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Short Communication

Clean benzylation of anisole with benzyl alcohol over recyclable partially sulfonated imidazole-exchanged heteropoly phosphotungstate

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ABSTRACT

A series of organic heteropoly acidic salts with high acid strength have been prepared via the partial replacement of protons in a neat phosphotungstic acid. These hybrid catalysts have exhibited good activity and selectivity in the benzylation of anisole with benzyl alcohol. The "liquid-phase reaction at high temperature, solid-state separation at room temperature" performance of obtained hybrid catalysts enables an easy recovery and steady reusability demonstrated by a three-run recycling test.

1. Introduction

The benzylation of aromatic compounds to produce diarylmethanes and their derivatives, which are key industrial compounds as pharmaceutical intermediates or fine chemicals, is one of the important reactions in organic chemistry [1,2]. The general benzylation methods, using benzyl chloride as reagent or employing homogeneous acid catalysts such as $AlCl_3$, $FeCl_3$, and H_2SO_4, suffer from many problems like pollution, corrosion and difficulty in the separation and recovery of catalysts [3–5]. Considering that benzyl alcohol (BA) is a relatively friendly benzylation reagent due to water as the byproduct, a cleaner benzylation route can be carried out to reduce environmental pollution [6,7]. Solid catalysts have been studied in benzylation reactions with benzyl alcohol to overcome the problems of mineral acids [8,9]. However, these heterogeneous catalysts have disadvantages as well, for example, water instability, the tendency to deactivate, and high mass transfer resistance.

Acidic functionalized ionic liquids have been revealed as promising green acid catalysts in view of their high activity, easiness in separation and recovery, just like the advantages of both homogeneous and heterogenous catalysts [10,11]. Especially, owing to the variety of ionic liquid structure available, "temperature-controlled liquid–solid separation" or "reaction-controlled phase-transfer" catalysis can be actualized by ionic liquid catalysts [10,12]. The organic salts of heteropolyacids, which possess the structural characteristics of both ionic liquids and heteropoly compounds, have raised much concern as novel "task-specific" catalysts for acid catalyzed reaction [13]. Shi [14] employed $[BMIM]_3PW_{12}O_{40}$($[1\text{-butyl-3-methylimidazolium}]_3PW_{12}O_{40}$) as the catalyst for esterification of ethanol with acetic acid. Ivanova [15] studied the catalytic performances of $[BMIM]_3PW_{12}O_{40}$ and $[BMIM]_3PMo_{12}O_{40}$ in the dehydration of methanol. Dai [16] found that $[HMIM]_3PW_{12}O_{40}$($[1\text{-methylimidazolium}]_3PW_{12}O_{40}$) could form a "temperature-controlled phase-separation" system in the acetalation reaction of carbonyl compounds. Leng [13,17] synthesized a series of heteropoly ionic liquids containing propane sulfonate (PS) functionalized organic cations $[MIMPS]_3PW_{12}O_{40}$($[3\text{-(1-methylimidazolium-3-yl)propane-1-sulfonate}]_3PW_{12}O_{40}$), $[PyPS]_3PW_{12}O_{40}$ ($[\text{pyridinium propane sulfonate}]_3PW_{12}O_{40}$) and $[TEAPS]_3PW_{12}O_{40}$($[3\text{-(triethylammonio)propane sulfonate}]_3PW_{12}O_{40}$). It was found that the use of the PS group was an effective approach to improve the acid strength of heteropoly ionic liquids. More importantly, $PW_{12}O_{40}^{3-}$ existing in the catalysts would lead to higher melting points than conventional ionic liquids. The above heteropoly ionic liquids with solid nature could act as "reaction induced self-separation catalysts" in some esterification reactions due to their different solubility in reactants and products. However, the PS group in organic cations could only provide enough acid strength for some specific reactions which were easy to realize, such as esterification [18–20]. In our benzylation study of aromatic compounds with benzyl alcohol using $[MIMPS]_3PW_{12}O_{40}$, considerable dibenzyl ether (DBE), the dehydrated product of benzyl alcohol, was produced due to insufficient acid strength of the catalyst.

In this paper, heteropoly acidic salts with acid strength even higher than a neat phosphotungstic acid have been prepared via the partial replacement of protons by the organic cation with highly acidic PS groups. These heteropoly acidic salts, which have enough water resistance and the similar structure of ionic liquids, have exhibited good activity, selectivity and stability in the benzylation of anisole with benzyl alcohol.

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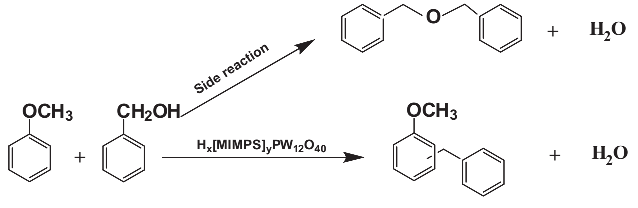

Scheme 1. Benzylation of anisole with benzyl alcohol.

What's more, designed catalysts can be readily reused according to their “liquid-phase reaction at high temperature, solid-state separation at room temperature” performance.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical grade and used without further purification. The ^1H NMR spectra of the designed catalysts were recorded with a 500 MHz BRUKER spectrometer in D_2O or DMSO. FT-IR spectra for catalyst samples in KBr disks were recorded on a Nicolet iS10 FT-IR instrument. Melting points of the catalysts were measured by a conventional method using X-4 type micromelting point apparatus. TG analysis was carried out with NETZSCH-TG 209 F1 Libra instruments in dry N_2 at a heating rate of 20 °C/min from 30 to 800 °C.

The acidity of prepared catalysts was determined by potentiometric titration [14,21]. A mixture containing 0.5 g sample and 30 mL acetonitrile was mixed with the stable potential. Then it was titrated with 0.05 mol/L acetonitrile solution of n-$C_4H_9NH_2$. The initial and jump potential values were registered by a pH meter to determine the acid strength and total acid amount of catalyst samples.

2.2. The preparation of hybrid catalysts

$[HMIM]_3PW_{12}O_{40}$ was obtained from Keggin phosphotungstic acid and N-methyl imidazole at room temperature [16]. $[BMIM]_3PW_{12}O_{40}$ was prepared from 1-butyl-3-methylimidazolium bromide ([BMIM]Br) and heteropolyacids $H_3PW_{12}O_{40}$ [14,22].

The sulfonated imidazole cations partially-exchanged heteropoly acid phosphotungstate $H_x[MIMPS]_yPW_{12}O_{40}$ ($x + y = 3$) was synthesized following the below procedure [17]. N-methylimidazole (0.10 mol) and 1,3-propanesultone (0.10 mol) were dissolved in 100 mL toluene and stirred at 50 °C for 24 h under nitrogen atmosphere. The white precipitate MIMPS was filtered, washed with acetic ether for three times and dried in a vacuum for 4 h. The aqueous solution of $H_3PW_{12}O_{40}$ was dropped into the stoichiometric intermediate MIMPS to obtain acidic salts. The mixture was stirred at room temperature for 24 h, then was distilled and dried in a vacuum to give heteropoly acid phosphotungstate $H_x[MIMPS]_yPW_{12}O_{40}$ ($x + y = 3$).

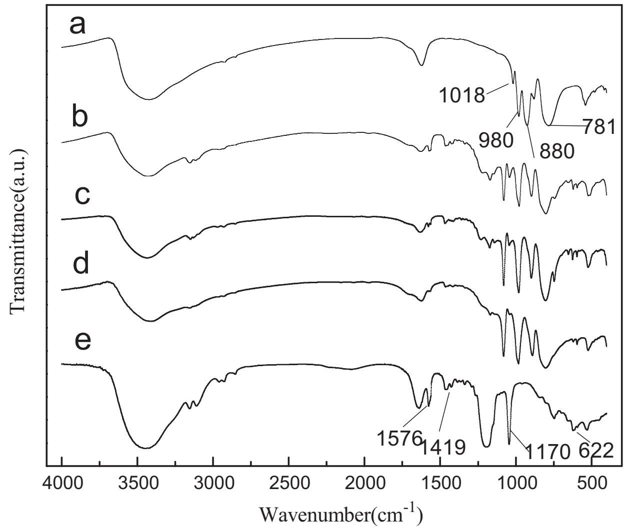

Fig. 1. FT-IR spectra for hybrid catalysts, (a) $H_3PW_{12}O_{40}$ (b) $[MIMPS]_3PW_{12}O_{40}$ (c) $H[MIMPS]_2PW_{12}O_{40}$ (d) $H_2[MIMPS]PW_{12}O_{40}$ and (e) MIMPS.

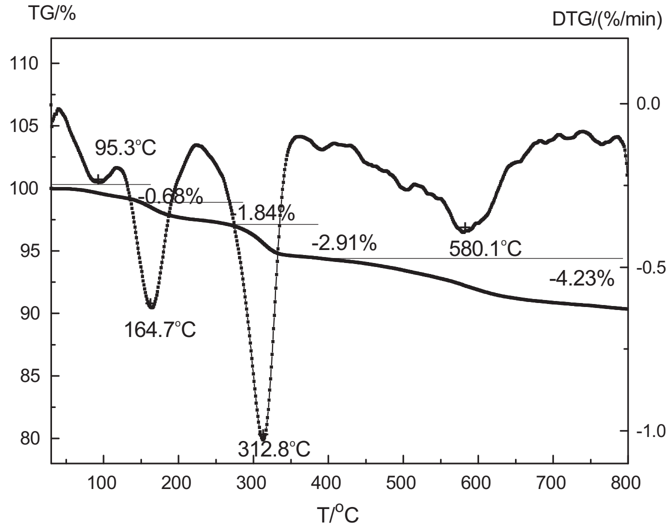

Fig. 2. TG–DTG profiles of $H_2[MIMPS]PW_{12}O_{40}$.

2.3. General procedure for the benzylation with benzyl alcohol

The typical procedure for benzylation reactions was as follows (see Scheme 1): Anisole, benzyl alcohol, and catalyst $H_x[MIMPS]_yPW_{12}O_{40}$ were added proportionally to a round-bottomed flask with a thermometer, a magnetic stirrer and a reflux condenser. The resulting reaction mixture was stirred vigorously at 160 °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 using a gas chromatography(GC-9790) equipped with an FID detector and a capillary column (DB-35 ms, 30 m × 0.25 mm × 0.25 μm) to determine the conversion of benzyl alcohol and the selectivity of methoxy diphenyl methane (MDM) products.

3. Results and discussion

3.1. Characterization of hybrid catalysts

Similar ^1H NMR (500 MHz, DMSO) spectra of $[MIMPS]_3PW_{12}O_{40}$, $H[MIMPS]_2PW_{12}O_{40}$, $H_2[MIMPS]PW_{12}O_{40}$ and their intermediate are observed: δ 2.21(quint, 2H), 2.83(t, 2H), 3.83(s, 3H), 4.26(t, 2H), 7.38(d, 1H), 7.46(d, 1H), 8.70(s, 1H), which support the correct structure of organic cations. Moreover, their FT-IR spectra are illustrated in Fig. 1, comparing with that of the neat $H_3PW_{12}O_{40}$. It can be seen that $[MIMPS]_3PW_{12}O_{40}$, $H[MIMPS]_2PW_{12}O_{40}$ and $H_2[MIMPS]PW_{12}O_{40}$ catalysts gave similar four featured peaks (around 1018 (P–O), 980 (W=O), 880 ($W-O_{b1}-W$) and 781 cm^{-1} ($W-O_{b2}-W$)) with those of $H_3PW_{12}O_{40}$ assigned to the Keggin structure. On the other hand, featured peaks at 1576 (C=N), 1419 ($S-CH_2$), 1170 (S=O stretching vibration) and 622 (C–H of imidazole ring) cm^{-1} of MIMPS also appear in the spectra of all the hybrid catalysts. The above results indicate that both $MIMPS^+$ and $PW_{12}O_{40}^{3-}$ are combined in all the hybrid catalysts.

Fig. 2 shows that $H_2[MIMPS]PW_{12}O_{40}$ will lose crystalliferous water (calculated weight loss: 2.52%) during 30–275 °C. Moreover, decomposition peaks of the imidazole ring and sulfonic group in $MIMPS^+$ are