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Nanoparticle Supported, Magnetically Separable Metalloporphyrin as an Efficient Retrievable Heterogeneous Nanocatalyst in Oxidation Reactions

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Abstract : Metalloporphyrins are well known to mimic the activity of monooxygenase enzymes. In this regard, metalloporphyrin complexes have been largely employed as valuable biomimetic catalysts, owing to the critical roles they play in oxygen transfer processes in catalytic oxidation reactions. Investigating in this area is based on different strategies to design selective, stable and high turnover catalytic systems. Immobilization of expensive metalloporphyrin catalysts onto supports appears to be a good way to improve their stability, selectivity and the catalytic performance because of the support environment and other advantages with respect to recovery, reuse. In other words, supporting metalloporphyrins provides a physical separation of active sites, thus minimizing catalyst self-destruction and dimerization of unhindered metalloporphyrins. Furthermore, heterogeneous catalytic oxidations have become an important target since their process are used in industry, helping to minimize the problems of industrial waste treatment. Hence, the immobilization of these biomimetic catalysts is much desired. An attractive approach is the preparation of the heterogeneous catalyst involves immobilization of complexes on silica coated magnetic nano-particles. Fe3O4@SiO2 magnetic nanoparticles have been studied extensively due to their superparamagnetism property, large surface area to volume ratio and easy functionalization. Using heterogenized homogeneous catalysts is an attractive option to facile separation of catalyst, simplified product work-up and continuity of catalytic system. Homogeneous catalysts immobilized on magnetic nanoparticles (MNPs) surface occupy a unique position due to combining the advantages of both homogeneous and heterogeneous catalysts. In addition, superparamagnetic nature of MNPs enable very simple separation of the immobilized catalysts from the reaction mixture using an external magnet. In the present work, an efficient heterogeneous catalyst was prepared by immobilizing manganese porphyrin on functionalized magnetic nanoparticles through the amino propyl linkage. The prepared catalyst was characterized by elemental analysis, FT-IR spectroscopy, X-ray powder diffraction, atomic absorption spectroscopy, UV-Vis spectroscopy, and scanning electron microscopy. Application of immobilized metalloporphyrin in the oxidation of various organic substrates was explored using Gas chromatographic (GC) analyses. The results showed that the supported Mn-porphyrin catalyst (Fe3O4@SiO2-NH2@MnPor) is an efficient and reusable catalyst in oxidation reactions. Our catalytic system exhibits high catalytic activity in terms of turnover number (TON) and reaction conditions. Leaching and recycling experiments revealed that nanocatalyst can be recovered several times without loss of activity and magnetic properties. The most important advantage of this heterogenized catalytic system is the simplicity of the catalyst separation in which the catalyst can be separated from the reaction mixture by applying a magnet. Furthermore, the separation and reuse of the magnetic Fe3O4 nanoparticles were very effective and economical.

Keywords : Fe3O4 nanoparticle, immobilized metalloporphyrin, magnetically separable nanocatalyst, oxidation reactions
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