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Synthesis and characterization of a green composite of $H_3PW_{12}O_{40}$ and starch-coated magnetite nano particles as a magnetically-recoverable nano catalyst in Friedel-Crafts alkylation

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ABSTRACT

Preparation and characterization of a magnetic composite of 12-tungstophosphoric acid (HPW) and starch coated magnetite nano particles (SMNs) were reported. Magnetite nano particles coated with starch were prepared using controlled chemical coprecipitation of magnetite phase from aqueous solution in a polymeric starch matrix. HPW was immobilized on this nano particles in order to produce a composite of SMNs and HPW (HPW/SMNs) as a nano catalyst. The as-prepared HPW/SMNs catalyst was characterized by transmission electron microscopy, laser particle size analyzer, Fourier transform infrared spectroscopy, vibrating sample magnetometer and chemical composition of the HPW/SMNs was estimated by elemental analysis. The results show that HPW/SMNs had a well-defined composite structure and an average size of approximately 29 nm. The characterization data derived from FT-IR reveal that basic structure and geometry of the Keggin anion are preserved after synthesis of HPW/SMNs. Activity of the catalyst was probed through alkylation of aromatic compounds from benzhydrol. The excellent conversions show that the catalyst has strong acidity, which are responsible for its catalytic performance. The catalyst could be recovered simply by using an external magnetic field and reused several times without appreciable loss of its catalytic activity.

1. Introduction

In recent years, in order to replace problematic mineral acid catalysts (e.g., H_2SO_4 and HCl) widely applied in a number of chemical processes, solid acid catalysts such as clays, zeolites, sulfated metal oxides or carbons and heteropoly acids (HPAs) have already attracted extensive research interests [1–4]. Among these solid acid catalysts, HPA compounds are unique due to their strong Brönsted acidity, lower corrosivity and higher catalytic activity, etc. The HPA compounds have been used as acid catalysts in several large scale industrial processes [5–7]. However, the HPAs 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 HPAs by using different strategies such as pillaring layered clays with polyanions, dispersing of HPAs on solid supports with high surface area, changing counter cations in HPAs, immobilizing HPAs into an organic polymer and prepare nano scale polyoxometalate (POM) particles [5,9–11]. However, for those potentially promising reactions to be used in practise, complete recovery and reduction of the amount of rather expensive POM catalysts used will be required. During recent years, the advances in nano science and nano technology have led to a new research interest in employing nano meter-sized particles to construct a magnetically recyclable nano catalyst system in the heterogeneous catalysis [12,13]. The magnetic nano particles are often used to immobilize catalytic materials in this system. Several investigations have been carried out in the field of superparamagnetic iron oxide nano particles because of their high magnetic susceptibility and relatively low cytotoxicy [14]. Superparamagnetic nano particles possess an advantage in that they do not retain any magnetization after removal of an external magnetic field [15]. In particular, magnetic materials are the most commonly selected substrates as affinity probes because of the ease of isolation. A recurrent problem, however, is that the direct use of these particles result in formation of agglomerates. Agglomeration of iron oxide nano particles reduces the superparamagnetic properties [16]. Agglomeration was occurred because of the high surface area to volume and consequently high

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surface energy of iron oxide nano particles [17]. Researchers have been studying different techniques to overcome these difficulties by engineering the surface of iron oxide nano particles [18,19]. Several methods have been reported for surface modification of superparamagnetic iron oxide nano particles. Most works focused on synthesis of nano composite materials with magnetic particles dispersed in organic or inorganic matrices.

Recently, various studies on nano metric magnetic particles have been reported including ultrafine metallic iron and iron alloy particles, as well as nano metric iron, and iron oxide particles, which were embedded in inorganic matrices (e.g., Al_2O_3, SiO_2) [20–23] and polymer matrices (e.g., ion-exchanging resin) [24–26]. Among the natural polymers, starch is an ideal material to this purpose because of the abundant availability of starch, low cost, renewability, biocompatibility, biodegradability, and non-toxicity [27]. Furthermore starch nano crystals have also been found to be excellent reinforcements [28,29]. In this study, starch coated magnetic nano particles (SMNs) were used as supports for the immobilization of HPAs. 12-Tungestophosphoric acid (HPW) on SMNs (HPW/SMNs) can be employed to derive a novel heterogeneous catalyst system that possesses both high separation efficiency and relatively high surface area to maximize catalyst loading and activity. Then, reactivity of the produced catalyst was investigated in alkylation of aromatic compounds with benzhydrol. The Friedel-Crafts alkylation is a well-known widely uses organic reaction for C-C bond formation between aromatic compounds and alkyl halides, alcohols, or carbonyl compounds. The ideal Friedel-Crafts reaction would employ an alcohol as the electrophile, and therefore generate water as the only byproduct. Several systems for the alkylation of aromatic compounds with alcohols have been reported so far [30–37]. To the best of our knowledge this is the first attempt on using of starch coated magnetic nano particles as a green material coated magnetite nano particles as a support for HPW.

2. Experimental

2.1. Preparation of starch-coated iron oxide nano particles (SMNs)

$FeCl_3{\cdot}6H_2O$ (99%) and $FeSO_4{\cdot}7H_2O$ (99%), NaOH (98%), HCl (37%), starch, HPW (>99), other reagents and solvents used in this work were obtained from Merck, Aldrich or Fluka without further purification.

SMNs were prepared in a polymeric starch matrix, by controlled chemical coprecipitation of magnetite phase from aqueous solution containing suitable salts of Fe^{2+} and Fe^{3+} mainly based on the van der Waals interaction between starch and magnetite nano particles. Starch (6 g) was dissolved in 40 mL of deionized water at 80 °C. Starch solution was added to an aqueous solution of Fe^{3+} (0.8 M) ions and Fe^{2+} (0.4 M) ions in 40 mL H_2O under vigorous stirring. Then a solution of NaOH (1.0 M) was added dropwise into the mixture of starch and iron salts until the pH of the solution achieved 9–11. After 2 h, the resulting black suspension was neutralized with HCl (0.1 M). The suspension was centrifuged for 15 min at 1500 rpm. Finally, the SMNs were washed with deionized water several times to remove little free starch exists. The resulting aqueous suspension of SMNs was used for the next step synthesis of the catalyst.

2.2. Preparation of HPW/SMNs

For the preparation of HPW/SMNs a solution of HPW (2 g in 10 mL water) was added to the aqueous solution of SMNs (3.3 g in 10 mL water to produce 60 wt.% of PW to support) that thoroughly dispersed by sonication and stirred overnight at room temperature. Finally, the solvent was removed by using rotary evaporator and dried. After preparation, the catalyst calcinated at different temperature (100, 150, 200, 250, 300 °C) for 2 h.

2.3. Catalyst characterization

Transmission electron microscopy (TEM) was obtained using a TEM microscope (Jeol JEM-2100 with an accelerating voltage of 200 kV). The size distribution of the samples was obtained using a laser particle size analyzer (HPPS 5001, Malvern, UK). Fourier transform infrared (FT-IR) spectra were recorded with KBr pellets using a FT-IR spectrometer ALPHA. UV–vis spectra were obtained with an Agilent (8453) UV–vis diode-array spectrometer using quartz cells of 1 cm optical path. NMR spectra were recorded on a Bruker Avance 200 MHz NMR spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Elemental analyses (C, H, and N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analyses system, GmbH). Magnetic properties of SMNs and HPW/SMNs were measured using a BHV-55, Riken, Japan vibrating sample magnetometer (VSM).

2.4. Catalytic experiments

The solid acid catalyst (0.25 g), was added to a mixture of benzhydrol (1 mmol) and various aromatic compounds (2.5 ml) at 75 °C. The reaction was preceded for a short period of time. Progress of the reaction was monitored by thin-layer chromatography (TLC). At the end of the reaction, the catalyst was separated from the product solution using an external magnet, followed by decantation of reaction mixture. The solvent was evaporated to generate the crude product. The crude product was purified by column chromatography on silica gel using hexane/ethyl acetate 4:1 as eluent. All products were identified by comparing their spectral data with those of the authentic samples [30–37].

The remaining catalyst was washed with diethyl ether, dried under vacuum and reused in a subsequent reaction. More than 85 wt.% of the catalyst could usually be recovered from each run.

To check the leaching stability of the catalyst, 0.001 g of the catalyst was stirred in 5 mL methanol for 30 min. UV–vis spectra of the diluted solution was recorded after removal of solid. The content of HPW in solution was determined with the aid of calibration curves.

2.5. Large scale synthesis

Reaction of benzhydrol and benzene was selected for large-scale synthesis. The reaction of **1a** (20.0 mmol) with **2b** (50 ml), in the presence of HPW/SMNs (4.8 g) was done at 75 °C.

3. Results and discussion

The purpose nano catalyst, HPW/SMNs, were prepared in two steps, Scheme 1 presents the synthetic strategy for HPW/SMNs.

(1) SMNs were prepared by controlled chemical coprecipitation of magnetite phase from aqueous solutions containing suitable salts of Fe^{2+} and Fe^{3+}.

(2) Immobilization of SMNs with a water solution of HPW occurs via formation of hydrogen bonding between hydroxyl group on the surface of starch and HPW molecule.

Fig. 1(a–d) show the TEM images, size histogram and electron diffraction (ED) pattern for the HPW/SMNs. As shown in Fig. 1(a,b) TEM observation indicated that HPW/SMNs had well-defined composite structure composed of several magnetite particles, HPW and starch chains which surrounds these particles. Histogram of size distribution by means of microstructure measurement software was obtained by measuring several spot from TEM image. As shown