Front. Chem. China 2009, 4(2): 132–135
DOI 10.1007/s11458-009-0032-9

RESEARCH ARTICLE

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Preparation of 1-butyl-3-methylimidazolium dodecatungstophosphate and its catalytic performance for esterification of ethanol and acetic acid

Abstract 1-Butyl-3-methylimidazolium dodecatungstophosphate catalyst ([bmim]$_3$PW$_{12}$O$_{40}$) with high water tolerance was prepared from 1-butyl-3-methylimidazolium bromide ([bmim]Br) and phosphotungstic acid ($H_3PW_{12}O_{40}$). The catalyst was characterized by means of Fourier transform infrared spectroscopy, thermogravimetry-differential scanning calorimetry, *n*-BuNH$_2$ potentiometric titration, elemental analysis and so on. Its catalytic activity for esterification of ethanol and acetic acid to ethyl acetate was measured. The results show that there were three crystal-water molecules in the [bmim]$_3$PW$_{12}$O$_{40}$ catalyst, and it preserved the primary Keggin structure and acid strength of $H_3PW_{12}O_{40}$. The acid amount of [bmim]$_3$PW$_{12}$O$_{40}$ catalyst was less than that of $H_3PW_{12}O_{40}$. The [bmim]$_3$PW$_{12}$O$_{40}$ catalyst exhibited higher catalytic activity and reusability in the esterification of ethanol and acetic acid to ethyl acetate.

Keywords 1-butyl-3-methylimidazolium bromide, 12-phosphotungstic acid, heteropoly acid, 1-butyl-3-methylimidazolium dodecatungstophosphate, ethanol, acetic acid, esterification, ethyl acetate

Heteropolyacids (or their salts) and supported heteropolyacids (or their salts), as one kind of environmentally friendly catalysts, have attracted greater attention because they possess many advantages, such as, simple composition, definite structure, easily modified component,strong acidic and redox properties, unique reaction fields such as pseudoliquid, high-activity in low temperature and high thermal stability [1, 2]. Most of the heteropolyacids (or their salts) homogeneous catalysts are difficult to recover, which can lose the expensive heteropolyacids (or their salts) and pollute the environment, and are hence not suitable for industrial applications. The heteropolyacids (or their salts) supported on different porous supporters can resolve the problem of catalyst recovery, increase the surface area and enhance the catalytic performance, consequently improving the product quality and reducing the production cost [3, 4]. However, when the supported heteropolyacids (or their salts) catalysts are prepared by a physical adsorption method, there is a desorption problem of the active components from the supporter, and the catalysts are not ideal for recycled use. Therefore, the preparation of new heteropolyacids (or their salts) catalysts has attracted great attention. Chiang M-H *et al.* [5] reported the redox properties of 1-pentyl-3-methylimidazolium dodecatungstophosphate characterized by electrochemistry. So far, the application of 1-butyl-3-methylimidazolium dodecatungstophosphate in catalytic reactions has not yet been reported. Based on our earlier work, we prepared 1-butyl-3-methylimidazolium dodecatungstophosphate catalyst in order to realize the heterogenizing application of $H_3PW_{12}O_{40}$ homogeneous catalyst, which is insoluble in water, alcohol and ester. The catalyst was characterized by means of Fourier transform infrared spectroscopy (FT-IR), thermogravimetry-differential scanning calorimetry (TG-DSC), *n*-BuNH$_2$ potentiometric titration and elemental analysis, and its catalytic activity for esterification of ethanol and acetic acid to ethyl acetate was measured.

1 Experimental

1.1 Preparation of Catalyst

0.2 mole of *N*-methylimidazole (Linhai Kaile Chemical Factory) was dissolved into 0.2 mole of 1-bromobutane

Translated from *Chinese Journal of Catalysis*, 2008, 29(7) (in Chinese)

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(Shanghai Wulian Chemical Factory) and then heated to 110°C and stirred for 12 h. The mixture was cooled to room temperature, and a yellow and viscous 1-butyl-3-methylimidazolium bromide ([bmim]Br) was obtained [6].

0.01 mole of dodecatungstophosphoric acid was dissolved into 100 mL water, and 0.06 mole of ([bmim]Br) was added into the above solution. The mixture was stirred at room temperature for 12 h. The white solid precipitated was filtered and washed with water until no detectable bromide ions were present in the solution. The white solid was dried at 80°C for 24 h, and white $[bmim]_3PW_{12}O_{40}$ catalyst powder was obtained.

1.2 Characterization of catalysts

Analysis of C, H and N elements in the sample was performed using Flash EA1112 Elemental analysis instrument (Thermofinigan). P and W elements in sample were measured using IRIS full spectrum direct reading ICP spectrometer (Fisher Scientific). The TG-DSC patterns were recorded at 20°C/min on TG-50 thermal analysis instrument (Shimadzu) in N_2 (20 mL/min). The FT-IR spectra of $H_3PW_{12}O_{40}$, [bmim]Br and $[bmim]_3PW_{12}O_{40}$ were recorded on a Nicolet 5700 FT-IR at room temperature in KBr pellets over the range of 400–4000 cm^{-1} under atmospheric conditions. The acidity of $[bmim]_3PW_{12}O_{40}$ catalyst was measured by means of potentiometric titration. The $[bmim]_3PW_{12}O_{40}$ catalyst (0.5 g) was added to 30 mL of acetonitrile and the mixture was agitated until electrode potential stabilization. The suspension was titrated with 50 mmol/L *n*-butylamine in acetonitrile at 0.05 mL/min. The electrode potential variation was measured with a digital pH meter. According to the titration jump, the acid amount of the catalyst was measured.

1.3 Synthesis of ethyl acetate

Acetic acid (AR, Sinopharm Chemical Reagent Co. Ltd), ethanol (AR, Anhui Ante Biochemistry Co. Ltd), $[bmim]_3PW_{12}O_{40}$ catalyst and toluene (AR, Hangzhou Chemical Reagent Co. Ltd) were added to a flask with a temperature controller, water separator, magnetic stirrer and condenser. The mixture was stirred at the reflux temperature for required time. Then, the mixture was cooled and filtered, and the concentrations of ethanol and ethyl acetate in reaction solution were determined by gas chromatography. The catalytic activities were evaluated on the base of the yield of ethyl acetate.

2 Results and discussion

2.1 Characterization of catalysts

Figure 1 shows the FT-IR spectra of different catalyst samples. The four absorption bands at 1081, 983, 890 and 805 cm^{-1} can be observed for $H_3PW_{12}O_{40}$, which are the fingerprints of the Keggin structure of $H_3PW_{12}O_{40}$, usually assigned to P–O, W═O, W–O_{b1}–W in corner shared octahedral and W–O_{b2}–W in edge shared octahedral associated with the asymmetric vibrations, respectively [7]. Similarly, there are four characteristic bands of Keggin structure at 1079, 982, 890 and 804 cm^{-1} for $[bmim]_3PW_{12}O_{40}$, indicating that the $[bmim]_3PW_{12}O_{40}$ catalyst preserves the primary Keggin structure of $H_3PW_{12}O_{40}$. The absorption bands at 3141, 2960, 1571 and 1169.7 cm^{-1} are observed in $[bmim]_3Br$ catalyst as shown in Fig. 1, which are assigned to C–H stretching vibration in the imidazole ring, C–H stretching vibration of substitute group, –C═N– stretching vibration and imidazole ring stretching vibration, respectively. Similar observations have been reported in reference [6]. For the $[bmim]_3PW_{12}O_{40}$ catalyst, there are characteristic bands of [bmim]Br at 3147, 2958, 1568 and 1165 cm^{-1} respectively, indicating that there is $[bmim]^+$ ion in the $[bmim]_3PW_{12}O_{40}$ catalyst.

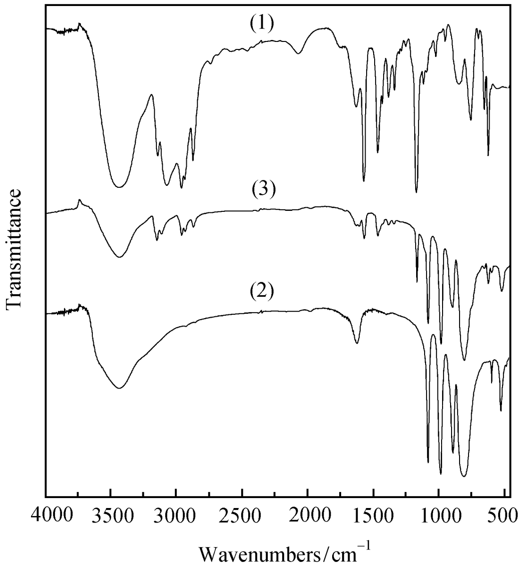

Fig. 1 FT-IR spectra of different catalyst samples
(1) [bmim]Br, (2) $H_3PW_{12}O_{40}$, (3) $[bmim]_3PW_{12}O_{40}$

Figure 2 shows TG-DSC profiles of the different catalyst samples. It can be seen that $H_3PW_{12}O_{40}$ shows two endothermic peaks accompanied by the loss of water at 82°C and 200°C, respectively, and one exothermic peak associated to the decomposition of $H_3PW_{12}O_{40}$ into corresponding single oxides at 613°C. The $[bmim]_3PW_{12}O_{40}$ catalyst shows one broad endothermic dehydration peak at the range of 40–350°C (1.57% weight loss) and four exothermic peaks associated to the decomposition at 396°C, 472°C, 590°C and 608°C, respectively, which are accompanied by the weight loss. It indicates that the thermal decomposition of

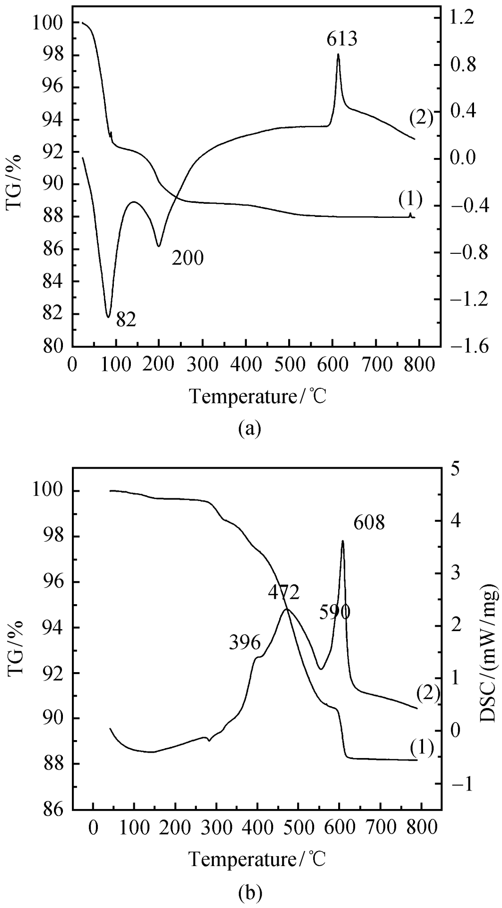

Fig. 2 TG-DSC profiles of different catalyst samples
(a) $H_3PW_{12}O_{40}$, (b) $[bmim]_3PW_{12}O_{40}$; (1) TG, (2) DSC

$[bmim]_3PW_{12}O_{40}$ catalyst is carried out gradually. The $[bmim]^+$ ion is firstly decomposed in the range of 400–600°C, the dodecatungstophosphoric acid anion is decomposed at near 610°C.

The elemental analysis results show that the contents of C, H, N, P and W in the $[bmim]_3PW_{12}O_{40}$ catalyst are 9.08%, 1.48%, 2.47%, 0.94% and 66.26%, respectively. Therefore, the structural formula of $[bmim]_3PW_{12}O_{40}$ catalyst possesses three molecules of crystal water (the calculated contents of C, H, N, P and W are 8.61%, 1.54%, 2.51%, 0.92% and 65.88%, respectively).

According to the above deduction, the weight loss of $[bmim]_3PW_{12}O_{40}$ catalyst should be about 14%. However, the weight loss from Fig. 2 (about 12% in N_2) is less than the theory value. It is possibly due to the carbonization in the decomposition process of $[bmim]^+$ ion in N_2.

2.2 Acidity of the catalysts

The acidity of the catalysts were measured by means of potentiometric titration with *n*-butylamine because the $[bmim]_3PW_{12}O_{40}$ catalyst decomposes easily during heating. Fig. 3 shows the potentiometric titration curves of different samples with acetonitrile solution of *n*-butylamine. Generally, the initial electrode potential indicates the maximum acid strength of the sites, and the titration jump indicates the total number of acid sites when the acidity of solid acid catalysts is measured by the mean of *n*-butylamine potentiometric titration. The acid strength of these sites may be classified according to the following scale: $E > 100\,\text{mV}$ (very strong sites), $0\,\text{mV} < E < 100\,\text{mV}$ (strong sites), $-100\,\text{mV} < E < 0\,\text{mV}$(weak sites) and $E < -100\,\text{mV}$ (very weak sites) [8]. Figure. 3 shows that the initial electrode potentials of $[bmim]_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ are 561 and 567 mV respectively, and their titration jump electrode potentials are 368 and 328 mV, respectively. It indicates that the acid sites of $[bmim]_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ catalysts are very strong and the acid strengths of them are about the same, but the numbers of acid sites are obviously different. The acid amount of $H_3PW_{12}O_{40}$ (1.0 mmol/g) is greater than that of $[bmim]_3PW_{12}O_{40}$ catalyst (0.08 mmol/g). It is due to the different manners of producing acidity. The $H_3PW_{12}O_{40}$ catalyst is a typical Bronsted's acid, and the latter's acidity can be from H^+ produced by hydrolysis.

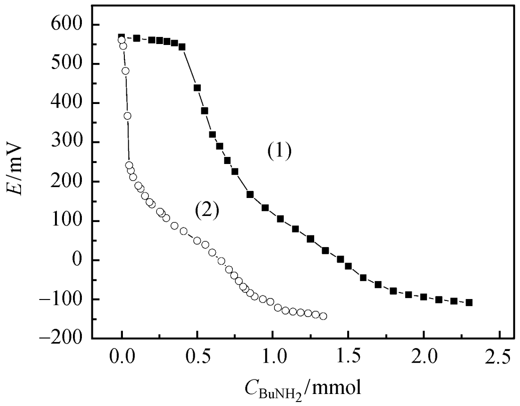

Fig. 3 Potentiometric titration curves of different catalyst samples with acetonitrile solution of butylamine
(1) $H_3W_{12}O_{40}$, (2) $[bmim]_3PW_{12}O_{40}$

2.3 Catalytic activity of the catalysts

Table 1 shows the catalytic activity of different samples for esterification of ethanol and acetic acid to ethyl acetate. As can be seen from Table 1, because of the autocatalysis of acetic acid, a certain amount of ethyl acetate was obtained (yield 57.8%) in the absence of catalyst. The yield of ethyl acetate in the presence of [bmim]Br is about the same as in the absence of catalyst, indicating that the [bmim]Br has no catalytic activity for the esterification ethanol and acetic acid. As shown in Table 1, $H_3PW_{12}O_{40}$ and $[bmim]_3PW_{12}O_{40}$ catalysts exhibit catalytic activity. The catalytic activity of $H_3PW_{12}O_{40}$ is a little higher than that

Table 1 Catalytic activity of different samples for esterification of ethanol (EtOH) and acetic acid (AA) to ethyl acetate (EA)

Sample	Solubility	*Y* (EA) / %
—	—	57.8
[bmim]Br	Soluble	57.0
$[bmim]_3PW_{12}O_{40}$	Insoluble	98.4
$H_3PW_{12}O_{40}$	Soluble	99.7

Reaction conditions: n(EtOH)= 0.1 mol, n(AA)/n(EtOH)= 3, m(Catalyst)= 0.3 g, V(phMe)= 4.0 mL (water-taken agent), T= 100°C (refluxing), t= 3 h

of $[bmim]_3PW_{12}O_{40}$, because both the catalysts have the same acid strength and the acid amount of the former is greater than that of the latter. In addition, the solubilities of $[bmim]_3PW_{12}O_{40}$ catalyst in water, ethanol, acetic acid and ethanol acetate are very little (0.39, 0.38, 0.29 and 0.40 mg/L, respectively). The solubility of $[bmim]_3PW_{12}O_{40}$ catalyst in the reaction solution is only 0.40 mg/L. In other words, the weight loss of catalyst after being used once was about 0.004%. It indicates that the $[bmim]_3PW_{12}O_{40}$ catalyst is separated from reaction solution in this reaction , thus realizing the heterogenizing application of the $H_3PW_{12}O_{40}$ homogeneous catalyst.

2.4 Stability of $[bmim]_3PW_{12}O_{40}$ catalyst

Table 2 shows the recycle performance of $[bmim]_3PW_{12}O_{40}$ catalyst. It can be seen from Table 2 that, the yield of ethyl acetate is 99.7% when the fresh catalyst is used. When the catalyst is reused, the catalytic activity decreases. Then, the catalytic activity is invariable in subsequent uses. It indicates that the $[bmim]_3PW_{12}O_{40}$ catalyst exhibits good stability in the esterification of ethanol and acetic acid to ethyl acetate. The reason why the activity of the second used $[bmim]_3PW_{12}O_{40}$ catalyst decreases is that ethyl acetate is strongly adsorbed on the surface of the catalyst. The absorption bands of C=O and C–O–C at near 1740 cm^{-1} and 1238 cm^{-1} on the used catalyst were observed by IR determination. The ester on the used catalyst cannot be removed by washing with water and alcohol, indicating that the adsorption of ester on the surface of catalyst is very strong.

Table 2 Catalytic performance of reused $[bmim]_3PW_{12}O_{40}$ catalyst

No.	Catalyst	*Y* (EA) / %
1	Fresh	99.7
2	First repeat	88.5
3	Second repeat	88.5
4	Third repeat	89.9
5	Fourth repeat	87.4

Reaction conditions: n(EtOH)= 0.2 mol, n(AA)/n(EtOH)= 3, m(Cat)= 0.6 g, V (phMe)= 8.0 mL (water-taken agent), T= 100°C (refluxing), t= 5.5 h

3 Conclusions

There are three crystal-water molecules in the $[bmim]_3PW_{12}O_{40}$ catalyst which preserves the primary Keggin structure of $H_3PW_{12}O_{40}$. The catalytic activities of $H_3PW_{12}O_{40}$ and $[bmim]_3PW_{12}O_{40}$ in the synthesis of ethyl acetate are almost the same because they have the same acid strength. The $[bmim]_3PW_{12}O_{40}$ catalyst can be reused with high catalytic activity and the recycling use of $H_3PW_{12}O_{40}$ homogeneous catalyst is realized.

References

1. Hu Y H, Shi J H, Wang G L, Lin B P, Jiang F. Application of heteropoly acids or their salt catalysts in organic synthesis. Modern Chem Ind, 2004, 24(Suppl): 32 (in Chinese)
2. Li X, Shi J H, Jin D, Zhou L, Yan W. Application of heteropoly acids and their salts catalysts in catalytic oxidation reaction. Modern Chem Ind, 2006, 26(Suppl): 51 (in Chinese)
3. Chen D Y, Wu Zh X. New progress of the loaded heteropolyacids catalyst. Appl Chem Ind, 2006, 35(10): 802 (in Chinese)
4. Zhao X Q, Han Y T, Sun X L, Wang Y J. Structure and Catalytic Performance of $H_3PW_{12}O_{40}/SiO_2$ Prepared by Several Methods.Chin J Catal , 2007, 28(1): 91 (in Chinese)
5. Chiang M H, Dzielawa J A, Dietz M L, Antonio M R. Redox chemistry of the Keggin heteropolyoxotungstate anion in ionic liquids. J Electroanal Chem, 2004, 567(1): 77
6. Song S Q. Preparation of [bmin]Cl/$FeCl_3$ ionic liquid and its characterization. Technol & Deve of Chem Ind, 2006, 35(6): 8 (in Chinese)
7. Wang E B, Hu Ch W, Xu L. Introduction to Polyacid Chemistry. Beijing: Chem Ind Press, 1998, 14 (in Chinese)
8. Vazquez P, Pizzio L, Caceres C, Blanco M, Thomas H, Alesso E, Finkielsztein L, Lantano B, Moltrasio G, Aguirre J. Silica-supported heteropolyacids as catalysts in alcohol dehydration reactions. J Mol Catal A, 2000, 161(1–2): 223