Journal of Molecular Catalysis A: Chemical 373 (2013) 30–37

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Controlled immobilization of Keggin-type heteropoly acids on the surface of silica encapsulated γ-Fe_2O_3 nanoparticles and investigation of catalytic activity in the oxidative esterification of arylaldehydes with methanol

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ARTICLE INFO

Article history:
Received 12 December 2012
Received in revised form 23 February 2013
Accepted 25 February 2013
Available online 5 March 2013

Keywords:
Supported heteropoly acid
Maghemite iron oxides
Magnetically recoverable catalyst
Oxidative esterification

ABSTRACT

Preparation, leaching and solid acidity measurements of $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ supported on silica-encapsulated γ-Fe_2O_3 nanoparticles were performed. The impregnating solvent and calcination temperature were optimized using various techniques. Catalytic activity of samples was examined by carrying out oxidative esterification of benzaldehyde with methanol under the same conditions. The acidity of the catalysts that was determined by NH_3-temperature-programmed desorption technique and chemisorption of pyridine. The best catalyst was characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and laser particle size analyzer. Finally, a mild, simple and clean procedure was presented for the one-pot oxidative esterification of arylaldehydes with methanol using magnetically recoverable nanocatalyst and hydrogen peroxide as a green oxidant.

1. Introduction

The development of new strategies for the recycling of catalysts is a task of great economic and environmental importance in chemical and pharmaceutical industries. Immobilization of homogeneous catalysts on various insoluble supports (especially porous materials with high surface areas) can lead to simplify catalyst recycling via filtration or centrifugation. However, a substantial decrease in the activity of the immobilized catalyst is frequently observed due to the loss of the catalyst in the separation processes and/or diffusion factors [1]. At present, nanoparticles (NPs) are attractive candidates as solid supports for the immobilization of well-defined homogeneous catalysts [2]. Because of the nanometer dimensions of NPs, such catalysts have better reaction kinetics as compared to the traditional heterogeneous catalysts on mesoporous solid supports. Additionally, due to their large surface area, which can carry a high payload of catalytically active species, these supported catalysts exhibit very high activity under mild conditions.

In NPs-based heterogeneous catalysis, the use of silica coated magnetic NPs can be of additional values: the magnetic nature of these particles allows for facile recovery and recycling of catalysts. Thus far, various catalytic species, including organometallic [3–5] and organic catalysts [6,7] and biocatalysts [8–10], were immobilized on the modified surface of magnetic NPs. Following this line of research, we have previously reported interesting results in the immobilization of heteropoly acids (HPAs) with Keggin anion structure [11]. In our work, the primary motivation was to create the novel magnetically recoverable nanocatalyst by immobilization of Keggin-structured $H_3PW_{12}O_{40}$ (PW) on silica-coated magnetic NPs. This synthesized catalyst possesses both magnetic separation and strong acidic sites. Moreover, the nano scale support materials have the high surface area. Consequently, NPs could have higher catalyst loading capacity and higher dispersion than many conventional support matrices, leading to an improved catalytic activity and high leaching stability of HPA species even in polar reaction media.

However, the effects of various processing parameters, including the concentration of impregnating solutions, the solvent used, calcination temperature and the type of HPA have remained a challenge. Literature survey showed that the above-mentioned parameters are major factors contributing to the catalytic activity of HPA immobilized on conventional solid supports [12–14]. Nevertheless, there has been scant investigation of HPA catalyst supported on magnetic NPs [15–20] and to the best of our knowledge, the detailed studies of the effective parameters on catalyst preparation have not been well developed.

Keeping in mind these statements, herein, we propose a simple method for the synthesis of magnetically recoverable HPA-based catalyst that relies on our pervious paper, but with an examination and subsequently careful choice of processing parameters.

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http://dx.doi.org/10.1016/j.molcata.2013.02.024

The synthesis of silica coated magnetic NPs, covering a wide range of compositions and tunable sizes, has made substantial progress, especially over the past decade [21,22]. Most of these researches focused on the generation of uniform particles, often of distinct size, shape, and structure, with little consideration of the expensive precursors used to prepare them or the cost of processes to produce them. On the other hand, for the large-scale application in industry, an important consideration will be to prepare NPs economically using relatively low-grade reagents under aerobic conditions. So, a simple ferric oxide, γ-Fe_2O_3, was chosen as the magnetic material for its low price, air stability and non-toxicity. It was prepared simply through chemical coprecipitation [23], and subsequently was coated with silica shell by the ordinary Stöber process [24] without expensive systems. After the surface coating by silica, magnetic solid (designed as Fe@Si) was used as support for immobilization of HPA. Preparation conditions including the impregnating solvent used, calcination temperature and the type of HPA have been optimized. Ultimately, the efficiencies of obtained catalysts were evaluated in oxidative esterification of benzaldehyde with methanol as the test reaction. The ever-increasing concern for the catalytic oxidative esterification of aldehydes as an interesting and potentially valuable alternative transformation [25–29] and the wide application of aromatic esters in pharmaceuticals, agrochemicals, and food additives [30–32] encouraged us to evaluate the scope and generality of the catalytic system by using various substituted benzaldehyde. To the best of our knowledge, the application of magnetically recoverable HPA-based catalyst in the oxidative esterification of arylaldehydes has not yet been studied.

2. Experimental

2.1. Catalyst preparation

$FeCl_2{\cdot}4H_2O$ (99%) and $FeCl_3{\cdot}6H_2O$ (99%), concentrated ammonium hydroxide (25%), tetraethyl orthosilicate (TEOS, 98%), PW (>99%), $H_4SiW_{12}O_{40}$ (SiW, >99%), $H_3PMo_{12}O_{40}$ (PMo, >99%) and other reagents and solvents used in this work were obtained from Merck, Aldrich or Fluka and used without further purification.

Magnetic γ-Fe_2O_3 NPs were prepared through the chemical co-precipitation method [23]. $FeCl_2{\cdot}4H_2O$ (2.0 g) and $FeCl_3{\cdot}6H_2O$ (5.4 g) were dissolved in water (20 mL) separately. These solutions were being mixed together under vigorous stirring (1200 rpm). A concentrated NH_4OH solution (25% w/w) was then added to the stirring mixture at room temperature to maintain the pH between 11 and 12. The resulting black dispersion was continuously stirred (1200 rpm, 1 h) at room temperature and then heated to reflux for 1 h to yield a brown dispersion. The γ-Fe_2O_3 NPs were then purified by a four times repeated centrifugation (3000–6000 rpm, 20 min), decantation and redispersion cycle until a stable brown magnetic dispersion was obtained.

Coating of a layer of silica on the surface of the γ-Fe_2O_3 NPs was achieved by mixing a dispersion of the purified NPs (8.5% w/w, 20 mL) obtained previously with ethanol (80 mL) for 1 h at 40 °C. A concentrated ammonia solution (15 mL) was added and the resulting mixture stirred at 40 °C (800 rpm, 30 min). Subsequently, TEOS (1.0 mL) was charged to the reaction mixture and the mixture continuously stirred at 40 °C (800 rpm, 24 h). The Fe@Si NPs were collected using a permanent magnet, followed by washing three times with ethanol, diethyl ether and drying in a vacuum for 24 h [33].

In order to study the effect of preparation conditions on leaching stability, acidity and activity of supported HPA catalysts, a series of samples were prepared using different impregnating solvents (water, MeOH and MeCN), calcination temperatures (100, 150, 200, 250 and 300 °C) and HPA types (PW, SiW and PMo).

All supported HPA catalysts were generally prepared by impregnating 1.0 g of Fe@Si with an aqueous or organic solution of HPA (1.2 g in 50 mL of solvent) with stirring at about 60 °C for 24–72 h. The catalyst was dried using a rotary evaporator. Further calcination of the catalyst was carried out at corresponding temperature in air for 2 h.

2.2. Catalyst characterization

The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30 and S-4160) with gold coating. Transmission electron microscopy (TEM) image was obtained using a TEM microscope (Philips CM 120 KV, The Netherlands). The size distribution of the samples was obtained using a laser particle size analyzer (HPPS 5001, Malvern, UK). X-ray diffraction (XRD) measurements were performed using a Bruker axs Company, D8 ADVANCE diffractometer (Germany). Fourier transform infrared (FTIR) 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. The tungsten (W) content in the catalyst was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Spectro Ciros CCD spectrometer. NH_3-temperature programmed desorption (NH_3-TPD) measurements were carried out with 200 mg samples on a Micromeritics 2900 TPD/TPR apparatus with a thermal conductivity detector (TCD).

The equilibrium adsorption of the support with different PW solutions was performed by contacting 1.0 g of support with 50 mL of solution, at 60 °C, under constant stirring during 72 h. At regular intervals, the samples of this mixture were taken for their UV–vis analyses.

To check the leaching stability of the catalysts, 0.02 g of each catalyst was stirred in 5 mL methanol for 1 h. UV–vis spectra of the diluted solutions were recorded after removal of solid. The content of HPA in solution was determined with the aid of calibration curves.

The surface acidity of the catalysts was determined by chemisorption of pyridine [34]. 1.0 g of solid was suspended in hexane (100 mL). The suspension was titrated with a 0.1 M solution of pyridine in hexane. Equilibrium concentration of pyridine in hexane solution between each addition was measured by UV–vis spectroscopy based on the fact that pyridine molecule has an absorbance at λ_{max} = 251 nm. For each measurement, 1 mL of solution was separated (1 mL of hexane was added into suspension in order to maintain a constant volume). Then the absorption value of this separated solution was measured, and the equilibrium concentration of pyridine can be calculated using calibration curves, considering the diluted factor. Since the amount of pyridine added was known, the amount of base adsorbed by the solid was calculated by difference.

Time dependent UV adsorption measurements were performed. It was observed that the absorbance was constant for standing times above 15 min. Therefore, the experiments were performed in the time scale of 15 min between each addition of pyridine. All the measurements were repeated at least three times and the reported values are average of the individual runs.

2.3. Catalytic experiments

The oxidative esterification was carried out as follows: catalyst (25 mg), aldehyde (1 mmol) and alcohol (4 mL) were magnetically stirred in the reaction flask. H_2O_2 (6 mmol) was progressively added to the reaction mixture using a syringe. The completion of reaction was monitored by thin layer chromatography (TLC). At