts of 0.025, 0.0375, and 0.050 g were

employed. Increasing the catalyst loading enhanced the O₂ consumption rate for the metal-modified MWCNT-based catalysts (Figure 5.9); however, the effect was more pronounced in the case of Cu-MWCNTs. Similarly, increasing the catalyst loading from 0.025 g to 0.0375 g, Cu-MWCNTs exhibited a significant increase in the catalytic activity, with EB conversion increasing from 15.3% to 19.3% and AcPO selectivity increasing from 56% to 66.2% (entry 9 vs 12). In contrast, Co- and Mn-MWCNTs exhibited only modest improvements in activity, with EB conversion increasing from 10.8% to 12.5% and from 11.7% to 13.2%, respectively, accompanied by increased AcPO selectivity (entries 13-14). A further increase to 0.050 g (entries 15-17) yielded only a slight improvement in EB conversion across all catalysts. This could be attributable to the reaction mixture, which became more slurry-like at higher catalyst loadings. The results indicate that a catalyst amount of 0.0375 g offers the most favorable balance between activity and reaction conditions.

5.1.2.3 Recyclability of the metal-modified MWCNTs

The recyclability and reusability of the metal-modified CNTs were thoroughly evaluated, and the results are presented in Table 5.6 and Figure 5.10. During the recyclability test, after each reaction cycle, the catalyst was separated from the reaction mixture, thoroughly washed with methanol and acetone, dried, and reused in subsequent cycles. The beneficial loading (0.0375 g) of the metal-modified catalysts was used for the recyclability test. All the metal-modified catalysts were relatively stable and maintained high activity. The product distribution somehow fluctuated slightly across the cycles, which could be associated with NHPI accumulation on the solid catalyst, minor catalyst loss due to adherence to the filtration membrane, and leaching of metal agglomerates or weakly bound surface species. The loss and/or leaching of metal content in the recycled samples (after the 4th cycle) was confirmed by ICP-MS analysis, which decreased to 0.49, 0.73, and 3.11% for Co, Mn, and Cu, respectively, from 0.70, 1.09, and 3.85% for Co, Mn, and Cu, respectively, in the fresh samples.

Table 5.6. Recyclability of the metal-modified MWCNTs.

Entry	Cycle	Catalyst	Con. (%)	Sel. (%)			
				PEHP	PEA	AcPO	BA
1	0	Cu-MWCNTs	19.3	22.3	9.3	66.2	2.2
2	1	Cu-MWCNTs	19.4	29.0	13.4	56.0	1.6
3	2	Cu-MWCNTs	17.4	35.0	4.8	58.5	1.7
4	3	Cu-MWCNTs	15.9	45.2	7.7	45.5	1.6
5	4	Cu-MWCNTs	16.8	40.1	21.5	37.0	1.4
6	0	Co-MWCNTs	12.5	50.3	13.5	31.4	4.8
7	1	Co-MWCNTs	9.5	60.1	14.8	21.0	4.1
8	2	Co-MWCNTs	9.0	58.0	14.6	23.2	4.2
9	3	Co-MWCNTs	11.0	52.5	22.7	20.9	3.9
10	4	Co-MWCNTs	14.3	53.3	13.5	31.4	1.8
11	0	Mn-MWCNTs	13.2	33.0	14.3	47.5	5.2
12	1	Mn-MWCNTs	13.3	37.5	18.4	40.1	4.0
13	2	Mn-MWCNTs	13.0	44.9	11.1	40.5	3.5
14	3	Mn-MWCNTs	11.3	41.5	15.4	38.2	4.9
15	4	Mn-MWCNTs	11.5	57.0	10.8	29.3	2.9

Reaction conditions: EB: 16.33 mmol; M-MWCNTs: 0.0375 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. For cycle *i*, the EB, NHPI, and AIBN amounts were adjusted according to the mass of recovered catalyst.

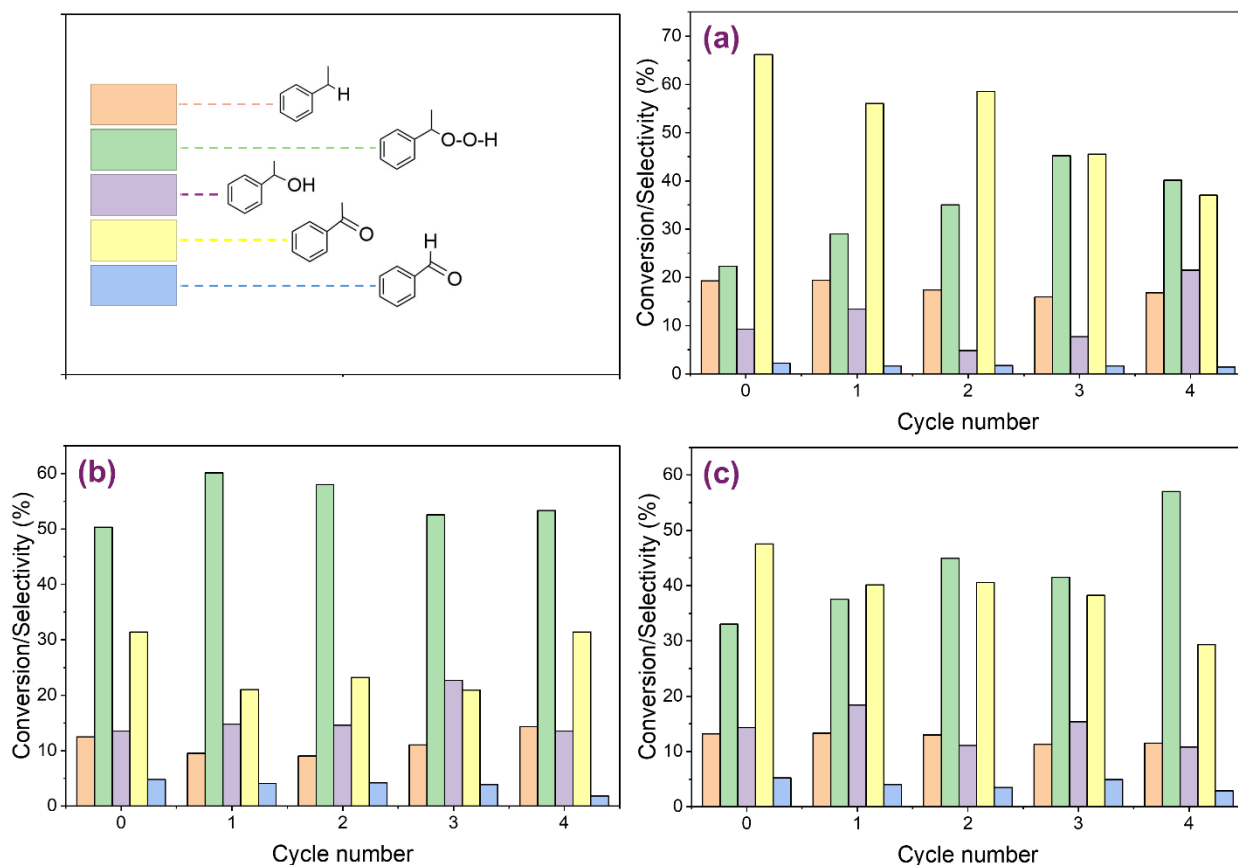


Figure 5.10. Recyclability of (a) Cu-MWCNTs, (b) Co-MWCNTs, and (c) Mn-MWCNTs. Reaction conditions: EB: 16.33 mmol; M-MWCNTs: 0.0375 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. For cycle i , the EB, NHPI, and AIBN amounts were adjusted according to the mass of recovered catalyst.

5.1.3 Metal-functionalized carboxylated MWCNTs

It has been reported that Cu(II), Co(II), and Mn(II) salts of carboxylated MWCNTs with NHPI as a cocatalyst enhanced the rate of EB oxidation [126]. The metal contents in these metal-functionalized MWCNTs were in the range of 0.89 – 1.16 wt.%. Among the reported metal salts of the carboxylated MWCNTs, the Cu(II) functionalized MWCNTs (MWCNT-COO-Cu) displayed higher catalytic activity.

Herein, the Cu(II) functionalized industrial-grade carboxylated MWCNTs (IGMWCNT-COO-Cu) were obtained by means of the reported procedure [126] and employed in the EB oxidation reaction under similar conditions as for the metal-rich MWCNT composites and metal-modified

MWCNTs to make a comparison. Furthermore, the physicochemical properties of the produced Cu(II) functionalized IGMWCNTs were thoroughly investigated.

5.1.3.1 Catalyst preparation and characterization

Industrial-grade carboxylated MWCNTs (IGMWCNT-COOH) were employed for Cu(II) functionalization (IGMWCNT-COO-Cu), due to their lower cost and commercial availability. The synthesis procedure was as simple as presented in Figure 5.11. First, IGMWCNT-COOH was sonicated in 10% aqueous ammonia solution. In the following step, the obtained IGMWCNT-COONH₄ was added to the CuCl₂ solution and sonicated again. The resulting IGMWCNT-COO-Cu was then filtered and dried. It is presumed that divalent copper cations could be immobilized by ionic bonds on the CNT surface in the form of (IGMWCNT-COO)₂Cu or IGMWCNT-COO-CuCl. The structural and physicochemical properties of the synthesized IGMWCNT-COO-Cu were thoroughly investigated using SEM, TEM/EDS, FTIR, ICP-MS, and N₂ physisorption and compared with those of the precursor pristine IGMWCNT-COOH.

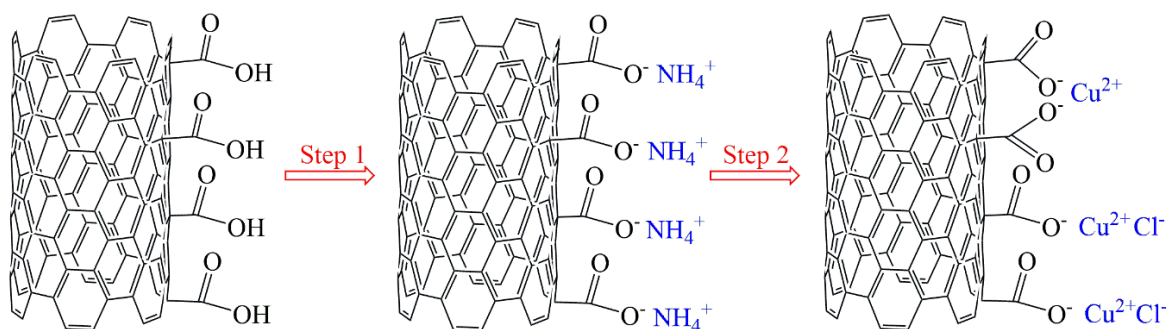


Figure 5.11. Scheme of the Cu(II) functionalization for carboxylated IGMWCNTs.

SEM analysis was performed to observe the morphology of the MWCNTs before (IGMWCNT-COOH) and after Cu(II) functionalization (IGMWCNT-COO-Cu), as can be observed in Figure 5.12 (a-b). Furthermore, the morphology of the recovered IGMWCNT-COO-Cu after the oxidation reaction was also examined (Figure 5.12 (c)). SEM images of IGMWCNT-COOH showed tangled, agglomerated nanotubes with no visible impurities. In the case of IGMWCNT-COO-Cu, agglomerated Cu(II) particles were observed on the surface, indicating non-uniform metal dispersion. Small, bright Cu(II) agglomerates were observed on the surface of the Cu(II)-functionalized CNTs.

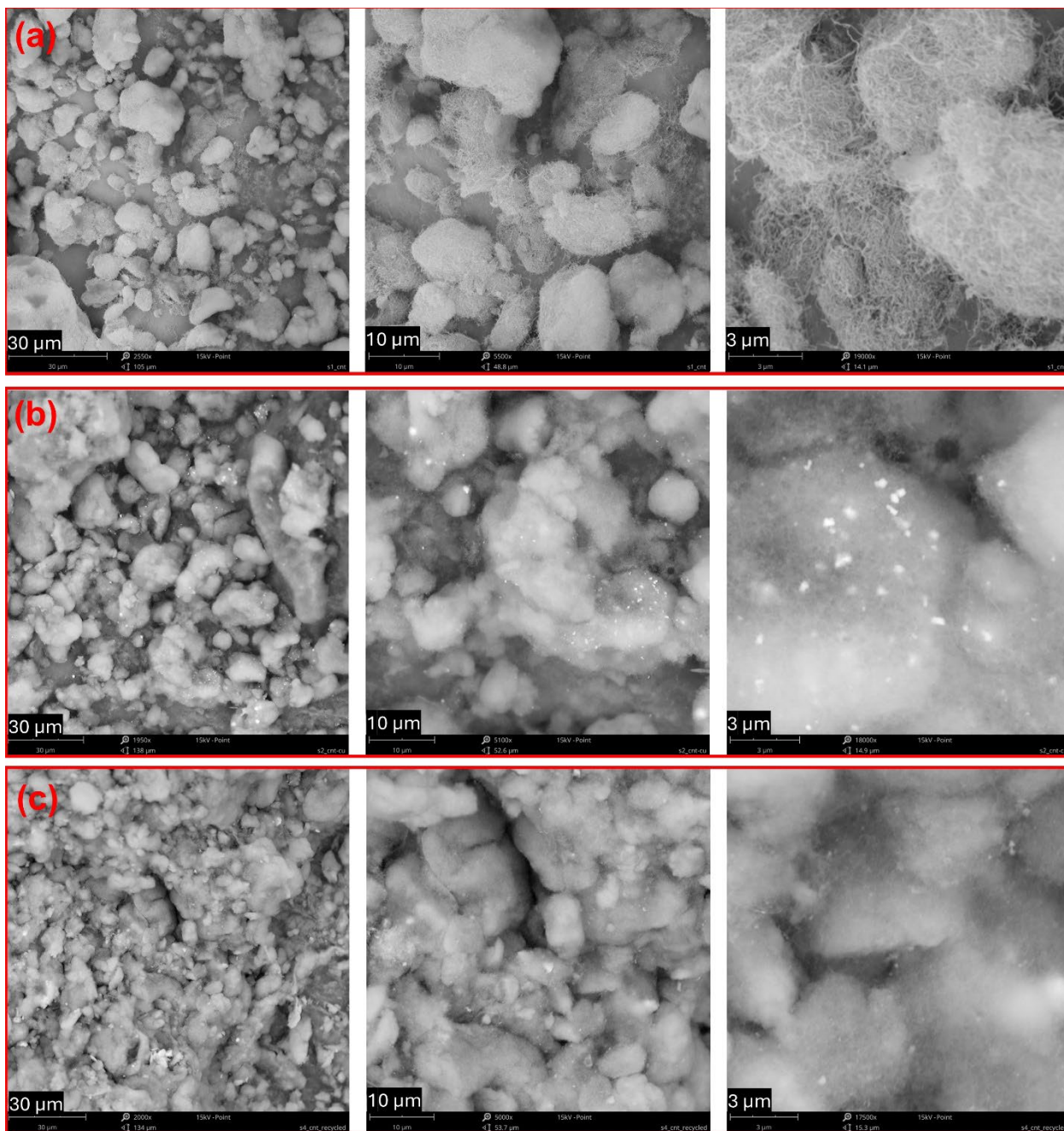


Figure 5.12. SEM image of (a) IGMWCNT-COOH, (b) IGMWCNT-COO-Cu, (c) Recycled IGMWCNT-COO-Cu (after V cycles).

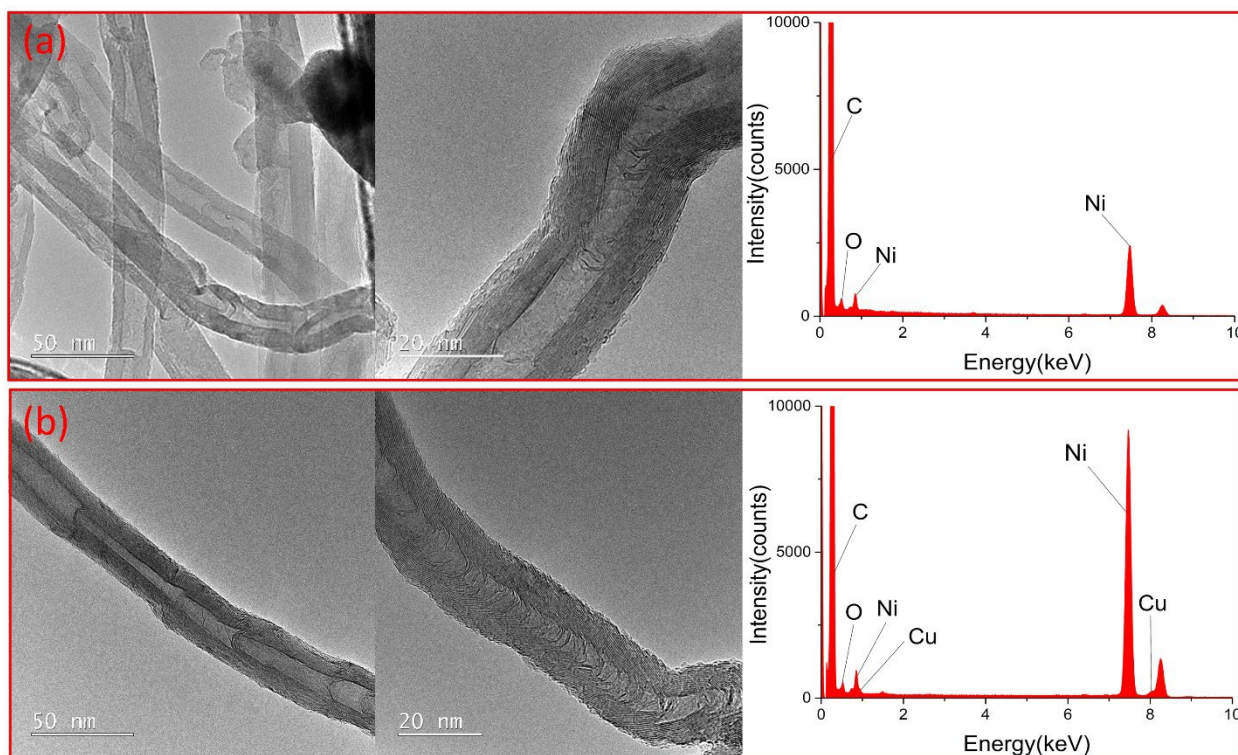


Figure 5.13. TEM images with EDS analyses of (a) IGMWCNT-COOH, and (b) IGMWCNT-COO-Cu.

TEM and EDS analyses were carried out for both the IGMWCNT-COOH and IGMWCNT-COO-Cu (Figure 5.13). As shown in Figure 5.13 (a), the pristine IGMWCNT-COOH sample exhibited smooth, entangled nanotubes with clean outer surfaces and outer diameters ranging from 20 to 40 nm. After Cu(II) functionalization (Figure 5.13 (b)), the nanotubes developed surface defects. The Cu(II) nanoparticles were not distinctly visible in the TEM image because of their irregular dispersion (Figure 5.12 (b)); however, EDS analysis performed at selected regions confirmed their presence. The corresponding EDS spectra are also provided in the Appendices (Figure A1). Weak copper signals in the EDS spectra of IGMWCNT-COO-Cu further verify the incorporation of Cu(II) species on the nanotube surface (Figure 5.13 (b)). The Cu(II) loading, determined by ICP-MS, was 1.26 wt.% for the prepared IGMWCNT-COO-Cu catalyst.

The FTIR spectra of IGMWCNT-COOH and IGMWCNT-COO-Cu are shown and compared in Figure 5.14. The broad and intense band at 3435 cm^{-1} corresponds to the stretching vibrations of -OH groups, which may originate from carboxylic functionalities, surface hydroxyl groups,

or sorbed water molecules. The band observed at $\sim 1633\text{ cm}^{-1}$ is ascribed to C=C stretching vibrations of the CNTs backbone, while the peak at $\sim 1059\text{ cm}^{-1}$ is attributed to the C-O stretching mode of surface oxygenated groups. In the case of IGMWCNT-COO-Cu, the absorption bands at 2923 and 2855 cm^{-1} are associated with the asymmetric and symmetric stretching of methylene ($-\text{CH}_2$) groups. These bands are typically attributed to defect sites formed on the nanotube sidewalls [281]. Such defects are likely introduced during the Cu(II) functionalization process. A weak shoulder around 1710 cm^{-1} corresponds to C=O stretching, whereas the low-intensity band at 1384 cm^{-1} is due to C-O-H stretching vibrations. The persistence of the band at 3435 cm^{-1} in IGMWCNT-COO-Cu suggests that only a portion of the surface carboxylic groups formed copper salts. Generally, carboxylate anions produce a strong band in the $1650\text{--}1550\text{ cm}^{-1}$ region and a weaker one near 1400 cm^{-1} ; nonetheless, in this case, the stronger band likely overlaps with the C=C stretching vibration observed at $\sim 1633\text{ cm}^{-1}$.

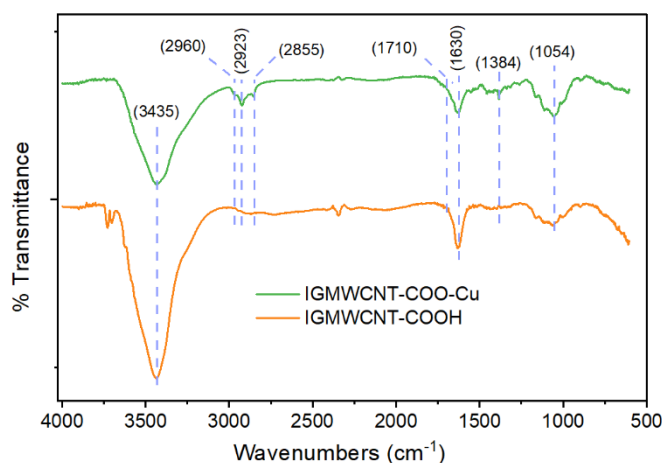


Figure 5.14. FTIR spectra of IGMWCNT-COOH and IGMWCNT-COO-Cu.

N_2 physisorption analysis was performed for IGMWCNT-COOH and IGMWCNT-COO-Cu, and the resulting isotherms and pore-size distributions are presented in Figure 5.15. The adsorption-desorption isotherms of IGMWCNT-COOH and the corresponding IGMWCNT-COO-Cu exhibit type IV behavior with an H_2 -type hysteresis loop, characteristic of irregular mesoporous structures according to the IUPAC classification [282]. A summary of the textural parameters obtained from these analyses is provided in Table 5.7 and Appendices (Table A1). The BET surface area of IGMWCNT-COOH slightly increased after Cu(II) immobilization, suggesting that the introduction of Cu(II) species granted additional accessible surface sites for

gas adsorption. This observation is also consistent with the Langmuir surface area values, which increased after Cu(II) incorporation, indicating that the metal species contributes to enhanced monolayer formation.

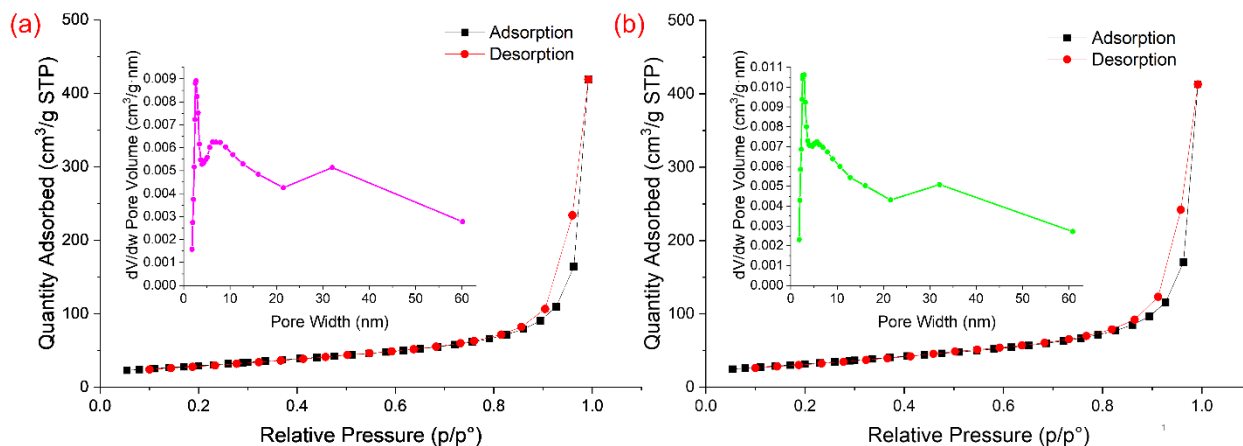


Figure 5.15. N₂ sorption isotherms and pore size distributions of IGMWCNT-COOH and IGMWCNT-COO-Cu.

Table 5.7. Textural properties derived from N₂ physisorption analysis at 77.258 K.

Catalysts	S_{BET}^1	S_{Lang}^2	S_{Micro}^3	V_{micro}^4	S_{Mes}^5	V_{Mes}^6	S_{Total}^7	V_{Total}^8
IGMWCNT-COOH	105.03	134.35	5.530	0.002305	41.860	0.35717	49.442	0.64108
IGMWCNT-COO-Cu	114.20	168.41	6.700	0.002721	45.250	0.35667	52.540	0.62968

¹ BET surface area (m².g⁻¹). ² Langmuir surface area (m².g⁻¹). ³ Micropore surface area (m².g⁻¹). ⁴ Micropore volume (cm³.g⁻¹). ⁵ Mesopore surface area (m².g⁻¹). ⁶ Mesopore volume (cm³.g⁻¹). ⁷ Total area in pores (m².g⁻¹). ⁸ Total volume in pores (cm³.g⁻¹).

5.1.3.2 Catalytic activity of IGMWCNT-COO-Cu

The catalytic activity of IGMWCNT-COO-Cu was investigated in the solvent-free oxidation of EB with oxygen, using NHPI as a cocatalyst. For comparison, parallel reactions were also performed with commercially available pristine MWCNTs and the precursor IGMWCNT-COOH under the same conditions. The corresponding EB conversions and product selectivities are summarized in Table 5.8.

Table 5.8. Effect of Cu(II) functionalized MWCNTs in the presence and absence of NHPI on the solvent-free oxidation of EB with oxygen.

Entry	Catalyst	AIBN (mol%)	NHPI (mol%)	Con. (%)	Sel. (%)			
					PEHP	PEA	AcPO	BA
1	-	0.186	-	4.1	84.5	4.6	10.9	-
2		-	1	3.2	80.9	19.1	-	-
3		0.186	1	6.4	73.2	21.1	5.7	-
4	MWCNTs	-	-	1.6	9.9	90.1	-	-
5		0.186	-	5.2	43.8	51.3	4.9	-
6		0.186	1	6.3	91.2	4.9	3.9	-
7	IGMWCNT-COOH	-	-	1.3	9.9	90.1	-	-
8		0.186	-	3.9	56.5	39.6	4	-
9		0.186	1	4.7	72.7	27.3	-	-
10	IGMWCNT-COO-Cu	-	-	5.2	16.7	4.7	78.6	-
11		0.186	-	6.8	13.1	13.4	73.5	-
12		0.186	1	26.3	24.6	13.4	60.7	1.2

Reaction conditions: EB: 16.33 mmol; catalyst: 0.025; 80 °C; 0.1 MPa; 6 h.

The introduction of either commercial MWCNTs or IGMWCNT-COOH had only a slight impact on EB conversion (entries 1 vs. 5 and 8) but led to a pronounced decrease in PEHP selectivity. This observation indicates that both materials may facilitate the decomposition of PEHP. When NHPI was introduced into the reaction system (entries 3, 6, and 9), the selectivity toward PEHP increased, with a slight improvement in EB conversion. The positive impact of NHPI on enhancing PEHP selectivity has also been reported in earlier studies [283,284], and the associated mechanism is presented and discussed in Section 2.2.2 (Figure 2.9).

As anticipated, the catalytic performance of CNTs in the free-radical oxidation reaction improved significantly after Cu(II) functionalization. Compared with IGMWCNT-COOH, the conversion of EB increased when using IGMWCNT-COO-Cu alone or in combination with

AIBN, NHPI, or both. A comparative analysis of EB conversion (α) and product selectivity (S_{PEHP} , S_{PEA} , S_{BA} , S_{AcPO}) for MWCNTs, IGMWCNT-COOH, and IGMWCNT-COO-Cu in the presence of NHPI is presented in Figure 5.16. It is well established that transition-metal compounds promote free-radical oxidation reactions by accelerating the decomposition of intermediate hydroperoxides such as PEHP, a trend consistent with our experimental observations (entries 7-9 vs. 10-12). AcPO dominated among the products when IGMWCNT-COO-Cu was applied (entries 10-12). Previous studies have revealed that the ketone-to-alcohol ratio in the product from hydrocarbon oxidation depends on the type of transition-metal salt. For instance, Cu(II)-based catalysts typically produce higher amounts of ketone compared with Co(II)- or Mn(II)-containing systems, owing to differences in their redox potentials [280].

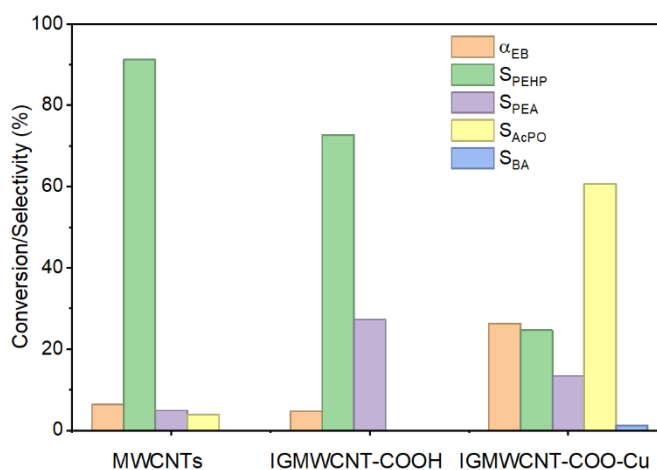


Figure 5.16. EB conversion (%) and product selectivity (%) over MWCNTs, IGMWCNT-COOH, and IGMWCNT-COO-Cu. Reaction conditions: EB: 16.33 mmol; catalyst: 0.025 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

It is worth noting that the use of IGMWCNT-OO-Cu alone (entry 10) resulted in the highest selectivity toward AcPO (78.6%) among other catalysts Table 5.8. However, the corresponding EB conversion remained low (5.2%). When the radical initiator was added, typically to shorten the induction period, the conversion slightly increased to 6.8%. On the other hand, the addition of NHPI as a cocatalyst together with IGMWCNT-COO-Cu and the initiator not only soared the EB conversion from 6.8% to 26.3%, but also improved the selectivity of AcPO (entry 12). This observation suggests that in the presence of NHPI, the Cu(II) salt of the carboxylated CNTs not only facilitated PEHP decomposition but also accelerated the formation of PINO radicals

from NHPI, thereby enhancing the overall reaction rate. This finding aligns well with previous literature reports on Co(II)-based systems that demonstrated similar synergistic effects [273]. The highest catalytic activity was obtained for the combination of IGMWCNT-COO-Cu and NHPI system (entry 12), where EB conversion soared from 4.7% to 26.3% upon immobilization of Cu(II) species onto industrial-grade carboxylated CNTs.

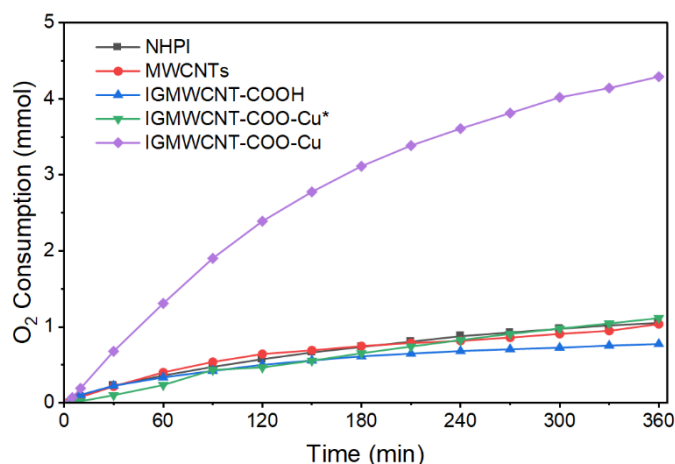


Figure 5.17. Oxygen consumption vs. time of EB oxidation reaction with NHPI, MWCNTs, IGMWCNT-COOH, IGMWCNT-COO-Cu*(without NHPI), and IGMWCNT-COO-Cu. Reaction conditions: EB:16.33 mmol; CNTs: 0.025 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6h.

The reaction profiles for the O₂ consumption during the oxidation of EB over IGMWCNT-COO-Cu in the presence and absence of NHPI are presented in Figure 5.17. The results are also compared with those of reactions performed with NHPI alone, MWCNTs with NHPI, and IGMWCNT-COOH with NHPI under similar reaction conditions. It can be observed that the O₂ consumption profiles over the reaction time are almost identical for NHPI, MWCNTs with NHPI, IGMWCNT-COOH with NHPI, and Cu(II) functionalized IGMWCNTs without NHPI. Interestingly, when the Cu(II) functionalized IGMWCNTs are employed with NHPI, the O₂ consumption is enhanced substantially, indicating a synergistic catalytic effect between NHPI and IGMWCNT-COO-Cu.

5.1.3.3 Recyclability of the IGMWCNT-COO-Cu system

The recyclability and reusability of the IGMWCNT-COO-Cu catalyst in the oxidation reaction were examined by scaling up the reaction volume of EB from 2 cm³ to 10 cm³. After completion

of each reaction, the catalyst was separated from the reaction mixture through filtration, washed with ethanol by passing it over the filter cake several times, dried, and employed in the subsequent oxidation cycles. For every cycle, fresh NHPI were introduced.

Table 5.9. Recyclability of IGMWCNT-COO-Cu catalyst.

Entry	Cycle	Con.(%)	Sel. (%)			
			PEHP	PEA	AcPO	BA
1	0	15.8	2.2	20.0	74.8	3.0
2	1	11.7	2.5	22.4	70.5	4.6
3	2	9.7	3.2	22.3	70.4	4.1
4	3	14.4	42.3	6.0	50.5	1.2
5	4	14.8	53.1	6.8	38.7	1.4
6	5	10.3	35.7	7.9	49.2	7.2

Reaction conditions: EB: 81.7 mmol; IGMWCNT-COO-Cu: 0.125 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. For cycle i , the EB, NHPI, and AIBN amounts were adjusted according to the mass of the recovered catalyst.

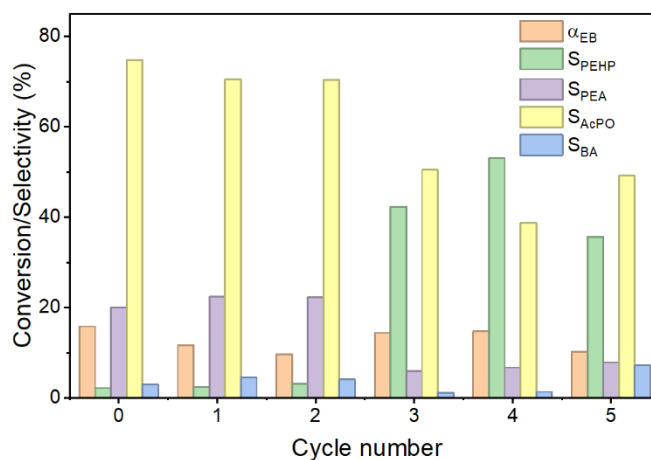


Figure 5.18. Recyclability of IGMWCNT-COO-Cu catalyst. Reaction conditions: EB: 81.7 mmol; IGMWCNT-COO-Cu: 0.125 g; NHPI: 1 mol%; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. For cycle i , the EB, NHPI, and AIBN amounts were adjusted according to the mass of the recovered catalyst.

The recyclability test was evaluated over five consecutive reaction cycles, and the results are presented in Table 5.9 and Figure 5.18. Upon scaling up the reaction from 2 cm³ to 10 cm³, the conversion of EB decreased from 26.3% to 15.8%. In the first and second reuse cycles, the EB conversion values further dropped to 11.7% and 9.7%, respectively. This decline in catalytic activity could be due to incomplete removal of reaction residues, as washing the filter cake only with ethanol was insufficient for thorough cleaning. Some oxidation products could remain trapped between the entangled CNT agglomerates and inside the nanotube channels, covering the active sites and thereby reducing catalytic performance.

To address this issue, the recovered catalyst was subsequently subjected to ethanol washing followed by 30 min of ultrasonication before reuse. After this treatment, the catalyst regained activity comparable to that of the fresh material. Applying the same regeneration step in the fourth cycle resulted in almost identical performance. However, when the sonication step was omitted during the fifth cycle, a pronounced decrease in EB conversion was observed, demonstrating the crucial role of ultrasonication in catalyst recycling. Moreover, the observed decline in AcPO selectivity suggested leaching of agglomerated Cu(II), as evidenced by SEM and ICP-MS analyses. After the fifth catalytic cycle, SEM imaging of the recycled catalyst (Figure 5.12 (c)) revealed the leaching of Cu(II) agglomerates originally present on the IGMWCNT-COO-Cu surface. Consistently, ICP-MS analysis further confirmed Cu(II) agglomerates leaching, with the metal content decreasing from 1.26 wt.% in the fresh catalyst to 0.99 wt.% for the recycled catalyst.

5.1.4 Summary

Metal-rich MWCNT composites were synthesized using Cu(II), Co(II), and Mn(II) nitrate precursors, resulting in high metal loadings. Under solvent-free EB oxidation using dioxygen with NHPI as a cocatalyst, these materials exhibited significantly higher activity than pristine MWCNTs. Structural characterization (TEM and ICP-OES) confirmed substantial metal incorporation, with species distributed on the external surface (dispersed and as localized agglomerates) and within CNT channels. The enhanced activity is attributed to facilitated electron-transfer processes, which promote the decomposition of the PEHP into AcPO.

To assess the role of metal loading, metal-modified MWCNTs with lower metal content were prepared and evaluated under identical reaction conditions. Among these, Cu-MWCNTs showed the best performance, achieving 15.3% EB conversion with 56% AcPO selectivity at 0.025 g, which increased to 19.3% conversion and 66.2% selectivity at 0.0375 g. A further increase to 0.050 g yielded only a slight enhancement in EB conversion across all catalysts. This could be attributed to the reaction mixture, which became more slurry-like at higher catalyst loadings. These catalysts also demonstrated good stability and recyclability, with slight fluctuations in the product distribution, which could be attributed to NHPI accumulation on the solid catalyst, minor catalyst loss due to membrane adherence during separation, and the leaching of the metal agglomerates or weakly bound surface species.

In contrast, Cu(II)-functionalized carboxylated IGMWCNTs exhibited superior activity, achieving 26.3% EB conversion and 60.7% AcPO selectivity in the presence of NHPI. Under similar conditions, control experiments using pristine and carboxylated MWCNTs favored PEHP formation, highlighting the crucial role of Cu(II) sites. These sites not only facilitate PINO radical formation from NHPI but also accelerate the selective decomposition of PEHP into AcPO. The IGMWCNT-COO-Cu catalyst remained recyclable, with only a moderate decrease in Cu content (from 1.26 wt.% to 0.99 wt.% after five cycles), attributed to partial leaching of loosely bound surface agglomerates.

Overall, these results indicate that high metal loading does not necessarily translate into superior catalytic performance. Instead, well-defined Cu(II) functionalization at low loading (~1.26 wt.%) provides enhanced activity and selectivity. The findings highlight that controlled metal incorporation, rather than excessive loading, governs catalytic efficiency in NHPI-mediated EB oxidation. The enhanced activity observed across all transition metal-modified MWCNTs may arise from a synergistic interaction with NHPI, reflecting the dual role of the system: the metal species promote PINO generation and accelerate PEHP decomposition, while NHPI facilitates PEHP formation, thereby collectively enhancing the overall reaction rate.

5.2 SCILL and SCILL-SILP Hybrid Catalytic System Based on IGMWCNT-COO-Cu and [emim][OcOSO₃]

The rational design of CNT-based catalysts has opened a new horizon for the solvent-free oxidation of hydrocarbons in the liquid phase using molecular oxygen as a green oxidant. By tailoring the surface chemistry of CNTs, both substrate conversion and selectivity towards specific products can be substantially improved under mild and sustainable conditions. In this context, the investigation in the previous section demonstrated that Cu(II)-functionalized carboxylated IGMWCNTs in the presence of NHPI displayed the highest activity in the EB oxidation with oxygen by achieving 26.3% EB conversion with 60.7% selectivity toward AcPO, thereby outperforming the other studied MWCNT-based catalysts. The enhanced catalytic activity reflects the synergistic interaction between Cu(II)-functionalized IGMWCNTs and NHPI in promoting the EB oxidation in the liquid phase using molecular oxygen as an oxidant.

Despite the catalytic advantage, the poor solubility of NHPI in nonpolar hydrocarbons such as EB, along with the challenge in recovery and reuse, remained the major drawback. The concept of thin-film ionic liquid (IL) catalysis can be employed to dissolve and stabilize catalytically active species, such as NHPI, while modulating the catalytic activity. Such a concept can simplify the separation of homogeneous catalysts and reduce solvent-derived waste. In addition, the IL film or layer can tune the interfacial polarity while enhancing oxygen solubility and mass transport [260,261]. In this context, in the previous study [273], 1-ethyl-3-methylimidazolium octylsulfate ([emim][OcOSO₃]) containing CoCl₂ coated onto NHPI-grafted (via an ester bond) polystyrene support was examined. The developed [emim][OcOSO₃]-based SCILL/SILP systems were employed in the solvent-free oxidation of EB using dioxygen. The catalytic systems demonstrated enhanced selectivity towards AcPO and were recyclable over multiple times without any substantial loss in catalytic activity.

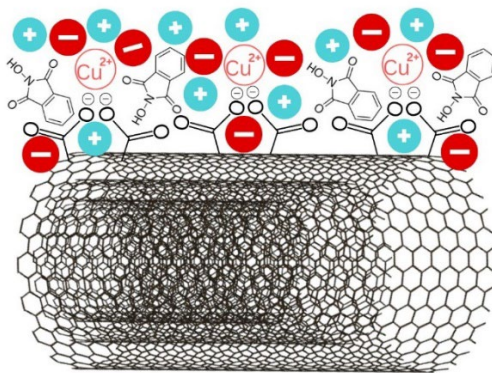


Figure 5.19. SCILL-SILP hybrid catalytic system.

Considering the advantages of IL thin film catalysis and the recyclability of [emim][OcOSO₃] IL-based SCILL/SILP systems [273], the present study integrates Cu(II)-functionalized carboxylated IGMWCNTs (IGMWCNT-COO-Cu), NHPI, and the [emim][OcOSO₃] IL into novel SCILL and SCILL-SILP hybrid catalytic systems for the liquid-phase solvent-free oxidation of EB using molecular oxygen. In the SCILL configuration, IGMWCNT-COO-Cu were coated with a thin layer of IL. In contrast, the SCILL-SILP hybrid catalytic system consists of IGMWCNT-COO-Cu coated with an IL layer containing dissolved NHPI, thereby simultaneously fulfilling the defining criteria of both SCILL and SILP concepts (Figure 5.19). Specifically, dissolution of NHPI within the IL phase corresponds to the SILP concept, while the immobilization of this layer onto an active solid catalyst satisfies the SCILL framework.

The primary objectives of this study are (i) to effectively heterogenize NHPI and the IL to facilitate catalyst recovery and reuse, and (ii) to integrate the properties of Cu(II) functionalized CNTs, NHPI, and IL to design a system (Figure 5.20) that exhibits synergistically to catalyze EB. It is worth noting that the proposed SCILL and SCILL-SILP hybrid catalytic system employing CNTs and functionalized CNTs has not been previously reported, underscoring the novelty of the present approach. This study introduced and coined the term SCILL-SILP hybrid catalytic system. Furthermore, the recyclability and reusability of the IGMWCNT-COO-Cu and SCILL-SILP systems were thoroughly investigated.

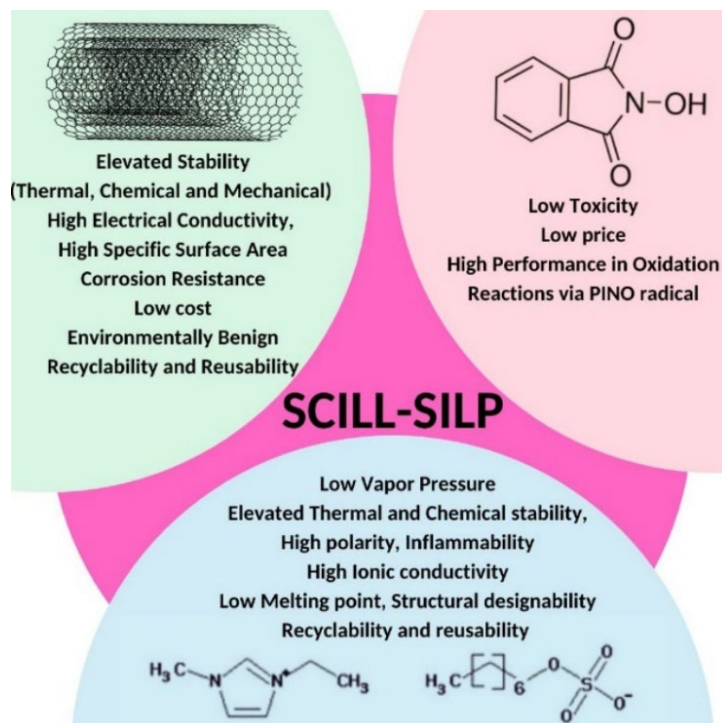


Figure 5.20. Synergistic effect in the SCILL-SILP hybrid catalytic system.

5.2.1 Catalyst preparation and characterization

The Cu(II)-functionalized IGMWCNTs reported in Section 5.1.3 were employed as the support material for developing both SCILL and SCILL-SILP hybrid catalytic systems. In the SCILL system, [emim][OscSO₃] was coated directly onto IGMWCNT-COO-Cu. For the SCILL-SILP hybrid catalytic system, [emim][OscSO₃] containing dissolved NHPI was coated onto the same support. The effect of IL loading was also investigated using amounts of 0.0125, 0.025, and 0.0375 g to prepare the SCILL and SCILL-SILP systems.

The preparation of the SCILL system was adapted from the previous work [272,273], employing the solvent evaporation technique with a minor modification involving the introduction of an ultrasonication step before stirring. The selected amounts of IL and support catalyst (IGMWNT-COO-Cu) were dispersed in acetone, ultrasonicated, stirred, and then the acetone was evaporated to yield the final SCILL system. The SCILL-SILP system was prepared following the same technique, with the addition of NHPI to the mixture before ultrasonication. The structural and physicochemical properties of the obtained catalysts (IGMWNT-COO-Cu

and the SCILL-SILP system) were thoroughly investigated using SEM, TEM/EDS, FTIR, ICP-MS, N₂ physisorption, and TGA.

SEM analysis was performed to observe the morphology of the obtained system before and after coating with the NHPI-dissolved IL (Figure 5.21). In the case of IGMWCNT-COO-Cu (Figure 5.21 (a)), agglomerated Cu(II) particles were observed on the surface, indicating non-uniform metal dispersion. Small, bright Cu(II) agglomerates were observed on the surface of the Cu(II)-functionalized CNTs. On the contrary, in the SEM images of the SCILL-SILP hybrid system (Figure 5.21 (b)), the Cu(II) agglomerates were not observed, which could be attributed to the uniform coating of the IL-NHPI mixture over the surface of IGMWCNT-COO-Cu.

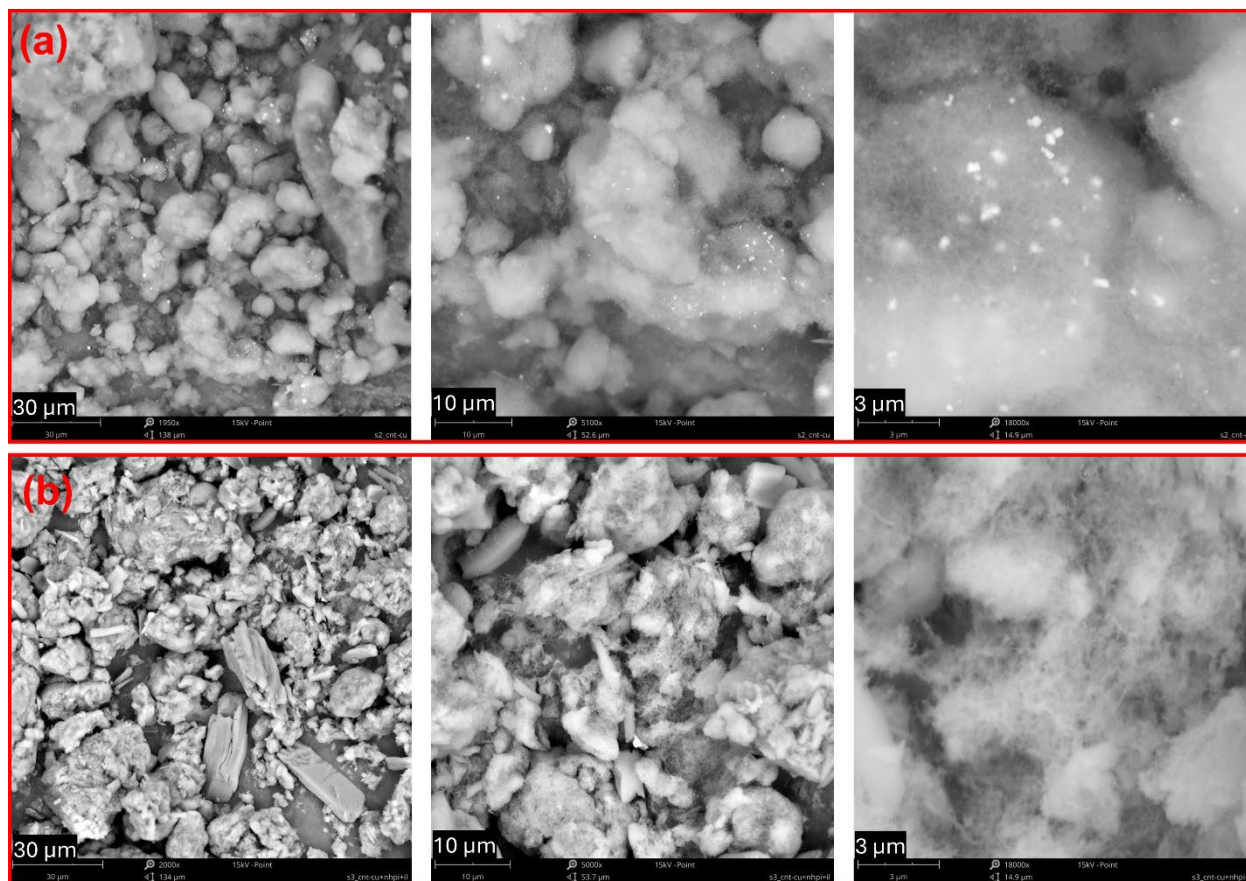


Figure 5.21. SEM image of (a) IGMWCNT-COO-Cu (b) and IGMWCNT-COO-Cu@2([emim][OcOSO₃])+NHPI.

TEM and EDS analyses were carried out for IGMWCNT-COO-Cu and for the SCILL-SILP hybrid catalytic system (Figure 5.22). As observed in Figure 5.22 (b), a thin and uneven layer

of the mixture of NHPI and IL is evident across the surface of IGMWCNT-COO-Cu, confirming the coating. Weak copper signals detected in the EDS spectra of both IGMWCNT-COO-Cu and the SCILL-SILP system further verify the presence of Cu(II) species on the nanotube surface. EDS analyses performed at selected regions for both materials are provided in the Appendices (Figure A1).

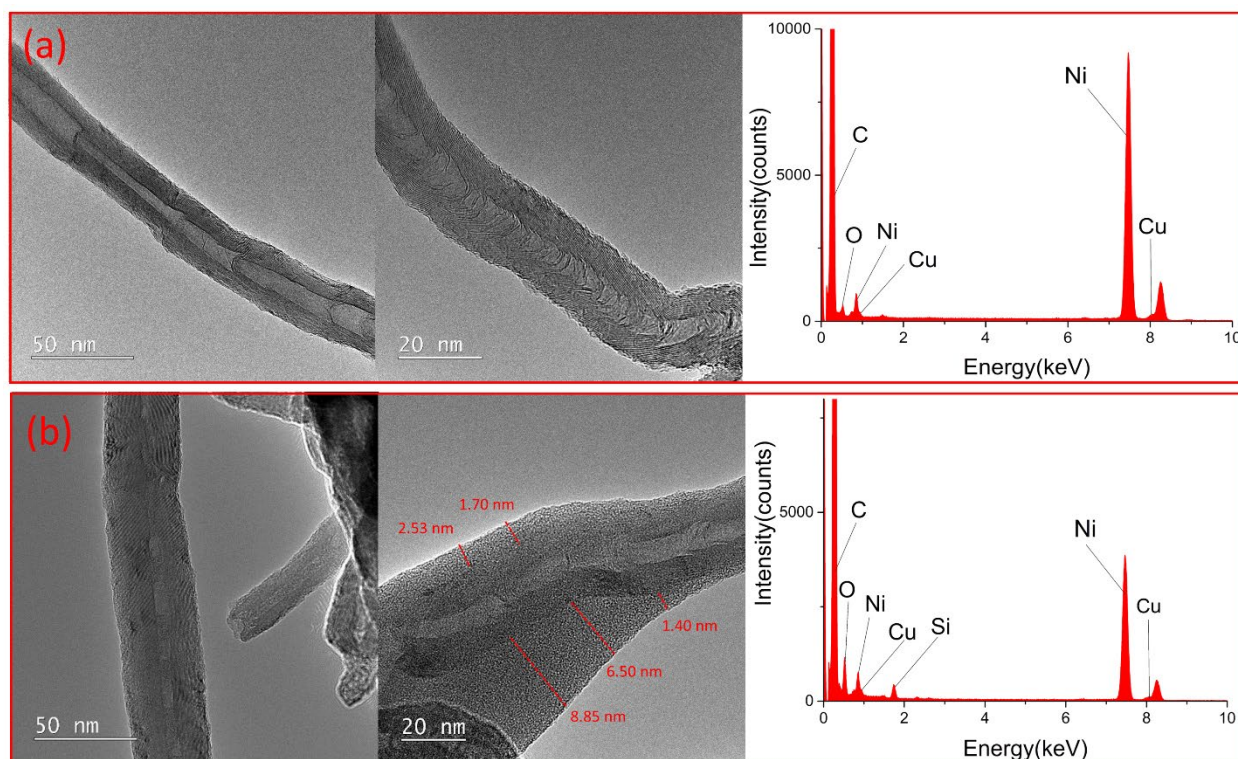


Figure 5.22. TEM images with EDS analyses of (a) IGMWCNT-COO-Cu, (b) IGMWCNT-COO-Cu@[emim][OcOSO₃]+NHPI.

The FTIR spectra of IGMWCNT-COOH and IGMWCNT-COO-Cu were presented and discussed in *Section 5.1.3.1* (Figure 5.14). Here, the FTIR spectra of the SCILL-SILP hybrid catalytic system before and after recycling are presented in Figure 5.23 (b). As a basis for comparison, the spectra of pristine NHPI and [emim][OcOSO₃] were also acquired and presented in Figure 5.23 (a). The FTIR spectrum of the hybrid SCILL-SILP system retains the characteristic absorption bands of the individual constituents, with slight shifts in band positions that are evident, consistent with weak intermolecular interactions and partial overlap of vibrational modes in the regions of similar frequencies. Strong absorption bands at 1790 and 1727 cm⁻¹, along with a medium-intensity band at 1137 cm⁻¹, correspond to the C=O and N-O

stretching vibrations, respectively, confirming the presence of NHPI [285]. The bands at 1574 and 1224 cm^{-1} are attributed to the N=C and O-C stretching vibrations, demonstrating the presence of the IL. Furthermore, a distinct absorption band near 623 cm^{-1} , associated with sulfate ion bending, also confirms the incorporation of the IL within the hybrid catalytic system [286].

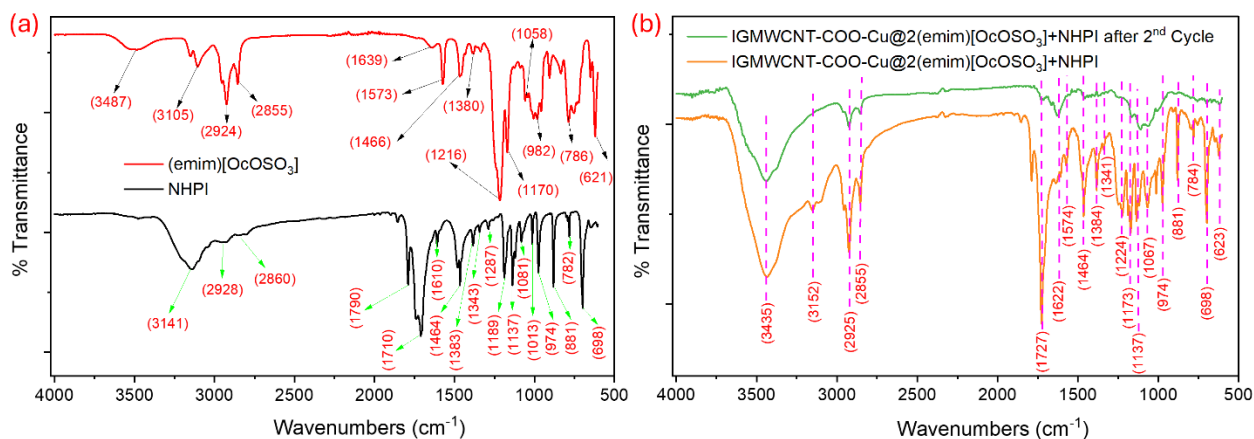


Figure 5.23. FTIR spectra of (a) NHPI and [emim][OcOSO₃] and (b) fresh and recycled SCILL-SILP system after 2nd recycle.

Table 5.10. Textural properties derived from N₂ physisorption analysis at 77.258 K.

Catalysts	S_{BET}^1	S_{Lang}^2	S_{Micro}^3	V_{micro}^4	S_{Mes}^5	V_{Mes}^6	S_{Total}^7	V_{Total}^8
IGMWCNT-COO-Cu	114.20	168.41	6.700	0.002721	45.25	0.35667	52.540	0.62968
IGMWCNT-COO-Cu@2([emim][OcOSO ₃]) +NHPI	4.85	-	-	-	1.42	0.01420	2.222	0.04461

¹ BET surface area ($\text{m}^2.\text{g}^{-1}$). ² Langmuir surface area ($\text{m}^2.\text{g}^{-1}$). ³ Micropore surface area ($\text{m}^2.\text{g}^{-1}$). ⁴ Micropore volume ($\text{cm}^3.\text{g}^{-1}$). ⁵ Mesopore surface area ($\text{m}^2.\text{g}^{-1}$). ⁶ Mesopore volume ($\text{cm}^3.\text{g}^{-1}$). ⁷ Total area in pores ($\text{m}^2.\text{g}^{-1}$). ⁸ Total volume in pores ($\text{cm}^3.\text{g}^{-1}$).

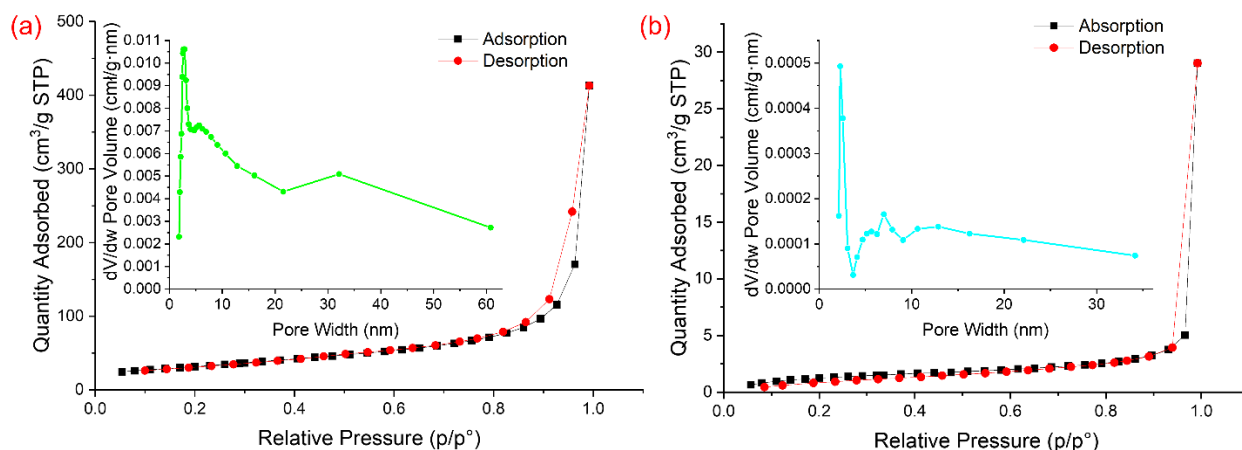


Figure 5.24. N₂ sorption isotherms and pore size distributions (a) IGMWCNT-COO-Cu, and (b) SCILL-SILP system.

N₂ physisorption analysis was performed for both the IGMWCNT-COO-Cu and the SCILL-SILP hybrid catalytic system, and the resulting isotherms and pore-size distributions are presented in Table 5.10 and Figure 5.24. The adsorption-desorption isotherm of IGMWCNT-COO-Cu (Figure 5.24 (a)) exhibits type IV behavior with an H₂-type hysteresis loop, characteristic of irregular mesoporous structures according to the IUPAC classification [282]. In contrast, the SCILL-SILP system (Figure 5.24 (b)) adsorbed significantly less N₂ than the Cu(II)-functionalized CNTs support, which can be attributed to the covering and/or partial blocking of the mesopores by the IL-NHPI coating. The corresponding pore-size distribution further confirms this observation. A summary of the textural parameters obtained from these analyses is provided in the Appendices (Table A1). The BET surface area of the support catalyst decreased substantially upon coating with the NHPI-dissolved IL, accompanied by significant reductions in total pore volume and total pore area. These results collectively indicate that the IL-NHPI layer not only covers the external surfaces of the nanotubes but may also partially and/or complete blocked the mesopores, ultimately reducing the total specific surface area of the SCILL-SILP hybrid system.

5.2.2 Catalytic activities of SCILL and SCILL-SILP hybrid catalytic system

The catalytic activities of the synthesized SCILL and SCILL-SILP catalytic systems were studied in the solvent-free oxidation of EB in the liquid phase using molecular oxygen, with and without the addition of initiator (AIBN). The obtained results are summarized in Table 5.11. In the absence of an initiator, EB oxidation did not occur for the SCILL systems (entries 1-3). This inactivity was attributed to the high viscosity of the IL, which covered the active metallic sites on the catalyst surface, consequently hindering the formation of reactive radicals crucial to driving the oxidation process. In contrast, a positive influence of IL coating on the catalytic performance of IGMWCNT-COO-Cu was observed in the presence of the initiator (entries 4-6). The EB conversion increased to 14.1% for IGMWCNT-COO-Cu@2([emim][OcOSO₃]), along with enhanced selectivity toward AcPO (entry 5). These results indicate that, once radicals were generated by AIBN, both the MWCNT-COO-Cu and the IL in the SCILL system contributed synergistically to the overall reaction performance. The ketone-to-alcohol ratio for all three IL loadings in the SCILL systems was relatively high, remaining in the range of 3.4 - 4.3.

The catalytic activities of the hybrid SCILL-SILP catalytic system in EB oxidation were further evaluated both in the absence and presence of the initiator. In all cases, high EB conversions were obtained along with augmented selectivity toward AcPO (entries 7-12). The EB conversions obtained employing the hybrid SCILL-SILP catalytic systems (entries 7-12) were comparable to those achieved with the Cu(II) functionalized CNTs in the presence of NHPI (entry 12, Table 5.8). The IGMWCNT-COO-Cu@2([emim][OcOSO₃])+NHPI system, prepared at a 1:1 (w/w) ratio of IL to IGMWCNT-COO-Cu, was identified as the beneficial SCILL-SILP system, achieving a maximum AcPO selectivity of 77% with ~27% EB conversion.

Table 5.11. Effect of SCILL and SCILL-SILP systems on the solvent-free oxidation of EB with oxygen.

Entry	Catalyst	Con. (%)	Sel. (%)			
			PEHP	PEA	AcPO	BA
1	IGMWCNT-COO-Cu@1([emim][OcOSO ₃])	-	-	-	-	-
2	IGMWCNT-COO-Cu@2([emim][OcOSO ₃])	-	-	-	-	-
3	IGMWCNT-COO-Cu@3([emim][OcOSO ₃])	-	-	-	-	-
4 ^a	IGMWCNT-COO-Cu@1([emim][OcOSO ₃])	8.2	3.1	18.2	78	0.7
5 ^a	IGMWCNT-COO-Cu@2([emim][OcOSO ₃])	14.1	4.7	21.4	72.9	1
6 ^a	IGMWCNT-COO-Cu@3([emim][OcOSO ₃])	10.9	4.5	20.2	74.4	1
7	IGMWCNT-COO-Cu@1([emim][OcOSO ₃])+NHPI	22.3	13.9	13.5	69.3	3.4
8	IGMWCNT-COO-Cu@2([emim][OcOSO ₃])+NHPI	26.4	10.9	11.1	75.3	2.7
9	IGMWCNT-COO-Cu@3([emim][OcOSO ₃])+NHPI	19.3	15.4	13	60.8	10.8
10 ^a	IGMWCNT-COO-Cu@1([emim][OcOSO ₃])+NHPI	21.1	26.6	11	57.4	5.1
11 ^a	IGMWCNT-COO-Cu@2([emim][OcOSO ₃])+NHPI	26.6	9.2	11.2	77.1	2.5
12 ^a	IGMWCNT-COO-Cu@3([emim][OcOSO ₃])+NHPI	25.5	9.4	14.8	72.7	3.1

Reaction conditions: EB: 16.33 mmol; IGMWCNT-COO-Cu: 0.025 g; NHPI: 1 mol%; 1, 2, and 3 denote IL loadings of 0.0125, 0.025, and 0.0375 g, respectively; 80 °C; 0.1 MPa; 6 h; ^a 0.186 mol% AIBN was added.

The enhanced AcPO selectivity was attributed, among other factors, to the solvent cage effect [287]. In the SCILL-SILP system, the IL, acting as a solvent, likely encapsulated the generated alkoxy radicals (Ph-CH(O[•])-CH₃), thereby confining the alkoxy radicals within the solvent cage and hindering their subsequent interaction with EB that would otherwise yield PEA. This confinement instead promoted the β-scission of the alkoxy radicals, leading predominantly to the formation of AcPO. Additionally, the viscosity of the solvent was a critical factor governing the residence time of radicals within the solvent cage; therefore, the highly viscous IL [emim][OcOSO₃] [288] adversely influenced this process.

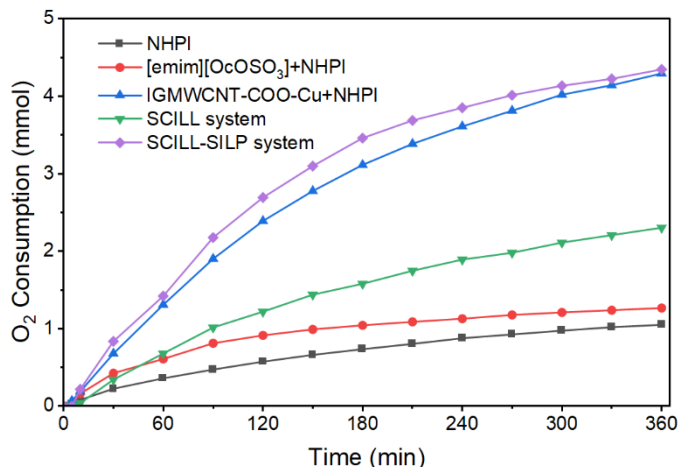


Figure 5.25. Oxygen consumption vs. time of EB oxidation reaction with NHPI (1 mol%); [emim][OcOSO₃](0.025 g) + NHPI (1 mol%); IGMWCNT-COO-Cu (0.025 g) + NHPI(1 mol%); [emim][OcOSO₃]-based SCILL System (IGMWCT-COO-Cu: 0.025 g and 0.025 g IL); and [emim][OcOSO₃]-based SCILL-SILP system (IGMWCT-COO-Cu: 0.025 g, 1 mol% NHPI, and 0.025 g IL). Reaction conditions: EB:16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6h.

The O₂ consumption in the oxidation reactions as a function of reaction time over SCILL and SCILL-SILP catalytic systems is presented in Figure 5.25. The results are also compared with reactions performed with only NHPI, [emim][OcOSO₃] with NHPI, and IGMWCNT-COO-Cu with NHPI under similar reaction conditions. The slight positive influence of IL [emim][OcOSO₃] can be observed as the O₂ consumption increased after the introduction of the IL with NHPI. For the [emim][OcOSO₃]-based SCILL system, in the presence of AIBN initiator, the O₂ consumption over the reaction time was further enhanced, suggesting the positive influence of the coated IL and IGMWCNT-COO-Cu catalyst support. A further slight enhancement in the O₂ consumption over the reaction time was recorded for the [emim][OcOSO₃]-based SCILL-SILP system (at 0.025 g IL loading), which explicitly corroborates the synergistic catalytic interaction between the metal functionalized catalyst support, IL, and the NHPI. Overall, the catalytic activity of the SCILL-SILP system (1:1 w/w, IL/IGMWCNT-COO-Cu) was comparable to that of the IGMWCNT-COO-Cu (with NHPI) system; however, the incorporation of IL as a thin film containing dissolved NHPI resulted in considerably higher selectivity towards AcPO. Furthermore, the SCILL-SILP system can offer

the practical advantage of simultaneous recovery of NHPI, IL, and the solid catalyst support, simplifying the recyclability.

5.2.3 Recyclability of the SCILL-SILP hybrid catalytic system

The recyclability and the reusability of the SCILL-SILP catalyst were evaluated, and the results are presented in Figure 5.26. After each reaction, the catalyst was separated from the reaction mixture, washed with fresh EB, dried, and reused in a new batch of EB with the addition of the initiator (Figure 5.26 (a)). However, the EB conversion decreased from 26.6% for the fresh catalyst to 9.0% and 8.1% after the first and second cycles, respectively. This decline suggested that a significant portion of NHPI, along with a small amount of the IL, had been leached out during the recovery step, probably due to the increased polarity of the reaction medium, which promoted dissolution of the hydrophilic NHPI. Additionally, the influence of NHPI reintroduction after each cycle on the performance of the SCILL-SILP system was investigated (Figure 5.26 (b)). The results revealed that the EB conversion gradually declined with successive cycles. Simultaneously, PEHP selectivity increased steadily, while AcPO selectivity decreased. These trends suggest that a portion of NHPI, and possibly the IL, remained on the catalyst surface after reuse, thereby influencing the oxidation process in terms of both conversion and product distribution.

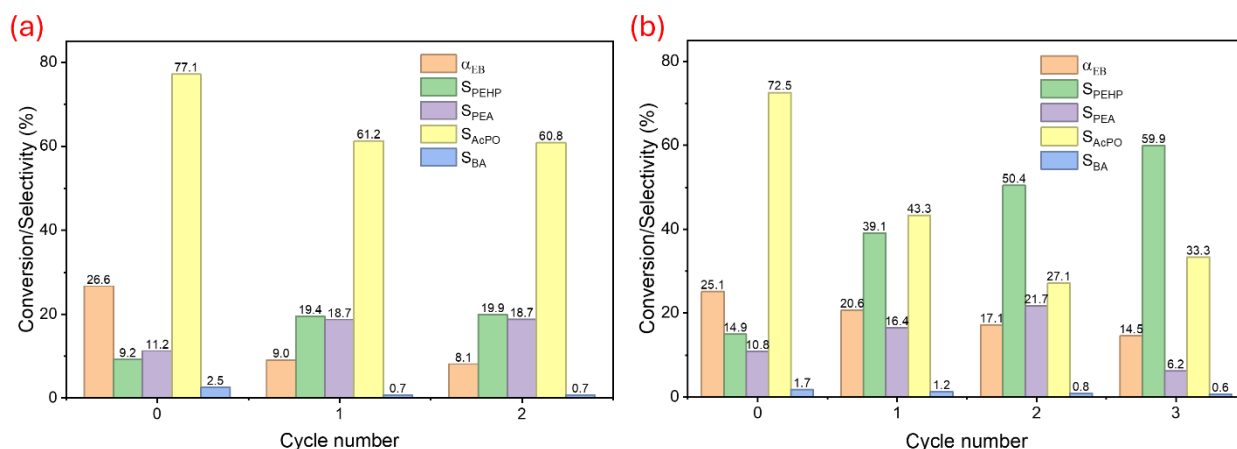


Figure 5.26. Recyclability SCILL-SILP system: (a) without additional NHPI and (b) with NHPI (1 mol%) added in subsequent cycles. Reaction conditions: EB: 16.33 mmol; IGMWCNT-COO-Cu: 0.025 g; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

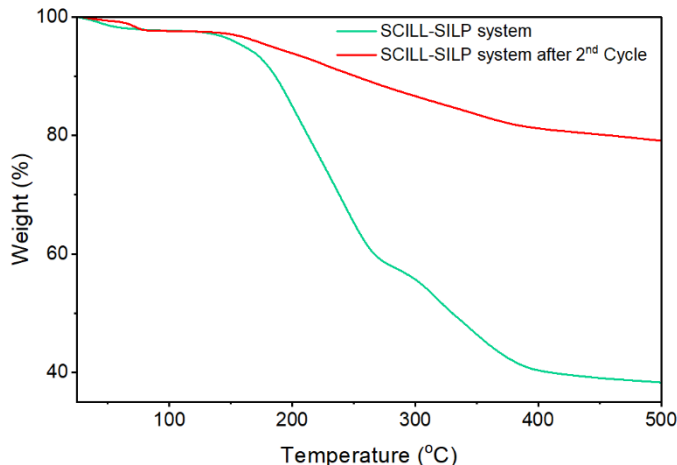


Figure 5.27. TGA curves of fresh IGMWCNT-COO-Cu@2([emim][OcOSO₃])+NHPI and after the second reaction cycle.

To evaluate the extent of NHPI and IL mixture leaching from the recycled SCILL-SILP system, TGA analysis was conducted for both the fresh catalyst and the sample recovered after the second cycle (Figure 5.27). The initial weight losses observed between 25-100 °C were approximately identical for both catalysts. However, between 100-500 °C, the fresh catalyst lost 59.41% of its weight, while the recycled sample showed an 8.53% loss, indicating that a fraction of the IL and NHPI was still retained on the Cu(II) functionalized CNT surfaces. This observation was further supported by the FTIR spectrum of the SCILL-SILP hybrid catalyst after the second cycle (Figure 5.23 (b)), which showed a noticeable decrease in the intensities of the characteristic bands corresponding to the IL and, in particular, to NHPI. The reduction of these bands' intensities confirmed that most of the NHPI and a portion of the IL had been leached out during the recycling process.

To further investigate the recyclability and reusability of the SCILL-SILP system, a leaching test was performed. A freshly prepared SCILL-SILP system was employed in the oxidation reaction, and after 30 minutes, the hybrid catalytic system was separated from the reaction mixture. The filtrate was then allowed to proceed and complete the reaction time under similar conditions. The overall EB conversion profile is compared with that obtained in the presence of the SCILL-SILP system in Figure 5.28. After the catalyst separation, the conversion rate decreased significantly, and the final conversion reached (11.1%) is less than half of that obtained in the presence of the catalyst (26.6%). It is noteworthy that more than half of this

final conversion had already been reached during the first 30 minutes before the catalyst separation, indicating that the filtrate contributed only marginally to the overall conversion after separation.

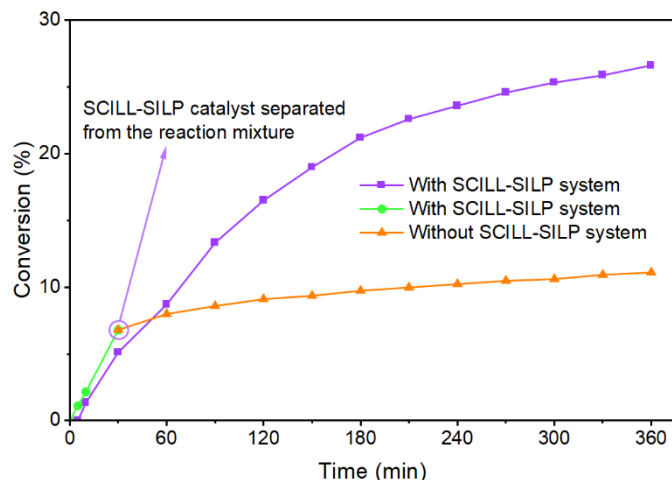


Figure 5.28. Comparison of EB conversion as a function of time for the SCILL-SILP system and for the corresponding reaction in which the hybrid catalyst was separated during the reaction, allowing the filtrate to proceed and complete the specified reaction time.

To investigate the results thoroughly, the product distribution for the filtrate after the completion of the reaction time was compared with reactions performed in the presence of [emim][OcOSO₃] and NHPI, and the SCILL-SILP system, and the results are presented in Table 5.12. In the presence of [emim][OcOSO₃] and NHPI, 7.8% EB conversion was obtained with 53% and 43.9% selectivity towards PEHP and AcPO, respectively. On the other hand, for the SCILL-SILP system, selectivity is more inclined towards AcPO (77.1) with 26.6% EB conversion. In contrast, for the SCILL-SILP leaching test (entry 4), 22.8% selectivity was observed, with 66.4% selectivity towards AcPO. Since more than half of the EB conversion was obtained before the catalyst separation, it has also contributed to the product distribution. Nevertheless, the significant decrease in the EB conversion rate after the catalyst separation, together with the product distribution (increase in PEHP selectivity), suggests that a portion of NHPI, probably with a small amount of IL, has been leached out.

Table 5.12. Leaching test for SCILL-SILP system.

Entry	Catalyst	Con. (%)	Sel. (%)			
			PEHP	PEA	AcPO	BA
1 ^a	[emim][OcOSO ₃] + NHPI	7.8	53	3.1	43.9	-
2 ^b	IGMWCNT-COO-Cu + [bmim][OcOSO ₃] + NHPI (mixture)	25.1	12.2	10	76.1	1.7
3 ^c	SCILL-SILP system	26.6	9.2	11.2	77.1	2.5
4 ^d	SCILL-SILP leaching test	11.1	22.8	2.5	66.4	8.3

Reaction conditions: EB: 16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h; ^a 0.025 g IL and 1 mol% of NHPI; ^b mixture of 0.025 g MWCNTs, 0.025 g IL and 1mol% NHPI added separately to EB; ^c [emim][OcOSO₃]-based SCILL-SILP (0.025 g IL, 1 mol% NHPI, and 0.025 g IGMWCNT-COO-Cu); ^d [emim][OcOSO₃]-based SCILL-SILP system was separated from the reaction mixture during the reaction, and the filtrate was allowed to proceed and complete the reaction time.

5.2.4 Summary

The novel SCILL-SILP hybrid catalytic systems developed as a part of the doctoral research were first reported by us in the Chemical Engineering Journal in the article entitled: “SCILL–SILP hybrid catalytic system employing carbon nanotubes as a support for the selective oxidation of ethylbenzene to acetophenone” (Chemical Engineering Journal 457 (2023)141207; <https://doi.org/10.1016/j.cej.2022.141207>).

Cu(II)-functionalized carboxylated IGMWCNTs (IGMWCNT-COO-Cu) were employed as the solid catalyst support, onto which [emim][OcOSO₃] containing dissolved NHPI was coated to obtain the SCILL-SILP hybrid catalytic system. For comparison, SCILL systems were also prepared by coating the pristine IL [emim][OcOSO₃] onto the same support in the absence of NHPI. These hybrid catalytic systems were subsequently employed in the liquid-phase solvent-free selective oxidation of EB to AcPO using molecular oxygen as an oxidant under mild conditions.

In SCILL systems, the viscous [emim][OcOSO₃] IL layer covered the active sites of the CNTs support, suppressing the interaction between the substrate and the catalytically active sites, thereby hindering the radical formation and impeding the oxidation initiation. However, in the presence of AIBN as a radical initiator, the positive effect of the coated IL was observed, increasing both the EB conversion and selectivity towards AcPO. Among the SCILL systems with various IL loadings, the highest EB conversion (14.1%) was observed for the SCILL system with 72.9% AcPO selectivity, where 0.025 g of IL was employed.

On the other hand, the SCILL-SILP hybrid catalytic system (0.025 g IL) outperformed, realizing ~27% EB conversion with ~77% AcPO selectivity. These results suggest that ILs promote a more selective, controlled oxidation environment, possibly via the solvent cage effect. Recyclability tests supported by TGA, FTIR analyses, and leaching tests revealed partial leaching of NHPI with a small portion of IL from the solid catalyst surface during the reaction and recycling process.

5.3 SILP and SCILL-SILP Hybrid Catalytic Systems Based on MWCNTs, MWCNT-COO-Cu and Various ILs

In Section 5.2, we reported [emim][OcOSO₃]-based SCILL and SCILL-SILP hybrid catalytic systems, employing Cu(II)-immobilized industrial-grade MWCNTs as the support. The SCILL system demonstrated diminished catalytic activity in the absence of a radical initiator (AIBN), attributed to active site masking, which restricted the substrate accessibility to the catalytically active sites, thereby suppressing the radical formation and inhibiting oxidation initiation. However, in the presence of AIBN as a radical initiator, the positive effect of the coated IL was observed, increasing both the EB conversion and selectivity towards AcPO to 14.1% and 72.9%, respectively (SCILL system, IL/IGMWCNT-COO-Cu = 1:1 w/w).

The SCILL-SILP system demonstrated enhanced activity in the absence and presence of the radical initiator, with activity comparable to that of the support catalyst (IGMWCNT-COO-Cu) with NHPI. In the presence of AIBN, the SCILL-SILP system realized ~27% EB conversion with ~77% AcPO selectivity. However, the recyclability tests, supported by TGA and FTIR analyses, revealed partial leaching of NHPI with a small portion of IL from the SCILL-SILP system, leading to a progressive loss of activity over the subsequent cycles. The limited recyclability of the developed SCILL-SILP system restricts its applicability. This limitation made it imperative to develop a more resilient and reusable hybrid catalytic system. Interestingly, the previous study has explored [bmim]-cationic ILs-based SCILL systems previously using NHPI-grafted silica as the solid support [272], which remarkably improved the solvent-free aerobic oxidation of EB. Furthermore, the [bmim][OcOSO₃] and silica-based SCILL system was somewhat recyclable, with a slight decline in activity in the fourth cycle.

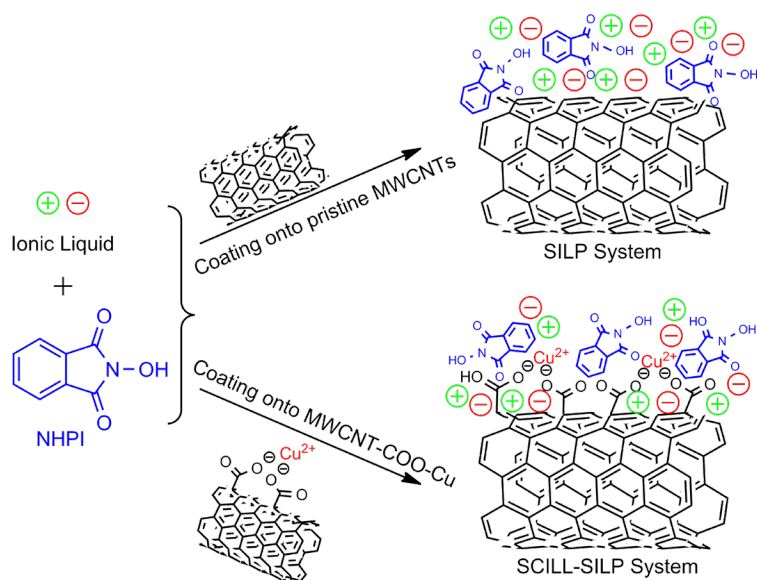


Figure 5.29. Scheme for the preparation of SILP and SCILL-SILP hybrid catalytic systems.

In this section, [Rmim]-based ILs (R-alkyl) were utilized to develop novel SILP and SCILL-SILP hybrid catalytic systems. The SILP systems were produced by depositing a thin layer of NHPI dissolved in a selected IL layer onto pristine MWCNTs, whereas the SCILL-SILP systems were obtained by depositing a layer of the same mixture onto Cu(II) functionalized carboxylated MWCNTs (Figure 5.29). To the best of our knowledge, these SILP and SCILL-SILP hybrid catalytic systems are novel and have not been previously reported, except for the [emim][OcOSO₃]-based SCILL-SILP system, which was reproduced from the previous section for comparison. The recyclability and reusability of all the catalysts were thoroughly investigated.

5.3.1 Catalyst preparation and characterization

In this study, carboxylated MWCNTs (MWCNT-COOH) were employed for Cu(II) functionalization following the same preparation procedure as described in Section 5.1.3. The SILP systems were prepared by adopting the solvent evaporation coating technique reported in previous work [272,273], with a minor modification involving the introduction of an ultrasonication step before stirring. The appropriate amount of selected IL, NHPI, and pristine MWCNTs was dispersed in acetone, ultrasonicated, stirred, and then the acetone was evaporated to yield the final SILP system. The SCILL-SILP systems were prepared following

the same technique, while replacing pristine MWCNTs with the MWCNT-COO-Cu in the mixture before ultrasonication.

To improve the stability, reusability, and catalytic efficiency, a broad set of ILs with different cation-anion combinations was explored, including [emim], [bmim], [omim], and [C₁₀mim] cations in combination with [Cl], [Br], [BF₄], [PF₆], [OcOSO₃], or [NTf₂] anions. The stability of all catalytic systems was rigorously examined through recyclability and reusability tests. Additionally, leaching tests were performed for the more stable SILP and SCILL-SILP systems to investigate the stability of the immobilized active layer under reaction conditions.

For representative characterization, the [bmim][OcOSO₃]-based SILP and SCILL-SILP hybrid catalysts were characterized using TEM, ATR-FTIR, and TGA/DTG analyses. The TEM image of pristine MWCNTs (Figure 5.30 (a)) shows smooth, defect-free nanotubes with outer diameters in the range of 20-50 nm (supplier reports 20-40 nm) and no detectable impurities. On the other hand, the SILP and SCILL-SILP samples exhibit a non-uniform, thin coating of the mixture of NHPI-IL phase on the surfaces of pristine and MWCNT-COO-Cu, respectively, as demonstrated in Figure 5.30 (b) and (c). As demonstrated in Section 5.2, coating the NHPI-IL mixture onto the IGMWCNT-COO-Cu drastically decreases the BET surface area, total pore volume, and overall porosity of the resulting hybrid catalytic system.

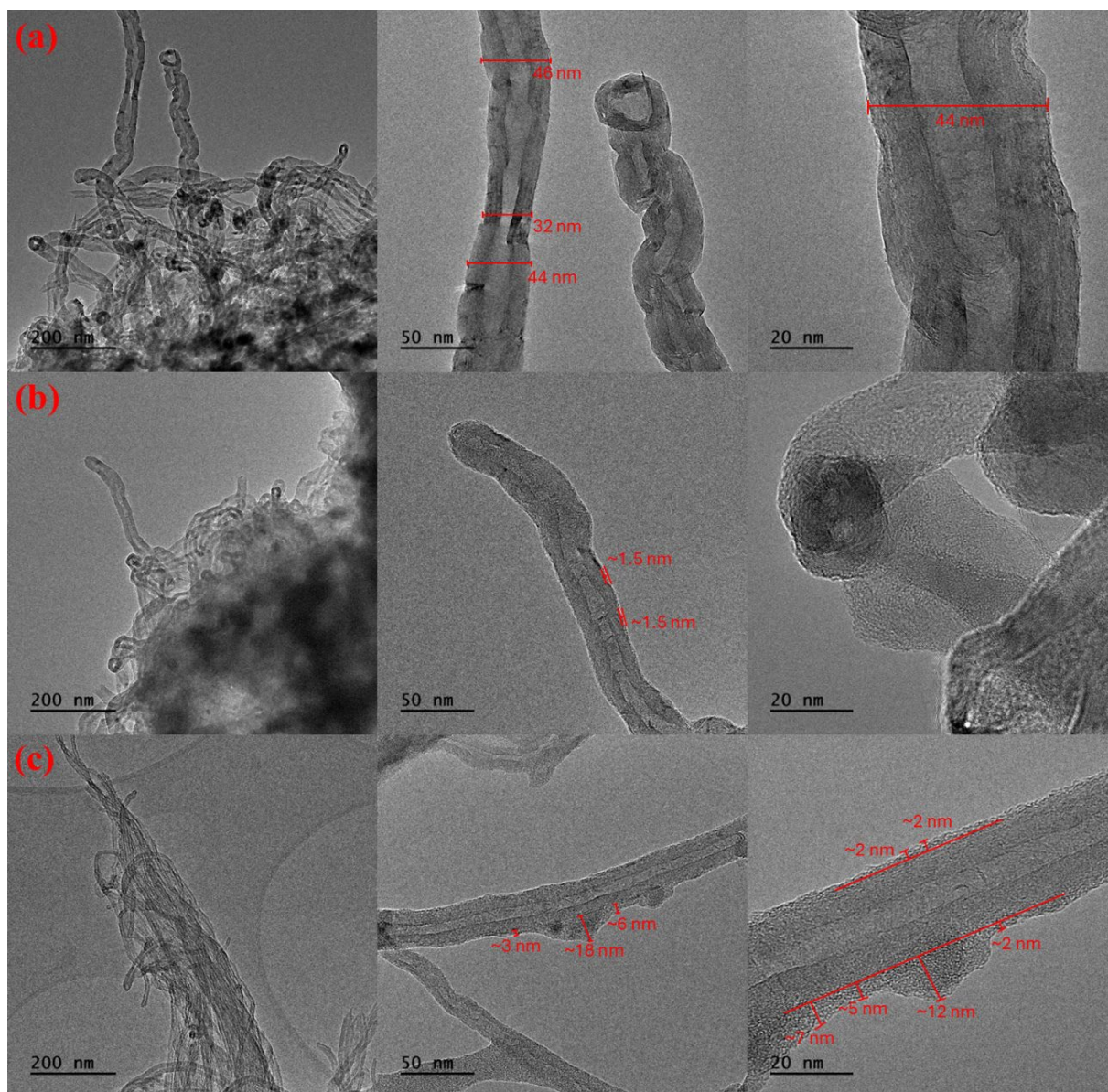


Figure 5.30. TEM image of (a) Pristine MWCNTs, (b) [bmim][OcOSO₃]-based SILP system, (c) [bmim][OcOSO₃]-based SCILL-SILP system.

The ATR-FTIR spectra of the [bmim][OcOSO₃]-based SILP and SCILL-SILP systems, together with the corresponding spectra of the constituent components, were acquired and analyzed (Figure 5.31). As shown in Figure 5.31 (a), the MWCNT-COOH displayed a characteristic absorption peak around $\sim 3380\text{ cm}^{-1}$, corresponding to the O-H stretching vibration of the surface carboxyl groups. The bands observed at around ~ 2923 and $\sim 2853\text{ cm}^{-1}$ are assigned to the asymmetric and symmetric stretching modes of methylene ($-\text{CH}_2$) groups, which are typically associated with structural and/or surface defects on the nanotube [281]. The absorption

band at $\sim 1704\text{ cm}^{-1}$ can be attributed to the C=O stretching vibration of the surface carboxyl groups. The band near $\sim 1611\text{ cm}^{-1}$ can be attributed to the C=C stretching vibration of the graphitic framework, whereas the band at $\sim 1577\text{ cm}^{-1}$ could be related to the carboxylate anion stretching vibrations [289]. Upon Cu(II) functionalization, the corresponding MWCNT-COO-Cu (Figure 5.31 (a)) demonstrated a reduction in the intensities of the O-H ($\sim 3380\text{ cm}^{-1}$), C=O ($\sim 1702\text{ cm}^{-1}$), and the carboxylate anion ($\sim 1577\text{ cm}^{-1}$) vibrational bands. These results collectively support the coordination of Cu(II) ions with the surface carboxylate groups. The divalent Cu(II) species could have been coordinated in the form of (MWCNT-COO)₂Cu or MWCNT-COOCuCl.

The ATR-FTIR spectrum of the MWCNTs (Figure 5.31 (c)) reveals the presence of surface defects and oxygen-containing functional groups, as its spectral features closely resemble those of the MWCNTs. Following the coating of the NHPI dissolved [bmim][OcOSO₃] onto the MWCNTs surfaces, the resulting SILP system (Figure 5.31 (c)) displayed a broad band at 3380 cm^{-1} , attributable to the sorbed water and/or the oxygenated functional groups on the MWCNTs. The absorption peaks at ~ 3100 , 1784 , and 1704 cm^{-1} correspond to the N-OH stretching vibration and the symmetric and asymmetric C=O stretching modes of the carbonyl groups in NHPI [285].

The ATR-FTIR spectrum of [bmim][OcOSO₃] IL is shown in Figure 5.31 (b). The absorption band at $\sim 3111\text{ cm}^{-1}$ corresponds to the C-H stretching vibration of the imidazolium ring. The absorption bands at ~ 2926 and $\sim 2853\text{ cm}^{-1}$ are associated with asymmetric and symmetric C-H stretching modes of the alkyl chains. The peak at $\sim 1571\text{ cm}^{-1}$, reflecting the C=C and C=N stretching vibrations in the imidazolium ring, whereas the peak at $\sim 1467\text{ cm}^{-1}$ originates from CH₂ bending within the alkyl chains of the [bmim] cation and [OcOSO₃] anion. A strong, sharp peak at 1215 cm^{-1} could be associated with the S=O stretching vibration of the sulfate anion [290]. In the SILP catalytic system, these characteristic peaks were overlapped with the NHPI and MWCNTs absorption bands. A similar effect can also be observed in the case of the SCILL-SILP system (Figure 5.31 (d)), where the prominent bands at ~ 3095 , ~ 1784 , and $\sim 1704\text{ cm}^{-1}$ confirm the presence of NHPI, yet the distinctive IR bands of [bmim][OcOSO₃] remain obscured due to peaks overlapping.

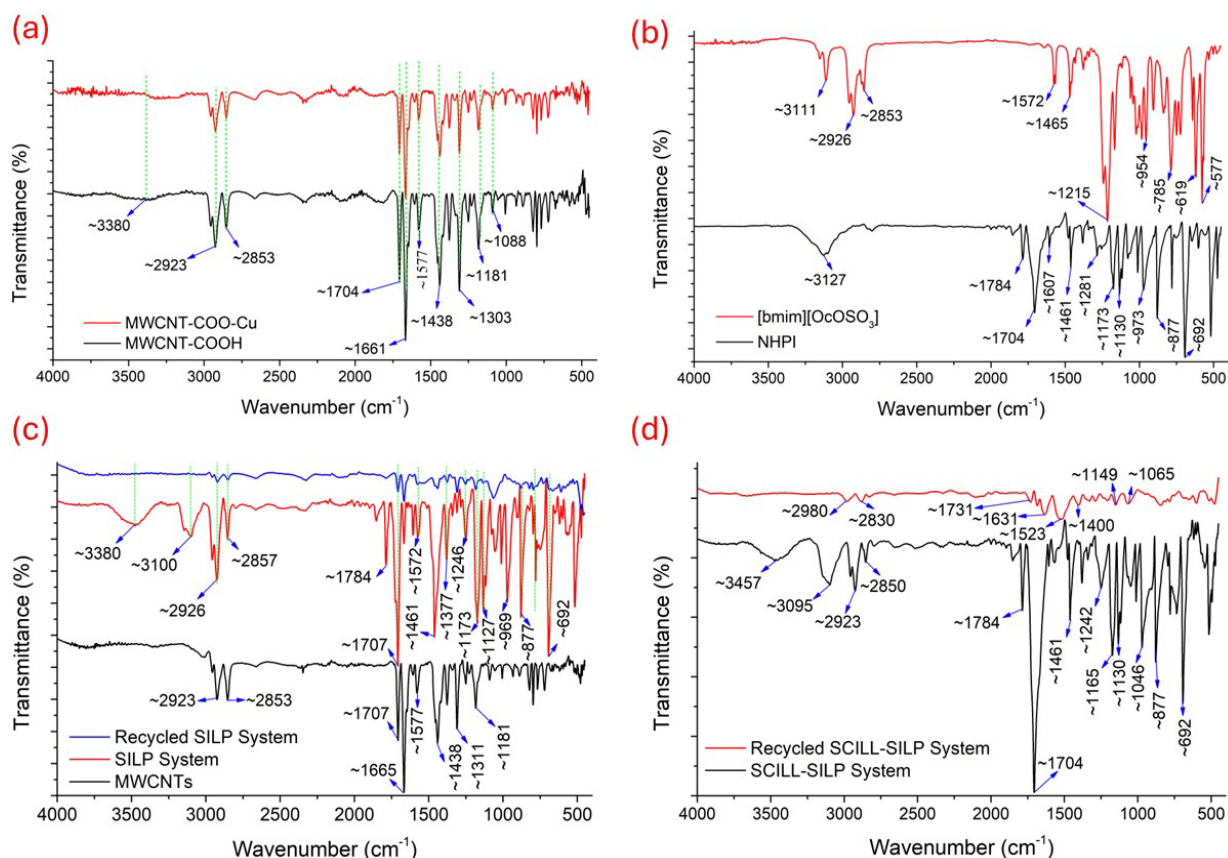


Figure 5.31. FTIR Spectra of (a) MWCNT-COOH and MWCNT-COO-Cu, (b) NHPI and [bmim][OcOSO₃], (c) MWCNTs, fresh and recycled [bmim][OcOSO₃]-based SILP systems, and (d) fresh and recycled [bmim][OcOSO₃]-based SCILL-SILP systems.

5.3.2 Catalytic activities of the SILP systems

The SILP systems were developed to integrate the established catalytic activities of CNTs, NHPI, and ILs in the liquid-phase oxidation of hydrocarbons with oxygen. Their catalytic activities under solvent-free conditions for the oxidation of EB are presented in Table 5.13 and Figure 5.32. Both the NHPI and MWCNTs have slightly increased the conversion of EB. The reduced selectivity toward PEHP observed with MWCNTs alone indicates their capability to decompose the intermediate hydroperoxides. In contrast, combining NHPI with MWCNTs resulted in a pronounced increase in PEHP selectivity, which is consistent with the previous reports, which demonstrate the capability of NHPI to selectively promote the formation of hydroperoxide in these processes [283,284].

Table 5.13. Effect of SILP systems on the solvent-free oxidation of EB with oxygen.

Entry	Catalyst	Con. (%)	Sel. (%)				
			PEHP	PEA	AcPO	BA	BzA
1	Blank	4.0	84.5	4.6	10.9	-	
2	NHPI	5.6	75.6	14.9	9.5	-	
	MWCNTs	4.1	46.9	42.2	10.9	-	
3	MWCNTs+NHPI	5.7	90.6	5.9	3.6	-	
4	MWCNTs@[bmim][Cl]+NHPI	12.2	10.1	4.8	84.1	1.1	-
5	MWCNTs@[bmim][Br]+NHPI	8.9	3.7	5.7	88.2	1.5	1.4
6	MWCNTs@[bmim][BF ₄]+NHPI	9.4	40.3	25	23.2	9.9	1.7
7	MWCNTs@[bmim][OcOSO ₃]+NHPI	9.7	56.8	9.7	25.9	6.6	1.2
8	MWCNTs@[bmim][NTf ₂]+NHPI	10.3	53.6	9.2	22.4	13.7	1.2
9	MWCNTs@[bmim][PF ₆]+NHPI	7.6	32.2	14.3	29.1	21.8	2.5
10	MWCNTs@[omim][Cl] + NHPI	21.9	6.5	1.8	90.1	1.2	0.5
11	MWCNTs@[C ₁₀ mim][Cl] + NHPI	27.6	5.1	5.5	87.9	1.3	0.5
12	MWCNTs@[emim][NTf ₂]+NHPI	5.3	11.7	0.9	16.5	63.0	7.9
13	MWCNTs@[emim][OcOSO ₃]+NHPI	9.6	59.8	9.1	24.0	6.9	0.3

Reaction conditions: SILP systems (MWCNTs: 0.025 g, 1 mol% NHPI (0.027 g), and 0.025 g IL); EB:16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

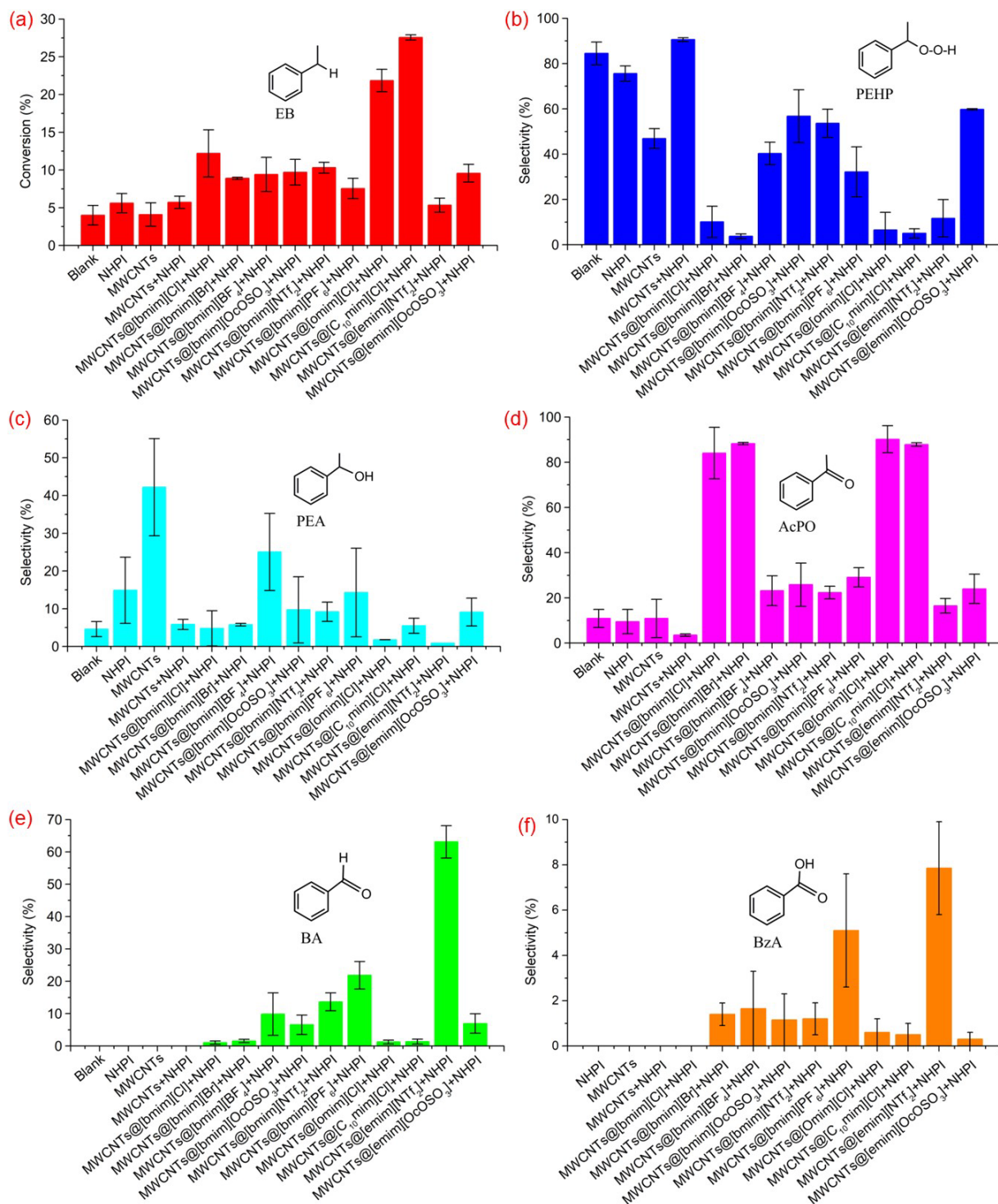


Figure 5.32. Catalytic activities of SILP systems: (a) EB conversion (%), (b) PEHP selectivity (%), (c) PEA selectivity (%), (d) AcPO selectivity (%), (e) BA selectivity (%), and (f) BzA selectivity (%). Reaction conditions: EB: 16.33 mmol; MWCNTs: 0.025 g; NHPI: 0.027 g (1 mol%); IL: 0.025 g; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

All SILP systems based on the [bmim] cation exhibited enhanced catalytic activities in the oxidation reactions compared to pristine MWCNTs or the MWCNTs/NHPI combination. Several factors may contribute to the improved catalytic activities, including the activities of ILs to promote hydroperoxide decomposition, positive interaction of IL with NHPI that facilitates the generation of PINO radical, improved solubility of the reagents and NHPI within the IL layer, and the influence of IL polarity and viscosity. Possible leaching of the IL and NHPI from the MWCNTs surfaces may also contribute to the observed behavior.

The highest EB conversion (12.2%) was obtained for [bmim][Cl] based SILP system, which also displayed the highest selectivity toward AcPO (84.1%). The superior performance of MWCNTs@[bmim][Cl] relative to MWCNTs@[bmim][Br] is consistent with the trends reported by Talik et al. [258] for NHPI-catalyzed hydrocarbon oxidations in the presence of halide-based ILs. Their studies showed that the catalytic activity of 1-alkyl-3-methylimidazolium cation and halide anion, [Rmim][X], decreases in the order [Cl] > [Br] > [I]. They attributed this behavior to a specific interaction between the halide anion and the hydrogen atom of the -NOH group in NHPI (Figure 5.33), which may weaken the NO-H bond in the NHPI and ultimately accelerate the generation of the PINO radical. The strength of this interaction can be correlated with the acidity of the corresponding HX acids, which is governed by the nature of the halide anion and increases in the order [Cl] < [Br] < [I]. Because weaker acids have stronger conjugate bases, [Cl] is the most basic of the three anions, resulting in a more pronounced -NOH---[Cl] interaction compared to -NOH---[Br] and -NOH---[I] interactions, thereby expediting PINO generation and ultimately enhancing the catalytic performance.

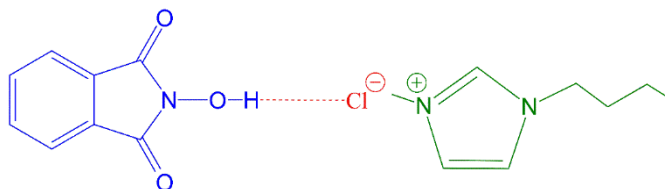


Figure 5.33. Interaction between NHPI and [bmim][Cl]. Adapted with permission from Ref. [258]. Copyright 2021, Wiley-VCH.

The SILP systems synthesized employing [bmim][NTf₂] and [bmim][OcOSO₃] exhibited enhanced selectivity towards PEHP. Although their limited ability to decompose the

intermediate hydroperoxides, these systems still displayed substantial catalytic activity, which could be attributed to the higher oxygen solubility of the corresponding ILs. For [bmim] cation-based ILs, oxygen solubility follows the order $[\text{NTf}_2] > [\text{PF}_6] \sim [\text{OcOSO}_3] > [\text{BF}_4]$ [245]. While [bmim][PF₆] has an oxygen solubility comparable to [bmim][OcOSO₃], NHPI is only sparingly soluble in this specific IL, which consequently limits its efficiency in the corresponding SILP system compared to the others.

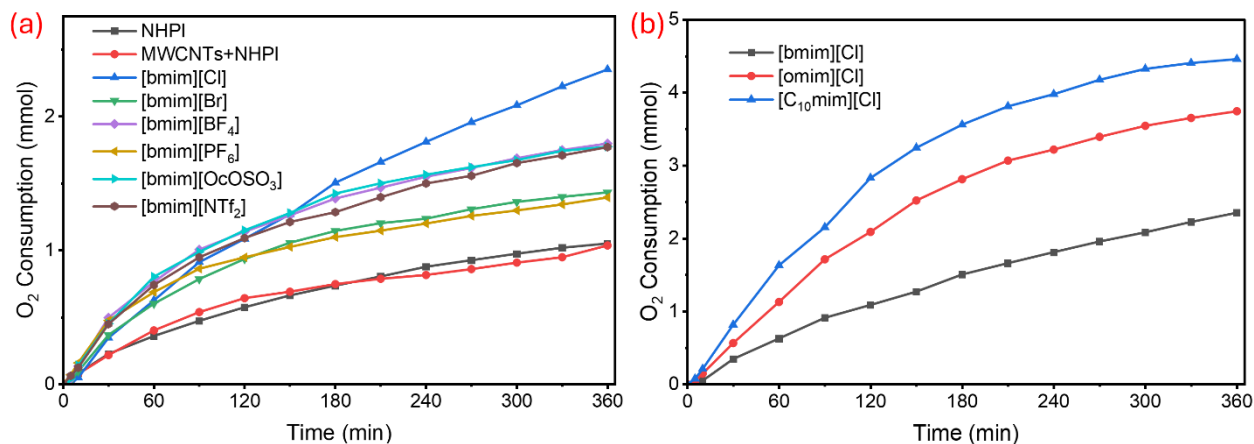


Figure 5.34. Oxygen consumption vs. time for EB oxidation reaction: (a) [bmim] cation IL-based SILP systems and (b) the effect of cation lipophilicity in [Cl] anion IL-based SILP systems. SILP systems (MWCNTs: 0.025 g, 1 mol% NHPI (0.027 g), and 0.025 g IL); EB:16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

The O₂ consumption profiles during the oxidation of EB over [bmim] cation IL-based SILP systems are presented in Figure 5.34 (a) and compared with the NHPI and MWCNT/NHPI system (in the same proportion as in the SILP system) under similar reaction conditions. The O₂ consumption profiles over the reaction time are approximately similar for NHPI and MWCNTs with the NHPI system. On the other hand, O₂ consumption during the oxidation reaction increases significantly for all the investigated [bmim] cation IL-based SILP systems, with the [bmim][Cl]-based system exhibiting the highest value.

The influence of the IL cation structure on the catalytic performance of the SILP systems was also investigated. An increase in the alkyl chain length of the cation, such as in [omim][Cl] and [C₁₀mim][Cl], significantly enhanced the O₂ consumption (Figure 5.34 (b)), while also increasing EB conversion and selectivity towards AcPO. It is well established that increasing the cation's lipophilicity enhances the solubility of both hydrocarbons and oxygen in the IL,

and also increases the solubility of ILs in nonpolar media and/or systems [258,272,291]. However, this increased lipophilicity may also promote undesired leaching of the IL from the MWCNTs surface.

For comparison, substituting the [bmim] cation in [OcOSO₃] and [NTf₂] with the less lipophilic [emim] cation resulted in a dramatic decrease in EB conversion for the [emim][NTf₂]-based SILP system. However, this particular IL-based SILP system displayed a higher selectivity toward BA (61.0%). BA is formed via β -C-C cleavage in the 1-phenylethyloxy radical [21,292]. The results suggest that [emim][NTf₂] strongly promotes alkoxy-radical scission. Among all SILP systems, the [emim][NTf₂]-based SILP catalyst demonstrated the highest selectivity to BA, followed by those incorporating [bmim][PF₆] and [bmim][BF₄]. On the other hand, [emim][OcOSO₃]-based SILP system maintained higher selectivity toward the intermediate hydroperoxide and achieved an EB conversion comparable to that of the [bmim][OcOSO₃] analogue.

5.3.3 Catalytic activities of SCILL-SILP hybrid systems

The SCILL-SILP hybrid systems were designed to integrate the known catalytic activities of Cu(II) functionalized MWCNTs, NHPI, and ILs, producing a synergistic catalyst capable of promoting the liquid-phase aerobic oxidation of hydrocarbons. The catalytic activities of the produced SCILL-SILP systems in the liquid-phase solvent-free oxidation of EB with oxygen are presented in Table 5.14 and Figure 5.35. For comparison purposes, the activity of MWCNT-COO-Cu was also evaluated under similar conditions with NHPI as a cocatalyst.

Table 5.14. Effect of SCILL-SILP systems on the solvent-free oxidation of EB with oxygen.

Entry	Catalyst	Con. (%)	Sel. (%)				
			PEHP	PEA	AcPO	BA	BzA
1	MWCNT-COO-Cu	5.4	8.9	8.2	82.9	-	-
2	MWCNT-COO-Cu + NHPI	27.9	10.7	6.7	81.5	1.1	-
3	MWCNT-COO-Cu@[bmim][Cl]+NHPI	15.6	1.4	3.8	94.5	0.4	-
4	MWCNT-COO-Cu@[bmim][Br]+NHPI	13.9	3.3	2.6	94.2	-	-
5	MWCNT-COO-Cu@[bmim][NTf ₂]+NHPI	22.6	15.6	7.8	70.1	6.1	0.6
6	MWCNT-COO-Cu@[bmim][BF ₄]+NHPI	22.2	9.0	2.8	86.0	1.7	0.6
7	MWCNT-COO-Cu@[bmim][PF ₆]+NHPI	18.8	8.4	5.0	82.7	3.5	0.5
8	MWCNT-COO-Cu@[bmim][O ₂ SO ₃]+NHPI	21.0	9.8	5.1	83.9	1.3	-
9	MWCNT-Cu@[omim][Cl]+NHPI	19.4	2.5	3.6	93.3	0.6	-
10	MWCNT-Cu@[C ₁₀ mim][Cl]+NHPI	15.1	2.2	6.0	91.0	0.8	-
11	MWCNT-COO-Cu@[emim][NTf ₂]+NHPI	10.0	3.7	0.7	57.9	34.1	3.6
12	MWCNT-COO-Cu@[emim][O ₂ SO ₃]+NHPI	24.4	11.7	5.8	80.3	1.7	0.4

Reaction conditions: SCILL-SILP systems (MWCNT-COO-Cu: 0.025 g, 1 mol% NHPI (0.027 g), and 0.025 g IL); EB:16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

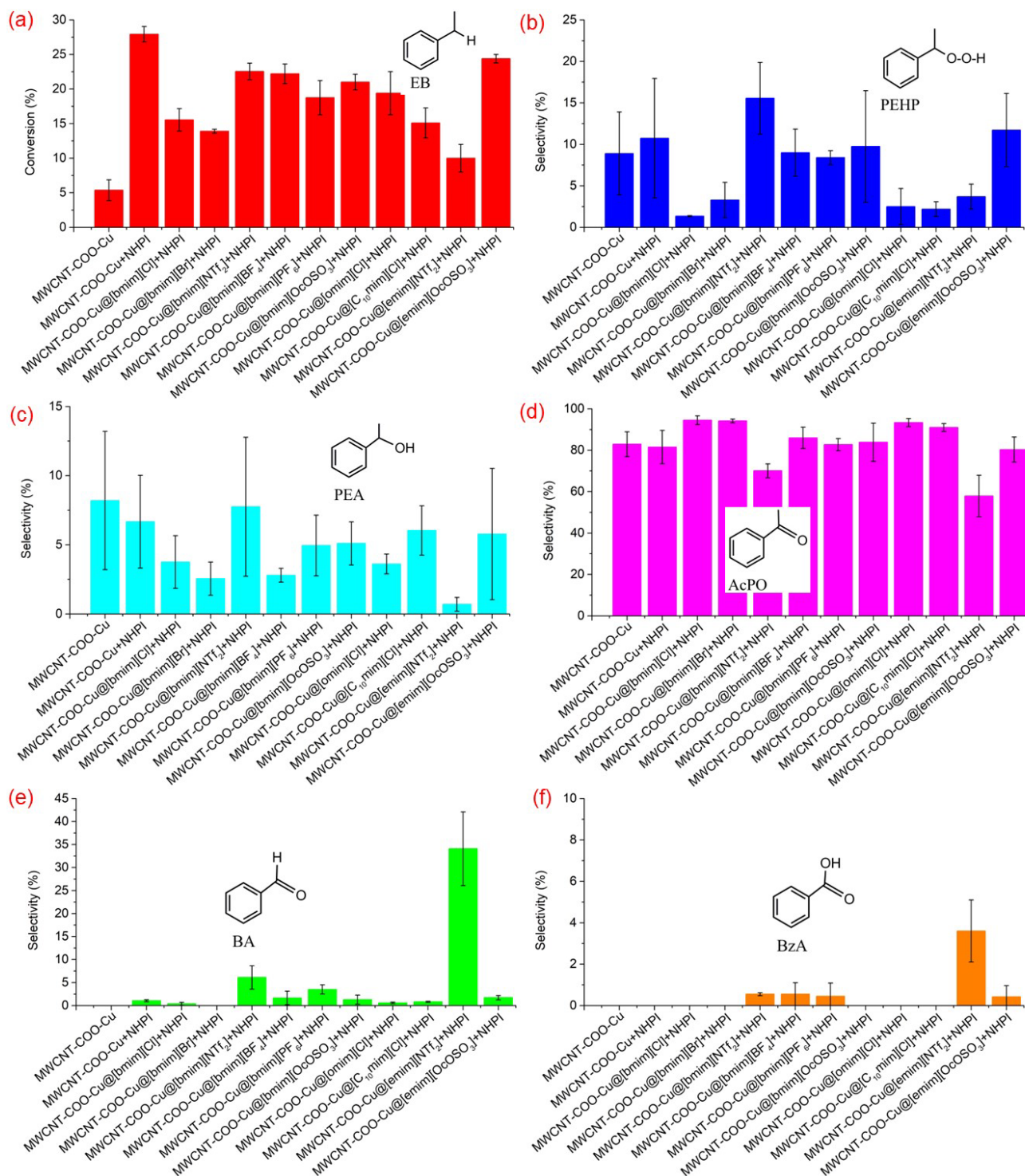


Figure 5.35. Catalytic activities of SCILL-SILP systems: (a) EB conversion (%), (b) PEHP selectivity (%), (c) PEA selectivity (%), (d) AcPO selectivity (%), (e) BA selectivity (%), and (f) BzA selectivity (%). Reaction conditions: EB: 16.33 mmol; MWCNT-COO-Cu: 0.025 g; NHPI: 0.027 g (1 mol%); IL: 0.025 g; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

The catalytic activity of the MWCNT-COO-Cu soared compared to the pristine MWCNTs, under identical reaction conditions, with the EB conversion increasing from 5.7% to 27.9%. The enhanced activity of the MWCNT-COO-Cu/NHPI system originates from the synergistic effect between the Cu(II)-functionalized CNTs and NHPI. Cu(II) salts and other transition-metal compounds are known to facilitate the decomposition of intermediate hydroperoxides into corresponding alcohol and ketone products, while boosting the overall reaction rate [131–134]. It can be observed from the comparison of the results presented in Table 5.13 and Table 5.14 that the Cu(II)-functionalized CNTs not only accelerate the decomposition of PEHP but also enhance the generation of PINO radicals from NHPI, ultimately enhancing the EB oxidation rate. Furthermore, it is well established that the product distribution in hydrocarbon oxidation is dependent upon the nature of the transition-metal salt being employed. Owing to their distinct redox potentials, Cu(II) salts generally favor a higher ketone-to-alcohol ratio compared with Co(II) and Mn(II) salts [280]. Consequently, the ketone-to-alcohol ratio for the MWCNT-COO-Cu/NHPI system was higher.

The SCILL-SILP hybrid catalytic systems exhibited lower catalytic activity in comparison with the MWCNT-COO-Cu/NHPI system, and their activities varied distinctly with the type of employed IL. For the SCILL-SILP systems based on [bmim] cations, the EB conversion decreased in the following order with respect to the IL anion: $[\text{NTf}_2] > [\text{BF}_4] \approx [\text{PF}_6] \approx [\text{OcOSO}_3] > [\text{Cl}] > [\text{Br}]$. The solubility of oxygen in [bmim]-based ILs at 50 °C (in $\text{mmol} \cdot \text{dm}^{-3} \cdot \text{atm}^{-1}$) follows the order: $[\text{NTf}_2] (3.75) > [\text{PF}_6] (2.67) > [\text{OcOSO}_3] (2.62) > [\text{BF}_4] (1.49)$ [293–295], while their viscosities at 30 °C (in $\text{mPa} \cdot \text{s}$) exhibit the opposite trend: $[\text{NTf}_2] (41.24) < [\text{bmim}][\text{BF}_4] (75) < [\text{bmim}][\text{PF}_6] (182) < [\text{bmim}][\text{OcOSO}_3] (447.9) < [\text{bmim}][\text{Cl}] (11,000)$ [235,296–298]. Therefore, the catalytic activities of the [bmim]-based SCILL-SILP systems are influenced by the oxygen solubility and viscosity of the IL. Among the SCILL-SILP systems investigated, the [bmim] $[\text{NTf}_2]$ -based catalyst exhibited the highest EB conversion, attributable to its superior oxygen solubility and relatively low viscosity. A similar trend can be observed in the O_2 consumption profiles during the EB oxidation over [bmim] cation IL-based SCILL-SILP systems, as presented in Figure 5.36 (a). Moreover, all SCILL-SILP systems presented enhanced selectivity towards AcPO compared with their corresponding SILP analogues.

The results indicate that the effective availability of Cu(II) is a decisive factor and can be influenced, among other parameters, by the viscosity of the IL. The EB conversions obtained for the [bmim][Cl]-based SILP and SCILL-SILP systems were almost comparable (entry 4, Table 5.13 vs. entry 3, Table 5.14), accompanied by a sustained elevated selectivity towards AcPO. These results suggested that the exceptionally high viscosity of [bmim][Cl] restricts the accessibility of Cu(II) active sites. Moreover, the elevated selectivity towards AcPO may be further rationalized by the solvent-cage effect associated with the viscous [bmim][Cl]. The IL layer effectively confined the generated alkoxy radicals, limiting their ability to diffuse out of the cage and react with EB to form PEA, thereby favoring β -scission within the IL-confined environment [287].

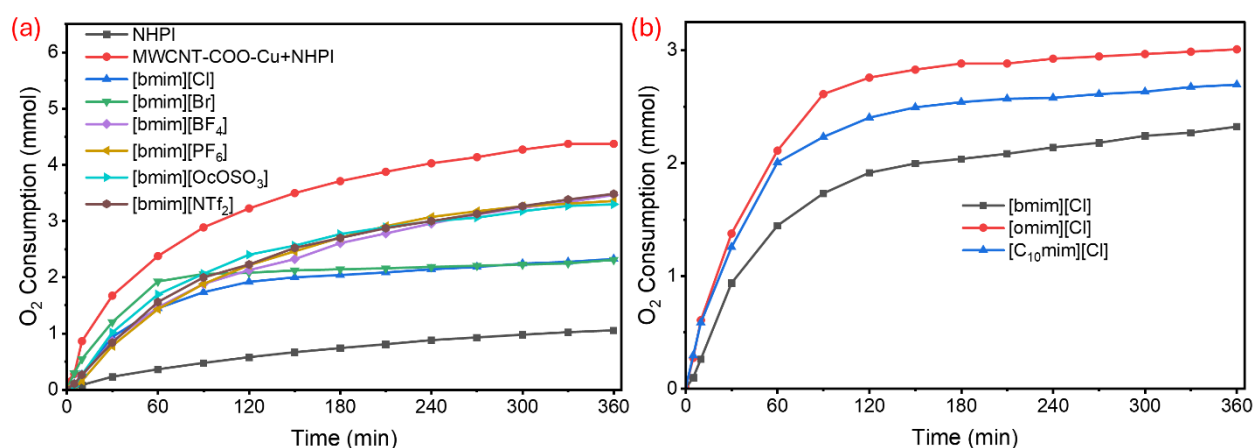


Figure 5.36. Oxygen consumption vs. time for EB oxidation reaction: (a) [bmim] cation IL-based IL SCILL-SILP systems and (b) the effect of cation lipophilicity in [Cl] anion IL-based SCILL-SILP systems. SCILL-SILP systems (MWCNT-COO-Cu: 0.025 g, 1 mol% NHPI (0.027 g), and 0.025 g IL); EB:16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6h.

The influence of cation lipophilicity in the SCILL-SILP systems was also examined. Increasing the lipophilicity of the cation in [Cl]-based ILs, by replacing [bmim] with [omim] and subsequently with [C₁₀mim], initially enhanced both the O₂ consumption and EB conversion for the [omim][Cl]-based system; however, a further increase in alkyl chain length to [C₁₀mim][Cl] led to a reduction in EB conversion (Figure 5.36 and Figure 5.35). The EB conversion for the [C₁₀mim][Cl]-based system remained comparable to that of the [bmim][Cl]-based SCILL-SILP catalyst. Both systems consistently exhibited high selectivity towards AcPO, although their overall activities were lower than those of the corresponding SILP

systems. This reduction in activity may be ascribed to the interactions between the [Cl] anion-based lipophilic ILs and the MWCNT-COO-Cu support catalyst. The more lipophilic ILs exhibited a greater tendency to leach from the SCILL-SILP system, potentially promoting interactions between the strongly coordinating [Cl] anions and the Cu(II) species immobilized on the nanotubes. Such interaction could diminish the availability of Cu(II) active sites and simultaneously weaken the positive interaction between [Cl] anions and the -N-OH group of NHPI, thus reducing the rate of PINO radical formation. As a consequence, these factors account for the lower catalytic performance of the [omim][Cl]- and [C₁₀mim][Cl]-based SCILL-SILP systems compared with their SILP counterparts.

5.3.4 Recyclability of SILP systems

The recyclability and reusability of the SILP catalysts were examined, and the corresponding results are displayed in Table 5.15 and Figure 5.37. After each reuse cycle, the SILP systems were separated employing filtration, washed with hexane, dried, and reused for oxidation of a fresh EB batch. Among the SILP systems examined, the system incorporating [bmim][OcOSO₃] exhibited more stability, outperforming the other IL-based SILP systems investigated in this study. This enhanced stability may be attributed to the amphiphilic character of the [OcOSO₃] anion, which contains a hydrophilic sulfate group and a hydrophobic octyl chain. Such dual functionality enables the anion to interact positively with both polar and non-polar components within the SILP system, as well as with the reaction medium. For instance, the hydrophobic octyl chain may enhance the interaction of this IL with the hydrophobic MWCNTs. Simultaneously, its partial hydrophilicity may promote improved dissolution of NHPI, thereby contributing to the improved stability of the system. It was also observed that the reusability of such a system declined gradually with increasing cation lipophilicity. For example, replacing the [bmim] cation in the [Cl]-based IL with more lipophilic cations, such as [omim] and [C₁₀mim], substantially enhanced EB conversion for the fresh catalysts. However, their activities declined significantly in the subsequent cycles, attributed to undesirable leaching of the IL from the support surface.

Table 5.15. Recyclability of SILP systems.

Entry	Cycle	Catalyst	Con. (%)	Sel. (%)				
				PEHP	PEA	AcPO	BA	BzA
1	0	MWCNTs@[bmim][Cl]+NHPI	14.4	5.2	1.5	92.1	1.2	-
2	1		14.3	6.8	3.6	88.9	0.7	-
3	2		7	4.5	2.9	92.6	-	-
4	0	MWCNTs@[bmim][Br]+NHPI	9	3	5.5	88.6	1.5	1.4
5	1		5.4	9.8	5.1	84.3	0.8	0
6	2		4.7	20.5	2	77.5	0	0
7	0	MWCNTs@[bmim][BF ₄]+NHPI	11	38.6	10.6	27.8	19.7	3.3
8	1		14.9	47.7	1.4	45.9	3.9	1.1
9	2		7.3	58.9	8.1	33	-	-
10	0	MWCNTs@[bmim][O ₃ SO ₃]+NHPI	10.9	48.5	3.5	32.6	13.1	2.3
11	1		9.9	63	15.4	21.6	-	-
12	2		11.1	65.1	10.9	24	-	-
13	0	MWCNTs@[bmim][NTf ₂]+NHPI	10.8	49.2	11	24.3	14.8	0.7
14	1		12.3	52.6	32.7	12.8	1.9	-
15	2		7.8	59	11.2	26.7	3.1	-
16	0	MWCNTs@[bmim][PF ₆]+NHPI	8.5	24.4	6	32.1	32.4	5.1
17	1		5.7	46.5	13.3	37.9	2.3	-
18	2		4	31.6	2.3	66.1	-	-
19	0	MWCNTs@[omim][Cl]+NHPI	20.8	12	1.8	83.8	1.8	0.6
20	1		11.7	13.2	0.4	85.2	1.2	0
21	2		5.6	50.5	0.7	48.8	0	0
22	0	MWCNTs@[C ₁₀ mim][Cl]+NHPI	27.8	8.6	1.8	87.3	1.8	0.5
23	1		9.3	17	5.5	77.5	0	0
34	2		7.2	37.2	24.7	38.1	0	0
25	0	MWCNTs@[emim][NTf ₂]+NHPI	6	17.5	0.9	14.2	61	6.4
26	1		12	20.9	4.6	73.4	1.1	0
27	2		8.5	76	4.4	18.6	1	0
28	0	MWCNTs@[emim][O ₃ SO ₃]+NHPI	10.4	59.6	11.7	19.4	9	0.3
29	1		14.3	51	20.8	22.1	6.1	-
30	2		8.4	73	0.6	24.6	1.8	-

Reaction conditions: EB:16.33 mmol; SILP systems (MWCNTs: 0.025 g, 1 mol% NHPI (0.027 g), and 0.025 g IL); AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6h.

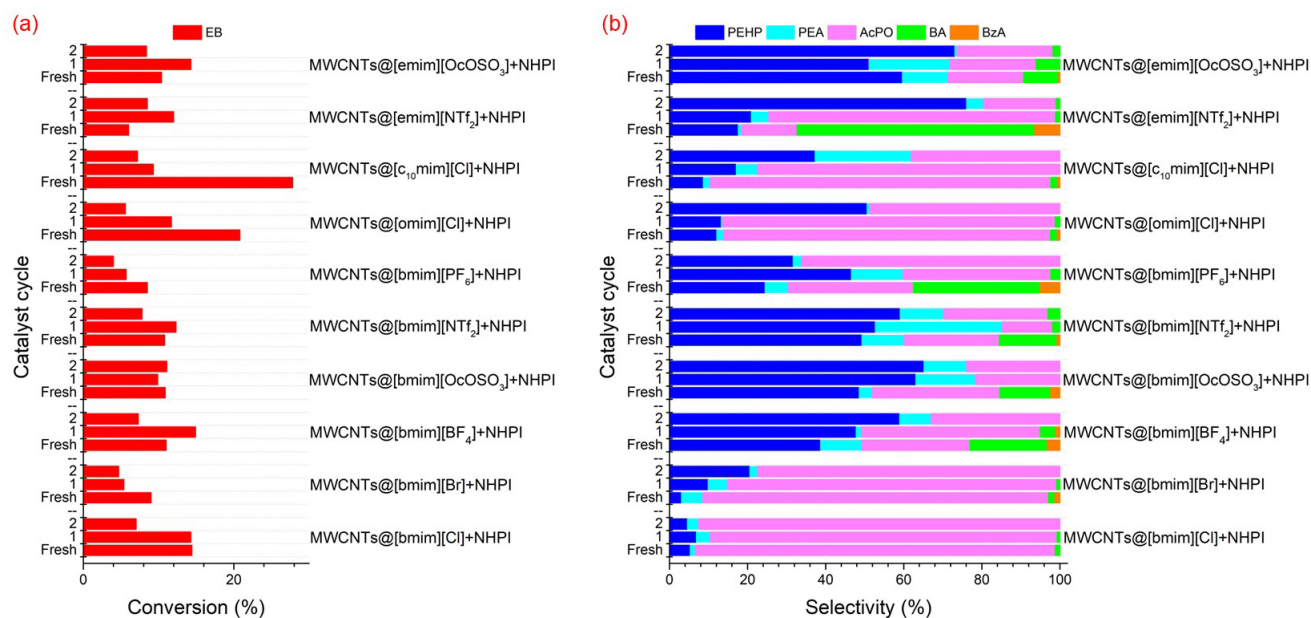


Figure 5.37. Recyclability of SILP systems. Reaction conditions: EB: 16.33 mmol; MWCNTs: 0.025 g; NHPI: 0.027 g (1 mol%); IL: 0.025 g; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

Table 5.16. Leaching test for the SILP system.

Entry	Catalyst	Con. (%)	Sel. (%)				
			PEHP	PEA	AcPO	BA	BzA
1 ^a	[bmim][OcOSO ₃]	4.5	41.3	11.6	47.1	-	-
2 ^b	[bmim][OcOSO ₃] + NHPI	8.7	64.8	4.2	31	-	-
3 ^c	MWCNTs + [bmim][OcOSO ₃] + NHPI	15.0	34.0	8.1	56.7	1.2	-
4 ^d	SILP system	10.9	48.5	3.5	32.6	13.1	2.3
5 ^e	SILP leaching test	11.1	28.5	11.3	55.8	4.4	-

Reaction conditions: EB: 16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h; ^a0.025 g IL; ^b0.025 g IL and 0.027 g of NHPI; ^c0.025 g MWCNTs, 0.025 g IL, and 0.027 g NHPI; ^d[bmim][OcOSO₃]-based SILP (0.025 g IL, 0.027 g NHPI, and 0.025 g MWCNTs); ^e[bmim][OcOSO₃]-based SILP system was separated from the reaction mixture during the reaction, and the effluent was allowed to proceed and complete the reaction time.

To investigate the reusability of the [bmim][OcOSO₃]-based SILP system, a leaching test was conducted. A freshly prepared SILP system was employed in the oxidation reaction, and after

30 minutes, the SILP system was separated from the reaction mixture. The filtrate was then allowed to proceed and complete the reaction time under similar conditions. To make a thorough comparison, additional reactions were carried out using [bmim][OcOSO₃] alone, [bmim][OcOSO₃] with NHPI, and MWCNTs combined with [bmim][OcOSO₃] and NHPI. The corresponding results are presented in Table 5.16 and Figure 5.38.

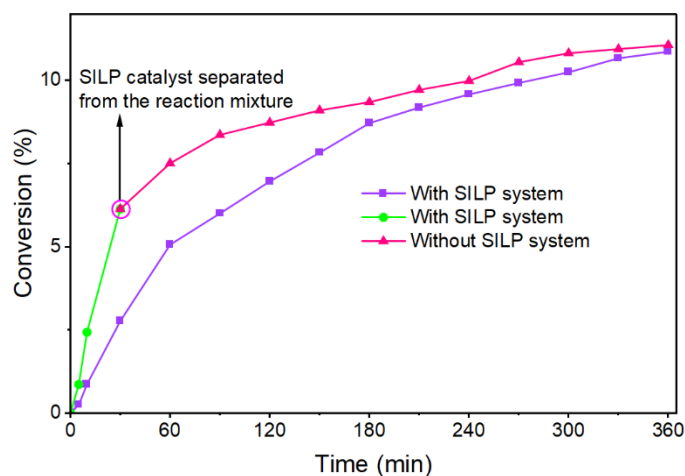


Figure 5.38. EB conversion vs time profiles for the SILP system, compared with the reaction progress of the filtrate after separating the SILP system during the reaction.

The results revealed that, following the separation of the SILP catalytic system from the reaction mixture, the reaction rate reduced slightly. However, the conversions measured after six hours for the reaction conducted with the SILP system and for the reaction continued after its separation were nearly identical, demonstrating undesirable leaching of catalytic components. The product distribution further suggests that the species predominantly leached from the MWCNT surface was the IL. Additionally, the selectivities to PEHP and AcPO obtained after SILP removal (entry 4) were comparable to those observed in the reaction carried out with pristine [bmim][OcOSO₃] (entry 1).

The undesirable leaching of NHPI and IL from the MWCNTs surfaces was further supported by TGA and DTG analyses conducted for both the fresh and recycled SILP samples (Figure 5.39). The fresh SILP sample, as can be observed from Figure 5.39 (a), exhibited two major thermal decomposition stages. The first stage showed a 32.76% weight loss with a pronounced degradation rate at 241 °C, attributable to the thermal decomposition of NHPI [299]. The second stage displayed a 31.13% weight loss with a maximum degradation rate at 310 °C,

corresponding to the decomposition of [bmim][OcOSO₃] IL [272]. Conversely, the recycled SILP system (Figure 5.37 (b)) presented a reduced two-step thermal degradation pattern. The first step accounted for a 20.29% weight loss, while the second contributed only 7.25%, with the maximum decomposition rate occurring at 183.71 °C. This reduced thermal profile confirms the partial leaching of both NHPI and IL during the recycling process. Furthermore, the FTIR spectrum of the recycled SILP system (Figure 5.31 (c)) confirmed the undesirable partial leaching of the mixture of NHPI and IL, as evidenced by the reduced and/or negligible characteristic IR bands.

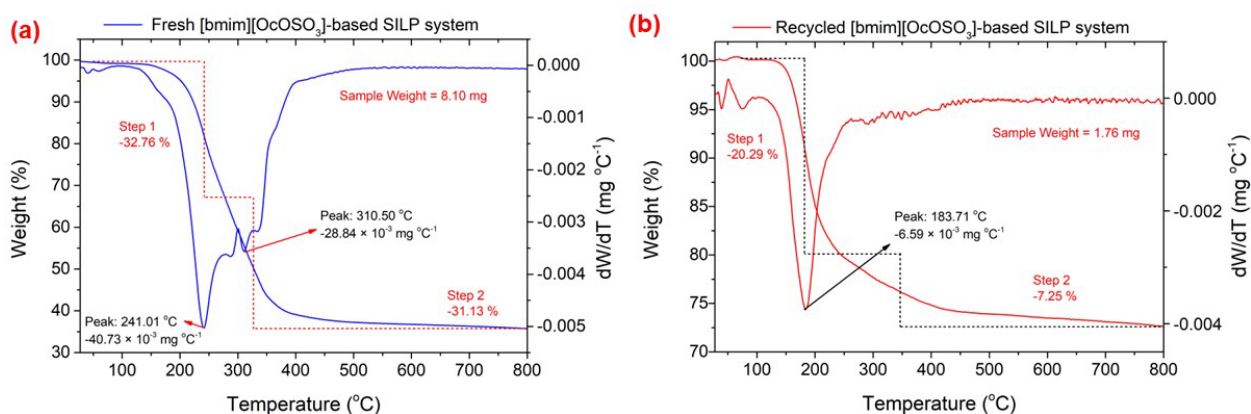


Figure 5.39. TGA and DTG curves, obtained for both the (a) fresh and (b) recycled SILP catalytic systems after the second cycle.

5.3.5 Recyclability of SCILL-SILP hybrid catalytic systems

The recyclability and reusability of the SCILL-SILP systems were also examined, and the results are presented in Table 5.17 and Figure 5.40. Unfortunately, all the SCILL-SILP systems exhibited a decline in activity upon recycling. The results indicate that the decline in catalytic activity is attributable not only to the leaching of the IL and NHPI mixture but also associated with the leaching of Cu(II) from the MWCNT-COO-Cu catalyst. This is supported by the observation that the activity of Cu(II) decreased in the second cycle, while simultaneously displaying a higher selectivity toward PEHP. Nonetheless, the catalytic performance of the [bmim][OcOSO₃]-based SCILL-SILP system remained more stable than that of the other IL-based hybrid systems, which could again be associated with the amphiphilic character of the [OcOSO₃] anion. The polar sulfate moiety of the [OcOSO₃] anion may interact with the Cu(II) sites on the functionalized MWCNTs within the SCILL-SILP hybrid systems, while the

hydrophilic character of this IL may simultaneously enhance the dissolution of NHPI, ultimately contributing to the improved stability and performance of this specific system.

Table 5.17. Recyclability of the SCILL-SILP system.

Entry	Cycle	Catalyst	Con. (%)	Sel. (%)				
				PEHP	PEA	AcPO	BA	Bz
1	0	MWCNT-COO-Cu + NHPI	26.8	3.6	8.4	87	1	-
2	1		22.7	37.4	6.8	55.2	0.6	-
3	2		18.6	34.5	4.8	60.7	-	-
4	0	MWCNT-COO-Cu+[bmim][Cl]+NHPI	14.4	1.3	5.1	93	0.6	-
5	1		6.3	6.7	1.1	92.2	-	-
6	2		2.9	9.2	8.5	82.3	-	-
7	0	MWCNT-COO-Cu+[bmim][Br]+NHPI	14.1	1.8	3.4	94.8	-	-
8	1		4	7.8	4.4	87.8	-	-
9	2		3.9	13	4.9	82.1	-	-
10	0	MWCNT-COO-Cu+[bmim][NTf ₂]+NHPI	23.4	12.5	11.3	67.7	7.9	0.6
11	1		14	41.5	23	31.7	3.8	-
12	2		13.8	44.7	44	10.1	1.2	-
13	0	MWCNT-COO-Cu+[bmim][BF ₄]+NHPI	21.2	11	2.8	82.4	2.7	1.1
14	1		13.7	40.6	10.3	47.1	2	-
15	2		7.2	56	6.5	35.1	2.4	-
16	0	MWCNT-COO-Cu+[bmim][PF ₆]+NHPI	20.5	7.8	6.5	80.6	4.2	0.9
17	1		7.3	32	6.2	60.6	1.2	-
18	2		5.5	61.5	7.2	31.3	-	-
19	0	MWCNT-COO-Cu+[bmim][OcOSO ₃]+NHPI	20.2	14.5	6.2	77.3	2	-
20	1		13	24.3	9.3	66.4	-	-
21	2		13.2	6.6	8.1	84.5	0.8	-
22	0	MWCNT-Cu@[omim][Cl]+NHPI	18.4	5	3	91.3	0.7	-
23	1		4.24	4.4	1	94.6	-	-
24	0	MWCNT-Cu@[C ₁₀ mim][Cl]+NHPI	16.5	1.9	8.1	89.1	0.9	-
25	1		4	5.9	9.4	84.7	-	-
26	0	MWCNT-COO-Cu+[emim][NTf ₂]+NHPI	10	3.7	0.7	57.9	34.1	3.6
27	1		9.7	21	6.1	38.1	32.8	2
28	2		4.8	50.2	7.8	31.7	10.3	-
29	0	MWCNT-COO-Cu+[emim][OcOSO ₃]+NHPI	24.3	7.7	3	87.3	1.4	0.6
30	1		9.3	54.7	21.8	17.5	6	-
31	2		8.7	75.7	4.8	17	2.5	-

Reaction conditions: EB:16.33 mmol; SCILL-SILP systems (MWCNT-COO-Cu: 0.025 g, 1 mol% NHPI (0.027 g), and 0.025 g IL); AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6h.

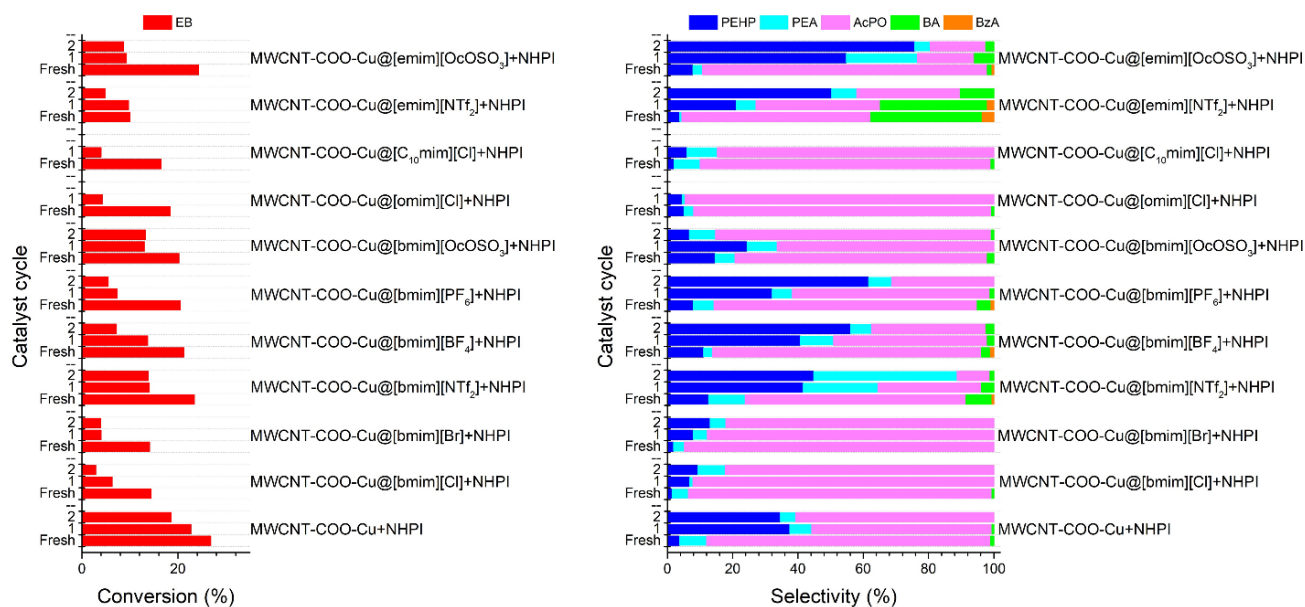


Figure 5.40. Recyclability of the SCILL-SILP system. Reaction conditions: EB: 16.33 mmol; MWCNTs: 0.025 g; NHPI: 0.027 g (1 mol%); IL: 0.025; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h.

Table 5.18. Leaching test for the SCILL-SILP system.

Entry	Catalyst	Con. (%)	Sel. (%)			
			PEHP	PEA	AcPO	BA
1 ^a	[bmim][OcOSO ₃]	4.5	41.3	11.6	47.1	-
2 ^b	[bmim][OcOSO ₃] + NHPI	8.7	64.8	4.2	31	-
3 ^c	MWCNT-COO-Cu [bmim][OcOSO ₃] + NHPI	25.5	18.8	1.5	77.3	2.4
4 ^d	SCILL-SILP system	20.2	14.5	6.2	77.3	2
5 ^e	SCILL-SILP Leaching test	12.54	8.4	5.5	81.6	4.5
6 ^f	Washed SCILL-SILP system	24.5	7.3	6.8	84.7	1.2

Reaction conditions: EB: 16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h; ^a 0.025 g IL; ^b 0.025 g IL and 0.027 g of NHPI added separately to EB; ^c mixture of 0.025 g MWCNTs, 0.025 g IL and 0.027 g NHPI added separately to EB; ^d [bmim][OcOSO₃]-based SCILL-SILP system (0.025 g IL, 0.027 g NHPI, and 0.025 g MWCNT-COOH-Cu; ^e SCILL-SILP system was separated from the reaction mixture during the reaction and the effluent (filtrate) was allowed

to proceed and complete the reaction time; ^f Fresh SCILL-SILP system was washed with hexane before oxidation testing.

The leaching test was also performed for the more stable SCILL-SILP system, which is the [bmim][OcOSO₃]-based system, to evaluate the leaching of the NHPI and IL layer, and the corresponding results are presented in Table 5.18. The catalytic system was separated from the reaction mixture after 30 minutes of the reaction run, and the filtrate was then allowed to proceed and complete the designated reaction time, as can be observed in Figure 5.41. The reaction rate decreased significantly after the SCILL-SILP catalyst was isolated, and the final conversion reached only about half of that obtained in its presence. This reveals that only a fraction of the NHPI and IL had leached from the surface of the MWCNT-COO-Cu.

The leaching of NHPI and IL from the hybrid system may be related to the increasing polarity of the reaction medium as the oxidation reaction progresses, since the formation of more polar products can enhance the solubility of both components. To support this statement, a fresh [bmim][OcOSO₃]-based SCILL-SILP catalyst was thoroughly washed with a nonpolar solvent (hexane) before being employed in the oxidation reaction (Table 5.18, entry 5). It is noteworthy that this pre-washing step did not affect the catalytic performance; in fact, the EB conversion (24.5%) and AcPO selectivity (84.7%) were slightly improved.

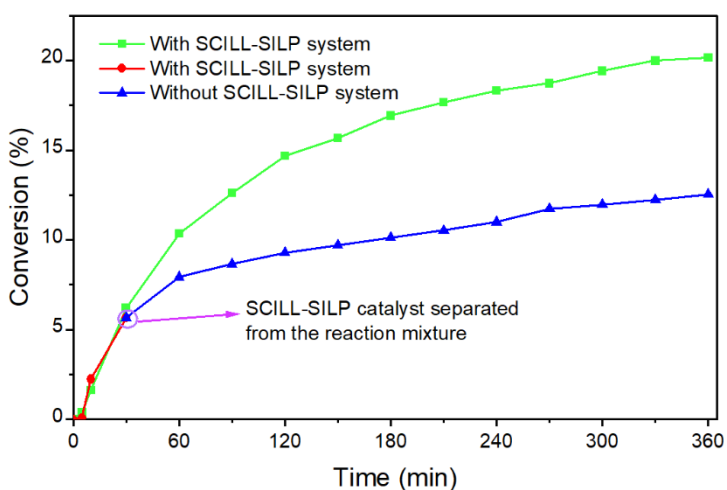


Figure 5.41. Comparison of EB conversion as a function of time for the SCILL-SILP catalytic system, with the system in which the SCILL-SILP was separated during the reaction, and the reaction mixture was allowed to proceed and complete the specified reaction

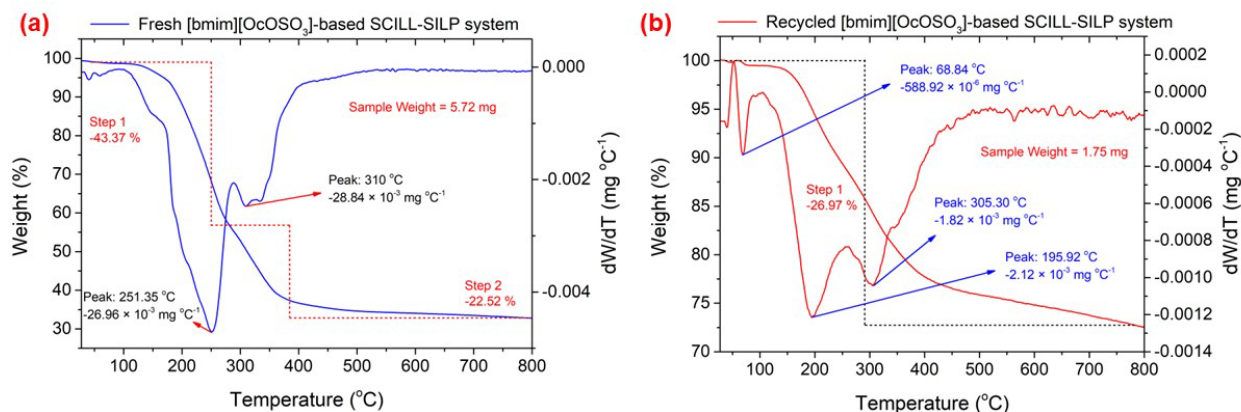


Figure 5.42. TGA and DTG curves, acquired for both the (a) fresh and (b) recycled SCILL-SILP catalytic systems after the second cycle.

TGA and DTG analyses were conducted on both the fresh and recycled SCILL-SILP systems (Figure 5.42) to further evaluate the leaching of NHPI and IL. As shown in Figure 5.42 (a), the fresh sample of the SCILL-SILP system undergoes two major weight-loss events. In the first step, a 43.37% mass loss was observed between 100 and 300 °C, with a maximum decomposition rate at 251.35 °C, which can be attributed to the thermal degradation of NHPI. In the second step, a 22.52% weight loss was recorded between 300 and 400 °C, with the maximum decomposition rate occurring at 310 °C, corresponding to the thermal degradation of [bmim][OcOSO₃]. In contrast, the recycled SCILL-SILP system (Figure 5.42 (b)) exhibited a reduced overall weight loss of 26.97%, indicating that a portion of the mixture of IL and NHPI was retained within the system after recycling. Three prominent DTG peaks were observed at 68.84 °C, 195.92 °C, and 305.30 °C, each corresponding to a distinct decomposition event. The initial peak at 68.84 °C, characterized by a modest mass-loss rate, is most plausibly associated with a minor weight-loss rate, is attributable to the desorption of residual volatiles or moisture. The subsequent peaks at 195.92 °C and 305.30 °C suggest the thermal degradation of the NHPI and IL retained within the recycled SCILL-SILP system. The ATR-FTIR spectrum of the recycled SCILL-SILP system (Figure 5.31 (d)) provides additional confirmation for the TGA and DTG results, as the characteristic absorption bands exhibit substantially reduced intensities.

5.3.6 Summary

SILP and SCILL-SILP systems were developed by depositing an NHPI dissolved in [Rmim]-based IL layer onto pristine MWCNTs and Cu(II)-functionalized MWCNTs, respectively, and

examined for solvent-free liquid-phase aerobic oxidation of EB under mild conditions. The [bmim]-SILP catalysts outperformed pristine MWCNTs; [bmim][Cl] was the most active (12.2% conversion, 84.1% AcPO selectivity), consistent with halide-assisted NHPI activation (PINO formation) and accelerated PEHP decomposition. Increasing cation lipophilicity improved initial activity but compromised recyclability, whereas [bmim][OcOSO₃] presented comparatively better stability despite clear evidence of gradual film loss (leaching tests, TGA/DTG, and ATR-FTIR).

SCILL-SILP systems were generally less active than the MWCNT-COO-Cu support because the viscous IL layer partially masks Cu sites and introduces mass-transfer limitations. Among [bmim] systems bearing [BF₄], [PF₆], [NTf₂], and [OcOSO₃] anions, activities were broadly similar, with [bmim][NTf₂] yielding the highest conversion (22.6%), while AcPO selectivity remained high for all the SCILL-SILP systems, consistent with the cage effect in the IL film together with Cu(II)-mediated pathways. In [Cl]-based SCILL-SILP systems, increasing cation lipophilicity increased conversion only up to [omim][Cl]; [C₁₀mim][Cl] returned to ~[bmim][Cl] levels, plausibly due to enhanced leaching and stronger [Cl] anions and Cu(II) sites interactions that reduce accessible Cu(II) sites and weaken NHPI activation.

Across both SILP and SCILL-SILP systems, [bmim][OcOSO₃]-based systems were comparatively more stable, which could be associated with the amphiphilic [OcOSO₃] anion (sulfate headgroup with an octyl chain), enhancing film retention and NHPI stabilization in the IL layer. In the SCILL-SILP system, the sulfate moiety in the IL may also interact with Cu(II) sites to enhance the film retention. Overall, the activity of all the SILP (except [bmim][OcOSO₃]) and SCILL-SILP systems declined gradually in the subsequent cycle, primarily through progressive leaching as oxidation products increased medium polarity, indicating partially non-heterogeneous operation. Thus, covalent grafting of NHPI and/or IL onto the CNT surface is a promising strategy to suppress leaching and enhance long-term stability.

The results presented in this section have been published in ACS Omega in the article entitled: “*N-Hydroxyphthalimide dissolved in ionic liquids supported on carbon nanotubes as a hybrid catalytic system for solvent-free aerobic oxidation of ethylbenzene*”. (ACS Omega 10 (2025) 47894–47913; <https://doi.org/10.1021/acsomega.5c01715>)

5.4 NHPI Grafting onto MWCNTs

5.4.1 Introduction

Because homogeneous NHPI remains difficult to recycle, we developed SILP and SCILL-SILP systems (Section 5.3-5.4) to heterogenize NHPI via an immobilized IL layer. Although these approaches improved handling and enabled reuse, gradual leaching of the NHPI-dissolved IL layer upon recycling remained a persistent limitation. To overcome this drawback and to improve recyclability, covalent grafting of NHPI onto a solid support has paved a new horizon in the design of recyclable NHPI-based catalysts [179]. In contrast to physical immobilization, covalent grafting of NHPI to a solid support provides a more robust attachment. This strategy not only effectively prevents the decomposition of NHPI but also addresses leaching and recyclability challenges. In addition, the choice of the support material, its functionalization, and the selection of the linker molecules can further enhance the robustness and activity of the resultant system. In the literature, various techniques have been employed to graft NHPI covalently onto solid supports, such as esterification [272,275,300–302], amidation [275,303], and other grafting techniques [303–305]. The resultant NHPI-based heterogeneous systems have exhibited enhanced activities while effectively addressing issues related to recyclability, reusability, and sustainability.

Herein, NHPI is grafted onto commercially available amine-functionalized MWCNTs (MWCNT-NH₂). Two MWCNT-NH₂ samples with amine functionalization degrees of ~0.45% and ~7% were initially employed to investigate NHPI grafting. Immobilization of NHPI was achieved via covalent attachment through amide bond formation using TAC, followed by in situ conversion of the anchored precursor into NHPI functionality. In addition, NHPI was grafted onto commercially available carboxylated industrial-grade MWCNTs (IGMWCNT-COOH) employing an EDC/NHS coupling strategy. Initially, the surface carboxyl groups were converted into amine-terminated CNTs via amide bond formation using 1,8-diaminooctane as a linker.

Meanwhile, 4-carboxy-NHPI was synthesized and temporarily protected with a trityl group to preserve the N-OH functionality. The protected NHPI was then covalently grafted via EDC/NHS-assisted amidation, followed by acid-mediated deprotection to regenerate the

catalytically active NHPI moiety. The produced NHPI-grafted IGMWCNTs were employed in the solvent-free liquid-phase aerobic oxidation of EB, and their catalytic activities were systemically evaluated. Additionally, catalyst recyclability and reusability were thoroughly investigated and compared.

5.4.2 NHPI grafting onto commercial MWCNT-NH₂

The grafting of NHPI onto commercially available amine-functionalized MWCNTs (amine functionalization degree of ~0.45% and ~7%) was adopted from a previously reported procedure [275], in which NHPI was grafted onto (aminomethyl) polystyrene via amide bond formation. MWCNT-NH₂ (~0.45 or ~7%) was dispersed in CH₂Cl₂ and reacted with TAC at 0 °C in the presence of Et₃N, followed by room-temperature stirring until completion. After filtration and washing, the TA-grafted MWCNTs were treated with NH₂OH·HCl in pyridine/1,2-dichloroethane at 75 °C to produce the NHPI moiety, followed by extensive washing and vacuum drying. The produced NHPI-grafted MWCNTs from ~0.45% and ~7% amine-functionalized MWCNT precursors were represented as MWCNT-NHPI-1 and MWCNT-NHPI-2, respectively.

FTIR analysis was performed for the TA-grafted MWCNTs and their precursor amine-functionalized MWCNTs, with the spectra presented in Figure 5.43. No distinct new peaks were observed after TA immobilization in either sample, making it difficult to confirm grafting by FTIR alone.

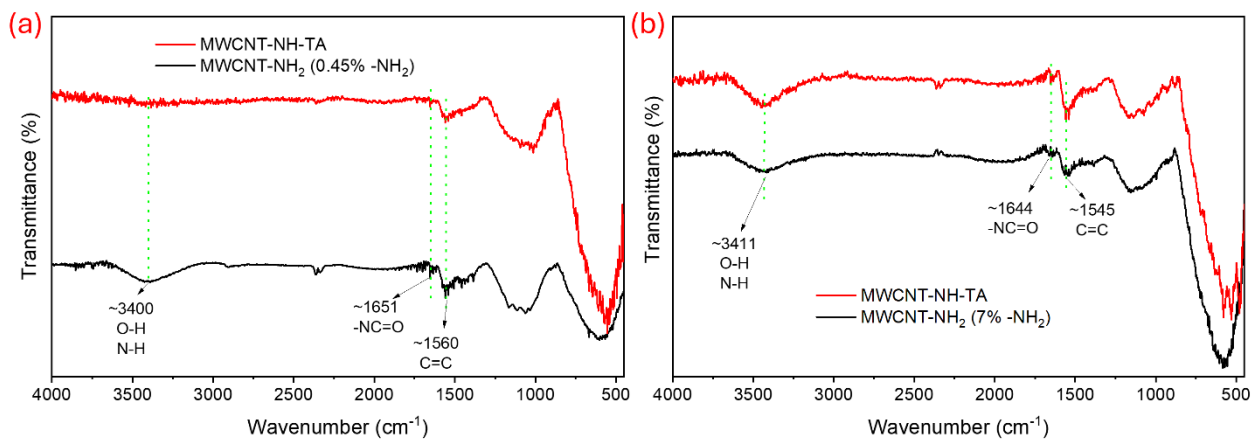


Figure 5.43. FTIR spectra of amine-functionalized MWCNTs and their corresponding TA grafting for (a) MWCNT-NH₂ (~0.45% -NH₂) and (b) MWCNT-NH₂ (~7% -NH₂).

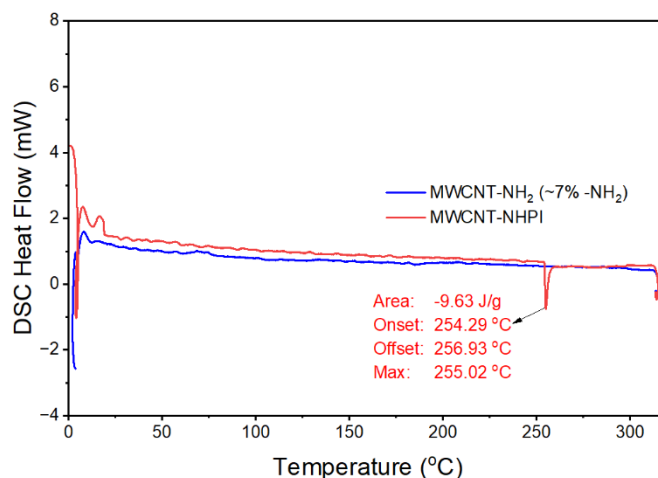


Figure 5.44. DSC profiles of MWCNT-NH₂ (~7%) and the corresponding NHPI-grafted MWCNTs (MWCNT-NHPI-2).

The DSC profiles of MWCNT-NH₂ (~7%) and the corresponding MWCNT-NHPI-2 exhibit distinct thermal responses (Figure 5.44), with the NHPI-grafted MWCNTs showing an additional thermal event centered at ~255 °C. This transition can be attributed to the thermal transformation of immobilized NHPI species and reflects overlapping processes involving constrained structural rearrangement and subsequent exothermic decomposition associated with N-O bond cleavage. Unlike the bulk NHPI (pristine), where melting is coupled with decomposition rather than occurring as a distinct phase transition [299], the grafted NHPI does not undergo a true melting transition due to surface confinement. The presence of this thermal peak relative to MWCNT-NH₂ supports the successful incorporation of NHPI, although DSC alone cannot distinguish between covalent grafting and physisorption. On the other hand, the DSC thermograms of MWCNT-NH₂ (~0.45%) and its corresponding MWCNT-NHPI-1 exhibited approximately the same features, which could be attributed to the limited density of amine functionalities, which restricts effective NHPI immobilization (Figure A5, Appendices).

5.4.3 Catalytic activity of MWCNT-NHPI

The catalytic activities of the NHPI grafted onto amine-functionalized MWCNTs (~0.45% and ~7% -NH₂, denoted as MWCNT-NHPI-1 and MWCNT-NHPI-2, respectively) were evaluated for the solvent-free aerobic oxidation of EB employing molecular oxygen as an oxidant. Both the MWCNT-NHPI catalysts were examined (i) with a minuscule amount of CuCl₂ as a

cocatalyst and (ii) under fully heterogeneous conditions employing the Cu(II) functionalized IGMWCNTs (IGMWCNT-COO-Cu), produced and described in the preceding section (5.1.3). The results were thoroughly compared with the precursor materials and are summarized in Table 5.19.

It can be observed that, under homogeneous conditions, the conversion of EB increases slightly upon the addition of NHPI in the absence of Cu(II) compound, with higher selectivity towards PEHP (entries 1 and 3). This observation is consistent with previous reports demonstrating NHPI's ability to selectively promote hydroperoxide formation in such oxidation processes [22,283,284]. The addition of a minuscule amount (0.08 mol%) of Cu(II) compound ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) enhanced the EB conversion with augmented selectivity towards AcPO (entries 1 and 2). This enhancement in catalytic performance is associated with the ability of the metallic compounds to accelerate the decomposition of intermediate hydroperoxides into the corresponding alcohols and ketones [22,131,273]. On the other hand, when 0.08 mol% of the Cu(II) compound was added with 1 mol% of NHPI (entry 4), the EB conversion soared to $31.4 \pm 1.5\%$ with augmented selectivity towards AcPO ($87.8 \pm 2.9\%$). This enhanced catalytic performance can be attributed to the synergistic effect between NHPI and the Cu(II) species within the reaction system. NHPI primarily promotes hydrogen-atom abstraction via the in situ formation of the PINO radical, thereby facilitating the formation of PEHP. In contrast, the Cu(II) compound selectively accelerates the decomposition of PEHP into AcPO, leading to improved overall EB conversion and AcPO selectivity.

The pristine MWCNTs showed a slight increase in EB conversion upon addition of NHPI, compared to MWCNTs without NHPI. However, the presence of NHPI in combination with MWCNTs dramatically increased the PEHP selectivity (entries 5 and 6). In contrast, amine-functionalized MWCNTs (entries 7-8) displayed higher activity than pristine MWCNTs, with overall activities comparable to those of MWCNTs used in the presence of NHPI. In these amine-functionalized MWCNTs, AcPO and PEHP were the predominant products. Moreover, employing amine-rich MWCNTs ($\sim 7\%$ $-\text{NH}_2$) enhanced EB conversion and shifted selectivity towards AcPO.

The NHPI grafting onto both amine-functionalized MWCNTs increased EB conversion and shifted the product distribution towards PEHP at a 0.025 g loading (entries 9-10). It is worth

noting that both the NHPI-grafted MWCNTs displayed higher EB conversion compared to the system using MWCNTs with homogeneous NHPI. The NHPI-grafted MWCNTs have also exhibited pronounced activities compared with the precursor amine-functionalized MWCNTs, with enhanced PEHP selectivities, suggesting the successful grafting. On the other hand, when both the NHPI-grafted MWCNTs loadings were increased to 0.050 g (entries 11-12), the EB conversion slightly decreased for the system that was produced employing ~0.45% amine-functionalized MWCNTs (MWCNT-NHPI-1), while it increased for MWCNT-NHPI-2 (produced using ~7% amine-functionalized MWCNTs). At this loading, the reaction mixture becomes slurry-like, which can hinder mixing and oxygen transfer and lower the fraction of accessible grafted NHPI sites. These diffusion and accessibility drawbacks may have affected MWCNT-NHPI-1 more strongly due to its lower NHPI density. In contrast, the higher NHPI grafting degree in MWCNT-NHPI-2 results in a higher density of active NHPI sites, enabling it to retain activity even under slurry conditions. In both cases, AcPO selectivity increased and became comparable to PEHP selectivity, consistent with faster conversion of intermediate PEHP at higher solid catalyst loading.

To make a more thorough comparison, a trace amount of CuCl_2 was added to both the NHPI-grafted MWCNTs (entries 13-14). Compared with the corresponding metal-free reactions at the same catalyst loading (entries 9-10), EB conversion increased slightly, while AcPO selectivity increased dramatically. To run the reactions under completely heterogeneous conditions, Cu(II) functionalized IGMWCNTs were employed with NHPI-grafted MWCNTs at various total loadings. The incorporation of the MWCNT-NHPI-1 with IGMWCNT-COO-Cu (entries 17-19) afforded consistently high EB conversions with elevated selectivity towards AcPO. Replacing the MWCNT-NHPI-1 with the NHPI-rich MWCNT-NHPI-2 at optimal loading (1:1 w/w, 0.025 g), the EB conversion further increased to $7.9 \pm 0.6\%$ with enhanced selectivity towards AcPO ($88.6 \pm 3.7\%$). The combined systems, both MWCNT-NHPIs with IGMWCNT-COO-Cu, exhibited enhanced activity with improved selectivity towards AcPO compared to the system with only IGMWCNT-COO-Cu at a loading of 0.0125 g (entry 16).

The O_2 consumption profiles during the oxidation of EB over NHPI-grafted amine-functionalized MWCNTs are presented in Figure 5.45 and compared with pristine NHPI, their amine-functionalized MWCNT precursors, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.08 mmol), IGMWCNT-COO-Cu, and their combination with IGMWCNT-COO-Cu, under similar reaction conditions. The O_2

consumption rate in the presence of MWCNT-NHPI was lower than that with pristine NHPI, which could be attributed to the greater amount of employed NHPI (1 mol%, 0.027 g) under homogeneous conditions. However, the O₂ consumption rate for the MWCNT-NHPI-1 (Figure 5.45 (a)) was slightly higher when employed with Cu(II) functionalized IGMWCNTs (1:1 w/w, 0.025 g). In contrast, the MWCNT-NHPI-2 (Figure 5.45 (b)) exhibited an enhanced O₂ consumption rate compared to the homogeneous NHPI when used alone and in combination with IGMWCNT-COO-Cu.

To estimate the upper limit of activity expected with fully functionalized ~7% amine-functionalized MWCNTs, a reference experiment was performed using 0.0179 g NHPI, corresponding to the theoretical maximum NHPI loading on 0.025 g of MWCNT-NH₂ (~7% -NH₂) under the assumptions of 100% grafting and 1:1 utilization of -NH₂ sites. Under these conditions, EB conversion reached to 12.5%, with PEHP as the major product (55.8% selectivity). On the other hand, an analogous run was performed using MWCNT-NHPI-2 at a mass calculated to provide the same NHPI-equivalent amount (0.0179 g), which corresponds to ~0.065 g of the grafted MWCNTs. In this case, EB conversion slightly decreased to 10.3%. The slightly reduced conversion is attributed to the pronounced increase in MWCNT-NHPI-2 content, which rendered the reaction medium highly slurry-like and could have introduced mixing and oxygen-transport limitations, as well as reduced accessibility to surface-bound active NHPI sites. At this high loading, the reaction mixture became slurry-type, which may have entered a transport-limited regime (mixing and O₂ transfer), thereby reducing the effective accessibility of surface-grafted NHPI sites. Consequently, the measured EB conversion no longer scaled with the nominal NHPI-equivalent loading. To probe this hypothesis, the amine-rich MWCNTs (MWCNT-NH₂, ~7% -NH₂) were evaluated at the same loading (entry 23), and the obtained EB conversion was comparable to that obtained with the corresponding NHPI-grafted MWCNTs.

Table 5.19. Catalytic activities of NHPI-grafted amine-functionalized MWCNTs.

Entry	Catalyst	Weight (g)	Con. (%)	Sel. (%)			
				PEHP	PEA	AcPO	BA
1	-	-	4.4 ± 0.4	83.5 ± 1.3	3.3 ± 1.8	13.2 ± 3.2	-
2 ^a	-	-	7.7 ± 0.3	6 ± 0.4	24.5 ± 0.8	68.6 ± 1.2	0.8 ± 0.1
3	NHPI	0.027	5.6 ± 1.3	75.6 ± 3.4	14.9 ± 8.8	9.5 ± 5.4	-
4 ^a	NHPI	0.027	31.4 ± 1.5	3.4 ± 1.2	8.4 ± 4	87.8 ± 2.9	0.5 ± 0.1
5	MWCNTs	0.025	4.1 ± 1.6	46.9 ± 4.4	42.2 ± 12.9	10.9 ± 8.5	-
6 ^b	MWCNTs	0.025	5.7 ± 0.8	90.6 ± 0.8	5.9 ± 1.3	3.6 ± 0.5	-
7	MWCNT-NH ₂ (~0.45 % -NH ₂)	0.025	4.7 ± 1.1	50.5 ± 9.2	12.3 ± 7.3	37.2 ± 13.3	-
8	MWCNT-NH ₂ (~7 % -NH ₂)	0.025	5.5 ± 0.4	47.1 ± 6.1	4.2 ± 2.0	48.7 ± 4.7	-
9	MWCNT-NHPI-1	0.025	5.3 ± 1.6	55 ± 13.1	22 ± 4	23 ± 9.1	-
10	MWCNT-NHPI-2	0.025	6.4 ± 0.6	57.8 ± 4.9	10.1 ± 4.7	32 ± 9.6	-
11	MWCNT-NHPI-1	0.050	4.2 ± 0.6	43.2 ± 0.8	4.3 ± 1.4	52.6 ± 0.6	-
12	MWCNT-NHPI-2	0.050	7 ± 0.3	48.5 ± 2.2	2.4 ± 1.8	49.2 ± 4	-
13 ^a	MWCNT-NHPI-1	0.025	6.1 ± 0.9	3.1 ± 1.8	9.2 ± 9.3	87.7 ± 10.2	-
14 ^a	MWCNT-NHPI-2	0.025	6.7 ± 0.8	2.3 ± 0.7	6.8 ± 10.1	90.8 ± 10.8	0.1 ± 0.2
15 ^b	IGMWCNT-COO-Cu	0.025	26.7 ± 0.1	6.6 ± 4.2	6.7 ± 2.4	85.8 ± 1.7	0.9 ± 0.04
16	IGMWCNT-COO-Cu	0.0125	7 ± 0.7	10.1 ± 8.3	17.3 ± 1	71.6 ± 9.7	1.1 ± 0.3
17	MWCNT-NHPI-1/IGMWCNT-COO-Cu (1:1 w/w)	0.050	7.3 ± 1	5.6 ± 3.1	11.5 ± 2.4	83 ± 1.2	-
18	MWCNT-NHPI-1/IGMWCNT-COO-Cu (1:1 w/w)	0.025	7.5 ± 0.1	10.4 ± 4.2	1.1 ± 0.5	88.6 ± 3.7	-
19	MWCNT-NHPI-1/IGMWCNT-COO-Cu (2:1 w/w)	0.0375	7.1	3	13	84	-
20	MWCNT-NHPI-2/IGMWCNT-COO-Cu (1:1 w/w)	0.025	7.9 ± 0.6	6.4 ± 1.8	4.7 ± 5.2	88.1 ± 5.2	0.7 ± 0.7
21 ^c	MWCNT-NH ₂ (7 % -NH ₂)	0.025	12.5	55.8	17.4	24.3	1.5
22 ^d	MWCNT-NHPI-2	0.065	10.3	28.3	4.8	66.9	-
23	MWCNT-NH ₂ (7% -NH ₂)	0.065	10.8	16.9	38.6	43.1	1.4

Reaction conditions: EB:16.32 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h; ^a 0.08 mmol of CuCl₂ was used; ^b 1 mol% (0.027g) of NHPI was used; ^c amount of NHPI (~0.0179) was used equivalent to the theoretical maximum loading on 0.025 g of 7% amine-functionalized

MWCNTs; ^d amount of MWCNT-NHPI-2 was used according to 0.027 g of NHPI, assuming a 100% grafting degree (0.9 % selectivity towards BzA was observed in this case).

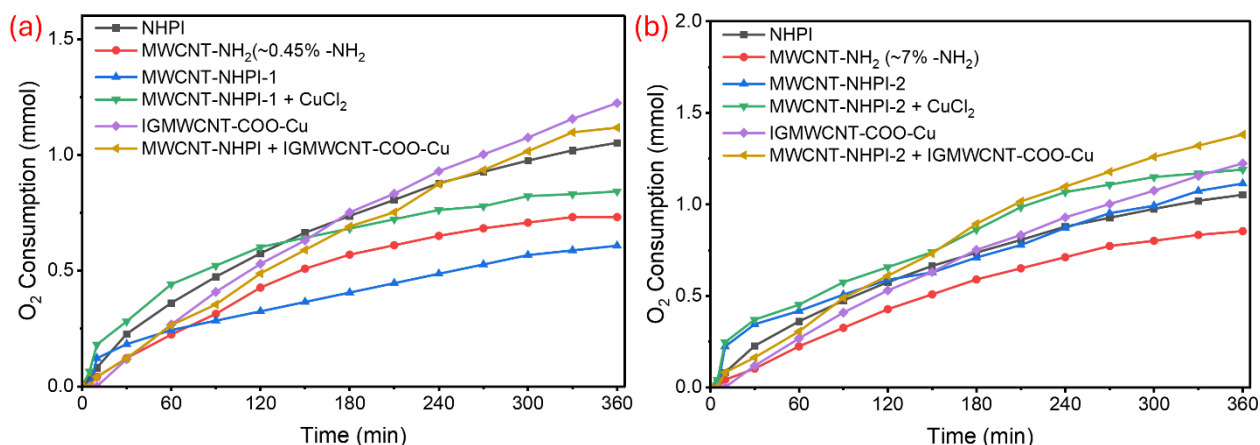


Figure 5.45. Oxygen consumption vs. time for EB oxidation reaction over (a) MWCNT-NHPI-1 and (b) MWCNT-NHPI-2, and compared with pristine NHPI (1 mol%, 0.027 g), their amine-functionalized MWCNT precursors (0.025 g), with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.08 mmol), IGMWCNT-COO-Cu (0.0125 g), and their combination with IGMWCNT-COO-Cu (1:1 w/w ratio, 0.025 g); EB:16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6h.

5.4.4 Recyclability of NHPI-grafted MWCNTs

The recyclability of both the NHP-grafted MWCNTs was evaluated in the solvent-free aerobic oxidation of EB using molecular oxygen as an oxidant. Recycling tests were performed either with a minuscule amount of CuCl_2 as a cocatalyst or under fully heterogeneous conditions using IGMWCNT-COO-Cu, applied at a beneficial catalyst loading (0.025 g total catalyst; 1:1 w/w mixture). The results are presented in Table 5.20 and Figure 5.46. After each reaction run, the catalyst was separated from the reaction mixture by filtration, washed with methanol and acetone, dried, and applied in the subsequent cycle to oxidize a fresh batch of EB under solvent-free conditions. The amount of EB in the subsequent reaction cycle was determined from the recovered catalyst mass.

It can be observed in Figure 5.46 (a) and (c) that, when CuCl_2 was employed together with the NHPI-grafted MWCNTs (MWCNT-NHPI-1 and MWCNT-NHPI-2, respectively), EB conversion remained approximately constant over the successive cycles, while selectivity was consistently inclined towards AcPO (entries 1-4, 8-11). Similarly, as shown in Figure 5.46 (b)

and (d), the hybrid systems formed by combining each NHPI-grafted MWCNT with IGMWCNT-COO-Cu maintained high EB conversion and enhanced AcPO selectivity across cycles. However, a gradual increase in the selectivities of PEHP and PEA was also observed. This trend may arise from cycle-to-cycle variations in the recovered catalyst mass and the corresponding adjustment of fresh EB, which changes the total reaction charge and can affect mixing, heat transfer, oxygen availability, and the effective accessibility of active sites on the recovered catalyst. Despite these secondary shifts in product distribution, the MWCNT-NHPI/MWCNT-COO-Cu systems exhibited excellent recyclability, demonstrating robustness under fully heterogeneous, solvent-free conditions.

Table 5.20. Recyclability of MWCNT-NHPI-1 and MWCNT-NHPI-2.

Entry	Cycle	Catalyst	Con. (%)	Sel. (%)				
				PEHP	PEA	AcPO	BA	BzA
1 ^a	0	MWCNT-NHPI-1	5.2	5.8	19.4	74.8	-	-
2 ^a	1		5.6	3.4	4.7	91.9	-	-
3 ^a	2		6.2	2.1	19.1	78.8	-	-
4 ^a	3		5.8	1	2.3	96.7	-	-
5 ^b	0	MWCNT-NHPI-1	7.5	13.3	0.7	86	-	-
6 ^b	1		8.2	11.1	19.1	68.5	1.3	-
7 ^b	2		7.7	19.4	37.7	41.7	1.2	-
8 ^a	0	MWCNT-NHPI-2	7.3	3.5	24.5	72	-	-
9 ^a	1		6.1	2	5.9	91.6	0.5	-
10 ^a	2		6.9	1.8	0.9	97.3	-	-
11 ^a	3		7.6	1.7	2	96.3	-	-
12 ^b	0	MWCNT-NHPI-2	8.5	4.5	3.4	90.7	1.4	-
13 ^b	1		7.7	6.9	10.4	82.1	0.6	-
14 ^b	2		10.5	17.6	25.2	55.9	1.3	-

Reaction conditions: EB: 16.33 mmol; Fresh catalyst: 0.025 g; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. ^a in the presence of CuCl₂ (0.08 mmol); ^b MWCNT-NHPI/IGMWCNT-COO-Cu (1:1 w/w for fresh catalyst). For cycle *i*, the EB and AIBN amounts were adjusted based on the recovered catalyst mass.

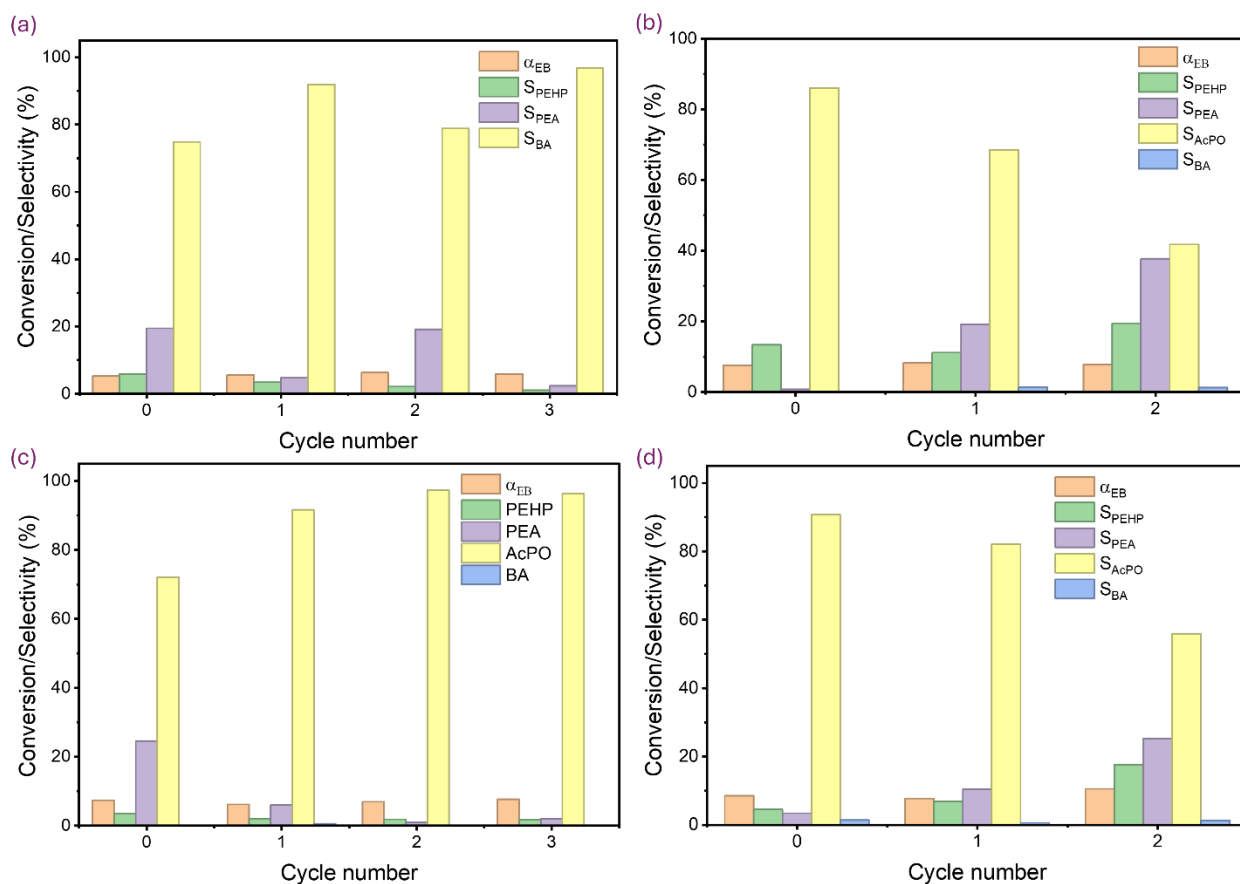


Figure 5.46. Recyclability of (a) MWCNT-NHPI-1 in the presence of CuCl_2 (0.08 mmol), (b) MWCNT-NHPI-1/MWCNT-COO-Cu (1:1 w/w; fresh catalyst = 0.025 g), (c) MWCNT-NHPI-2 in the presence of CuCl_2 (0.08 mmol), and (d) MWCNT-NHPI-2/IGMWCNT-COO-Cu (1:1 w/w; fresh catalyst = 0.025 g). Reaction conditions: EB: 16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. For cycle i , the EB and AIBN amounts were adjusted based on the recovered catalyst mass.

5.4.5 NHPI grafting onto IGMWCNT-COOH

The grafting of NHPI onto IGMWCNT-COOH was achieved via a sequential EDC/NHS-mediated coupling procedure, as described in Section 4.7. Briefly, surface carboxyl (-COOH) groups on the IGMWCNTs were activated and converted into amine-terminated CNTs through amide bond formation using 1,8-diaminooctane as a linker. In parallel, 4-carboxy-NHPI was synthesized, and its N-OH functionality was temporarily protected to suppress undesired side reactions and preserve the structural integrity of the NHPI moiety. The protected 4-carboxy-NHPI was subsequently covalently immobilized onto the amine-functionalized CNTs via

EDC/NHS-assisted amidation, after which acid-mediated trityl deprotection regenerated the catalytically active NHPI functionality.

FTIR spectra illustrating the complete NHPI grafting process onto IGMWCNTs, from the starting material to the final NHPI-grafted IGMWCNTs, are presented in Figure 5.47. The FTIR spectrum of IGMWCNT-COOH exhibits a distinct absorption band at approximately 1730 cm^{-1} , which could be assigned to the C=O stretching vibration of -COOH groups. A broad absorption band observed in the $\sim 3427\text{ cm}^{-1}$ region is primarily associated with O-H stretching vibrations and may also indicate the presence of adsorbed moisture. The band near 1572 cm^{-1} can be assigned to skeletal stretching vibrations of the sp^2 -hybridized C=C framework in the CNTs. Nevertheless, this wavenumber region also coincides with the stretching vibration of carboxylate (-COO-) species [281,289,306]. The presence of a single, sharp, and intense absorption indicates that these vibrational modes have overlapped.

On the other hand, the absorption band around 1064 cm^{-1} could be assigned to the C-O stretching modes [306]. After grafting a long amine spacer through EDC/NHS-assisted coupling with 1,8-diaminooctane, a distinct band appearing at $\sim 1630\text{ cm}^{-1}$ confirms amide bond formation, which could be assigned to the amide carbonyl stretching mode [307,308]. The elemental analysis (Table 5.21) further corroborated the successful amine grafting, as evidenced by an increase in nitrogen weight percent from $<0.1\text{ wt.}\%$ to $1.64\text{ wt.}\%$. The carbon weight percent also increased, likely due to the incorporation of the long aliphatic carbon chain of the grafted octylamine moiety.

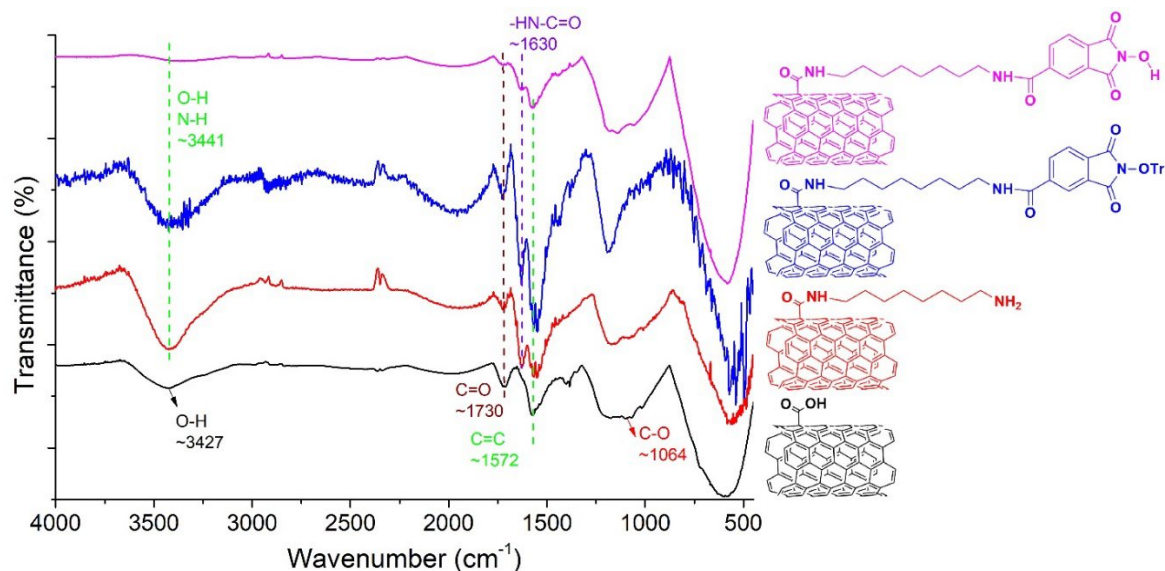


Figure 5.47. FTIR spectra of IGMWCNT-COOH, amine-functionalized IGMWCNTs, protected NHPI-grafted IGMWCNTs, and the NHPI-grafted IGMWCNTs.

Table 5.21. Elemental analysis of carboxylated and amine-functionalized IGMWCNTs.

Sample	N (wt.%)	STD DEV	C (wt.%)	STD DEV	H (wt.%)	STD DEV	S (wt.%)	STD DEV
IGMWNT-COOH	< 0.1	-	93.92	± 0.1	< 0.1	-	< 0.5	-
IGMWNT-CO-NH-C ₈ H ₁₆ - NH ₂	1.64	± 0.1	>>	-	1.71	± 1.35	< 0.5	-

Pristine NHPI exhibits characteristic absorption bands approximately at ~ 3100 , ~ 1784 , and 1704 cm^{-1} , which are assigned to the N-OH stretching vibration and the symmetric and asymmetric C=O stretching modes of the imide carbonyl groups, respectively [285]. After grafting of the protected NHPI onto the amine-functionalized CNTs, the corresponding FTIR spectrum remains dominated by a broad absorption band in the $\sim 3441\text{ cm}^{-1}$ region, which can be attributed to adsorbed moisture with overlapping contributions from O-H and N-H stretching vibrations. Following the deprotection of the trityl group, no significant changes in the positions of the characteristic NHPI-related bands were observed, as all the associated peaks lie in the existing pattern.

FTIR analysis confirms the successful grafting of the long-chain amine spacer onto the surface of carboxylated MWCNTs via EDC/NHS-assisted coupling with 1,8-diaminooctane. However, FTIR alone does not provide unequivocal evidence of NHPI incorporation. In contrast, NMR spectroscopy, performed at different stages of the synthesis, directly verified the successful grafting of NHPI. The NMR results confirmed the synthesis of 4-COOH-NHPI (Figure A2, Appendices) and the effective introduction of the trityl protecting group to shield the catalytically active -N-OH functionality (Figure A3, Appendices). Furthermore, NMR analysis of the residue obtained after drying the filtrate collected during the deprotection step revealed the recovery of the trityl group, most probably as trityl trifluoroacetate (Figure A4, Appendices), providing robust evidence for the integrity of the protection-deprotection strategy and, consequently, for the successful grafting process. Before deprotection, the protected NHPI-grafted IGMWCNTs were thoroughly washed with water, acetone, and ethyl acetate to remove residual reagents, thereby ensuring the unambiguous identification and recovery of the trityl group during deprotection.

Thermogravimetric analysis demonstrated the high thermal stability of the carboxylated IGMWCNTs (under N₂ atmosphere), which exhibited only a limited mass loss at low temperatures (Figure 5.48 (a)). A minor weight loss of approximately 0.55 wt.% below ~150 °C is attributed to the removal of physisorbed moisture and weakly bound surface species, followed by an additional ~0.73 wt.% loss up to ~325 °C, associated with the gradual decomposition of oxygen-containing surface functionalities introduced during acid treatment. Beyond this temperature range, the mass remained largely constant, with a high residual weight of ~95.6 wt.% at 900 °C, confirming the preservation of the graphitic CNT framework.

In contrast, the amine-functionalized IGMWCNTs exhibited an intensely different thermal behavior when analyzed in air (Figure 5.48 (b)). Two minor weight-loss steps of ~1.05 wt.% around 200 °C and ~5.38 wt.% up to ~416 °C are attributed to the thermal degradation of grafted aliphatic amine spacers and amide linkages formed during the EDC/NHS-mediated coupling process. At higher temperatures, a pronounced and rapid weight loss occurs between ~600 and 700 °C, corresponding to the oxidative combustion of the CNT framework. Consequently, the TGA curve shows a total weight loss of ~93.44 wt.% at 900 °C, leaving a small inorganic residue of ~6.56 wt.%. This interpretation is further corroborated by the DTG profiles, which show

broad, weak features for IGMWCNT-COOH, whereas sharp, intense decomposition peaks are observed for the amine-functionalized IGMWCNTs under an air atmosphere.

It should be noted that the TGA/DTG measurement for IGMWCNT-COOH and amine-functionalized IGMWCNTs was conducted under different atmospheres (N₂ and air, respectively). Therefore, a direct quantitative comparison of residual masses is not appropriate; however, a qualitative comparison of the degradation profiles provides valuable insight into the presence of surface functionalities and their thermal decomposition behavior under inert and oxidative conditions.

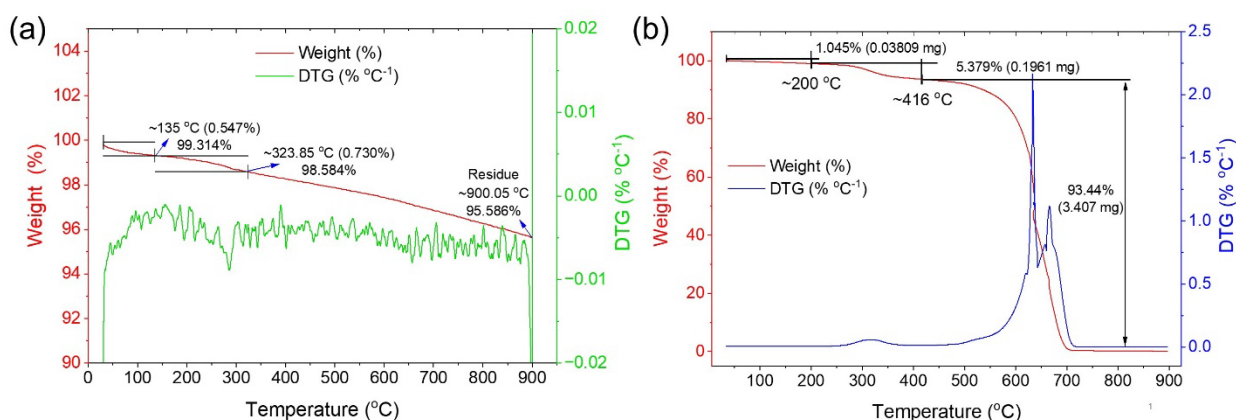


Figure 5.48. TGA and DTG curves obtained for (a) IGMWCNT-COOH (measured under N₂) and (b) amine-functionalized IGMWCNTs (measured under air).

5.4.6 Catalytic activity of the IGMWCNT-NHPI

NHPI was covalently grafted onto IGMWCNTs to transform the homogeneous organocatalyst into a heterogeneous system, thereby facilitating efficient catalyst recovery and reuse, while preserving its intrinsic catalytic performance under heterogeneous conditions. The catalytic activity of the NHPI-grafted IGMWCNTs under solvent-free liquid-phase aerobic oxidation of EB is presented in Table 5.22 and compared with that of the precursor materials under identical reaction conditions. For a broader context, these results can be compared with the EB oxidation data reported in Table 5.19 (blank, using CuCl₂, NHPI, MWCNTs, MWCNTs+NHPI, and Cu(II) functionalized IGMWCNTs with and without NHPI), which were acquired under similar reaction conditions.

Table 5.22. Catalytic activity of IGMWCNT-NHPI.

Entry	Catalyst	Weight (g)	Con. (%)	Sel. (%)			
				PEHP	PEA	AcPO	BA
1	IGMWCNT-COOH	0.025	3.9	56.5	39.6	4	-
2 ^a	IGMWCNT-COOH	0.025	4.7	72.7	27.3	-	-
3 ^b	IGMWCNT-COOH	0.025	4.3 ± 0.3	9.4 ± 0.9	16.6 ± 1.6	74 ± 0.7	-
4	IGMWCNT-NHPI	0.025	2.45 ± 0.2	66 ± 9.9	9 ± 9.3	25 ± 19.23	-
5 ^c	IGMWCNT-NHPI	0.025	3.3	50.1	4.9	45	-
6 ^a	IGMWCNT-NHPI	0.025	6.9 ± 0.2	1.9 ± 0.6	0.7 ± 0.2	97.4 ± 0.8	-
7 ^a	IGMWCNT-NHPI	0.05	5.5 ± 0.2	3.5 ± 1.4	17 ± 5.1	79.6 ± 3.7	-
8	IGMWCNT-NHPI/IGMWCNT-COO-Cu (1:1 w/w)	0.025	6.9 ± 0.4	22.8 ± 12.1	13.9 ± 5.2	62.1 ± 12.5	1.2 ± 0.4
9	IGMWCNT-NHPI/IGMWCNT-COO-Cu (1:1 w/w)	0.05	3.4	5.2	19.8	73.7	1.3

Reaction conditions: EB: 16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h; ^a 1 mol% NHPI; ^b 0.08 mol% of CuCl₂·2H₂O; and ^c Recycle of entry 4.

The industrial-grade carboxylated MWCNTs demonstrated a slight increase in activity, in terms of EB conversion, after the addition of NHPI compared to IGMWCNT-COOH in the absence of NHPI. However, the presence of NHPI, in combination with IGMWCNT-COOH, shifted selectivity towards PEHP (entries 1-2). The activity of IGMWCNT-COOH (both in the absence and presence of NHPI) was lower compared to the pristine MWCNTs system (Table 5.19, entries 5-6) under similar conditions, which could be associated with the oxygen-containing functional groups that hurt the activity of CNTs in the oxidation of hydrocarbons [40]. The EB conversion obtained in the presence of carboxylated IGMWCNTs, along with 0.08 mol% Cu(II) species, remained comparable to that achieved with carboxylated IGMWCNTs in combination with NHPI. However, the addition of Cu(II) species shifted the selectivity towards AcPO.

As expected, the NHPI-grafted IGMWCNTs were more selective towards PEHP in the absence of Cu(II) species (entry 4). However, in the presence of 0.8 mol% of Cu(II) compound (entry 6), the NHPI-grafted IGMWCNTs exhibited enhanced EB conversion (6.9 ± 0.2%) with an augmented selectivity towards AcPO, reaching as high as 97.4 ± 0.8%, compared with the precursor carboxylated IGMWCNTs under similar reaction conditions (entry 3), indicating a

clear positive influence of NHPI grafting. The enhancement in the selectivity towards AcPO can again be attributed to the synergistic effect between the grafted NHPI, which promotes the PEHP formation, and the Cu(II) species, which efficiently accelerates the decomposition of the produced PEHP to AcPO. The literature further indicates that the nature of the transition-metal salts plays a decisive role in determining the product distribution. Owing to their distinct redox potentials, Cu(II) salts generally favor a higher ketone-to-alcohol ratio than Co(II) and Mn(II) salts [280].

The lower EB conversion observed for the NHPI-grafted IGMWCNT/Cu(II) system (entry 6), compared with the homogeneous NHPI/Cu(II) system (Table 5.19, entry 4), can be ascribed to surface confinement of the active NHPI moieties, which may limit their accessibility to reagents because of mass-transfer limitations. As a consequence, the radical chain-propagation length is shortened, resulting in reduced overall catalytic activity. Furthermore, the grafting degree of NHPI onto the amine-functionalized carboxylated IGMWCNTs is lower than the effective NHPI concentration employed under homogeneous conditions, resulting in a reduced number of active hydrogen-atom transfer sites and, consequently, lower catalytic activity. On the other hand, when the amount of NHPI-grafted IGMWCNTs was increased to 50 mg (entry 7), a slight decrease in catalytic activity was observed. This reduction suggests that a threshold CNT loading was exceeded, leading to an overpopulation of CNTs in the reaction medium, which in turn hindered effective access of the oxidant to the active sites.

The combination of Cu(II)-functionalized IGMWCNTs with the NHPI-grafted IGMWCNTs (1:1 w/w, 0.025 g; entry 8) enabled fully heterogeneous operation and delivered an EB conversion comparable to that obtained with homogeneous CuCl₂ (entry 6), along with elevated AcPO selectivity. A similar trend is also observed in the O₂ consumption profile during oxidation over IGMWCNT-NHPI (Figure 5.49), where the O₂ consumption rate increases upon incorporation of IGMWCNT-COO-Cu. In contrast, when the total catalyst mass was increased to 0.050 g at the same IGMWCNT-NHPI/IGMWCNT-COO-Cu ratio, EB conversion decreased (entry 9). This reduction in the activity could be associated with the higher catalyst content in the reaction system, which could have exceeded the threshold catalyst loading and imposed mixing/oxygen-transport constraints.

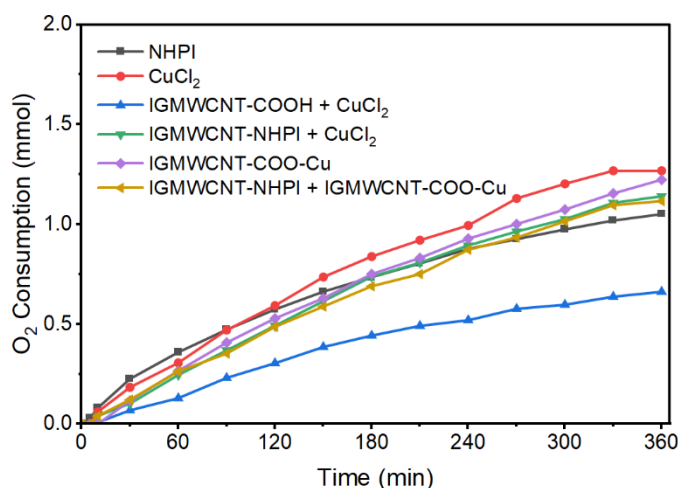


Figure 5.49. Oxygen consumption vs. time for EB oxidation reaction over IGMWCNT-NHPI and compared with pristine NHPI (1 mol%, 0.027 g), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.08 mmol), the precursor IGMWCNT-COOH (0.0125 g) in the presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.08 mmol), in combination with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.08 mmol), IGMWCNT-COO-Cu (0.0125 g) and in combination with IGMWCNT-COO-Cu (1:1 w/w ratio, 0.025 g); EB:16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6h.

5.4.7 Recyclability of IGMWCNT-NHPI

The recyclability and reusability of the IGMWCNT-NHPI were examined for both cases, using homogeneous CuCl_2 and IGMWCNT-COO-Cu, and the results are presented in Table 5.23 and Figure 5.50. After each run, the catalyst was recovered by filtration. The isolated catalyst was thoroughly washed with methanol and acetone, dried, and applied in the subsequent cycle to oxidize a fresh batch of EB under solvent-free conditions. In each run, a very small amount of CuCl_2 (0.08 mol%) was used as a cocatalyst for the case presented in entries 1-5 and in Figure 5.50 (a). The catalyst maintained its activity throughout the cycles, with AcPO as the dominant product. Similarly, when the homogeneous CuCl_2 was replaced with IGMWCNT-COO-Cu at the optimal loading, the resultant hybrid system (IGMWCNT-NHPI and IGMWCNT-COO-Cu) displayed remarkable stability while retaining the activity across the cycles (entries 6-8 and in Figure 5.50 (b)). These results collectively demonstrate the robustness of NHPI-grafted IGMWCNTs in the oxidation reaction under the applied conditions.

Table 5.23. Recyclability of IGMWCNT-NHPI.

Entry	Cycle	Catalyst	Con. (%)	Sel. (%)				
				PEHP	PEA	AcPO	BA	BzA
1 ^a	0	IGMWCNT-NHPI	7.0	2.3	0.9	96.8	-	-
2 ^a	1		6.2	5.2	18.9	74.3	1.6	-
3 ^a	2		6.4	2.9	15.0	81.0	1.1	-
4 ^a	3		9.2	2.3	14.4	82.1	1.2	-
5 ^a	4		8.1	6.5	31.9	55.6	6.0	-
6 ^b	4	IGMWCNT-NHPI	6.8	13.3	9.6	75.6	1.5	-
7 ^b	1		7	35	9.3	54.4	1.3	-
8 ^b	2		7.48	31.3	19.2	48.9	0.6	-

Reaction conditions: EB: 16.33 mmol; Fresh catalyst: 0.025 g; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. ^a in the presence of CuCl₂ (0.08 mmol); ^b IGMWCNT-NHPI/IGMWCNT-COO-Cu (1:1 w/w for fresh catalyst). For cycle *i*, the EB and AIBN amounts were adjusted based on the recovered catalyst mass.

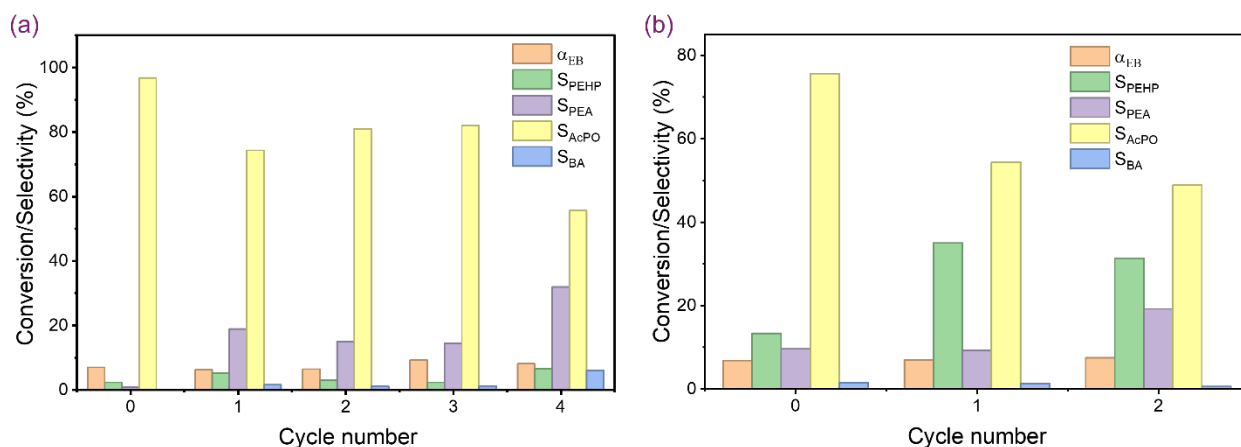


Figure 5.50. Recyclability of (a) IGMWCNT-NHPI in the presence of CuCl₂ (0.08 mmol), (b) MWCNT-NHPI/MWCNT-COO-Cu (1:1 w/w; fresh catalyst = 0.025 g). Reaction conditions: EB: 16.33 mmol; AIBN: 0.186 mol%; 80 °C; 0.1 MPa; 6 h. For cycle *i*, the EB and AIBN amounts were adjusted based on the recovered catalyst mass.

5.4.8 Summary

The covalent grafting of NHPI onto MWCNTs was performed to enhance its stability and recyclability. NHPI was grafted onto commercially available amine-functionalized MWCNTs (two precursors: ~0.45 wt.% and ~7 wt.% -NH₂) via TAC-mediated amide formation, followed by the conversion of grafted TA to NHPI functionality employing NH₂OH·HCl. On the other hand, NHPI was also grafted onto IGMWCNT-COOH via an EDC/NHS coupling strategy. The carboxyl groups on the CNTs were first converted to amine-terminated surfaces using a 1,8-diaminooctane long spacer. In parallel, 4-carboxy-NHPI was synthesized and temporarily protected with trityl chloride to preserve the N-OH group during the coupling. The protected NHPI was then grafted onto the long-spacer amine-functionalized IGMWCNTs. The NHPI moiety was regenerated by acid-mediated deprotection.

In the solvent-free aerobic oxidation of EB, NHPI-grafted MWCNTs increased PEHP selectivity relative to their precursor support material and, with the addition of trace CuCl₂, presented higher EB conversion with enhanced AcPO selectivity. Interestingly, replacing CuCl₂ with Cu(II) functionalized IGMWCNTs preserved activity and selectivity in a fully heterogeneous configuration. All the NHPI-grafted MWCNTs were recyclable, indicating that covalent grafting effectively eliminates the key limitations in recyclability and stability of homogeneous NHPI while retaining the advantage of NHPI-mediated HAT chemistry.

6. Summary and Conclusion of the Study

The liquid-phase oxidation of hydrocarbons is a key industrial route for upgrading hydrocarbon feedstocks into valuable oxygenated products, including hydroperoxides, alcohols, ketones, and acids. However, achieving high substrate conversion and selectivity towards the target product remains challenging. These reactions require activation of strong C-H bonds, yet the resulting radical pathways can propagate beyond the desired oxidation level, leading to over-oxidation and complex by-product mixtures. This challenge is particularly pronounced in the liquid-phase oxidation with oxygen, where radical-chain mechanisms and the formation and decomposition of hydroperoxides govern both catalytic performance and process safety. From the perspective of sustainability and green chemistry, air or molecular oxygen is an attractive oxidant because it is abundant and offers high atom economy. Nonetheless, the greenness of an oxidation process is not defined solely by the oxidant. A practically green oxidation process must also minimize or eliminate solvent use and associated waste, avoid corrosive or toxic components, control hydroperoxide accumulation and decomposition to maintain selective oxidation, and employ catalysts that are economical and environmentally benign, readily separable and reusable without loss of activity.

Within this framework, the doctoral dissertation systematically evaluated the catalytic activities of CNTs, including pristine CNTs, metal-modified CNTs, and CNT-based hybrid catalytic systems, as well as NHPI-grafted CNTs. The study developed and compared CNT-based catalytic systems that combine: (i) CNT surfaces as stable supports that can promote radical reactions, (ii) transition-metal sites that accelerated the decomposition of intermediate hydroperoxides via redox cycle, (iii) NHPI, either as a cocatalyst, physically immobilized (using ILs) on CNTs surfaces, or covalently grafted onto CNTs, serving as a HAT organocatalyst operating via in situ generation of the PINO radical, and (iv) IL thin films that influence the catalytic activity while providing tunable interfacial microenvironment to adjust polarity, oxygen transport, and product selectivity. EB was employed as the model hydrocarbon for solvent-free liquid-phase oxidation using molecular oxygen as a green oxidant under mild conditions (80 °C, 0.1 MPa, 6 h, with AIBN initiation), enabling direct and consistent comparison across the catalytic systems.

Transition metal-modified MWCNTs were prepared using Cu(II), Co(II), and Mn(II) salts according to previously reported methods, yielding three types of catalysts: metal-rich MWCNT composites, metal-modified MWCNTs, and metal-functionalized MWCNTs.

To investigate whether simply increasing metal content enhances the radical oxidation, metal-rich MWCNT composites were prepared via harsh oxidative pretreatment of MWCNTs in concentrated HNO₃ (68%) for 6 or 14 h, followed by the incorporation of Cu, Co, and Mn nitrate precursors and calcination under an inert atmosphere. TEM images and ICP-OES analyses confirmed very high metal loadings (619, 667, and 706 g·kg⁻¹ for Mn, Cu, and Co, respectively), with nanoparticles deposited on the outer surface and also encapsulated within CNT channels, facilitated by defect formation and open nanotube ends. The obtained metal-rich MWCNTs significantly enhanced the EB conversion compared to pristine MWCNTs under similar reaction conditions (0.025 g catalyst, 1 mol% NHPI). EB conversion increased from 6.3% (MWCNTs) to 24.4% (Cu-MWCNT@14h), 20.8% (Cu-MWCNT@6h), 18% (Co-MWCNT@6h), and 21.1% (Mn-MWCNT@6h), corresponding to an approximately 3-4 fold improvement. All composites also exhibited enhanced AcPO selectivity. The composite catalyst loading had little effect on catalytic activity, likely due to the high metal loadings. Recyclability tests demonstrated that all composite catalysts retained their activity over successive cycles, with only a marginal decline attributed to partial catalyst loss and metal leaching, as supported by ICP-OES analysis.

While the metal-rich MWCNT composites demonstrated enhanced catalytic activities, the role of metal loading was further investigated by preparing metal-modified MWCNTs with significantly lower metal contents (0.70, 1.09, and 3.85% for Co, Mn, and Cu, respectively). Among these, Cu-MWCNTs displayed the highest activity, while Mn- and Co-based systems exhibited comparable activities, consistent with their respective metal loadings. Cu-MWCNTs achieved 15.3% EB conversion with 56% AcPO selectivity at 0.025 g, increasing to 19.3% conversion and 66.2% selectivity at 0.0375 g. A further increase to 0.050 g yielded only a slight increase. This could be attributed to the reaction mixture, which became more slurry-like at higher catalyst loadings. These catalysts also demonstrated good stability and recyclability, with minor fluctuations attributed to NHPI accumulation, catalyst loss during recycling, and leaching of metal agglomerates or weakly bound surface species.

In contrast, Cu(II)-functionalized carboxylated IGMWCNTs exhibited superior activity, achieving 26.3% EB conversion and 60.7% AcPO selectivity in the presence of NHPI under similar reaction conditions. Control experiments using pristine and carboxylated MWCNTs favored PEHP formation, highlighting the crucial role of Cu(II) sites. These sites facilitate both the generation of PINO radicals and the selective decomposition of PEHP into AcPO. The IGMWCNT-COO-Cu catalyst maintained good recyclability, with only a moderate decrease in Cu content (from 1.26 wt.% to 0.99 wt.% after five cycles), attributed to partial leaching of loosely bound surface agglomerates.

The enhanced activity observed across all transition metal-modified MWCNTs could be attributed to a synergistic interaction with NHPI, in which the metal species promote PINO radical generation and accelerate PEHP decomposition. At the same time, NHPI facilitates PEHP formation, collectively enhancing the overall oxidation rate.

Based on the previous findings, Cu(II) functionalized carboxylated IGMWCNTs exhibited the highest catalytic performance in the presence of NHPI. Despite the catalytic advantage, the poor solubility of NHPI in nonpolar hydrocarbons such as EB, along with the challenges of recovery and reuse, remained the major drawbacks. To address this, the concept of thin-film IL catalysis was adopted to solubilize NHPI while modulating the catalytic activity. Accordingly, SCILL and SCILL-SILP hybrid catalytic systems were developed. The SCILL systems were prepared by coating selected IL ([emim][OcOSO₃]) directly onto IGMWCNT-COO-Cu, while the SCILL-SILP hybrid catalytic system was prepared by coating NHPI-dissolved [emim][OcOSO₃] onto the same support.

In SCILL systems, the IL layer covered the active sites of the IGMWCNT-COO-Cu support, limiting substrate access and suppressing radical initiation. However, in the presence of AIBN as a radical initiator, the positive effect of the coated IL was observed, increasing EB conversion and enhancing selectivity towards AcPO. Among SCILL systems with varying IL loading, the highest EB conversion (14.1%) was observed for the SCILL system with 72.9% AcPO selectivity, using 0.025 g of IL. In contrast, the SCILL-SILP hybrid (0.025 g IL) outperformed, achieving ~27% EB conversion with ~77% AcPO selectivity, suggesting that the NHPI-containing IL film creates a more selective interfacial oxidation environment (consistent with confinement/cage effects). However, recyclability tests supported by TGA and FTIR revealed

partial loss of the IL and NHPI layer after reuse, indicating that leaching and film retention remain critical constraints for long-term operation of physically immobilized systems.

The limited recyclability of the developed [emim][OcOSO₃]-based SCILL-SILP system restricts its practical applicability. This limitation made it imperative to develop a more resilient and reusable hybrid catalytic system. Consequently, a broad set of ILs with different cation-anion combinations was explored, including [emim], [bmim], [omim], and [C10mim] cations in combination with [Cl], [Br], [BF₄], [PF₆], [OcOSO₃], or [NTf₂] anions, and were investigated to develop SILP and SCILL-SILP hybrid catalytic systems. SILP systems were prepared by depositing an NHPI-dissolved IL layer onto pristine MWCNTs, whereas SCILL-SILP hybrid catalytic systems were obtained by coating the same NHPI-dissolved IL onto Cu(II)-functionalized MWCNTs. All the produced [Rmim]-based SILP systems were more active compared to the pristine MWCNTs or the MWCNT/NHPI combination, reflecting combined effects of (i) IL-assisted PEHP decomposition, (ii) favorable interaction between NHPI and IL that facilitates PINO generation, (iii) improved solubility of the reagents and NHPI within the IL layer, and (iv) the influence of IL polarity and viscosity. Among the [bmim]-based SILP systems, the [bmim][Cl] based system outperformed, achieving the highest EB conversion (12.2%), while maintaining elevated AcPO selectivity (84.1%), consistent with halide-assisted NHPI activation (PINO formation) and accelerated PEHP decomposition.

SCILL-SILP systems were generally less active than the MWCNT-COO-Cu support because the viscous IL layer partially covered the active Cu(II) sites, introducing additional mass-transfer limitations. Nevertheless, these systems delivered higher AcPO selectivity than their SILP analogs, supporting a robust cage or confinement selectivity mechanism in the IL thin film combined with Cu(II) mediated hydroperoxide decomposition pathways. The catalytic activities of [bmim]-based SCILL-SILP systems bearing [BF₄], [PF₆], [NTf₂], and [OcOSO₃] anions were broadly similar, with [bmim][NTf₂] yielding the highest conversion (22.6%), consistent with its favorable combination of higher oxygen solubility and lower viscosity relative to the more viscous analogues.

A key outcome of this study was the identification of stability. Increasing cation lipophilicity sometimes improved the initial conversion, but it often reduced the recyclability because the IL phase leached more readily as more oxygenated products accumulated and the reaction mixture

became more polar. On the other hand, [bmim][OcOSO₃]-based systems were comparatively more stable in both the SILP and SCILL-SILP systems, which could be attributed to the amphiphilic sulfate anion, which enhances film retention on hydrophobic CNT surfaces while still stabilizing NHPI within the interfacial layer. Overall, these findings establish a clear structure-property-performance relationship: activity and selectivity are controlled not only by NHPI and Cu(II) chemistry but also by IL viscosity, oxygen transport, and thin-film resilience under solvent-free aerobic oxidation conditions.

The NHPI-dissolved IL layer in the SILP and SCILL-SILP hybrid catalytic system was prone to gradual loss, which could be partially attributed to leaching during reaction and partially to recycling. Therefore, this study shifted to covalent grafting of NHPI onto MWCNTs to improve the stability and recyclability. NHPI was grafted onto amine-functionalized MWCNTs (two precursors: ~0.45 % and ~7% -NH₂) via TAC-mediated amide formation, followed by the conversion of grafted TA to NHPI functionality employing NH₂OH.HCl. On the other hand, NHPI was also grafted onto IGMWCNT-COOH via an EDC/NHS coupling strategy. The carboxyl groups on the CNTs were first converted to amine-terminated surfaces using a 1,8-diaminooctane long spacer. In parallel, 4-carboxy-NHPI was produced and temporarily protected with trityl chloride to preserve the N-OH group during the coupling. The protected NHPI was then grafted onto the long-spacer amine-functionalized IGMWCNTs. The NHPI functionality was restored via acid-mediated deprotection.

The catalytic evaluation confirmed the expected behavior of all the NHPI-grafted MWCNTs. In the absence of any metallic compounds, they exhibited higher PEHP selectivity (an attribute of NHPI-based systems) in the solvent-free aerobic oxidation of EB, compared to their respective support precursors. In the presence of a minuscule amount of homogeneous CuCl₂, all the NHPI-grafted CNTs exhibited an enhanced EB conversion, with elevated selectivities towards AcPO. Interestingly, when the CuCl₂ was replaced with Cu(II)-functionalized IGMWCNTs to transition to a completely heterogeneous system, all the NHPI-grafted CNTs retained their catalytic activity, with elevated selectivity towards AcPO. Furthermore, all the produced NHPI-grafted MWCNTs were stable and recyclable in both cases, with CuCl₂ and under a completely heterogeneous system with IGMWCNT-COO-Cu. Overall, these results indicated that covalent grafting of NHPI onto a solid support is the most effective route to overcome the key limitations associated with the homogeneous NHPI, and with SILP and

SCILL-SILP systems, while preserving the mechanistic benefits of NHPI-mediated HAT oxidations.

References

- [1] R. Sheldon, *Metal-Catalyzed Oxidations of Organic Compounds: Mechanistic Principles and Synthetic Methodology Including Biochemical Processes*, Elsevier, 2012.
- [2] L. Gómez-Hortigüela, F. Cora, C.R.A. Catlow, Aerobic oxidation of hydrocarbons catalyzed by Mn-doped nanoporous aluminophosphates (IV): Regeneration mechanism, *ACS Catalysis* 1 (2011) 1475–1486. <https://doi.org/10.1021/cs200402b>
- [3] R.A. Sheldon, R.A. Van Santen, *Catalytic Oxidation: Principles and Applications*, World Scientific, 1995.
- [4] A.K. Suresh, M.M. Sharma, T. Sridhar, Engineering aspects of industrial liquid-phase air oxidation of hydrocarbons, *Industrial & Engineering Chemistry Research* 39 (2000) 3958–3997. <https://doi.org/10.1021/ie0002733>
- [5] M.N. Siddiquee, M.M. Hossain, N. Nazemifard, Liquid phase oxidation of hydrocarbons to high-value chemicals in microfluidic reactors – prospects and challenges, *The Chemical Record* 22 (2022) e202200022. <https://doi.org/10.1002/tcr.202200022>
- [6] N.M. Emanuel, Z.K. Maizus, I.P. Skibida, The catalytic activity of transition metal compounds in the liquid-phase oxidation of hydrocarbons, *Angewandte Chemie International Edition in English* 8 (1969) 97–107. <https://doi.org/10.1002/anie.196900971>
- [7] X. Liu, Y. Ryabenkova, M. Conte, Catalytic oxygen activation versus autoxidation for industrial applications: a physicochemical approach, *Physical Chemistry Chemical Physics* 17 (2015) 715–731. <https://doi.org/10.1039/C4CP04144B>
- [8] L.I. Simándi, *Dioxygen Activation and Homogeneous Catalytic Oxidation*, Elsevier, 1991.
- [9] D.H.R. Barton, A.E. Martell, D.T. Sawyer, *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, Springer Science & Business Media, 2012.

- [10] J.-E. Bäckvall, *Modern Oxidation Methods*, John Wiley & Sons, 2011.
- [11] G. Centi, F. Cavani, F. Trifirò, *Selective Oxidation by Heterogeneous Catalysis*, Springer, 2001.
- [12] E. Roduner, W. Kaim, B. Sarkar, V.B. Urlacher, J. Pleiss, R. Gläser, W. Einicke, G.A. Sprenger, U. Beifuß, E. Klemm, Selective catalytic oxidation of C–H bonds with molecular oxygen, *ChemCatChem* 5 (2013) 82–112. <https://doi.org/10.1002/cctc.201200266>
- [13] G. Ertl, Wilhelm Ostwald: Founder of physical chemistry and Nobel laureate 1909, *Angewandte Chemie International Edition* 48 (2009) 6600–6606. <https://doi.org/10.1002/anie.200901193>
- [14] E. Roduner, Understanding catalysis, *Chemical Society Reviews* 43 (2014) 8226–8239. <https://doi.org/10.1039/C4CS00210E>
- [15] W. Buijs, Challenges in oxidation catalysis, *Topics in Catalysis* 24 (2003) 73–78. <https://doi.org/10.1023/B:TOCA.0000003078.34848.23>
- [16] M.O. Azeez, S.A. Nafiu, T.A. Olarewaju, A.B. Olabintan, A. Tanimu, Y. Gambo, A. Aitani, Selective catalytic oxidation of ethylbenzene to acetophenone: a review of catalyst systems and reaction mechanisms, *Industrial & Engineering Chemistry Research* 62 (2023) 12795–12828. <https://doi.org/10.1021/acs.iecr.3c01588>
- [17] O.U. Isocyanates, *Ullmann's Encyclopedia of Industrial Chemistry*, (1985).
- [18] C.A. Hone, D.M. Roberge, C.O. Kappe, The use of molecular oxygen in pharmaceutical manufacturing: is flow the way to go?, *ChemSusChem* 10 (2017) 32–41. <https://doi.org/10.1002/cssc.201601321>
- [19] P.L. Mills, R.V. Chaudhari, Reaction engineering of emerging oxidation processes, *Catalysis Today* 48 (1999) 1–30. [https://doi.org/10.1016/S0920-5861\(98\)00354-X](https://doi.org/10.1016/S0920-5861(98)00354-X)
- [20] E.T. Denisov, I.B. Afanas'ev, *Oxidation and Antioxidants in Organic Chemistry and Biology*, CRC Press, 2005.

- [21] I. Hermans, J. Peeters, P.A. Jacobs, Autoxidation of ethylbenzene: the mechanism elucidated, *Journal of Organic Chemistry* 72 (2007) 3057–3064. <https://doi.org/10.1021/jo070040m>
- [22] F. Recupero, C. Punta, Free radical functionalization of organic compounds catalyzed by *N*-hydroxyphthalimide, *Chemical Reviews* 107 (2007) 3800–3842. <https://doi.org/10.1021/cr040170k>
- [23] Statista Research Department, Global purified terephthalic acid market volume 2015–2030, (2024). <https://www.statista.com/statistics/1245249/purified-terephthalic-acid-market-volume-worldwide/>
- [24] Mordor Intelligence, Dimethyl terephthalate (DMT) market size & share analysis–growth trends and forecast (2026–2031), (2026). <https://www.mordorintelligence.com/industry-reports/dimethyl-terephthalate-dmt-market>
- [25] Market Reports World, Cumene market size, share, growth, and industry analysis, by type (GC, AR, General), by application (production of phenol and acetone, chromatography, others), regional insights, and forecast to 2033, (2026). <https://www.marketreportsworld.com/market-reports/cumene-market-14716184>
- [26] Statista Research Department, Global benzoic acid market volume 2015–2030, Statista. <https://www.statista.com/statistics/1245227/benzoic-acid-market-volume-worldwide/>
- [27] A. Vomeri, M. Stucchi, A. Villa, C. Evangelisti, A. Beck, L. Prati, New insights for the catalytic oxidation of cyclohexane to K-A oil, *Journal of Energy Chemistry* 70 (2022) 45–51. <https://doi.org/10.1016/j.jechem.2022.02.008>
- [28] Prismane Consulting Pvt. Ltd., Adipic acid capacity, production, market size, average price, and forecast, 2018–2034, 2025. <https://prismaneconsulting.com/report-details/adipic-acid-market>
- [29] Everchem Specialty Chemicals, Chinese propylene oxide update, (2021). <https://everchem.com/chinese-propylene-oxide-update-4/>

- [30] D. Lisicki, A. Maciej, B. Orlinska, Selective aerobic oxidation of toluene in the presence of Co^{2+} and task-specific organic salts, including ionic liquids, *Industrial & Engineering Chemistry Research* 60 (2021) 11579–11589. <https://doi.org/10.1021/acs.iecr.1c00927>
- [31] W. Partenheimer, Methodology and scope of metal/bromide autoxidation of hydrocarbons, *Catalysis Today* 23 (1995) 69–158. [https://doi.org/10.1016/0920-5861\(94\)00138-R](https://doi.org/10.1016/0920-5861(94)00138-R)
- [32] R.A. Sheldon, Green solvents for sustainable organic synthesis: state of the art, *Green Chemistry* 7 (2005) 267–278. <https://doi.org/10.1039/B418069K>
- [33] R.A. Sheldon, The E factor 25 years on: the rise of green chemistry and sustainability, *Green Chemistry* 19 (2017) 18–43. <https://doi.org/10.1039/C6GC02157C>
- [34] R.A. Sheldon, The E factor: fifteen years on, *Green Chemistry* 9 (2007) 1273–1283. <https://doi.org/10.1039/B713736M>
- [35] C.J. Clarke, W.-C. Tu, O. Levers, A. Brohl, J.P. Hallett, Green and sustainable solvents in chemical processes, *Chemical Reviews* 118 (2018) 747–800. <https://doi.org/10.1021/acs.chemrev.7b00571>
- [36] Y. Yan, J. Miao, Z. Yang, F.-X. Xiao, H. Bin Yang, B. Liu, Y. Yang, Carbon nanotube catalysts: recent advances in synthesis, characterization and applications, *Chemical Society Reviews* 44 (2015) 3295–3346. <https://doi.org/10.1039/C4CS00492B>
- [37] R.P. Rocha, O.S.G.P. Soares, J.L. Figueiredo, M.F.R. Pereira, Tuning CNT properties for metal-free environmental catalytic applications, *C–Journal of Carbon Research* 2 (2016) 17. <https://doi.org/10.3390/c2030017>
- [38] J.M. Schnorr, T.M. Swager, Emerging applications of carbon nanotubes, *Chemistry of Materials* 23 (2011) 646–657. <https://doi.org/10.1021/cm102406h>
- [39] J. John, E. Gravel, I.N.N. Namboothiri, E. Doris, Advances in carbon nanotube-noble metal catalyzed organic transformations, *Nanotechnology Reviews* 1 (2012) 515–539. <https://doi.org/10.1515/ntrev-2012-0025>

- [40] S.U. Azam, B. Orlńska, Carbon nanotubes as advanced catalysts and catalytic supports for the liquid-phase aerobic oxidation of hydrocarbons: A review, *Applied Catalysis A: General* 668 (2023) 119465. <https://doi.org/10.1016/j.apcata.2023.119465>
- [41] S. Iijima, Helical microtubules of graphitic carbon, *Nature* 354 (1991) 56–58. <https://doi.org/10.1038/354056a0>
- [42] M.N. Norizan, M.H. Moklis, S.Z.N. Demon, N.A. Halim, A. Samsuri, I.S. Mohamad, V.F. Knight, N. Abdullah, Carbon nanotubes: functionalisation and their application in chemical sensors, *RSC Advances* 10 (2020) 43704–43732. <https://doi.org/10.1039/D0RA09438B>
- [43] R. Rao, C.L. Pint, A.E. Islam, R.S. Weatherup, S. Hofmann, E.R. Meshot, F. Wu, C. Zhou, N. Dee, P.B. Amama, Carbon nanotubes and related nanomaterials: critical advances and challenges for synthesis toward mainstream commercial applications, *ACS Nano* 12 (2018) 11756–11784. <https://doi.org/10.1021/acsnano.8b06511>
- [44] N. Gupta, S.M. Gupta, S.K. Sharma, Carbon nanotubes: synthesis, properties and engineering applications, *Carbon Letters* 29 (2019) 419–447. <https://doi.org/10.1007/s42823-019-00068-2>
- [45] R.P. Rocha, M.F.R. Pereira, J.L. Figueiredo, Metal-free carbon materials as catalysts for wet air oxidation, *Catalysis Today* 356 (2020) 189–196. <https://doi.org/10.1016/j.cattod.2019.04.047>
- [46] S. Yang, X. Li, W. Zhu, J. Wang, C. Descorme, Catalytic activity, stability and structure of multi-walled carbon nanotubes in the wet air oxidation of phenol, *Carbon* 46 (2008) 445–452. <https://doi.org/10.1016/j.carbon.2007.12.006>
- [47] R.P. Rocha, O.S.G.P. Soares, A.G. Gonçalves, J.J.M. Órfão, M.F.R. Pereira, J.L. Figueiredo, Different methodologies for synthesis of nitrogen-doped carbon nanotubes and their use in catalytic wet air oxidation, *Applied Catalysis A: General* 548 (2017) 62–70. <https://doi.org/10.1016/j.apcata.2017.08.033>

- [48] G. Jing, M. Luan, T. Chen, Progress of catalytic wet air oxidation technology, *Arabian Journal of Chemistry* 9 (2016) S1208–S1213. <https://doi.org/10.1016/j.arabjc.2012.01.001>
- [49] W. Qi, W. Liu, B. Zhang, X. Gu, X. Guo, D. Su, Oxidative dehydrogenation on nanocarbon: identification and quantification of active sites by chemical titration, *Angewandte Chemie International Edition* 52 (2013) 14224–14228. <https://doi.org/10.1002/anie.201306825>
- [50] W. Liu, C. Wang, F. Herold, B.J.M. Etzold, D. Su, W. Qi, Oxidative dehydrogenation on nanocarbon: effect of heteroatom doping, *Applied Catalysis B: Environmental* 258 (2019) 117982. <https://doi.org/10.1016/j.apcatb.2019.117982>
- [51] A. Rinaldi, J. Zhang, B. Frank, D.S. Su, S.B.A. Hamid, R. Schlögl, Oxidative purification of carbon nanotubes and its impact on catalytic performance in oxidative dehydrogenation reactions, *ChemSusChem* 3 (2010) 254–260. <https://doi.org/10.1002/cssc.200900179>
- [52] Y. Shen, A.C. Lua, Synthesis of Ni and Ni-Cu supported on carbon nanotubes for hydrogen and carbon production by catalytic decomposition of methane, *Applied Catalysis B: Environmental* 164 (2015) 61–69. <https://doi.org/10.1016/j.apcatb.2014.08.038>
- [53] F.R. García-García, J. Álvarez-Rodríguez, I. Rodríguez-Ramos, A. Guerrero-Ruiz, The use of carbon nanotubes with and without nitrogen doping as support for ruthenium catalysts in the ammonia decomposition reaction, *Carbon* 48 (2010) 267–276. <https://doi.org/10.1016/j.carbon.2009.09.015>
- [54] J. Chen, Z.H. Zhu, S. Wang, Q. Ma, V. Rudolph, G.Q. Lu, Effects of nitrogen doping on the structure of carbon nanotubes (CNTs) and activity of Ru/CNTs in ammonia decomposition, *Chemical Engineering Journal* 156 (2010) 404–410. <https://doi.org/10.1016/j.cej.2009.10.062>
- [55] H. Zhang, Q. Gong, S. Ren, M.A. Arshid, W. Chu, C. Chen, Implication of iron nitride species to enhance the catalytic activity and stability of carbon nanotube-supported Fe catalysts for carbon-free hydrogen production via low-temperature ammonia

- decomposition, *Catalysis Science & Technology* 8 (2018) 907–915. <https://doi.org/10.1039/C7CY02270K>
- [56] M. Mu, W. Fang, Y. Liu, L. Chen, Iron(III)-modified tungstophosphoric acid supported on titania catalyst: synthesis, characterization, and Friedel-Craft acylation of m-xylene, *Industrial & Engineering Chemistry Research* 54 (2015) 8893–8899. <https://doi.org/10.1021/acs.iecr.5b01861>
- [57] A.H. Nia, A. Amini, S. Taghavi, H. Eshghi, K. Abnous, M. Ramezani, A facile Friedel-Crafts acylation for the synthesis of polyethylenimine-grafted multi-walled carbon nanotubes as efficient gene delivery vectors, *International Journal of Pharmaceutics* 502 (2016) 125–137. <https://doi.org/10.1016/j.ijpharm.2016.02.034>
- [58] H. Zhang, A. Dong, B. Liu, J. Chen, Y. Xu, X. Liu, Hydrogen spillover effects in the Fischer-Tropsch reaction over carbon nanotube-supported cobalt catalysts, *Catalysis Science & Technology* 13 (2023) 1888–1904. <https://doi.org/10.1039/D3CY00014A>
- [59] H. Zhang, C. Lancelot, W. Chu, J. Hong, A.Y. Khodakov, P.A. Chernavskii, J. Zheng, D. Tong, The nature of cobalt species in carbon nanotubes and their catalytic performance in Fischer-Tropsch reaction, *Journal of Materials Chemistry* 19 (2009) 9241–9249. <https://doi.org/10.1039/B911355J>
- [60] C. Xing, G. Yang, D. Wang, C. Zeng, Y. Jin, R. Yang, Y. Suehiro, N. Tsubaki, Controllable encapsulation of cobalt clusters inside carbon nanotubes as effective catalysts for Fischer-Tropsch synthesis, *Catalysis Today* 215 (2013) 24–28. <https://doi.org/10.1016/j.cattod.2013.02.018>
- [61] S. Wang, T. Wu, J. Lin, Y. Ji, S. Yan, Y. Pei, S. Xie, B. Zong, M. Qiao, Iron-potassium on single-walled carbon nanotubes as an efficient catalyst for CO₂ hydrogenation to heavy olefins, *ACS Catalysis* 10 (2020) 6389–6401. <https://doi.org/10.1021/acscatal.0c00810>
- [62] R.S. Oosthuizen, V.O. Nyamori, Carbon nanotubes as supports for palladium and bimetallic catalysts for use in hydrogenation reactions, *Platinum Metals Review* 55 (2011) 154–169. <https://doi.org/10.1595/147106711X577274>

- [63] X. Yang, X. Wang, J. Qiu, Aerobic oxidation of alcohols over carbon nanotube-supported Ru catalysts assembled at the interfaces of emulsion droplets, *Applied Catalysis A: General* 382 (2010) 131–137. <https://doi.org/10.1016/j.apcata.2010.04.046>
- [64] X. Hu, M. Fan, Y. Zhu, Q. Zhu, Q. Song, Z. Dong, Biomass-derived phosphorus-doped carbon materials as efficient metal-free catalysts for selective aerobic oxidation of alcohols, *Green Chemistry* 21 (2019) 5274–5283. <https://doi.org/10.1039/C9GC01910C>
- [65] A. Maleki, Green oxidation protocol: selective conversions of alcohols and alkenes to aldehydes, ketones, and epoxides by using a new multiwall carbon nanotube-based hybrid nanocatalyst via ultrasound irradiation, *Ultrasonics Sonochemistry* 40 (2018) 460–464. <https://doi.org/10.1016/j.ultsonch.2017.07.020>
- [66] J. Luo, F. Peng, H. Yu, H. Wang, Selective liquid phase oxidation of benzyl alcohol catalyzed by carbon nanotubes, *Chemical Engineering Journal* 204 (2012) 98–106. <https://doi.org/10.1016/j.cej.2012.07.098>
- [67] J. Luo, F. Peng, H. Yu, H. Wang, W. Zheng, Aerobic liquid-phase oxidation of ethylbenzene to acetophenone catalyzed by carbon nanotubes, *ChemCatChem* 5 (2013) 1578–1586. <https://doi.org/10.1002/cctc.201200603>
- [68] S. Liao, F. Peng, H. Yu, H. Wang, Carbon nanotubes as catalyst for the aerobic oxidation of cumene to cumene hydroperoxide, *Applied Catalysis A: General* 478 (2014) 1–8. <https://doi.org/10.1016/j.apcata.2014.03.024>
- [69] Y. Cao, H. Yu, J. Tan, F. Peng, H. Wang, J. Li, W. Zheng, N.-B. Wong, Nitrogen-, phosphorous- and boron-doped carbon nanotubes as catalysts for the aerobic oxidation of cyclohexane, *Carbon* 57 (2013) 433–442. <https://doi.org/10.1016/j.carbon.2013.02.016>
- [70] E. Zeynalov, N.S. Allen, N. Salmanova, V. Vishnyakov, Carbon nanotubes catalysis in liquid-phase aerobic oxidation of hydrocarbons: influence of nanotube impurities, *Journal of Physics and Chemistry of Solids* 127 (2019) 245–251. <https://doi.org/10.1016/j.jpcs.2018.12.031>

- [71] H. Fu, K. Huang, G. Yang, Y. Cao, H. Wang, F. Peng, Q. Wang, H. Yu, Synergistic effect of nitrogen dopants on carbon nanotubes on the catalytic selective epoxidation of styrene, *ACS Catalysis* 10 (2019) 129–137. <https://doi.org/10.1021/acscatal.9b03584>
- [72] P.S. Engel, W.E. Billups, D.W. Abmayr, K. Tsveygboym, R. Wang, Reaction of single-walled carbon nanotubes with organic peroxides, *The Journal of Physical Chemistry C* 112 (2008) 695–700. <https://doi.org/10.1021/jp0770054>
- [73] H. Yu, F. Peng, J. Tan, X. Hu, H. Wang, J. Yang, W. Zheng, Selective catalysis of the aerobic oxidation of cyclohexane in the liquid phase by carbon nanotubes, *Angewandte Chemie International Edition* 50 (2011) 4064–4068. <https://doi.org/10.1002/anie.201007932>
- [74] P. Ayala, R. Arenal, M. Rmmeli, A. Rubio, T. Pichler, The doping of carbon nanotubes with nitrogen and their potential applications, *Carbon* 48 (2010) 575–586. <https://doi.org/10.1016/j.carbon.2009.10.009>
- [75] W.J. Lee, U.N. Maiti, J.M. Lee, J. Lim, T.H. Han, S.O. Kim, Nitrogen-doped carbon nanotubes and graphene composite structures for energy and catalytic applications, *Chemical Communications* 50 (2014) 6818–6830. <https://doi.org/10.1039/C4CC00146J>
- [76] Y. Su, J. Huang, G. Yang, H. Wang, H. Yu, Q. Zhang, Y. Cao, F. Peng, Elucidating mechanism of ethylbenzene oxidation catalyzed by carbon-based catalysts with kinetic modeling, *AIChE Journal* 69 (2023) e18007. <https://doi.org/10.1002/aic.18007>
- [77] S. Liao, Y. Chi, H. Yu, H. Wang, F. Peng, Tuning the selectivity in the aerobic oxidation of cumene catalyzed by nitrogen-doped carbon nanotubes, *ChemCatChem* 6 (2014) 555–560. <https://doi.org/10.1002/cctc.201300909>
- [78] X. Lin, Z. Nie, L. Zhang, S. Mei, Y. Chen, B. Zhang, R. Zhu, Z. Liu, Nitrogen-doped carbon nanotubes encapsulate cobalt nanoparticles as efficient catalysts for aerobic and solvent-free selective oxidation of hydrocarbons, *Green Chemistry* 19 (2017) 2164–2173. <https://doi.org/10.1039/C7GC00415J>

- [79] X. Yang, Y. Cao, H. Yu, H. Huang, H. Wang, F. Peng, Unravelling the radical transition during the carbon-catalyzed oxidation of cyclohexane by in situ electron paramagnetic resonance in the liquid phase, *Catalysis Science & Technology* 7 (2017) 4431–4436. <https://doi.org/10.1039/C7CY00958E>
- [80] X. Yang, H. Wang, J. Li, W. Zheng, R. Xiang, Z. Tang, H. Yu, F. Peng, Mechanistic insight into the catalytic oxidation of cyclohexane over carbon nanotubes: kinetic and in situ spectroscopic evidence, *Chemistry – A European Journal* 19 (2013) 9818–9824. <https://doi.org/10.1002/chem.201300676>
- [81] Y. Cao, X. Luo, H. Yu, F. Peng, H. Wang, G. Ning, sp^2 - and sp^3 -hybridized carbon materials as catalysts for aerobic oxidation of cyclohexane, *Catalysis Science & Technology* 3 (2013) 2654–2660. <https://doi.org/10.1039/C3CY00361B>
- [82] X. Duan, H. Sun, Y. Wang, J. Kang, S. Wang, N-doping-induced nonradical reaction on single-walled carbon nanotubes for catalytic phenol oxidation, *ACS Catalysis* 5 (2015) 553–559. <https://doi.org/10.1021/cs5017613>
- [83] W. Li, Y. Gao, W. Chen, P. Tang, W. Li, Z. Shi, D. Su, J. Wang, D. Ma, Catalytic epoxidation reaction over N-containing sp^2 carbon catalysts, *ACS Catalysis* 4 (2014) 1261–1266. <https://doi.org/10.1021/cs500062s>
- [84] P. Tang, G. Hu, M. Li, D. Ma, Graphene-based metal-free catalysts for catalytic reactions in the liquid phase, *ACS Catalysis* 6 (2016) 6948–6958. <https://doi.org/10.1021/acscatal.6b01668>
- [85] M. Martin-Martinez, R.S. Ribeiro, B.F. Machado, P. Serp, S. Morales-Torres, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Role of nitrogen doping on the performance of carbon nanotube catalysts: a catalytic wet peroxide oxidation application, *ChemCatChem* 8 (2016) 2068–2078. <https://doi.org/10.1002/cctc.201600123>
- [86] Y. Cao, H. Yu, F. Peng, H. Wang, Selective allylic oxidation of cyclohexene catalyzed by nitrogen-doped carbon nanotubes, *ACS Catalysis* 4 (2014) 1617–1625. <https://doi.org/10.1021/cs500187q>

- [87] Y. Gao, G. Hu, J. Zhong, Z. Shi, Y. Zhu, D.S. Su, J. Wang, X. Bao, D. Ma, Nitrogen-doped sp^2 -hybridized carbon as a superior catalyst for selective oxidation, *Angewandte Chemie International Edition* 52 (2013) 2109–2113. <https://doi.org/10.1002/anie.201207918>
- [88] C. Mu, Y. Cao, H. Wang, H. Yu, F. Peng, A kinetics study on cumene oxidation catalyzed by carbon nanotubes: effect of N-doping, *Chemical Engineering Science* 177 (2018) 391–398. <https://doi.org/10.1016/j.ces.2017.11.016>
- [89] Y. Su, Y. Li, Z. Chen, J. Huang, H. Wang, H. Yu, Y. Cao, F. Peng, New understanding of selective aerobic oxidation of ethylbenzene catalyzed by nitrogen-doped carbon nanotubes, *ChemCatChem* 13 (2021) 646–655. <https://doi.org/10.1002/cctc.202001503>
- [90] L. He, F. Weniger, H. Neumann, M. Beller, Synthesis, characterization, and application of metal nanoparticles supported on nitrogen-doped carbon: catalysis beyond electrochemistry, *Angewandte Chemie International Edition* 55 (2016) 12582–12594. <https://doi.org/10.1002/anie.201603198>
- [91] Z. Ma, H. Zhang, Z. Yang, G. Ji, B. Yu, X. Liu, Z. Liu, Mesoporous nitrogen-doped carbons with high nitrogen contents and ultrahigh surface areas: synthesis and applications in catalysis, *Green Chemistry* 18 (2016) 1976–1982. <https://doi.org/10.1039/C5GC01920F>
- [92] H. Wang, T. Maiyalagan, X. Wang, Review on recent progress in nitrogen-doped graphene: synthesis, characterization, and its potential applications, *ACS Catalysis* 2 (2012) 781–794. <https://doi.org/10.1021/cs200652y>
- [93] J. Long, X. Xie, J. Xu, Q. Gu, L. Chen, X. Wang, Nitrogen-doped graphene nanosheets as metal-free catalysts for aerobic selective oxidation of benzylic alcohols, *ACS Catalysis* 2 (2012) 622–631. <https://doi.org/10.1021/cs3000396>
- [94] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts, *Science* 351 (2016) 361–365. <https://doi.org/10.1126/science.aad0832>

- [95] Y. Cao, Y. Li, H. Yu, F. Peng, H. Wang, Aerobic oxidation of α -pinene catalyzed by carbon nanotubes, *Catalysis Science & Technology* 5 (2015) 3935–3944. <https://doi.org/10.1039/C5CY00136F>
- [96] M. Liu, Z. Xiao, J. Dai, W. Zhong, Q. Xu, L. Mao, D. Yin, Manganese-containing hollow TS-1: description of the catalytic sites and surface properties for solvent-free oxidation of ethylbenzene, *Chemical Engineering Journal* 313 (2017) 1468–1479. <https://doi.org/10.1016/j.cej.2016.11.054>
- [97] L. Fu, S. Zhao, Y. Chen, Z. Liu, One-pot synthesis of mesoporous silica hollow spheres with Mn–N–C integrated into the framework for ethylbenzene oxidation, *Chemical Communications* 52 (2016) 5577–5580. <https://doi.org/10.1039/C6CC00907G>
- [98] H. Ma, J. Xu, C. Chen, Q. Zhang, J. Ning, H. Miao, L. Zhou, X. Li, Catalytic aerobic oxidation of ethylbenzene over Co/SBA-15, *Catalysis Letters* 113 (2007) 104–108. <https://doi.org/10.1007/s10562-007-9019-7>
- [99] N.N. Tušar, S.C. Laha, S. Cecowski, I. Arčon, V. Kaučič, R. Gläser, Mn-containing porous silicates as catalysts for the solvent-free selective oxidation of alkyl aromatics to aromatic ketones with molecular oxygen, *Microporous and Mesoporous Materials* 146 (2011) 166–171. <https://doi.org/10.1016/j.micromeso.2011.05.001>
- [100] S.E. Dapurkar, H. Kawanami, T. Yokoyama, Y. Ikushima, Solvent-free selective oxidation of benzylic compounds over chromium containing mesoporous molecular sieve catalyst at 1 atm O₂, *Catalysis Communications* 10 (2009) 1025–1028. <https://doi.org/10.1016/j.catcom.2008.12.053>
- [101] R. Zhao, D. Ji, G. Lv, G. Qian, L. Yan, X. Wang, J. Suo, A highly efficient oxidation of cyclohexane over Au/ZSM-5 molecular sieve catalyst with oxygen as oxidant, *Chemical Communications* (2004) 904–905. <https://doi.org/10.1039/B315098D>
- [102] B.P.C. Hereijgers, B.M. Weckhuysen, Aerobic oxidation of cyclohexane by gold-based catalysts: new mechanistic insight by thorough product analysis, *Journal of Catalysis* 270 (2010) 16–25. <https://doi.org/10.1016/j.jcat.2009.12.003>

- [103] Z.Y. Cai, M.Q. Zhu, J. Chen, Y.Y. Shen, J. Zhao, Y. Tang, X.Z. Chen, Solvent-free oxidation of cyclohexene over catalysts Au/OMS-2 and Au/La-OMS-2 with molecular oxygen, *Catalysis Communications* 12 (2010) 197–201. <https://doi.org/10.1016/j.catcom.2010.09.014>
- [104] L.-X. Xu, C.-H. He, M.-Q. Zhu, S. Fang, A highly active Au/Al₂O₃ catalyst for cyclohexane oxidation using molecular oxygen, *Catalysis Letters* 114 (2007) 202–205. <https://doi.org/10.1007/s10562-007-9058-0>
- [105] C. Yin, Z. Yang, B. Li, F. Zhang, J. Wang, E. Ou, Allylic oxidation of cyclohexene with molecular oxygen using cobalt resinate as catalyst, *Catalysis Letters* 131 (2009) 440–445. <https://doi.org/10.1007/s10562-009-9886-1>
- [106] H. Huang, H. Zhang, Z. Ma, Y. Liu, H. Ming, H. Li, Z. Kang, Tunable synthesis of metal-graphene complex nanostructures and their catalytic ability for solvent-free cyclohexene oxidation in air, *Nanoscale* 4 (2012) 4964–4970. <https://doi.org/10.1039/C2NR30962A>
- [107] S.E. Dapurkar, H. Kawanami, K. Komura, T. Yokoyama, Y. Ikushima, Solvent-free allylic oxidation of cycloolefins over mesoporous CrMCM-41 molecular sieve catalyst at 1 atm dioxygen, *Applied Catalysis A: General* 346 (2008) 112–116. <https://doi.org/10.1016/j.apcata.2008.05.012>
- [108] A. Nowacka, P. Briantais, C. Prestipino, F.X. Llabrés Xamena, Selective aerobic oxidation of cumene to cumene hydroperoxide over mono- and bimetallic trimesate metal-organic frameworks prepared by a facile "green" aqueous synthesis, *ACS Sustainable Chemistry & Engineering* 7 (2019) 6205–6214. <https://doi.org/10.1021/acssuschemeng.8b06472>
- [109] R. Chakrabarty, B.K. Das, J.H. Clark, Enhanced selectivity in green catalytic epoxidation using a supported cobalt complex, *Green Chemistry* 9 (2007) 845–848. <https://doi.org/10.1039/B618862A>
- [110] R. Raja, G. Sankar, J.M. Thomas, New catalysts for the aerobic selective oxidation of hydrocarbons: Mn(III)- and Co(III)-containing molecular sieves for the epoxidation of

- alkenes, Chemical Communications (1999) 829–830.
<https://doi.org/10.1039/A901127G>
- [111] N.V. Maksimchuk, M.N. Timofeeva, M.S. Melgunov, A.N. Shmakov, Y.A. Chesalov, D.N. Dybtsev, V.P. Fedin, O.A. Kholdeeva, Heterogeneous selective oxidation catalysts based on coordination polymer MIL-101 and transition metal-substituted polyoxometalates, Journal of Catalysis 257 (2008) 315–323.
<https://doi.org/10.1016/j.jcat.2008.05.014>
- [112] J. Sheng, B. Yan, W.D. Lu, B. Qiu, X.Q. Gao, D. Wang, A.H. Lu, Oxidative dehydrogenation of light alkanes to olefins on metal-free catalysts, Chemical Society Reviews 50 (2021) 1438–1468. <https://doi.org/10.1039/D0CS01174F>
- [113] W. Qi, P. Yan, D.S. Su, Oxidative dehydrogenation on nanocarbon: insights into the reaction mechanism and kinetics via in situ experimental methods, Accounts of Chemical Research 51 (2018) 640–648. <https://doi.org/10.1021/acs.accounts.7b00475>
- [114] T.D. Marforio, A. Bottoni, F. Zerbetto, M. Calvaresi, CNT-catalyzed oxidative dehydrogenation of ethylbenzene to styrene: DFT calculations disclose the pathways, ChemNanoMat 5 (2019) 499–505. <https://doi.org/10.1002/cnma.201800558>
- [115] W. Liu, C. Wang, D. Su, W. Qi, Oxidative dehydrogenation of ethylbenzene on nanocarbon: kinetics and reaction mechanism, Journal of Catalysis 368 (2018) 1–7.
<https://doi.org/10.1016/j.jcat.2018.09.023>
- [116] J. Zhang, X. Liu, R. Blume, A. Zhang, R. Schlögl, S.S. Dang, Surface-modified carbon nanotubes catalyze oxidative dehydrogenation of n-butane, Science 322 (2008) 73–77.
<https://doi.org/10.1126/science.1161916>
- [117] X. Liu, D.S. Su, R. Schlögl, Oxidative dehydrogenation of 1-butene to butadiene over carbon nanotube catalysts, Carbon 46 (2008) 547–549.
<https://doi.org/10.1016/j.carbon.2007.12.014>
- [118] Y. Chi, M. Zhu, Y. Li, H. Yu, H. Wang, F. Peng, The effect of surface oxygenated groups of carbon nanotubes on liquid phase catalytic oxidation of cumene, Catalysis Science & Technology 6 (2016) 2396–2402. <https://doi.org/10.1039/C5CY01631B>

- [119] X. Ren, C. Chen, M. Nagatsu, X. Wang, Carbon nanotubes as adsorbents in environmental pollution management: a review, *Chemical Engineering Journal* 170 (2011) 395–410. <https://doi.org/10.1016/j.cej.2010.08.045>
- [120] H.H. Cho, B.A. Smith, J.D. Wnuk, D.H. Fairbrother, W.P. Ball, Influence of surface oxides on the adsorption of naphthalene onto multiwalled carbon nanotubes, *Environmental Science & Technology* 42 (2008) 2899–2905. <https://doi.org/10.1021/es702363e>
- [121] Q. Liao, J. Sun, L. Gao, The adsorption of resorcinol from water using multi-walled carbon nanotubes, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 312 (2008) 160–165. <https://doi.org/10.1016/j.colsurfa.2007.06.045>
- [122] X. Yang, H. Yu, F. Peng, H. Wang, Confined iron nanowires enhance the catalytic activity of carbon nanotubes in the aerobic oxidation of cyclohexane, *ChemSusChem* 5 (2012) 1213–1217. <https://doi.org/10.1002/cssc.201100807>
- [123] Y. Su, Z. Chen, J. Huang, H. Wang, H. Yu, Q. Zhang, Y. Cao, F. Peng, Confined cobalt on carbon nanotubes in solvent-free aerobic oxidation of ethylbenzene: enhanced interfacial charge transfer, *ChemCatChem* 14 (2022) e202101378. <https://doi.org/10.1002/cctc.202101378>
- [124] J. Luo, H. Yu, H. Wang, F. Peng, Enhancing the catalytic activity of carbon nanotubes by filled iron nanowires for selective oxidation of ethylbenzene, *Catalysis Communications* 51 (2014) 77–81. <https://doi.org/10.1016/j.catcom.2014.03.031>
- [125] L. Fu, Y. Lu, Z. Liu, R. Zhu, Influence of the metal sites of MNC (M = Co, Fe, Mn) catalysts derived from metalloporphyrins in ethylbenzene oxidation, *Chinese Journal of Catalysis* 37 (2016) 398–404. [https://doi.org/10.1016/S1872-2067\(15\)60981-9](https://doi.org/10.1016/S1872-2067(15)60981-9)
- [126] K. Peckh, B. Orlńska, Transition metal salts of carboxylated multiwalled carbon nanotubes in combination with *N*-hydroxyphthalimide as catalytic systems for hydrocarbon oxidation, *Materials* 14 (2021) 2314. <https://doi.org/10.3390/ma14092314>

- [127] Y. Feng, A. Zeng, Selective liquid-phase oxidation of toluene with molecular oxygen catalyzed by Mn₃O₄ nanoparticles immobilized on CNTs under solvent-free conditions, *Catalysts* 10 (2020) 623. <https://doi.org/10.3390/catal10060623>
- [128] Z. Wang, Y. Qin, F. Pan, Z. Li, W. Zhang, F. Wu, D. Chen, W. Wen, J. Li, Mesoporous silica-supported manganese oxides for complete oxidation of volatile organic compounds: influence of mesostructure, redox properties, and hydrocarbon dimension, *Industrial & Engineering Chemistry Research* 57 (2018) 7374–7382. <https://doi.org/10.1021/acs.iecr.8b00630>
- [129] K. Machado, J. Mishra, S. Suzuki, G.S. Mishra, Synthesis of superparamagnetic carbon nanotubes immobilized Pt and Pd pincer complexes: highly active and selective catalysts towards cyclohexane oxidation with dioxygen, *Dalton Transactions* 43 (2014) 17475–17482. <https://doi.org/10.1039/C4DT02099E>
- [130] M. Araghi, F. Bokaei, Manganese(III) porphyrin supported on multi-wall carbon nanotubes: a highly efficient and reusable biomimetic catalyst for oxidative decarboxylation of α -arylcarboxylic acids and oxidation of alkanes with sodium periodate, *Polyhedron* 53 (2013) 15–19. <https://doi.org/10.1016/j.poly.2013.01.052>
- [131] B. Orlńska, I. Romanowska, *N*-Hydroxyphthalimide and transition metal salts as catalysts of the liquid-phase oxidation of 1-methoxy-4-(1-methylethyl) benzene with oxygen, *Open Chemistry* 9 (2011) 670–676. <https://doi.org/10.2478/s11532-011-0048-0>
- [132] N.V. Ulitin, K.A. Tereshchenko, N.A. Novikov, D.A. Shiyan, Y.L. Lyulinskaya, N.M. Nurullina, M.N. Denisova, V.I. Anisimova, T.S. Nurmurodov, K.E. Kharlampidi, Catalytic properties of metals of the 2nd and 12th groups in cumene oxidation, *Applied Catalysis A: General* 653 (2023) 119044. <https://doi.org/10.1016/j.apcata.2023.119044>
- [133] N. V Ulitin, K.E. Kharlampidi, K.A. Tereshchenko, N.A. Novikov, D.A. Shiyan, T.S. Nurmurodov, N.M. Nurullina, N.N. Ziyatdinov, N.P. Miroshkin, The cumene oxidation and cumene hydroperoxide decomposition in the presence of Zn, Cd or Hg 2-ethylhexanoate: kinetic model and analysis of its sensitivity, *Molecular Catalysis* 515 (2021) 111886. <https://doi.org/10.1016/j.mcat.2021.111886>

- [134] N. Turovskij, E. Raksha, Y. Berestneva, A. Eresko, Anion effect on the cumene hydroperoxide decomposition in the presence of Cu(II) 1,10-phenanthrolinates, *Journal of Organometallic Chemistry* 922 (2020) 121371. <https://doi.org/10.1016/j.jorganchem.2020.121371>
- [135] R.K. Srivastava, R.D. Srivastava, Kinetics of liquid phase oxidation of cumene with Cr_2O_3 , MnO_2 , and Fe_2O_3 catalysts, *Journal of Catalysis* 39 (1975) 390–396. [https://doi.org/10.1016/0021-9517\(75\)90297-3](https://doi.org/10.1016/0021-9517(75)90297-3)
- [136] X. Pan, X. Bao, The effects of confinement inside carbon nanotubes on catalysis, *Accounts of Chemical Research* 44 (2011) 553–562. <https://doi.org/10.1021/ar100160t>
- [137] T.T. Nguyen, P. Serp, Confinement of metal nanoparticles in carbon nanotubes, *ChemCatChem* 5 (2013) 3595–3603. <https://doi.org/10.1002/cctc.201300527>
- [138] Y. Chen, L. Fu, Z. Liu, Y. Wang, Ionic-liquid-derived boron-doped cobalt-coordinating nitrogen-doped carbon materials for enhanced catalytic activity, *ChemCatChem* 8 (2016) 1782–1787. <https://doi.org/10.1002/cctc.201600114>
- [139] Z. Chen, Y. Deng, G. Yang, Y.N. Zhu, Q. Zhang, Z. Liu, Y. Cao, F. Peng, Understanding of cumene oxidation catalyzed by metal-nitrogen-carbon through theoretical simulations and kinetic validation, *ACS Sustainable Chemistry & Engineering* 11 (2023) 5773–5781. <https://doi.org/10.1021/acssuschemeng.3c00676>
- [140] X. Pan, X. Bao, Reactions over catalysts confined in carbon nanotubes, *Chemical Communications* (2008) 6271–6281. <https://doi.org/10.1039/B810994J>
- [141] S.A. Miners, G.A. Rance, A.N. Khlobystov, Chemical reactions confined within carbon nanotubes, *Chemical Society Reviews* 45 (2016) 4727–4746. <https://doi.org/10.1039/C6CS00090H>
- [142] Z.-Q. Shi, Z.-P. Dong, J. Sun, F.-W. Zhang, H.-L. Yang, J.-H. Zhou, X.-H. Zhu, R. Li, Filled cobalt nanoparticles into carbon nanotubes as a rapid and high-efficiency catalyst for selective epoxidation of styrene with molecular oxygen, *Chemical Engineering Journal* 237 (2014) 81–87. <https://doi.org/10.1016/j.cej.2013.09.107>

- [143] G. Xiang, X. Wang, L. Zhang, Z. Liu, Influence of doping nitrogen on the catalytic performance of carbon nanotubes encapsulating cobalt for selective oxidation of arylalkanes, *Particuology* 58 (2021) 85–91. <https://doi.org/10.1016/j.partic.2021.02.002>
- [144] L. Zhao, Y. Zhang, L.B. Huang, X.Z. Liu, Q.H. Zhang, C. He, Z.Y. Wu, L.J. Zhang, J. Wu, W. Yang, L. Gu, J.S. Hu, L.J. Wan, Cascade anchoring strategy for general mass production of high-loading single-atomic metal-nitrogen catalysts, *Nature Communications* 10 (2019) 1278. <https://doi.org/10.1038/s41467-019-09290-y>
- [145] W. Yang, X. Liu, X. Yue, J. Jia, S. Guo, Bamboo-like carbon nanotube/Fe₃C nanoparticle hybrids and their highly efficient catalysis for oxygen reduction, *Journal of the American Chemical Society* 137 (2015) 1436–1439. <https://doi.org/10.1021/ja5129132>
- [146] S. Wang, L. Zhang, Z. Xia, A. Roy, D.W. Chang, J.B. Baek, L. Dai, BCN graphene as an efficient metal-free electrocatalyst for the oxygen reduction reaction, *Angewandte Chemie International Edition* 51 (2012) 4209–4212. <https://doi.org/10.1002/anie.201109257>
- [147] T.Y. Ma, S. Dai, M. Jaroniec, S.Z. Qiao, Graphitic carbon nitride nanosheet–carbon nanotube three-dimensional porous composites as high-performance oxygen evolution electrocatalysts, *Angewandte Chemie International Edition* 53 (2014) 7281–7285. <https://doi.org/10.1002/anie.201403946>
- [148] P. Zhou, B. Liu, J. Zhang, Y. Zhang, G. Zhang, C. Wei, J. Liang, Y. Liu, W. Zhang, Radicals induced from peroxomonosulfate by nanoscale zero-valent copper in the acidic solution, *Water Science and Technology* 74 (2016) 1971–1979. <https://doi.org/10.2166/wst.2016.381>
- [149] Y. Gao, Y. Chen, X. Ma, C. Chen, Collisional quenching of CCl₂ radicals in the A¹B¹ (0,4,0) and a³B¹ states by alcohols, *Chemical Physics Letters* 339 (2001) 209–215. [https://doi.org/10.1016/S0009-2614\(01\)00316-5](https://doi.org/10.1016/S0009-2614(01)00316-5)
- [150] C. Chen, F. Wang, Y. Chen, X. Ma, Temperature effect on quenching of CH(A²Δ), *Chemical Physics* 230 (1998) 317–325. [https://doi.org/10.1016/S0301-0104\(98\)00030-5](https://doi.org/10.1016/S0301-0104(98)00030-5)

- [151] C. Gong, F. Chen, Q. Yang, K. Luo, F. Yao, S. Wang, X. Wang, J. Wu, X. Li, D. Wang, G. Zeng, Heterogeneous activation of peroxymonosulfate by Fe-Co layered doubled hydroxide for efficient catalytic degradation of Rhoadmine B, *Chemical Engineering Journal* 321 (2017) 222–232. <https://doi.org/10.1016/j.cej.2017.03.117>
- [152] B. Chen, S. Li, S. Liu, M. Dong, B. Han, H. Liu, L. Zheng, Aerobic selective oxidation of methylaromatics to benzoic acids over Co@N/Co-CNTs with high loading CoN₄ species, *Journal of Materials Chemistry A* 7 (2019) 23543–23553. <https://doi.org/10.1039/C9TA10506A>
- [153] M. Biswal, V.V. Dhas, V.R. Mate, A. Banerjee, P. Pachfule, K.L. Agrawal, S.B. Ogale, C.V. Rode, Selectivity tailoring in liquid phase oxidation over MWNT-Mn₃O₄ nanocomposite catalysts, *Journal of Physical Chemistry C* 115 (2011) 14174–14184. <https://doi.org/10.1021/jp203318n>
- [154] E. Skliri, S. Papadogiorgakis, I.N. Lykakis, G.S. Armatas, Mesoporous assembled Mn₃O₄ nanoparticle networks as efficient catalysts for selective oxidation of alkenes and aryl alkanes, *ChemPlusChem* 82 (2017) 136–143. <https://doi.org/10.1002/cplu.201600460>
- [155] J. Gao, X. Tong, X. Li, H. Miao, J. Xu, The efficient liquid-phase oxidation of aromatic hydrocarbons by molecular oxygen in the presence of MnCO₃, *Journal of Chemical Technology and Biotechnology* 82 (2007) 620–625. <https://doi.org/10.1002/jctb.1717>
- [156] Y. Deng, Z. Chen, J. Huang, G. Yang, Q. Zhang, Z. Liu, Y. Cao, F. Peng, MnO₂ nanoparticles supported on CNTs for cumene oxidation: synergistic effect and kinetic modelling, *Chemical Engineering Journal* 444 (2022) 136666. <https://doi.org/10.1016/j.cej.2022.136666>
- [157] G. Ovejero, J.L. Sotelo, M.D. Romero, A. Rodríguez, M.A. Ocana, G. Rodríguez, J. García, Multiwalled carbon nanotubes for liquid-phase oxidation. Functionalization, characterization, and catalytic activity, *Industrial & Engineering Chemistry Research* 45 (2006) 2206–2212. <https://doi.org/10.1021/ie051079p>

- [158] Z. Chen, Y. Li, Y. Cao, Q. Zhang, H. Yu, F. Peng, Inhibitory effect of Zn^{2+} on the chain-initiation process of cumene oxidation, *International Journal of Quantum Chemistry* 121 (2021) e26780. <https://doi.org/10.1002/qua.26780>
- [159] J. Deng, Y. Li, Y. Cao, H. Wang, H. Yu, Q. Zhang, J. Zuo, F. Peng, Trace amounts of $\text{Cu}(\text{OAc})_2$ boost the efficiency of cumene oxidation catalyzed by carbon nanotubes washed with HCl, *Catalysis Science & Technology* 10 (2020) 2523–2530. <https://doi.org/10.1039/C9CY02536G>
- [160] N. Sezer, M. Koç, Oxidative acid treatment of carbon nanotubes, *Surfaces and Interfaces* 14 (2019) 1–8. <https://doi.org/10.1016/j.surfin.2018.11.001>
- [161] T.G. Ros, A.J. Van Dillen, J.W. Geus, D.C. Koningsberger, Surface oxidation of carbon nanofibres, *Chemistry – A European Journal* 8 (2002) 1151–1162. [https://doi.org/10.1002/1521-3765\(20020301\)8:5%3C1151::AID-CHEM1151%3E3.0.CO;2-%23](https://doi.org/10.1002/1521-3765(20020301)8:5%3C1151::AID-CHEM1151%3E3.0.CO;2-%23)
- [162] I.D. Rosca, F. Watari, M. Uo, T. Akasaka, Oxidation of multiwalled carbon nanotubes by nitric acid, *Carbon* 43 (2005) 3124–3131. <https://doi.org/10.1016/j.carbon.2005.06.019>
- [163] P.-X. Hou, C. Liu, H.-M. Cheng, Purification of carbon nanotubes, *Carbon* 46 (2008) 2003–2025. <https://doi.org/10.1016/j.carbon.2008.09.009>
- [164] Y. Ishii, S. Sakaguchi, Recent progress in aerobic oxidation of hydrocarbons by *N*-hydroxyimides, *Catalysis Today* 117 (2006) 105–113. <https://doi.org/10.1016/j.cattod.2006.05.006>
- [165] C. Punta, C. Gambarotti, *N*-Hydroxy derivatives: key organocatalysts for the selective free radical aerobic oxidation of organic compounds, *Ideas in Chemistry and Molecular Sciences: Advances in Synthetic Chemistry* (2010) 1–24. <https://doi.org/10.1002/9783527630554.ch1>
- [166] S. Coseri, Phthalimide-*N*-oxyl (PINO) radical, a powerful catalytic agent: its generation and versatility towards various organic substrates, *Catalysis Reviews* 51 (2009) 218–292. <https://doi.org/10.1080/01614940902743841>

- [167] S. Coseri, *N*-Hydroxyphthalimide (NHPI)/lead tetraacetate, a peculiar system for the phthalimide-*N*-oxyl (PINO) radical generation, *Mini-Reviews in Organic Chemistry* 5 (2008) 222–227. <https://doi.org/10.2174/157019308785161675>
- [168] C. Galli, P. Gentili, O. Lanzalunga, Hydrogen abstraction and electron transfer with aminoxyl radicals: synthetic and mechanistic issues, *Angewandte Chemie International Edition* 47 (2008) 4790–4796. <https://doi.org/10.1002/anie.200704292>
- [169] L. Melone, C. Punta, Metal-free aerobic oxidations mediated by *N*-hydroxyphthalimide. A concise review, *Beilstein Journal of Organic Chemistry* 9 (2013) 1296–1310. <https://doi.org/10.3762/bjoc.9.146>
- [170] L. Melone, C. Punta, *N*-Hydroxyphthalimide (NHPI)-organocatalyzed aerobic oxidations: advantages, limits, and industrial perspectives, *Liquid Phase Aerobic Oxidation Catalysis: Industrial Applications and Academic Perspectives* (2016) 253–265. <https://doi.org/10.1002/9783527690121.ch16>
- [171] M.A. Andrade, L.M. Martins, Organocatalysis meets hydrocarbon oxyfunctionalization: the role of *N*-hydroxyimides, *European Journal of Organic Chemistry* 2021 (2021) 4715–4727. <https://doi.org/10.1002/ejoc.202100479>
- [172] E. Grochowski, T. Bolesławska, J. Jurczak, Reaction of diethyl azodicarboxylate with ethers in the presence of *N*-hydroxyimides as catalysts, *Synthesis* 1977 (1977) 718–720. DOI: 10.1055/s-1977-24550
- [173] M. Masui, T. Ueshima, S. Ozaki, *N*-Hydroxyphthalimide as an effective mediator for the oxidation of alcohols by electrolysis, *Journal of the Chemical Society, Chemical Communications* (1983) 479–480. <https://doi.org/10.1039/C39830000479>
- [174] Y. Ishii, K. Nakayama, M. Takeno, S. Sakaguchi, T. Iwahama, Y. Nishiyama, Novel catalysis by *N*-hydroxyphthalimide in the oxidation of organic substrates by molecular oxygen, *Journal of Organic Chemistry* 60 (1995) 3934–3935. <https://doi.org/10.1021/jo00118a002>

- [175] R. Nakamura, Y. Obora, Y. Ishii, Selective oxidation of acetophenones bearing various functional groups to benzoic acid derivatives with molecular oxygen, *Advanced Synthesis & Catalysis* 351 (2009) 1677–1684. <https://doi.org/10.1002/adsc.200900099>
- [176] Z. Du, Z. Sun, W. Zhang, H. Miao, H. Ma, J. Xu, A free radical process for oxidation of hydrocarbons promoted by nonmetal xanthone and tetramethylammonium chloride under mild conditions, *Tetrahedron Letters* 50 (2009) 1677–1680. <https://doi.org/10.1016/j.tetlet.2009.01.077>
- [177] I. Hermans, L. Vereecken, P.A. Jacobs, J. Peeters, Mechanism of the catalytic oxidation of hydrocarbons by *N*-hydroxyphthalimide: a theoretical study, *Chemical Communications* (2004) 1140–1141. <https://doi.org/10.1039/B401050G>
- [178] O. Kushch, I. Hordieieva, K. Novikova, Y. Litvinov, M. Kompanets, A. Shendrik, I. Opeida, Kinetics of *N*-oxyl radicals' decay, *Journal of Organic Chemistry* 85 (2020) 7112–7124. <https://doi.org/10.1021/acs.joc.0c00506>
- [179] M. Caruso, S. Navalón, M. Cametti, A. Dhakshinamoorthy, C. Punta, H. García, Challenges and opportunities for *N*-hydroxyphthalimide supported over heterogeneous solids for aerobic oxidations, *Coordination Chemistry Reviews* 486 (2023) 215141. <https://doi.org/10.1016/j.ccr.2023.215141>
- [180] Z.-X. Wu, G.-W. Hu, Y.-X. Luan, Development of *N*-hydroxy catalysts for C–H functionalization via hydrogen atom transfer: challenges and opportunities, *ACS Catalysis* 12 (2022) 11716–11733. <https://doi.org/10.1021/acscatal.2c03261>
- [181] M. Caruso, M. Petroselli, M. Cametti, Design and synthesis of multipurpose derivatives for *N*-hydroxyimide and NHPI-based catalysis applications, *ChemistrySelect* 6 (2021) 12975–12980. <https://doi.org/10.1002/slct.202103792>
- [182] R. Amorati, M. Lucarini, V. Mugnaini, G.F. Pedulli, F. Minisci, F. Recupero, F. Fontana, P. Astolfi, L. Greci, Hydroxylamines as oxidation catalysts: thermochemical and kinetic studies, *Journal of Organic Chemistry* 68 (2003) 1747–1754. <https://doi.org/10.1021/jo026660z>

- [183] F. Minisci, F. Recupero, G.F. Pedulli, M. Lucarini, Transition metal salts catalysis in the aerobic oxidation of organic compounds: thermochemical and kinetic aspects and new synthetic developments in the presence of *N*-hydroxy-derivative catalysts, *Journal of Molecular Catalysis A: Chemical* 204–205 (2003) 63–90. [https://doi.org/10.1016/S1381-1169\(03\)00286-3](https://doi.org/10.1016/S1381-1169(03)00286-3)
- [184] C. Miao, H. Zhao, Q. Zhao, C. Xia, W. Sun, NHPI and ferric nitrate: a mild and selective system for aerobic oxidation of benzylic methylenes, *Catalysis Science & Technology* 6 (2016) 1378–1383. <https://doi.org/10.1039/C5CY01245G>
- [185] B. Orlńska, J. Zawadiak, Aerobic oxidation of isopropylaromatic hydrocarbons to hydroperoxides catalyzed by *N*-hydroxyphthalimide, *Reaction Kinetics, Mechanisms and Catalysis* 110 (2013) 15–30. <https://doi.org/10.1007/s11144-013-0581-2>
- [186] Y. Tashiro, T. Iwahama, S. Sakaguchi, Y. Ishii, A new strategy for the preparation of terephthalic acid by the aerobic oxidation of *p*-xylene using *N*-hydroxyphthalimide as a catalyst, *Advanced Synthesis & Catalysis* 343 (2001) 220–225. [https://doi.org/10.1002/1615-4169\(20010226\)343:2%3C220::AID-ADSC220%3E3.0.CO;2-N](https://doi.org/10.1002/1615-4169(20010226)343:2%3C220::AID-ADSC220%3E3.0.CO;2-N)
- [187] Y. Ishii, S. Sakaguchi, A new strategy for alkane oxidation with O₂ using *N*-hydroxyphthalimide (NHPI) as a radical catalyst, *Catalysis Surveys from Asia* 3 (1999) 27–35. <https://doi.org/10.1023/A:1019059315516>
- [188] I.A. Opeida, A.L. Plekhov, O.V. Kushch, M.A. Kompanets, On the mechanism of oxidation process initiation by the *N*-hydroxyphthalimide-cobalt(II) acetate system, *Russian Journal of Physical Chemistry A* 86 (2012) 366–368. DOI: 10.1134/S0036024412030235
- [189] M. Petroselli, L. Melone, M. Cametti, C. Punta, Lipophilic *N*-hydroxyphthalimide catalysts for the aerobic oxidation of cumene: towards solvent-free conditions and back, *Chemistry – A European Journal* 23 (2017) 10616–10625. <https://doi.org/10.1002/chem.201701573>
- [190] L. Melone, S. Prosperini, G. Ercole, N. Pastori, C. Punta, Is it possible to implement *N*-hydroxyphthalimide homogeneous catalysis for industrial applications? A case study of

- cumene aerobic oxidation, *Journal of Chemical Technology & Biotechnology* 89 (2014) 1370–1378. <https://doi.org/10.1002/jctb.4213>
- [191] Y. Ishii, T. Iwahama, S. Sakaguchi, K. Nakayama, Y. Nishiyama, Alkane oxidation with molecular oxygen using a new efficient catalytic system: *N*-hydroxyphthalimide (NHPI) combined with $\text{Co}(\text{acac})_n$ ($n = 2$ or 3), *Journal of Organic Chemistry* 61 (1996) 4520–4526. <https://doi.org/10.1021/jo951970l>
- [192] Y. Yoshino, Y. Hayashi, T. Iwahama, S. Sakaguchi, Y. Ishii, Catalytic oxidation of alkylbenzenes with molecular oxygen under normal pressure and temperature by *N*-hydroxyphthalimide combined with $\text{Co}(\text{OAc})_2$, *Journal of Organic Chemistry* 62 (1997) 6810–6813. <https://doi.org/10.1021/jo9710571>
- [193] Y. Ishii, S. Sakaguchi, T. Iwahama, Innovation of hydrocarbon oxidation with molecular oxygen and related reactions, *Advanced Synthesis & Catalysis* 343 (2001) 393–427. [https://doi.org/10.1002/1615-4169\(200107\)343:5%3C393::AID-ADSC393%3E3.0.CO;2-K](https://doi.org/10.1002/1615-4169(200107)343:5%3C393::AID-ADSC393%3E3.0.CO;2-K)
- [194] O. Fukuda, S. Sakaguchi, Y. Ishii, Preparation of hydroperoxides by *N*-hydroxyphthalimide-catalyzed aerobic oxidation of alkylbenzenes and hydroaromatic compounds and its application, *Advanced Synthesis & Catalysis* 343 (2001) 809–813. [https://doi.org/10.1002/1615-4169\(20011231\)343:8%3C809::AID-ADSC809%3E3.0.CO;2-1](https://doi.org/10.1002/1615-4169(20011231)343:8%3C809::AID-ADSC809%3E3.0.CO;2-1)
- [195] I.W.C.E. Arends, M. Sasidharan, A. Kühnle, M. Duda, C. Jost, R.A. Sheldon, Selective catalytic oxidation of cyclohexylbenzene to cyclohexylbenzene-1-hydroperoxide: a coproduct-free route to phenol, *Tetrahedron* 58 (2002) 9055–9061. [https://doi.org/10.1016/S0040-4020\(02\)01131-6](https://doi.org/10.1016/S0040-4020(02)01131-6)
- [196] I.W.C.E. Arends, M. Sasidharan, S. Chatel, R.A. Sheldon, C. Jost, M. Duda, A. Kühnle, Highly selective catalytic oxidation of alkylbenzenes to the corresponding hydroperoxides, *Catalysis of Organic Reactions* (2002) 143–150.
- [197] G.N. Koshel', E.V. Smirnova, E.A. Kurganova, I.D. Ekimova, N.V. Lebedeva, S.G. Koshel', V.V. Plakhtinskii, Intensifying the oxidation of isopropylbenzene, *Catalysis in Industry* 2 (2010) 255–258. <https://doi.org/10.1134/S2070050410030086>

- [198] G.N. Koshel', E.V. Smirnova, E.A. Kurganova, Y.B. Rumyantseva, V.V. Plakhtinskii, S.G. Koshel', Liquid-phase oxidation of isopropylbenzene in the presence of *N*-hydroxyphthalimide, *Catalysis in Industry* 4 (2012) 96–99. <https://doi.org/10.1134/S2070050412020080>
- [199] V.N. Sapunov, G.N. Koshel', Y.B. Rumyantseva, E.A. Kurganova, N.D. Kukushkina, The role of *N*-hydroxyphthalimide in the reaction mechanism of liquid-phase oxidation of *p*-cymene, *Petroleum Chemistry* 53 (2013) 171–176. <https://doi.org/10.1134/S0965544113030092>
- [200] V.N. Sapunov, E.A. Kurganova, G.N. Koshel, Kinetics and mechanism of cumene oxidation initiated by *N*-hydroxyphthalimide, *International Journal of Chemical Kinetics* 50 (2018) 3–14. <https://doi.org/10.1002/kin.21135>
- [201] A.S. Frolov, E.A. Kurganova, V.N. Sapunov, R.A. Kozlovskii, G.N. Koshel', E.M. Yarkina, Kinetic laws of oxidation of para-tert-butylcumene in the presence of *N*-hydroxyphthalimide, *Kinetics and Catalysis* 64 (2023) 750–758. <https://doi.org/10.1134/S0023158423060034>
- [202] E. Baciocchi, M.F. Gerini, O. Lanzalunga, Reactivity of phthalimide *N*-oxyl radical (PINO) toward the phenolic O–H bond. A kinetic study, *Journal of Organic Chemistry* 69 (2004) 8963–8966. <https://doi.org/10.1021/jo048656o>
- [203] A.D. Cohen, B.-B. Zeng, S.B. King, J.P. Toscano, Direct observation of an acyl nitroso species in solution by time-resolved IR spectroscopy, *Journal of the American Chemical Society* 125 (2003) 1444–1445. <https://doi.org/10.1021/ja028936f>
- [204] N. Koshino, B. Saha, J.H. Espenson, Kinetic study of the phthalimide *N*-oxyl radical in acetic acid. Hydrogen abstraction from substituted toluenes, benzaldehydes, and benzyl alcohols, *Journal of Organic Chemistry* 68 (2003) 9364–9370. <https://doi.org/10.1021/jo0348017>
- [205] C. Ueda, M. Noyama, H. Ohmori, M. Masui, Reactivity of phthalimide-*N*-oxyl: a kinetic study, *Chemical & Pharmaceutical Bulletin* 35 (1987) 1372–1377. <https://doi.org/10.1248/cpb.35.1372>

- [206] B.B. Wentzel, M.P.J. Donners, P.L. Alsters, M.C. Feiters, R.J.M. Nolte, *N*-Hydroxyphthalimide/cobalt(II) catalyzed low temperature benzylic oxidation using molecular oxygen, *Tetrahedron* 56 (2000) 7797–7803. [https://doi.org/10.1016/S0040-4020\(00\)00679-7](https://doi.org/10.1016/S0040-4020(00)00679-7)
- [207] X. Baucherel, I.W.C.E. Arends, S. Ellwood, R.A. Sheldon, A new catalytic system for the selective aerobic oxidation of large ring cycloalkanes to ketones, *Organic Process Research & Development* 7 (2003) 426–428. <https://doi.org/10.1021/op0340199>
- [208] N. Hirai, N. Sawatari, N. Nakamura, S. Sakaguchi, Y. Ishii, Oxidation of substituted toluenes with molecular oxygen in the presence of *N,N',N''*-trihydroxyisocyanuric acid as a key catalyst, *Journal of Organic Chemistry* 68 (2003) 6587–6590. <https://doi.org/10.1021/jo034313z>
- [209] C. Annunziatini, M.F. Gerini, O. Lanzalunga, M. Lucarini, Aerobic oxidation of benzyl alcohols catalyzed by aryl substituted *N*-hydroxyphthalimides. Possible involvement of a charge-transfer complex, *Journal of Organic Chemistry* 69 (2004) 3431–3438. <https://doi.org/10.1021/jo049887y>
- [210] M. Nechab, C. Einhorn, J. Einhorn, New aerobic oxidation of benzylic compounds: efficient catalysis by *N*-hydroxy-3,4,5,6-tetraphenylphthalimide (NHTPPI)/CuCl under mild conditions and low catalyst loading, *Chemical Communications* (2004) 1500–1501. <https://doi.org/10.1039/B403004D>
- [211] O.V. Kushch, Effect of the structure of *N*-hydroxyphthalimides on their catalytic activity in the oxidation of isopropylbenzene in the presence of cuprous salts, *Theoretical and Experimental Chemistry* 48 (2012) 252–257. <https://doi.org/10.1007/s11237-012-9269-3>
- [212] Q. Zhang, C. Chen, H. Ma, H. Miao, W. Zhang, Z. Sun, J. Xu, Efficient metal-free aerobic oxidation of aromatic hydrocarbons utilizing aryl-tetrahalogenated *N*-hydroxyphthalimides and 1,4-diamino-2,3-dichloroanthraquinone, *Journal of Chemical Technology & Biotechnology* 83 (2008) 1364–1369. <https://doi.org/10.1002/jctb.1977>
- [213] H. Wang, Q. Zhang, Z. Zhu, Y. Yang, Y. Ye, Z. Lv, C. Chen, High-efficient metal-free aerobic oxidation of aromatic hydrocarbons by *N,N*-dihydroxypyromellitimide and 1,4-

- diamino-2,3-dichloroanthraquinone, *Molecular Catalysis* 518 (2022) 112078. <https://doi.org/10.1016/j.mcat.2021.112078>
- [214] Y. Sun, W. Zhang, X. Hu, H. Li, Correlation analysis of the substituent electronic effects on the allylic H-abstraction in cyclohexene by phthalimide-*N*-oxyl radicals: A DFT study, *Journal of Physical Chemistry B* 114 (2010) 4862–4869. <https://doi.org/10.1021/jp911778k>
- [215] A. Shibamoto, S. Sakaguchi, Y. Ishii, Aerobic oxidation of ethane to acetic acid catalyzed by *N,N'*-dihydroxypyromellitimide combined with Co species, *Tetrahedron Letters* 43 (2002) 8859–8861. [https://doi.org/10.1016/S0040-4039\(02\)02197-1](https://doi.org/10.1016/S0040-4039(02)02197-1)
- [216] K.V. Novikova, M.O. Kompanets, O.V. Kushch, S.P. Kobzev, M.M. Khlietov, I.O. Opeida, Substituted *N*-hydroxyphthalimides as oxidation catalysts, *Reaction Kinetics, Mechanisms and Catalysis* 103 (2011) 31–40. <https://doi.org/10.1007/s11144-011-0289-0>
- [217] N. Sawatari, T. Yokota, S. Sakaguchi, Y. Ishii, Alkane oxidation with air catalyzed by lipophilic *N*-hydroxyphthalimides without any solvent, *Journal of Organic Chemistry* 66 (2001) 7889–7891. <https://doi.org/10.1021/jo010668v>
- [218] S.K. Guha, Y. Obora, D. Ishihara, H. Matsubara, I. Ryu, Y. Ishii, Aerobic oxidation of cyclohexane using *N*-hydroxyphthalimide bearing fluoroalkyl chains, *Advanced Synthesis & Catalysis* 350 (2008) 1323–1330. <https://doi.org/10.1002/adsc.200800057>
- [219] M. Petroselli, P. Franchi, M. Lucarini, C. Punta, L. Melone, Aerobic oxidation of alkylaromatics using a lipophilic *N*-hydroxyphthalimide: overcoming the industrial limit of catalyst solubility, *ChemSusChem* 7 (2014) 2695–2703. <https://doi.org/10.1002/cssc.201402393>
- [220] K. Kasperczyk, B. Orlińska, J. Zawadiak, Aerobic oxidation of cumene catalysed by 4-alkyloxycarbonyl-*N*-hydroxyphthalimide, *Open Chemistry* 12 (2014) 1176–1182. <https://doi.org/10.2478/s11532-014-0565-8>
- [221] T. Kaneiwa, K. Yamada, R. Nakano, M. Yamashita, Lipophilic *N*-hydroxyimide derivatives: design, synthesis, and application to aerobic alkane oxidation under neat

- p>conditions, ChemPlusChem 88 (2023) e202200380.
-
- <https://doi.org/10.1002/cplu.202200380>
- [222] N. Taha, Y. Sasson, Superior performance of NHPI cocatalyst in the autoxidation of methylbenzenes under solvent-free phase transfer conditions, Organic Process Research & Development 14 (2010) 701–704. <https://doi.org/10.1021/op100027s>
- [223] R.D. Patil, B. Fuchs, N. Taha, Y. Sasson, Solvent-free and selective autooxidation of alkylbenzenes catalyzed by Co/NHPI under phase transfer conditions, ChemistrySelect 1 (2016) 3791–3796. <https://doi.org/10.1002/slct.201600913>
- [224] C. Chiappe, D. Pieraccini, Ionic liquids: solvent properties and organic reactivity, Journal of Physical Organic Chemistry 18 (2005) 275–297. <https://doi.org/10.1002/poc.863>
- [225] R.D. Rogers, K.R. Seddon, Ionic liquids — solvents of the future?, Science 302 (2003) 792–793. <https://doi.org/10.1126/science.1090313>
- [226] M.J. Earle, K.R. Seddon, Ionic liquids. Green solvents for the future, Pure and Applied Chemistry 72 (2000) 1391–1398. <https://doi.org/10.1351/pac200072071391>
- [227] S. Mallakpour, M. Dinari, Ionic liquids as green solvents: progress and prospects, Green Solvents II: Properties and Applications of Ionic Liquids (2012) 1–32. https://doi.org/10.1007/978-94-007-2891-2_1
- [228] Z. Lei, B. Chen, Y.-M. Koo, D.R. MacFarlane, Introduction: ionic liquids, Chemical Reviews 117 (2017) 6633–6635. <https://doi.org/10.1021/acs.chemrev.7b00246>
- [229] H. Weingärtner, Understanding ionic liquids at the molecular level: facts, problems, and controversies, Angewandte Chemie International Edition 47 (2008) 654–670. <https://doi.org/10.1002/anie.200604951>
- [230] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis, Inorganic Chemistry 21 (1982) 1263–1264. <https://doi.org/10.1021/ic00133a078>

- [231] J.S. Wilkes, M.J. Zaworotko, Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids, *Journal of the Chemical Society, Chemical Communications* (1992) 965–967. <https://doi.org/10.1039/C39920000965>
- [232] J.H. Davis Jr., Task-specific ionic liquids, *Chemistry Letters* 33 (2004) 1072–1077. <https://doi.org/10.1246/cl.2004.1072>
- [233] D.D. Patel, J. Lee, Applications of ionic liquids, *The Chemical Record* 12 (2012) 329–355. <https://doi.org/10.1002/tcr.201100036>
- [234] N.V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry, *Chemical Society Reviews* 37 (2008) 123–150. DOI: [10.1039/B006677J](https://doi.org/10.1039/B006677J)
- [235] K.R. Seddon, A. Stark, Selective catalytic oxidation of benzyl alcohol and alkylbenzenes in ionic liquids, *Green Chemistry* 4 (2002) 119–123. <https://doi.org/10.1039/B111160B>
- [236] Y. Meng, B. Liang, S. Tang, A study on the liquid-phase oxidation of toluene in ionic liquids, *Applied Catalysis A: General* 439–440 (2012) 1–7. <https://doi.org/10.1016/j.apcata.2012.06.026>
- [237] Z. Li, C.-G. Xia, Oxidation of hydrocarbons with iodobenzene diacetate catalyzed by manganese(III) porphyrins in a room temperature ionic liquid, *Journal of Molecular Catalysis A: Chemical* 214 (2004) 95–101. <https://doi.org/10.1016/j.molcata.2004.01.012>
- [238] C. Chiappe, A. Sanzone, P.J. Dyson, Styrene oxidation by hydrogen peroxide in ionic liquids: the role of the solvent on the competition between two Pd-catalyzed processes, oxidation and dimerization, *Green Chemistry* 13 (2011) 1437–1441. <https://doi.org/10.1039/C0GC00881H>
- [239] S. Baj, A. Chrobok, Autooxidation of hydrocarbons with oxygen in ionic liquids as solvents, *International Journal of Chemical Kinetics* 40 (2008) 287–293. <https://doi.org/10.1002/kin.20315>

- [240] S. Xu, J. Zhang, B. Chen, Z. Lei, Process intensification on the selective catalytic oxidation of cumene with ionic liquids, *Chemical Engineering and Processing: Process Intensification* 130 (2018) 88–92. <https://doi.org/10.1016/j.cep.2018.06.003>
- [241] J.-R. Wang, L. Liu, Y.-F. Wang, Y. Zhang, W. Deng, Q.-X. Guo, Aerobic oxidation with *N*-hydroxyphthalimide catalysts in ionic liquid, *Tetrahedron Letters* 46 (2005) 4647–4651. <https://doi.org/10.1016/j.tetlet.2005.04.114>
- [242] D.S. Choi, D.H. Kim, U.S. Shin, R.R. Deshmukh, S. Lee, C.E. Song, The dramatic acceleration effect of imidazolium ionic liquids on electron transfer reactions, *Chemical Communications* (2007) 3467–3469. <https://doi.org/10.1039/B708044A>
- [243] S. Koguchi, T. Kitazume, Synthetic utilities of ionic liquid-supported NHPI complex, *Tetrahedron Letters* 47 (2006) 2797–2801. <https://doi.org/10.1016/j.tetlet.2006.02.148>
- [244] T. Lu, M. Lu, W. Yu, Z. Liu, Remarkable effect of PEG-1000-based dicationic ionic liquid for *N*-hydroxyphthalimide-catalyzed aerobic selective oxidation of alkylaromatics, *Croatica Chemica Acta* 85 (2012) 277–282. <https://doi.org/10.5562/cca2006>
- [245] G. Dobras, B. Orlńska, Aerobic oxidation of alkylaromatic hydrocarbons to hydroperoxides catalysed by *N*-hydroxyimides in ionic liquids as solvents, *Applied Catalysis A: General* 561 (2018) 59–67. <https://doi.org/10.1016/j.apcata.2018.05.019>
- [246] S. Xu, C. Huang, J. Zhang, J. Liu, B. Chen, Catalytic oxidation of 1,3-diisopropylbenzene using imidazolium ionic liquid as catalyst, *Korean Journal of Chemical Engineering* 26 (2009) 985–989. <https://doi.org/10.1007/s11814-009-0164-0>
- [247] L. Ding, X. Sun, C. Huang, J. Li, B. Chen, Insights into the mechanism of cumene catalytic oxidation using ionic liquid [Bmim]OH, *Molecular Catalysis* 538 (2023) 113008. <https://doi.org/10.1016/j.mcat.2023.113008>
- [248] T. Chen, J. Zhou, S. Xu, C. Huang, X. Sun, Experimental and theoretical studies on 1-butyl-3-methyl imidazolium bromine ionic liquids-promoted conversion of aerobic oxidation of cumene, *Catalysis Communications* 187 (2024) 106842. <https://doi.org/10.1016/j.catcom.2024.106842>

- [249] S. Mahmood, B.-H. Xu, T.-L. Ren, Z.-B. Zhang, X.-M. Liu, S.-J. Zhang, Cobalt/*N*-hydroxyphthalimide (NHPI)-catalyzed aerobic oxidation of hydrocarbons with ionic liquid additive, *Molecular Catalysis* 447 (2018) 90–96. <https://doi.org/10.1016/j.mcat.2017.12.028>
- [250] S.A. Pillai, V.I. Patel, D. Ray, J.K. Parikh, V.K. Aswal, P. Bahadur, Microstructural micellar transition in bile salt–ionic liquid mixed systems in water: a DLS and SANS study, *RSC Advances* 6 (2016) 108488–108497. <https://doi.org/10.1039/C6RA22418K>
- [251] C. Jungnickel, J. Łuczak, J. Ranke, J.F. Fernández, A. Müller, J. Thöming, Micelle formation of imidazolium ionic liquids in aqueous solution, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 316 (2008) 278–284. <https://doi.org/10.1016/j.colsurfa.2007.09.020>
- [252] B. Dong, X. Zhao, L. Zheng, J. Zhang, N. Li, T. Inoue, Aggregation behavior of long-chain imidazolium ionic liquids in aqueous solution: micellization and characterization of micelle microenvironment, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 317 (2008) 666–672. <https://doi.org/10.1016/j.colsurfa.2007.12.001>
- [253] A. Mezzetta, J. Łuczak, J. Woch, C. Chiappe, J. Nowicki, L. Guazzelli, Surface active fatty acid ILs: influence of the hydrophobic tail and/or the imidazolium hydroxyl functionalization on aggregates formation, *Journal of Molecular Liquids* 289 (2019) 111155. <https://doi.org/10.1016/j.molliq.2019.111155>
- [254] A. Cognigni, P. Gaertner, R. Zirbs, H. Peterlik, K. Prochazka, C. Schröder, K. Bica, Surface-active ionic liquids in micellar catalysis: impact of anion selection on reaction rates in nucleophilic substitutions, *Physical Chemistry Chemical Physics* 18 (2016) 13375–13384. DOI: [10.1039/C6CP00493H](https://doi.org/10.1039/C6CP00493H)
- [255] K. Dong, X. Liu, H. Dong, X. Zhang, S. Zhang, Multiscale studies on ionic liquids, *Chemical Reviews* 117 (2017) 6636–6695. <https://doi.org/10.1021/acs.chemrev.6b00776>
- [256] M. McCutchen, L.G. Chen, H. Bermudez, S. Matysiak, Interplay of dynamical properties between ionic liquids and ionic surfactants: mechanism and aggregation,

- Journal of Physical Chemistry B 119 (2015) 9925–9932.
<https://doi.org/10.1021/acs.jpcb.5b03799>
- [257] G. Dobras, M. Sitko, M. Petroselli, M. Caruso, M. Cametti, C. Punta, B. Orlńska, Solvent-free aerobic oxidation of ethylbenzene promoted by NHPI/Co(II) catalytic system: the key role of ionic liquids, *ChemCatChem* 12 (2020) 259–266.
<https://doi.org/10.1002/cctc.201901406>
- [258] G. Talik, B. Orlńska, New evidence for the key role of hydrogen bonding between *N*-hydroxyphthalimide and halide ionic liquids in hydrocarbons oxidation, *ChemCatChem* 13 (2021) 4578–4590. <https://doi.org/10.1002/cctc.202101061>
- [259] L. Ding, X. Sun, C. Huang, J. Li, B. Chen, Cooperative effect of NHPI and BmimBr for promoting cumene catalytic oxidation, *Applied Catalysis A: General* 679 (2024) 119731. <https://doi.org/10.1016/j.apcata.2024.119731>
- [260] O. Bartlewicz, I. Dąbek, A. Szymańska, H. Maciejewski, Heterogeneous catalysis with the participation of ionic liquids, *Catalysts* 10 (2020) 1227.
<https://doi.org/10.3390/catal10111227>
- [261] H.-P. Steinrück, P. Wasserscheid, Ionic liquids in catalysis, *Catalysis Letters* 145 (2015) 380–397. <https://doi.org/10.1007/s10562-014-1435-x>
- [262] C.P. Mehnert, R.A. Cook, N.C. Dispenziere, M. Afeworki, Supported ionic liquid catalysis – a new concept for homogeneous hydroformylation catalysis, *Journal of the American Chemical Society* 124 (2002) 12932–12933.
<https://doi.org/10.1021/ja0279865>
- [263] C.P. Mehnert, E.J. Mozeleski, R.A. Cook, Supported ionic liquid catalysis investigated for hydrogenation reactions, *Chemical Communications* (2002) 3010–3011.
<https://doi.org/10.1039/B210241K>
- [264] A. Riisager, P. Wasserscheid, R. van Hal, R. Fehrmann, Continuous fixed-bed gas-phase hydroformylation using supported ionic liquid-phase (SILP) Rh catalysts, *Journal of Catalysis* 219 (2003) 452–455. [https://doi.org/10.1016/S0021-9517\(03\)00256-7](https://doi.org/10.1016/S0021-9517(03)00256-7)

- [265] A. Riisager, K.M. Eriksen, P. Wasserscheid, R. Fehrmann, Propene and 1-octene hydroformylation with silica-supported, ionic liquid-phase (SILP) Rh-phosphine catalysts in continuous fixed-bed mode, *Catalysis Letters* 90 (2003) 149–153. <https://doi.org/10.1023/B:CATL.00000004109.46005.be>
- [266] U. Kernchen, B. Etzold, W. Korth, A. Jess, Solid catalyst with ionic liquid layer (SCILL) – a new concept to improve selectivity illustrated by hydrogenation of cyclooctadiene, *Chemical Engineering & Technology* 30 (2007) 985–994. <https://doi.org/10.1002/ceat.200700050>
- [267] I. Podolean, O.D. Pavel, H.G. Manyar, S.F.R. Taylor, K. Ralphs, P. Goodrich, V.I. Pârvolescu, C. Hardacre, SCILLs as selective catalysts for the oxidation of aromatic alcohols, *Catalysis Today* 333 (2019) 140–146. <https://doi.org/10.1016/j.cattod.2018.05.035>
- [268] J. Arras, M. Steffan, Y. Shayeghi, D. Ruppert, P. Claus, Regioselective catalytic hydrogenation of citral with ionic liquids as reaction modifiers, *Green Chemistry* 11 (2009) 716–723. <https://doi.org/10.1039/B822992A>
- [269] J. Arras, M. Steffan, Y. Shayeghi, P. Claus, The promoting effect of a dicyanamide based ionic liquid in the selective hydrogenation of citral, *Chemical Communications* (2008) 4058–4060. <https://doi.org/10.1039/B810291K>
- [270] B. Karimi, E. Badreh, SBA-15-functionalized TEMPO confined ionic liquid: an efficient catalyst system for transition-metal-free aerobic oxidation of alcohols with improved selectivity, *Organic & Biomolecular Chemistry* 9 (2011) 4194–4198. <https://doi.org/10.1039/C1OB05178D>
- [271] L. Liu, D. Liu, Z. Xia, J. Gao, T. Zhang, J. Ma, D. Zhang, Z. Tong, Supported ionic-liquid layer on polystyrene–TEMPO resin: a highly efficient catalyst for selective oxidation of activated alcohols with molecular oxygen, *Monatshefte für Chemie – Chemical Monthly* 144 (2013) 251–254. <https://doi.org/10.1007/s00706-012-0780-y>
- [272] G. Dobras, K. Kasperczyk, S. Jurczyk, B. Orlińska, *N*-hydroxyphthalimide supported on silica coated with ionic liquids containing CoCl₂ (SCILLs) as new catalytic system

- for solvent-free ethylbenzene oxidation, *Catalysts* 10 (2020) 252. <https://doi.org/10.3390/catal10020252>
- [273] G. Talik, A. Osial, M. Grymel, B. Orlńska, *N*-hydroxyphthalimide on a polystyrene support coated with Co(II)-containing ionic liquid as a new catalytic system for solvent-free ethylbenzene oxidation, *Catalysts* 10 (2020) 1367. <https://doi.org/10.3390/catal10121367>
- [274] O. Michalski, B. Kwiecień, K. Khachatryan, G. Khachatryan, L. Stobinski, P. Tomasik, Metal salts of carboxylic multiwalled carbon nanotubes – preparation, structure and thermal properties, *Physica Status Solidi C* 8 (2011) 2532–2537. <https://doi.org/10.1002/pssc.201001183>
- [275] K. Kasperczyk, B. Orlinska, E. Witek, P. Łątka, J. Zawadiak, L. Proniewicz, Polymer-supported *N*-hydroxyphthalimide as catalyst for toluene and *p*-methoxytoluene aerobic oxidation, *Catalysis Letters* 145 (2015) 1856–1867. <https://doi.org/10.1007/s10562-015-1578-4>
- [276] T. Rusconi, L. Riva, C. Punta, M. Solé, I. Corsi, Environmental safety of nanocellulose: an acute in vivo study with marine mussels *Mytilus galloprovincialis*, *Environmental Science: Nano* 11 (2024) 61–77. DOI: [10.1039/D3EN00135K](https://doi.org/10.1039/D3EN00135K)
- [277] S. Su, J.R. Giguere, S.E. Schaus, J.A. Porco Jr., Synthesis of complex alkoxyamines using a polymer-supported *N*-hydroxyphthalimide, *Tetrahedron* 60 (2004) 8645–8657. <https://doi.org/10.1016/j.tet.2004.05.109>
- [278] J. Zawadiak, D. Gilner, Z. Kulicki, S. Baj, Concurrent iodimetric determination of cumene hydroperoxide and dicumenyl peroxide used for reaction control in dicumenyl peroxide synthesis, *Analyst* 118 (1993) 1081–1083. <https://doi.org/10.1039/AN9931801081>
- [279] H. Yu, F. Peng, J. Tan, X. Hu, H. Wang, J. Yang, W. Zheng, Selective catalysis of the aerobic oxidation of cyclohexane in the liquid phase by carbon nanotubes, *Angewandte Chemie* 17 (2011) 4064–4068. <https://doi.org/10.1002/anie.201007932>

- [280] B. Orlńska, *N*-Hydroxyphthalimide in combination with Cu(II), Co(II) or Mn(II) salts as catalytic systems for the oxidation of isopropyl-aromatic hydrocarbons with oxygen, *Tetrahedron Letters* 51 (2010) 4100–4102. <https://doi.org/10.1016/j.tetlet.2010.05.128>
- [281] T.L. do Amaral Montanheiro, F.H. Cristóvan, J.P.B. Machado, D.B. Tada, N. Durán, A.P. Lemes, Effect of MWCNT functionalization on thermal and electrical properties of PHBV/MWCNT nanocomposites, *Journal of Materials Research* 30 (2015) 55–65. <https://doi.org/10.1557/jmr.2014.303>
- [282] E. Zong, X. Liu, J. Wang, S. Yang, J. Jiang, S. Fu, Facile preparation and characterization of lanthanum-loaded carboxylated multi-walled carbon nanotubes and their application for the adsorption of phosphate ions, *Journal of Materials Science* 52 (2017) 7294–7310. <https://doi.org/10.1007/s10853-017-0966-0>
- [283] M.M. Al-Taher, C. Kalamaras, M.A. Alqahtani, F.S. Alomar, Aerobic oxidation of hydrocarbons using *N*-hydroxyphthalimide (NHPI) catalysts for cetane enhancement, *Fuel* 324 (2022) 124563. <https://doi.org/10.1016/j.fuel.2022.124563>
- [284] N.I. Kuznetsova, L.I. Kuznetsova, O.A. Yakovina, I.E. Karmadonova, B.S. Bal'zhinimaev, An improved catalytic performance of Fe(III)-promoted NHPI in the oxidation of hydrocarbons to hydroperoxides, *Catalysis Letters* 150 (2020) 1020–1027. <https://doi.org/10.1007/s10562-019-02999-x>
- [285] M. Zhou, X. Li, L. Bao, X. Yuan, H. Luo, A new method for immobilization of NDHPI on SBA-15 carrier used as catalyst for selective oxidation of toluene, *Catalysis Letters* 146 (2016) 383–390. <https://doi.org/10.1007/s10562-015-1635-z>
- [286] O. Cabeza, L. Segade, M. Domínguez-Pérez, E. Rilo, D. Ausín, A. Martinelli, N. Yaghini, B. Gollas, M. Kriechbaum, O. Russina, Mesosstructure and physical properties of aqueous mixtures of the ionic liquid 1-ethyl-3-methyl imidazolium octyl sulfate doped with divalent sulfate salts in the liquid and the mesomorphic states, *Physical Chemistry Chemical Physics* 20 (2018) 8724–8736. <https://doi.org/10.1039/C7CP07999K>
- [287] D.A. Braden, E.E. Parrack, D.R. Tyler, Solvent cage effects. I. Effect of radical mass and size on radical cage pair recombination efficiency. II. Is geminate recombination of

- polar radicals sensitive to solvent polarity?, *Coordination Chemistry Reviews* 211 (2001) 279–294. [https://doi.org/10.1016/S0010-8545\(00\)00287-3](https://doi.org/10.1016/S0010-8545(00)00287-3)
- [288] S.K. Das, M. Sarkar, Rotational dynamics of coumarin-153 and 4-aminophthalimide in 1-ethyl-3-methylimidazolium alkylsulfate ionic liquids: effect of alkyl chain length on the rotational dynamics, *The Journal of Physical Chemistry B* 116 (2012) 194–202. <https://doi.org/10.1021/jp207528p>
- [289] M.A. Atieh, O.Y. Bakather, B. Al-Tawbini, A.A. Bukhari, F.A. Abuilaiwi, M.B. Fettouhi, Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water, *Bioinorganic Chemistry and Applications* 2010 (2010) 603978. <https://doi.org/10.1155/2010/603978>
- [290] Y. Chaker, H. Ilikti, M. Debdab, T. Moumene, E.H. Belarbi, A. Wadouachi, O. Abbas, B. Khelifa, S. Bresson, Synthesis and characterization of 1-(hydroxyethyl)-3-methylimidazolium sulfate and chloride ionic liquids, *Journal of Molecular Structure* 1113 (2016) 182–190. <https://doi.org/10.1016/j.molstruc.2016.02.017>
- [291] D. Pyszny, B. Orlńska, Solvent-free aerobic oxidative cleavage of alkenes catalyzed by *N*-hydroxyphthalimide, *Reaction Kinetics, Mechanisms and Catalysis* 124 (2018) 123–138. <https://doi.org/10.1007/s11144-017-1307-7>
- [292] S. Evans, J.R.L. Smith, The oxidation of ethylbenzene and other alkylaromatics by dioxygen catalysed by iron(III) tetrakis(pentafluorophenyl)porphyrin and related iron porphyrins, *Journal of the Chemical Society, Perkin Transactions 2* (2000) 1541–1552. <https://doi.org/10.1039/B000967I>
- [293] A. Chrobok, M. Swadźba, S. Baj, Oxygen solubility in ionic liquids based on 1-alkyl-3-methylimidazolium cations, *Polish Journal of Chemistry* 81 (2007) 337–344.
- [294] J. Kumelan, Á.P.-S. Kamps, I. Urukova, D. Tuma, G. Maurer, Solubility of oxygen in the ionic liquid [bmim][PF₆]: experimental and molecular simulation results, *Journal of Chemical Thermodynamics* 37 (2005) 595–602. <https://doi.org/10.1016/j.jct.2005.03.005>

- [295] W. Afzal, X. Liu, J.M. Prausnitz, Solubilities of some gases in four imidazolium-based ionic liquids, *Journal of Chemical Thermodynamics* 63 (2013) 88–94. <https://doi.org/10.1016/j.jct.2013.03.007>
- [296] M. Vraneš, N. Zec, A. Tot, S. Papović, S. Dožić, S. Gadžurić, Density, electrical conductivity, viscosity, and excess properties of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide + propylene carbonate binary mixtures, *Journal of Chemical Thermodynamics* 68 (2014) 98–108. <https://doi.org/10.1016/j.jct.2013.08.034>
- [297] H. Tokuda, S. Tsuzuki, M.A.B.H. Susan, K. Hayamizu, M. Watanabe, How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties, *Journal of Physical Chemistry B* 110 (2006) 19593–19600. <https://doi.org/10.1021/jp064159v>
- [298] P. Wasserscheid, R. van Hal, A. Bösmann, 1-*n*-Butyl-3-methylimidazolium ([bmim]) octylsulfate – an even 'greener' ionic liquid, *Green Chemistry* 4 (2002) 400–404. <https://doi.org/10.1039/B205425F>
- [299] D.K. Pronkin, I.N. Melnikov, D.B. Meerov, V.K. Lesnikov, A.Y. Sukhorukov, N.V. Muravyev, Thermal stability of several organic hydroxylamine derivatives and a broader look at explosive hazard identification, *Industrial & Engineering Chemistry Research* (2025). <https://doi.org/10.1021/acs.iecr.4c04227>
- [300] M. Jian, C. Jianlan, L. Dongmei, X. Meina, Catalytic properties of *N*-hydroxyphthalimide immobilized on a novel porous organic polymer in the oxidation of toluene by molecular oxygen, *RSC Advances* 6 (2016) 68170–68177. <https://doi.org/10.1039/C6RA14936G>
- [301] P. Łątka, K. Kasperczyk, B. Orlińska, M. Drozdek, B. Skorupska, E. Witek, *N*-hydroxyphthalimide immobilized on poly(HEA-co-DVB) as catalyst for aerobic oxidation processes, *Catalysis Letters* 146 (2016) 1991–2000. <https://doi.org/10.1007/s10562-016-1830-6>
- [302] J.F. Blandez, S. Navalón, M. Álvaro, H. García, *N*-Hydroxyphthalimide Anchored on Diamond Nanoparticles as a Selective Heterogeneous Metal-free Oxidation Catalyst of

- Benzylic Hydrocarbons and Cyclic Alkenes by Molecular O₂, *ChemCatChem* 10 (2018) 198–205. <https://doi.org/10.1002/cctc.201700886>
- [303] G. Shi, Y. Feng, S. Xu, Q. Lu, Y. Liang, E. Yuan, L. Ji, Covalent anchoring of *N*-hydroxyphthalimide on silica via robust imide bonds as a reusable catalyst for the selective aerobic oxidation of ethylbenzene to acetophenone, *New Journal of Chemistry* 45 (2021) 13441–13450. <https://doi.org/10.1039/D1NJ01268A>
- [304] R. Hosseinzadeh, M. Mavvaji, M. Tajbakhsh, Z. Lasemi, Synthesis and characterization of *N*-hydroxyphthalimide immobilized on NaY nano-zeolite as a novel and efficient catalyst for the selective oxidation of hydrocarbons and benzyl alcohols, *Reaction Kinetics, Mechanisms and Catalysis* 124 (2018) 839–855. <https://doi.org/10.1007/s11144-018-1354-8>
- [305] T. Berniak, P. Łatka, M. Drozdek, A. Rokicińska, A. Jaworski, A. Leyva-Pérez, P. Kuśtrowski, Covalent bonding of *N*-hydroxyphthalimide on mesoporous silica for catalytic aerobic oxidation of *p*-xylene at atmospheric pressure, *ChemPlusChem* 89 (2024) e202300631. <https://doi.org/10.1002/cplu.202300631>
- [306] S.C. Her, C.Y. Lai, Dynamic behavior of nanocomposites reinforced with multi-walled carbon nanotubes (MWCNTs), *Materials* 6 (2013) 2274–2284. <https://doi.org/10.3390/ma6062274>
- [307] F. Pompeo, D.E. Resasco, Water solubilization of single-walled carbon nanotubes by functionalization with glucosamine, *Nano Letters* 2 (2002) 369–373. <https://doi.org/10.1021/nl015680y>
- [308] K.Y. Chun, I.K. Moon, J.H. Han, S.H. Do, J.S. Lee, S.Y. Jeon, Highly water-soluble multi-walled carbon nanotubes amine-functionalized by supercritical water oxidation, *Nanoscale* 5 (2013) 10171–10174. <https://doi.org/10.1039/C3NR03784C>

Appendices: Supplementary Data

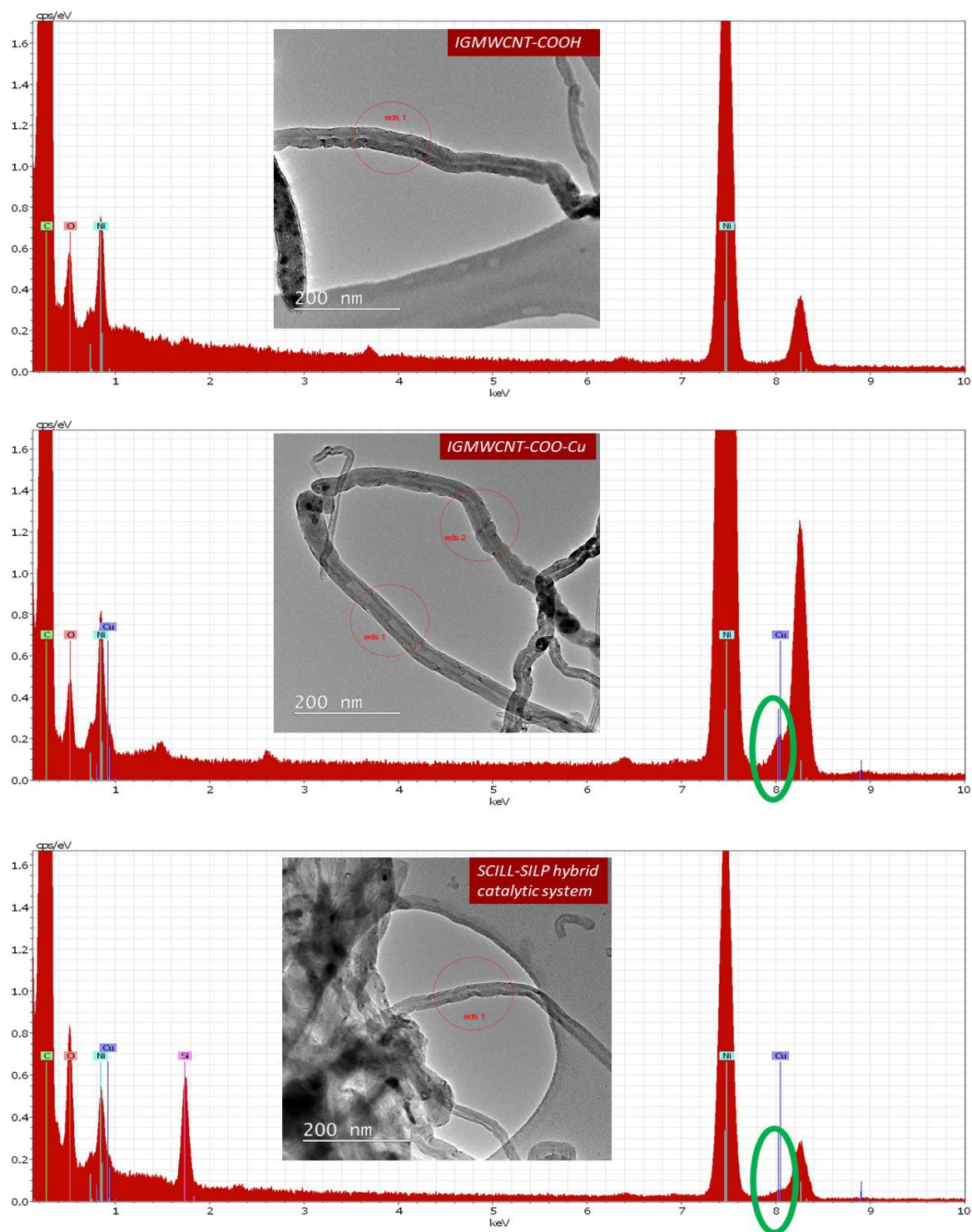


Figure A1. EDS analysis was performed at positions marked on the TEM images.

Table A1. Textural properties obtained from N₂ physisorption analysis at 77.258K

Quantity	IGMWCNT-COOH	IGMWCNT-COO-Cu	IGMWCNT-COO-Cu@2(emim)[O ₂ SO ₃]
Surface Area (m²/g)			
Single point surface area	103.0621 ^a	111.8406 ^a	4.438 ^b
BET Surface Area	105.0301	114.1975	4.8457
Langmuir Surface Area	134.3503	168.4139	-
t-Plot Micropore Area	5.5304	6.6936	-
t-Plot external surface area	99.4998	107.5039	-
BJH Adsorption cumulative surface area of pores	100.7381 ^c	108.8867 ^c	1.6478 ^d
BJH Desorption cumulative surface area of pores	109.3447 ^c	109.5999 ^c	5.5494 ^d
Pore Volume(cm³/g)			
Single-point adsorption total pore volume	0.625897 ^e	0.616128 ^e	0.04251 ^f
Single-point desorption total pore volume	0.559319 ^e	0.560758 ^e	0.03751 ^f
t-Plot micropore volume	0.002305	0.002721	-
BJH Adsorption cumulative volume of pores	0.644897 ^e	0.634773 ^e	0.00519 ^d
BJH Desorption cumulative volume of pores	0.650734 ^e	0.604989 ^e	0.04432 ^d
Pore Size (nm)			
Adsorption average pore diameter	23.8368	21.5812	35.092
Desorption average pore diameter	21.3013	19.6417	30.9652
BJH Adsorption average pore width	25.6069	23.3186	12.6066

BJH Desorption average pore width	23.8049	22.0799	31.9425
DFT Pore Size (Volume = cm³/g, Area = m²/g)			
Volume in Pores (< 2.002 nm width)	0.01094	0.01223	0.00031
Total Volume in Pores (<=159.355 nm width)	0.64108	0.62968	0.04461
Area in Pores (>159.355 nm width)	0.277	0.266	0.019
Total Area in Pores (>= 2.002 nm)	49.442	52.54	2.222

^a Determined at $p/p^\circ = 0.2998$; ^b Determined at $p/p^\circ = 0.26050$; ^c In between 1.7000-300.0000 nm width; ^d In between 2.0000-50.0000 nm width; ^e Pores less than 196.4359 nm width at $p/p^\circ = 0.9902$; ^f Pores less than 106.4200 nm width at $p/p^\circ = 0.9819$

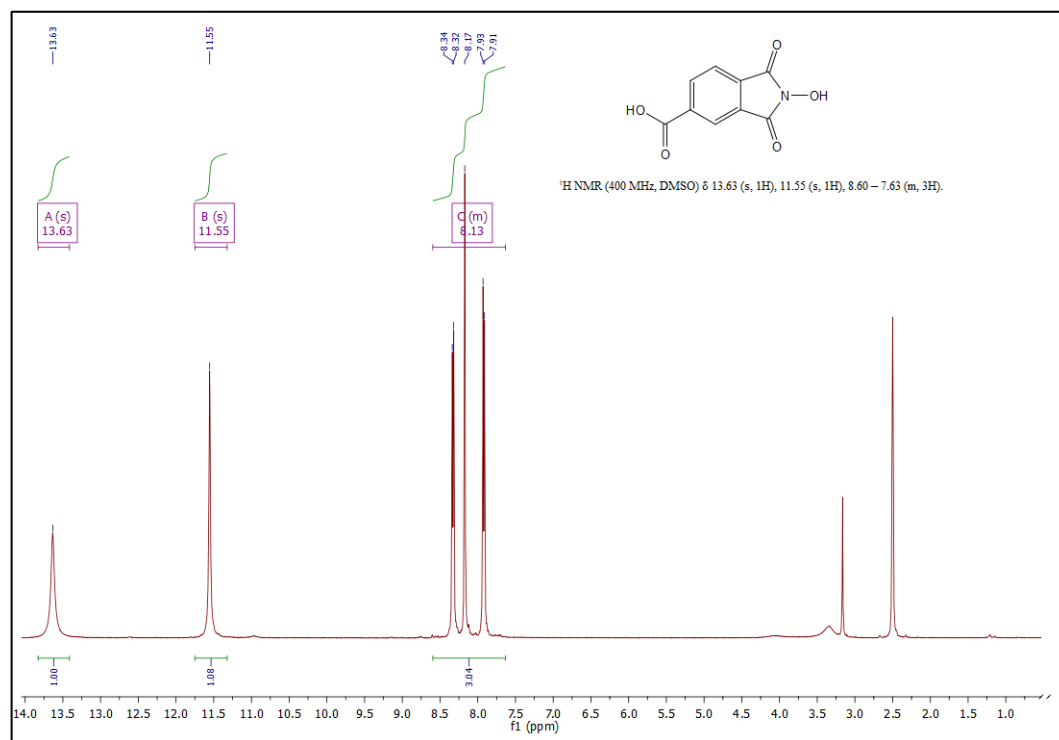


Figure A2. ¹H NMR spectrum of 4-carboxy-NHPI (400 MHz, DMSO-d₆).

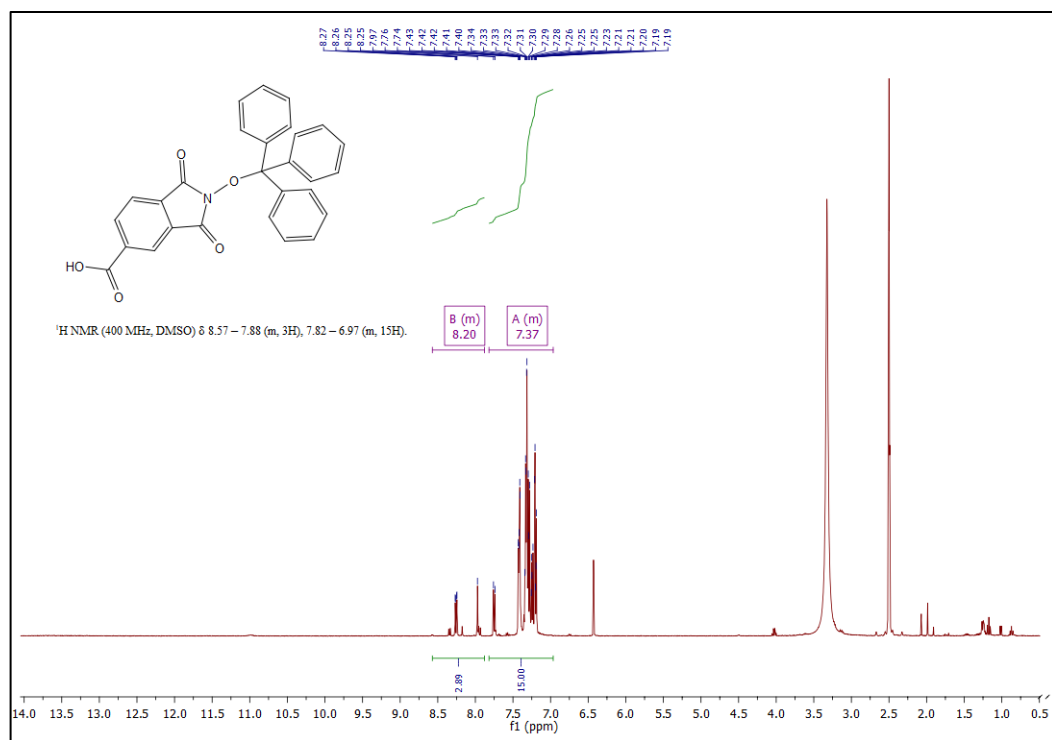


Figure A3. ^1H NMR spectrum of protected 4-carboxy-NHPI (400 MHz, DMSO- d_6).

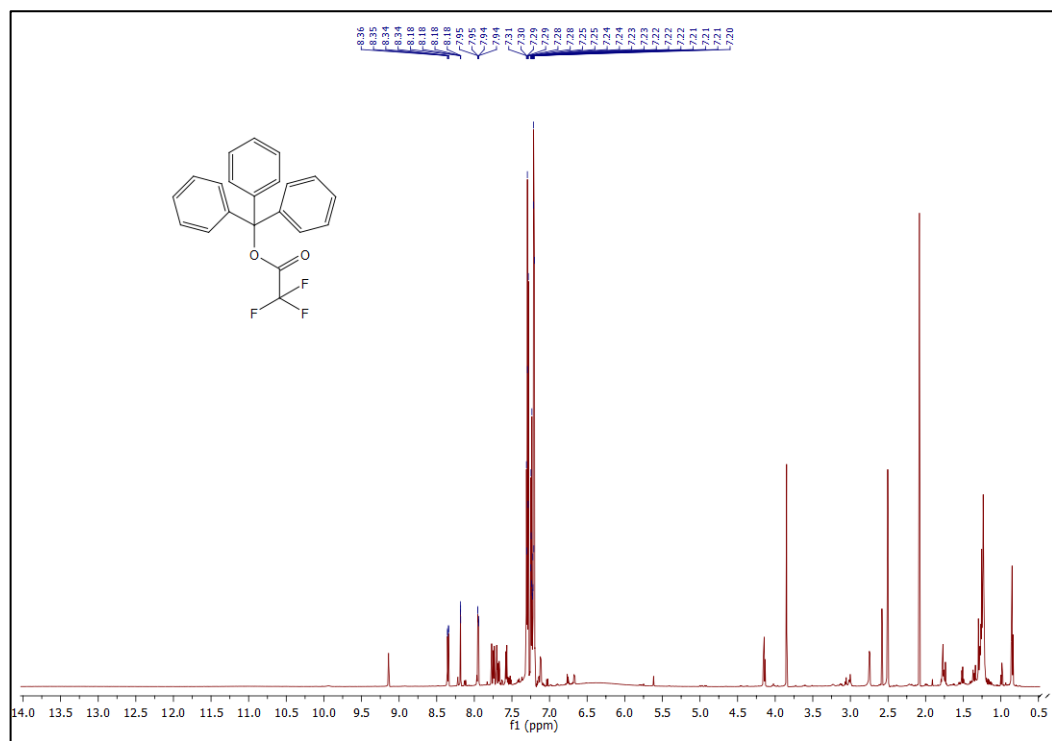


Figure A4. ^1H NMR of the solid residue, confirming the presence of the regenerated trityl group, probably as trityl trifluoroacetate (400 MHz, DMSO- d_6).

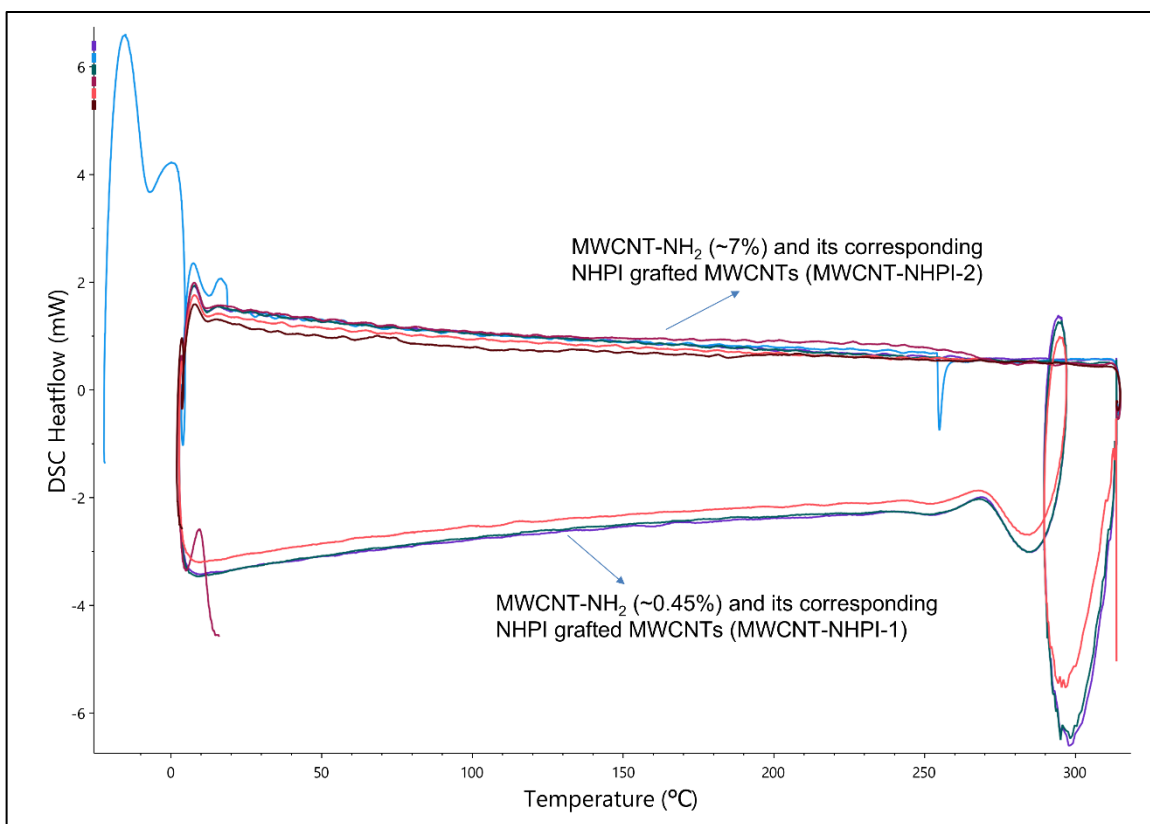


Figure A5. DSC profiles of MWCNT-NH₂ (~0.45% and ~7% -NH₂) and the corresponding NHPI-grafted MWCNTs, MWCNT-NHPI-1 and MWCNT-NHPI-2.

Scientific Achievements

Peer-Reviewed Journal Publications:

1. **Azam, S.U.**; Peckh, K.; Orlńska, B.
SCILL–SILP hybrid catalytic system employing carbon nanotubes as a support for the selective oxidation of ethylbenzene to acetophenone.
Chemical Engineering Journal 457 (2023) 141207.
Impact Factor: 16.744.
<https://doi.org/10.1016/j.cej.2022.141207>
2. **Azam, S.U.**; Peckh, K.; Orlńska, B.
N-Hydroxyphthalimide dissolved in ionic liquids supported on carbon nanotubes as a hybrid catalytic system for selective oxidation.
ACS Omega 10 (2025) 47894–47913.
Impact Factor: 5.2.
<https://doi.org/10.1021/acsomega.5c01715>
3. **Azam, S.U.**; Orlńska, B.
Carbon nanotubes as advanced catalysts and catalytic supports for liquid-phase aerobic oxidation of hydrocarbons: A review.
Applied Catalysis A: General 668 (2023) 119465.
Impact Factor: 4.8.
<https://doi.org/10.1016/j.apcata.2023.119465>

Conference Contributions

Conference proceedings

1. S.U. Azam, B. Orlńska
Solid Catalyst with Ionic Liquid Layer (SCILL), a novel catalytic system for hydrocarbon oxidation processes,
Interdyscyplinarne Badania Młodych Naukowców,
ISBN: 978-83-7880-857-2; Wydawnictwo Politechniki Śląskiej,
2. Shakir Ul Azam, Arianna De Santis, Beata Orlńska, Carlo Punta; *N-Hydroxyphthalimide supported multi-walled carbon nanotubes catalyzed solvent-free*

- aerobic oxidation of hydrocarbons*; **Konferencja ChemSpot 2026**, Gliwice, 18 czerwca 2026. Materiały konferencyjne / Marek Adam (eds.), 2026, Gliwice, Politechnika Śląska. Wydział Chemiczny, pp.34-34, Article number: BKM3, ISBN 978-83-917305-6-0.
3. David Lisicki, Mateusz Słaboń, Mateusz Cykowski, Shakir Ul Azam, Beata Orlińska; *Katalizatory typu SCDESL (Solid Catalyst with Deep Eutectic Solvent Layer) w selektywnym utlenianiu etylobenzenu do acetofenonu*; **Konferencja ChemSpot 2026**, Gliwice, 18 czerwca 2026. Materiały konferencyjne / Marek Adam (eds.), 2026, Gliwice, Politechnika Śląska. Wydział Chemiczny, pp.45-45, Article number: BKM14, ISBN 978-83-917305-6-0.
 4. Orlińska Beata, Lisicki Dawid, Azam Shakir Ul, Kacper Cykowski, Mateusz Słaboń; *Badania nad nowymi układami katalitycznymi dla procesów utleniania: XI Kongres Technologii Chemicznej*. Poznań, 16-19 września 2024. Materiały konferencyjne / Frankowski Robert (eds.), 2024, Poznań, Politechnika Poznańska, pp.81-81, ISBN 978-83-955437-6-0.

Oral and Poster Presentations:

1. ChemSpot 2026, Silesian University of Technology, Poland, 18 June 2026.
2. Ph.D Nexus -Wisław- Silesian University of Technology, Poland, 25-26 October 2024.
3. Società Chimica Italiana (SCI 2024) – XXVIII National Congress (Conference & Exhibition), Milan, Italy, 26-30 August 2024.
Laboratory of Organic Synthesis, Catalysis, and Materials (OSCM) lab day, Department Chemistry, Materials, and Chemical Engineering “G. Natta”, Politecnico di Milano, Via Mancinelli 7-20131, Milano, Italy, 21 June 2024.
4. 11 Kongres Technologii Chemicznej, Poznań, 16-20 September 2024
5. The 3rd Advances in Green Chemistry Conference – AGChem, Poznań, 26-30 September 2022.
6. 16th Freiberg Colloquium of Young Researchers: Responsible Consumption and Production in the Raw Material Sector, TU Bergakademie Freiberg, Germany, 07-11 June 2022.

7. International Interdisciplinary Conference of Doctoral Students of Technical Universities - InterTechDoc'2022, Ul. Zdrojowa 10, 43-450 Ustroń, Poland, 05-07 April 2022.

Research Funding and Grants:

1. Received BKM Project 2025-Grant No: 04/050/BKM25/0214
2. Received BKM Project 2024-Grant No: 04/050/BKM24/0198
3. Received BKM Project 2023-Grant No: BKM-555/RCH5/2023
4. Received BKM Project 2022-Grant No: BKM-614/RCH5/2022 /04/050/BKM22/0153

International Research Experience

1. Erasmus+ Long-Term Research Traineeship
Politecnico di Milano, Milan, Italy.
Duration: February 2024 – February 2025
Programme: ERASMUS + KA131
Project code: 2023-1-PL01-KA131-HED-000116082

Awards and Distinctions

1. Rector's Team Award (2023), Silesian University of Technology, Gliwice, Poland
2. Best PhD Student Award (three-time recipient, Silesian University of Technology, Gliwice, Poland)
 - Academic Year 2021/2022
 - Academic Year 2023/2024
 - Academic Year 2024/2025