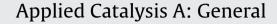
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Metalloporphyrins immobilized on core-shell CeO₂@SiO₂ nanoparticles prepared by a double-coating method for oxidation of diphenyl methane

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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 CeO₂@SiO₂ has been found to be very suitable inorganic support for metalloporphyrins because CeO₂ is well known to store and release oxygen via forming surface and bulk vacancies [10,11]. In addition, CeO₂ can be used as a promoter in combination with other elements to give mixed-oxide formation. On the other hand, SiO₂ 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 NH₄OH was used as the particle-forming agent, the surface charge of the CeO_2 precursor nanoparticle was negative [17]. It was considered that

ABSTRACT

Metalloporphyrins immobilized on CeO₂@SiO₂ core-shell nanoparticles were synthesized by a doublecoating method and used for catalytic oxidation of diphenyl methane. A variety of characterization techniques including FT-IR, UV-vis, SEM, TEM, XRD, N₂ 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 CeO₂@SiO₂ 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.

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electrostatic repulsion occurred between the surface of the CeO₂ precursor and SiO₂, and agglomeration of SiO₂ and CeO₂ 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 CeO₂ in order to solve this problem [16,17]. Because of the electrostatic affinity, the CeO₂ precursor nanoparticle was coated with SiO₂, and SiO₂-coated CeO₂ nanoparticles were obtained.

As illustrated in Scheme 1, we make use of the CeO₂ sol modified by sodium citrate and the double-coating method to achieve CeO₂@SiO₂ core-shell nanoparticles. Metalloporphyrins were immobilized, via amide bonds, on CeO₂@SiO₂ 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, N₂ 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 CeO₂@SiO₂ 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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