



Heteropoly acid encapsulated into zeolite imidazolate framework (ZIF-67) cage as an efficient heterogeneous catalyst for Friedel–Crafts acylation



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ARTICLE INFO

Article history:

Received 15 May 2015

Received in revised form

5 November 2015

Accepted 6 November 2015

Available online 7 November 2015

Keywords:

Heteropoly acid

Encapsulate

Zeolite imidazolate framework

Catalyst

Friedel–Crafts acylation

ABSTRACT

A new strategy has been developed for the encapsulation of the phosphotungstic heteropoly acid ($H_3PW_{12}O_{40}$ denoted as PTA) into zeolite imidazolate framework (ZIF-67) cage and the PTA@ZIF-67(ec) catalysts with different PTA content were prepared. The structure of the catalysts was characterized by XRD, BET, SEM, FT-IR, ICP-AES and TG. The catalytic activity and recovery properties of the catalysts for the Friedel–Crafts acylation of anisole with benzoyl chloride were evaluated. The results showed that 14.6–31.7 wt% PTA were encapsulated in the ZIF-67 cage. The PTA@ZIF-67(ec) catalysts had good catalytic activity for Friedel–Crafts acylation. The conversion of anisole can reach ~100% and the selectivity of the production can reach ~94% over 26.5 wt% PTA@ZIF-67(ec) catalyst under the reaction condition of 120 °C and 6 h. After reaction, the catalyst can be easily separated from the reaction mixture by the centrifugation. The recovered catalyst can be reused five times and the selectivity can be kept over 90%.

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1. Introduction

The production of various pharmaceutical, pesticides, dyes and agrochemicals at industrial scale involves the synthesis and further transformation of aromatic ketones. The Friedel–Crafts acylation of aromatic compounds is an essential route for the synthesis of the aromatic ketones that are intermediates in the manufacturing of fine and special chemicals as well as pharmaceuticals [1]. Traditionally Lewis acid catalysts i.e. $ZnCl_2$, $AlCl_3$, $FeCl_3$ and Brønsted acid catalysts i.e. HCl, HF and H_2SO_4 had been significantly used for the acylation of aromatic compounds [2]. Utilization of homogeneous acid catalyst for the acylation reactions caused a number of issues such as produced impurities along with desired products, production of large amounts of toxic waste, increase in expenditures, and utilization of catalyst more than stoichiometric quantity, and difficulty in recovery. For Friedel–Crafts reactions, incessant investigation for appropriate heterogeneous catalyst had led to growth of catalysts for example $Re-Br(CO)_5$, $LiClO_4$ -acyl anhydride complex [3], acid-treated clays [4], HZSM-5 zeolite [5], cation exchange resins [6], $Ln-(OTf)_3-LiClO_4$ [7], and heteropoly acids supported catalyst [8,9].

The literatures until now supply an array of catalysts and reage-

nts employ for the Friedel–Crafts acylation of aromatic compounds. However, there is ambit to develop heterogeneous acid catalysts for the Friedel–Crafts acylation reaction. Solid catalysts are secure, reasonable and benign. Furthermore the methods using solid catalysts have advantages for instance better selectivity, moderate reaction conditions, minimize waste and cheap construction of material [9,10]. Acetic acid, acetic anhydride and acetyl chloride as acylating agents have been utilized for the acylation of activated aromatic compounds in presence of zeolites [10], acid-treated metal oxides [11] and heteropoly acids [12]. However, heteropoly acids (HPAs) have been used in excess of organic reactions [9,12]. Nevertheless heteropoly acids in unsupported form present poor stability, fast deactivation and low efficiency. A variety of supports, as mesoporous alumina silicate, mesoporous silica, carbon, alumina, zirconia and metal-organic frameworks (MOFs) have been employed to build up the stability and effectiveness of heteropoly acids [13]. Indeed, the catalytic activity and acidity of the supported heteropoly acids rely mainly on the loading and the nature of carrier, i.e. strong interaction with activated carbons cause low catalytic activity than that of the heteropoly acid itself, while dramatic leaching cause by low interactions of heteropoly acid with support. Direct synthesis of the Keggin structures inside the zeolite cavities (FAU) has been used to achieve the encapsulation of heteropoly acids. This method is revealed to solve the leaching problem, since the windows of the zeolitic cavities are smaller than the heteropoly acid clusters, but only very low loadings can be utilized (< 5 wt%) if diffusion limitations are to be avoided [14].

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Metal-organic frameworks (MOFs) consist of metallic nodes bonded by organic linker, are currently receiving significant attention because of their versatile properties [15–17]. They have been extensively utilized as gas storage [18], separation [19], ion exchange [20], sensor drug delivery [21] and catalysis [22,23]. MOFs as compared to traditional microporous and mesoporous inorganic materials reveal advantages such as tunable pore sizes, high surface area, structural diversity, flexibility and geometrical control by the functionalization and controlling the size of organic linkers [24,25]. However, MOFs used in catalysis are limited because of limited thermal and moisture stability including often completely blocked metal sites by the organic linker or solvent, leaving no free position available for substrate chemisorption's [26]. Zeolite imidazolate frameworks (ZIFs) classified as a novel subclass of MOFs, have fascinated important attention as they unite advantages from both zeolite and conventional MOFs [27,28]. In the past decade, research works have directed on synthesizing new ZIFs and utilizations in different fields. In the literature, there are a small number of applications of ZIFs as catalyst or catalyst supports for transformation of organic compounds as compare to conventional MOFs [29–31].

In this work, we wish to report a direct, synthetic encapsulation of active species such as phosphotungstic acid (PTA) into MOFs. We demonstrate that incorporation of highly dispersed PTA into zeolite imidazolate frameworks-67 (ZIF-67) cage is possible to achieve by following the one-pot synthesis approach. As far as we know, the Friedel–Crafts acylation reaction catalyzed by PTA encapsulated in ZIF-67 are not previously mentioned in the literature. The novel composite material PTA@ZIF-67(ec) has been utilized as an efficient heterogeneous catalyst for Friedel–Crafts acylation reaction of anisole with benzoyl chloride. High conversions have been achieved with PTA@ZIF-67(ec) catalyst without an inert atmosphere. PTA@ZIF-67(ec) catalyst was easily separated from the reaction mixture and reused without significant degradation in activity.

2. Experimental

2.1. Materials

Cobalt nitrate hexahydrate (99%), 2-methylimidazole (98%) and phosphotungstic acid were purchased from Aladdin Chemical Co., Ltd., China. Anisole ($\geq 98\%$) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Benzoyl Chloride (98%) was purchased from Tianjin Fuchen Chemical Reagents, China. Diethyl ether and methanol were purchased from Beijing Yili Fine Chemical Co. Ltd., China. Hydrogen gas and nitrogen gas were purchased from HaiPu Gas Industry Co. Ltd., China. All these reagents were used as received without further purification.

2.2. Catalyst Preparation

2.2.1. Zeolite imidazolate framework (ZIF-67) preparation

For the synthesis of ZIF-67, 0.722 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.48 mmol) was dissolved in 25 mL methanol and 1.629 g of 2-methylimidazole (19.84 mmol) was dissolved in 25 mL methanol separately, were stirred until dissolved. When both reagents were entirely dissolved in methanol, the solution consists of 2-methylimidazole was slowly added to the solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The solution became purple immediately, and the resultant mixture was stirred for 2 h at room temperature. The solids were collected by centrifugation for 10 min and were washed with methanol for several times to remove excess 2-methylimidazole present on the surface and pores. Then solids were dried overnight in air oven, at room temperature. Finally, the sample was dried under vacuum at 130 °C for 2 h.

2.2.2. PTA@ZIF-67(ec) Preparation

The encapsulation of the phosphotungstic acid in ZIF-67 has been done by the same procedure as follow in the synthesis of ZIF-67 with same synthesis mixture. But the phosphotungstic acid (PTA) was dissolved in 11 mL deionized water and added to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. Different loadings of phosphotungstic acid in ZIF-67 structure were achieved (14.6 wt% to 46.4 wt% according to ICP-AES), depending on the amount of phosphotungstic acid introduced into the synthesis mixture.

2.3. Catalyst characterization

The power X-ray diffraction patterns of all samples were recorded at room temperature using a Cu $K\alpha$ radiation source ($\lambda = 1.54056 \text{ \AA}$), operating at 40 kV and 50 mA using a Rigaku D/Max 2500 VB2+/PC diffractometer. The BET surface areas and pore size distributions were obtained from N_2 adsorption–desorption isotherms measured on the Micrometrics ASAP 2020 adsorption analyzer at 77 K. Structure and morphology of samples were characterized by scanning electron microscopy (SEM) on a Zeiss Supra55. Fourier transform infrared (FT-IR) spectra of the samples were collected on a Bruker Tensor 27, by dispersing the samples on KBr pellets in the range of 600–4000 cm^{-1} . Thermogravimetric analysis (TGA) measurements were collected on a SETSYS Evolution from Setaram Instrumentation with a heating rate of 10 °C/min in air up to 800 °C. Elemental analysis was performed by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The samples were investigated with SPECTRO Analytical Instruments GmbH in order to calculate the amount of PTA encapsulated into the ZIF-67 structure. Gas chromatographic (GC) analyses were carried out using a Beijing Beifenruili SP-2100 with flame ionization detector (FID). GC–MS analyses were carried out using a Shimadzu GCMS-QP5000.

2.4. Catalytic performance testing

The Friedel–Crafts acylation of anisole with benzoyl chloride using PTA@ZIF-67(ec) catalyst was carried out in the magnetically stirred round-bottom flask. In a typical reaction, a mixture of anisole and benzoyl chloride with molar ratio 1:2, n-Dodecane as an internal standard was charged into a 50 mL flask containing the PTA@ZIF-67(ec) catalyst. The reaction mixture was then heated to 120 °C with continuously stirring for 6 h. After 6 h, the reaction mixture was quenched with an aqueous NaOH solution (1%, 0.15 mL). The organic components were extracted using diethyl ether (2 mL), dried over anhydrous Na_2SO_4 and the product was analyzed by GC. The structure of the product was defined by GC–MS. For the investigating the reusability of the catalyst, the PTA@ZIF-67(ec) catalyst was separated by simple centrifugation from the reaction mixture, washed with abundant amounts of dichloromethane (DCM), dried under vacuum at room temperature for 6 h and reused in reaction.

3. Results and discussion

3.1. XRD and BET

Fig. 1 illustrates the XRD patterns of bare ZIF-67 and PTA@ZIF-67(ec) samples. The XRD patterns of synthesized samples in this work were in good agreement with simulated single crystal structure patterns in the Cambridge Structural Database (CCDC code=GITTOT). In the bare ZIF-67 sample, a very sharp peak was detected at 7.3° on the XRD pattern, demonstrating that the material was obtained, is highly crystalline material.

In fact, whenever MOF-based materials are synthesized, highly

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