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Research paper

A Novel Brønsted-Lewis acidic catalyst based on heteropoly phosphotungstates: Synthesis and catalysis in benzylation of *p*-xylene with benzyl alcohol

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ABSTRACT

A novel Brønsted-Lewis acidic catalyst, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, has been prepared by the replacement of protons in neat phosphotungstic acid with both organic and metal cations and characterized by FT-IR, Py-IR, XRD, TG-DTG, ICP-AES, BET, elemental analysis and *n*-butylamine potentiometeric titration techniques. This hybrid heterogeneous catalyst with both Brønsted and Lewis acidity can efficiently promote the conversion of dibenzyl ether, the self-condensation product of benzyl alcohol, to the benzylation products, as well restrain the polybenzylation of aromatics. As a result, it exhibits excellent catalytic activity and selectivity in the benzylation of *p*-xylene with clean benzylation reagent benzyl alcohol. Thus, an environmentally friendly route for the benzylation reaction of *p*-xylene with high atomic economy has been developed by this reusable $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ catalyst.

1. Introduction

Friedel-Crafts benzylation of aromatic is a key direct carbon–carbon bond forming reaction in organic synthesis to produce diarylmethanes and their derivatives, commercial significance pharmaceutical intermediates [1,2]. This industrial process suffers from many problems like pollution, corrosion and difficulty in the separation and recovery of catalysts due to the employment of benzyl chloride as the reagent or homogeneous acid such as $AlCl_3$, $FeCl_3$, and H_2SO_4 as catalysts [3,4]. Benzyl alcohol (BA) is a friendly benzylation reagent to substitute benzyl chloride in view of atom economy and environment factor. Many environmentally friendly catalysts have been studied in benzylation reactions with BA to overcome the problems of mineral acids [5–11]. However, it has been found that the self-condensation of BA is more favorable than benzylation of aromatics with less reactivity over the catalyst without enough catalytic activities [12]. Moreover, the monobenzylated aromatics would further react with BA to produce bulky polybenzylated aromatics at high reaction temperature or strong acidity [10,13]. Some heteropoly compounds (HPCs) catalysts with specific heteropoly anions have exhibited good catalytic activities and selectivities for desired monobenzylated aromatics in the reaction with BA being the benzylation reagent. However, in most cases, these HPCs need to be impregnated onto or encapsulated into porous carriers to overcome the high solubility in polar substance (especially for instance, water generating during benzylation) or the low surface areas [14–17].

Recently, a new modification for heteropolyacid (HPA) catalysts has been developed *via* organic cations bonding ionically to heteropolyanion, just like ionic liquids (ILs) [18–27]. Leng [19] has found that the acid strength of heteropoly ionic liquids could be improved effectively by employing propane sulfonate (PS) functionalized organic cations. However, the PS group in organic cations could only provide enough acid strength for some reactions which were easy to realize, such as esterification [23–25]. In our previous work, heteropoly acidic salts with higher acid strength have been developed *via* the partial replacement of protons by the organic cation with acidic PS groups, and have exhibited good activity, selectivity and stability in the benzylation of anisole with BA [28]. Unfortunately, as to the case of *p*-xylene (PX) with less activation degree, it was difficult to achieve an excellent selectivity for monobenzylation *via* single Brønsted acid sites provided by the heteropoly organic acidic salts, due to the forming of dibenzyl ether (DBE) [29]. On the other hand, Hafnium-exchanged het-

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eropoly acid has been found a favorable catalytic and recycling performance due to the high Lewis acidity [30]. Herein, based on the high charge numbers of heteropoly anions, sulfated organic cations $[TEAPS]^+$ (TEAPS: 3-(triethylammonio) propane sulfonate) with Brønsted acidity and metal cations Hf^{4+} with Lewis acidity were introduced together as counter ions for heteropoly anions $PW_{12}O_{40}{}^{3-}$, establishing a novel heteropoly organic-inorganic salt catalyst, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, with both Brønsted and Lewis acidity. As a solid catalyst, this heteropoly organic-inorganic salt which has the similar structure of ionic liquids and enough water resistance has exhibited excellent activity, selectivity and reusability in the benzylation of PX with BA.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical grade and phosphotungstic acid hydrate was dried at 120 °C. The spectra of Fourier transform infrared spectroscopy (FT-IR) for catalyst samples (for Py-IR test, samples (0.50 g) were put in a vacuum drier together with pyridine (3.0 mL) at 2 Kpa for 12 h prior to measurement) in KBr disks was recorded on a Nicolet iS10 FT-IR instrument in the 400–4000 cm^{-1} range. The measurement of X-ray diffraction (XRD) was performed by used a Rigaku DMAX 2500 PC diffractometer equipped with Cu K_α radiation in the 2θ range of 5−90°. The thermal analysis (TG-DTG) was performed with Netzsch TG209F1 instrument in dry N_2 at a heating rate of 20 °C/min from 30 to 800 °C. The content of the elements in the catalyst was determined by Elementar Vario ELIII system and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) with a Prodigy XP ICP spectroscope. The acidity of prepared catalysts was determined by potentiometric titration [31,32]. The Brunauer Emmett Teller (BET) specific surface areas were determined with a Micromeritics ASAP 2010 apparatus.

2.2. Preparation of organic-inorganic heteropoly salts

Contrastive catalysts, $[TEAPS]_3PW_{12}O_{40}$ and $Hf_{0.5}HPW_{12}O_{40}$, were prepared according to the literatures [19,33]. Analogously, equimolar triethylamine and 1,3-propanesultone were dissolved in ethyl acetate and stirred at 50 °C for 24 h under nitrogen atmosphere. The obtained white precipitate, 3-(triethylammonio) propane sulfonate (TEAPS), was filtered, washed with ethyl acetate and dried at 100 °C for 6 h. Next, a solution of intermediate TEAPS and $HfCl_4$ in water was dropped into another aqueous solution of the calculated amount of $H_3PW_{12}O_{40}$. The solution was stirred at room temperature for 24 h, distilled to remove water, and washed with ethyl acetate. Finally, the obtained solid was dried in a vacuum at 80 °C for 6 h to give organic-inorganic heteropoly salts $Hf_x[TEAPS]_yH_zPW_{12}O_{40}(4x+y+z=3)$.

2.3. General procedure for the benzylation of p-xylene with benzyl alcohol

The typical procedure for benzylation reactions was as follows: PX, BA, and catalyst $Hf_x[TEAPS]_yH_zPW_{12}O_{40}$ were added proportionally to a round-bottomed flask with a thermometer, a magnetic stirrer and a reflux condenser. The resulting mixture was stirred vigorously at 140 °C for 2 h then was cooled to room temperature. The reaction solution, from which the generated water and precipitated catalyst had been removed, was analyzed by a gas chromatography (GC-9790) equipped with an FID detector and a capillary column (OV-1701, 50 m × 0.25 mm × 0.25 μm) to determine the conversion of BA and the selectivity of benzylation products.

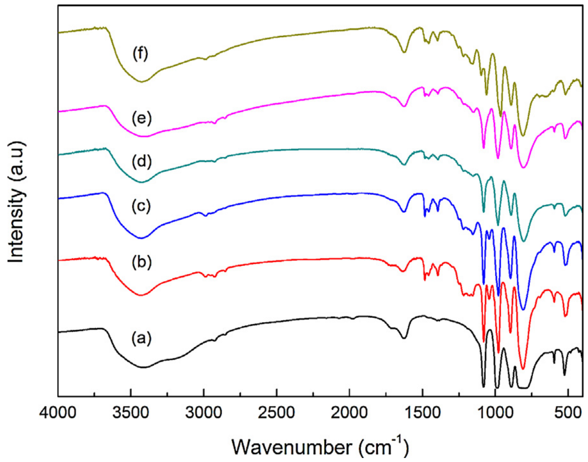

Fig. 1. FT-IR spectra of organic-inorganic heteropoly salts. (a) $H_3PW_{12}O_{40}$, (b) $[TEAPS]_3PW_{12}O_{40}$, (c) $Hf_{0.25}[TEAPS]HPW_{12}O_{40}$, (d) $Hf_{0.25}[TEAPS]_2PW_{12}O_{40}$, (e) $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, (f) Reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$.

The products were identified by GC–MS (HP6980/5973) analysis after the separation of products on a DB-35 column with He as carrier gas.

3. Results and discussion

3.1. Characterization of the organic-inorganic heteropoly salts

The FT-IR spectra (Fig. 1) of prepared organic-inorganic heteropoly salts, comparing with that of the neat $H_3PW_{12}O_{40}$, show that the catalysts $Hf_x[TEAPS]_yH_zPW_{12}O_{40}$, $[TEAPS]_3PW_{12}O_{40}$, and reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ have four featured peaks similar to those of $H_3PW_{12}O_{40}$ [1080 (P-O), 984 (W = O), 891 (W-O_{b1}-W) and 802 cm^{-1} (W-O_{b2}-W)], which are assigned to the Keggin structure. On the other hand, feature peaks at 2989, 1483, 1394 and 1150 cm^{-1} are detected to verify the presence of $[TEAPS]^+$ in these catalysts [20,24]. Obviously, for the organic-inorganic heteropoly salts, the still observed four peaks of Keggin structure together with the simultaneous occurrence of characteristic peaks of organic groups indicate that the structures of both organic cations and heteropoly anions are well preserved. Moreover, the FT-IR spectrum of the used $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ shows no obvious structural change in the catalyst during benzylation (Fig. 1).

Besides, the Py-IR results of prepared organic-inorganic heteropoly salts (Fig. 2) show the existence of featured peaks 1536 cm^{-1} (referred to Brønsted acid) and 1447 cm^{-1} (referred to Lewis acid), which proves the Brønsted-Lewis double acidity of these hybrids and also reveals that both metal ions and sulfated organic cations have been introduced into the structure of $H_3PW_{12}O_{40}$ successfully.

N-butylamine potentiometric titration results of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ and contrastive catalysts are shown in Table 1. Generally, in terms of *n*-butylamine potentiometric, the initial electrode potential indicates the acid strength of catalyst, and the titration jump indicates the total acid amount. It can be seen that introducing organic cations, even with highly acidic sulfonic acid groups (TEAPS), into $H_3PW_{12}O_{40}$ leads to a significant reduction in acid strength. However, there is no distinct influence on acid strength to introduce Hf^{4+} into phosphotungstic acid. Moreover, the total acid amount of these catalysts prevailingly depends on the volume of cations and anions, as well as their bonding. Therefore, the prepared organic-inorganic heteropoly salt, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, demonstrates higher acid strength and total acid amount than highly acidic heteropoly ionic liquid $[TEAPS]_3PW_{12}O_{40}$ because of the existing of Hf cations in struc-