Copper (II) Tetrasulfonated Phthalocyanine Immobilized on Superparamagnetic Nanoparticles Catalyzed Highly selective and Economical Heterogeneous Oxidation of Hydrocarbons in Water

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Abstract

In the age of environmental amity chemistry, heterogeneous reactions have become an important objective as these processes are used in industry, helping to minimize the problems of industrial disposal and waste treatment [1]. For practical applications of heterogeneous systems, the life time of catalyst and its recovery and extension of reusability are very important factor. Many attempts have been devoted for hetrogenization of porphyrin complexes as often-used bio-relevant catalysts within different organic and inorganic supports to enhance their chemical stability and allow catalyst recovery by simple filtration [2]. However, due to the diffusion of substrates and products through the pores of the support materials, a substantial decrease in the reaction rate is frequently observed compared to the homogeneous system [3]. To overcome this limitation the size of the support particles should be kept as small as possible providing nanoparticles with high external surface area. Consequently, a high loading of catalytically active sites is obtained and diffusion will no longer limit the kinetics.

Nanoparticles have recently emerged as efficient alternatives for the immobilization of homogeneous catalysts. Nevertheless, difficulties in recovering the nanometer-sized particles from the reaction mixture resulting from effective dispersion in solution by forming stable suspensions, severely limited their wide applications. There is currently intense interest in the use of magnetic nanoparticles (such as Fe_3O_4) for a wide range of biomedical and technological applications. They have been coated with metal catalysts or conjugated with enzymes, to combine the separating power of the magnetic properties with the catalytic activity of the metal surface or enzyme conjugate [4]. Furthermore, a recoverable catalyst requires a sustainable reaction media for application in scale-up procedures in practical goals. Discarding of harmful organic solvents is the major problem in chemical industries which accounts around 80% of their wastes. Thus, a new challenge is to make innovative, “clean” methods by using non-toxic solvents in particularly aqueous media. Moreover, it has been found that reactions in water can facilitate access to different reactivity and selectivity patterns compared with those observed in common organic solvents due to its unique physical and chemical properties. In this regard, the use of water as a reaction solvent has attracted great attention in the recent past and has become an active area of research in green chemistry [5].

In this work water soluble copper (II) tetrasulfonated phthalocyanine supported on nano-sized Fe_3O_4 coated with a silica layer (CuPcS@Fe_3O_4) has been used as a magnetically recoverable heterogeneous nanocatalyst for highly selective aqueous oxidation of hydrocarbons using tetra-n-butylammonium peroxomonosulfate (TBAOX). Organic co-solvents, surfactants, co-catalyst and hydrophilic auxiliaries were completely missed in this heterogeneous catalytic strategy. The catalyst could easily be recycled by an external magnetic field and reused without loss of activity and the oxidant’s by-product (n-Bu_4NHSO_4) could also be recycled.

References

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Figures

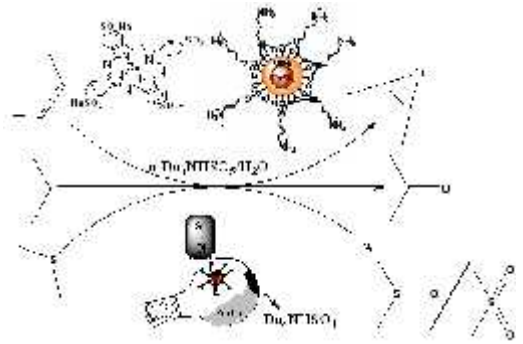

Fig. 1. The oxygenation of hydrocarbons using $CuPcS@Fe_3O_4$ by n-Bu_4NHSO_5 in neat water

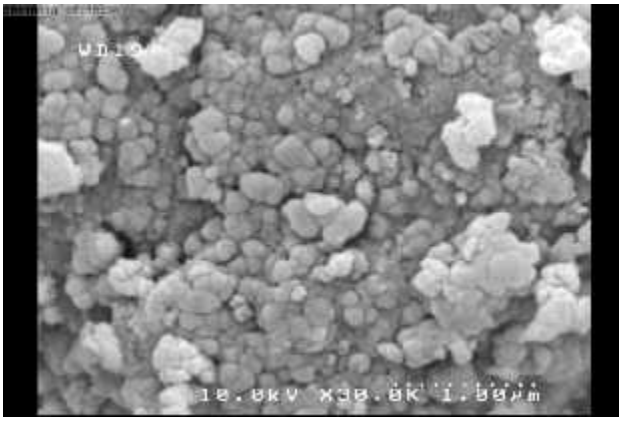

Fig. 2. SEM image of $CuPcS@Fe_3O_4$

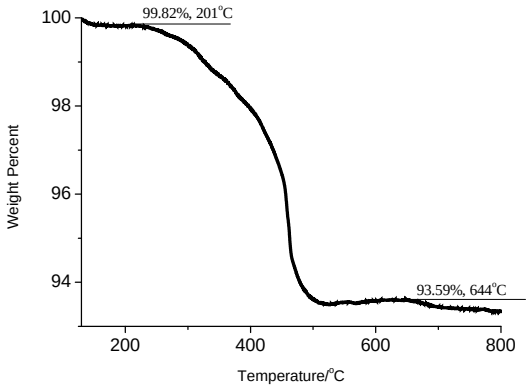

Fig. 3. TGA thermogram of $CuPcS@Fe_3O_4$