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Metalloporphyrins immobilized on core–shell $CeO_2@SiO_2$ nanoparticles prepared by a double-coating method for oxidation of diphenyl methane

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ABSTRACT

Metalloporphyrins immobilized on $CeO_2@SiO_2$ core–shell nanoparticles were synthesized by a double-coating method and used for catalytic oxidation of diphenyl methane. A variety of characterization techniques including FT-IR, UV–vis, SEM, TEM, XRD, N_2 adsorption–desorption and TGA were employed. The results show that the catalyst consists of regular nanoparticles (around 400 nm) with core–shell structure and metalloporphyrins were immobilized on $CeO_2@SiO_2$ core–shell nanoparticles via amide bonds. Moreover, these new developed catalysts for solvent-free selective oxidation of diphenyl methane exhibited an excellent catalytic activity, selectivity and stability. Furthermore, these catalysts could be reused 6 times without significant loss of their catalytic activity and the used catalysts maintained nearly the same physicochemical properties as the fresh.

1. Introduction

Metalloporphyrins have attracted much interest because of their recognized catalytic activity employed in the oxidation of hydrocarbons [1–3]. However, unsupported metalloporphyrins are easily degraded and difficult to reuse, which limits their practical application in actual industrial processes. Much attention has been paid to solid supported metalloporphyrins not only because of their increased stability and selectivity but also their ability to be recovered from reaction media and reused [4–7].

Generally, inorganic supports are preferred versus organic supports because they are more robust and more efficient in preventing catalyst deactivation caused by dimerization, e.g. formation of μ-oxo dimmers [8,9]. The $CeO_2@SiO_2$ has been found to be very suitable inorganic support for metalloporphyrins because CeO_2 is well known to store and release oxygen via forming surface and bulk vacancies [10,11]. In addition, CeO_2 can be used as a promoter in combination with other elements to give mixed-oxide formation. On the other hand, SiO_2 allows for ease of modification and immobilization of the metalloporphyrins onto its surface [12–15].

However, the charge between the precursor of CeO_2 and silica are contrast, which cause the bulk precipitation of CeO_2 or silica during the coating procedure [16]. For example, when NH_4OH was used as the particle-forming agent, the surface charge of the CeO_2 precursor nanoparticle was negative [17]. It was considered that electrostatic repulsion occurred between the surface of the CeO_2 precursor and SiO_2, and agglomeration of SiO_2 and CeO_2 particles observed would be ascribed to that repulsion. The surface modifiers such as oxalic acid and hexamethylenetetramine were used to adjust the electronic properties of the surface in CeO_2 in order to solve this problem [16,17]. Because of the electrostatic affinity, the CeO_2 precursor nanoparticle was coated with SiO_2, and SiO_2-coated CeO_2 nanoparticles were obtained.

As illustrated in Scheme 1, we make use of the CeO_2 sol modified by sodium citrate and the double-coating method to achieve $CeO_2@SiO_2$ core–shell nanoparticles. Metalloporphyrins were immobilized, via amide bonds, on $CeO_2@SiO_2$ core–shell nanoparticles. The oxidation of diphenyl methane to diphenyl ketone was used as the probing reaction. Variety of characterization techniques including FT-IR, UV–vis, SEM, TEM, XRD, N_2 adsorption–desorption and TGA were applied. As expected, the mixing of ceria has a beneficial influence on the catalytic performance, which has been generally attributed to the cooperative effect among metalloporphyrins, silica and ceria. The results show the superior ability to immobilize the metalloporphyrins onto $CeO_2@SiO_2$ core–shell nanoparticles.

2. Experimental

2.1. Materials

5-(4-Carboxyphenyl)-10,15,20-triphenyl porphyrin (TMCPP) was synthesized and purified in our laboratory. The metal oxides used in this work were prepared by coprecipitation method from

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