

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.