



One-pot fabrication of magnetically recoverable acid nanocatalyst, heteropolyacids/chitosan/Fe₃O₄, and its catalytic performance

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ABSTRACT

A magnetically recoverable acid nanocatalyst, heteropolyacids/chitosan/Fe₃O₄ (HSiW-CS-Fe₃O₄), was successfully prepared by a one-pot synthesis method. The characterized results by XRD, TEM, TGA, FT-IR and magnetic measurements testified that Keggin-type 12-silicotungstic acid (HSiW) was efficiently immobilized into the cross-linked chitosan (CS) coating on nanometer-sized Fe₃O₄ magnetic cores. The prepared HSiW-CS-Fe₃O₄ possesses a typical superparamagnetic behavior and has the acid capacity of 0.13 mmol/g. It exhibits higher catalytic activity in the acetalization reaction of benzaldehyde with ethylene glycol, and gives a 99% yield for acetal under mild reaction conditions. Furthermore, the prepared catalysts can be magnetically separated from the reaction system and reused 5 times without the significant loss of catalytic activities. It is also confirmed that the recovered catalysts are not dramatically changed in the physicochemical features. The prepared HSiW-CS-Fe₃O₄ may be the promising catalytic material in a mass production of the fine chemicals.

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1. Introduction

In recent years, in order to replace problematic mineral acid catalysts (e.g. H₂SO₄ and HCl) widely applied in a number of chemical processes, solid acid catalysts such as clays, zeolites, sulfated metal oxides or carbons and heteropolyacids have already attracted extensive research interests [1–4]. Among these solid acid catalysts, heteropolyacid compounds are unique due to their strong Brønsted acidity, lower corrosivity and higher catalytic activity, etc. The heteropolyacid compounds have been used as acid catalysts in several large scale industrial processes [5–7]. However, the heteropolyacids in the bulk form possess very low surface area and high solubility in polar medium, which limits the exertion of potentially catalytic performance and makes some difficulties in catalyst recovery [8]. For overcoming these disadvantages, considerable research endeavors have been devoted to improve the catalytic efficiency and stability of heteropolyacids by using different strategies such as pillaring layered clays with polyanions, dispersing heteropolyacids on solid supports with high surface area, changing counteranions in heteropolyacids, immobilizing heteropolyacids into an organic polymer and to prepare nanoscale polyoxometalate particles [5,9–11]. However, for those potentially promising

reactions to be used in practice, complete recovery and reduction of the amount of rather expensive polyoxometalate catalysts used will be required.

During recent years, the advances in nanoscience and nanotechnology have led to a new research interest in employing nanometer-sized particles to construct a magnetically recyclable nanocatalyst system in the heterogeneous catalysis [12,13]. The magnetic nanoparticles are often used to immobilize catalytic materials in this system. The magnetic catalysts can be well dispersed in the reaction mixtures during the absence of the magnetic field, which provides the large surface for the readily access of substrate molecules. At the end of reaction, these catalysts can be efficiently separated from the reaction mixtures by applying a permanent magnet externally via magnetic concentration step [13]. It is an attractive candidate in the development of a cost-effective catalysis process. Considerable efforts have been devoted to the studies of magnetically recyclable nanocatalyst system, especially due to the increasing demand for more sustainable and environmentally beneficial processes. A wide range of the magnetically recyclable nanocatalysts containing metal species, such as Pd [14–16], Pt [17,18], Ru [19], Cu [20] and Au nanoparticles [21,22] have already been prepared. Many magnetic nanocatalysts including palladium complexes [23–25], rhodium complexes [26,27] and copper complexes [28,29], etc. have also been obtained. Recently, a magnetically recoverable epoxidation catalyst based on molybdenum dioxide nanoparticles was reported [30]. At the

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