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Polyoxometalates Based Supported Ionic Liquid Catalysis for Alcohol Oxidation with Hydrogen Peroxide

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Abstract: Ionic liquid functionalized SiO_2 (SiO_2-IL) was demonstrated to be an appropriate support for polyoxometalates (POMs), and three kinds of commercially available POMs were immobilized on SiO_2-IL as supported ionic liquid catalysis for alcohol oxidation with H_2O_2. The catalysts were characterized by FTIR, XRD and XPS. PW/SiO_2-IL shows the best activity and high yields (most > 93 %) of corresponding carbonyl products were obtained. In addition, the catalyst can be easily recovered by filtration and reused seven times with good yields.

Key words: Polyoxometalates; supported ionic liquid catalysis; alcohol oxidation; hydrogen peroxide

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The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds (ketones, aldehydes, carboxylic acids) is one of the most important processes in both chemical laboratories and practical applications [1-3]. For example, cyclohexone, the product of cyclohexanol oxidation, is the raw material in the preparation of nylon-6 and nylon-66 [4]. Traditional methods for alcohol oxidation generally involve large amounts of chromium reagents ranging from stoichiometric to excess [5], however, these oxidants are toxic and corrosive. From economic and environmental viewpoint, new developments in this field require the use of clean oxidant, such as O_2 and H_2O_2 [6], together with recyclable catalyst.

Polyoxometalates (POMs) are a class of early transition metal oxygen clusters, which have received much attention in broad fields such as catalysis, materials science and medicine because of their chemical properties, such as hydrolytic and thermal stability, solubility in various media, tunable acid and redox properties at the molecular or atomic level [7]. Many kinds of POMs can act as effective catalysts for O_2 or H_2O_2 based green oxidation. Recently, there have been some publications [8-13] reporting on alcohol oxidation catalyzed by molybdenum and tungsten containing POMs. For example, using $[PMo_{10}V_2O_{40}]^{5-}$ as catalyst and air or O_2 as oxidant [8-9]; using $[PW_{12}O_{40}]^{3-}$ and $[SiW_{10}O_{36}]^{8-}$ as catalyst and H_2O_2 as oxidant [10-13], and so on in homogeneous or two-phase or emulsion systems. Although good yields were obtained in these systems, they have some disadvantages, such as complicated steps in the separation of products and recovery of the catalyst. To solve this problem, supporting POMs on an appropriate support without loss of the intrinsic activity and selectivity[14], is probably the best choice.

Ionic liquids (ILs), composed entirely of ions with a melting point below or near 100 ℃, have attracted significant attention in the scientific community due to

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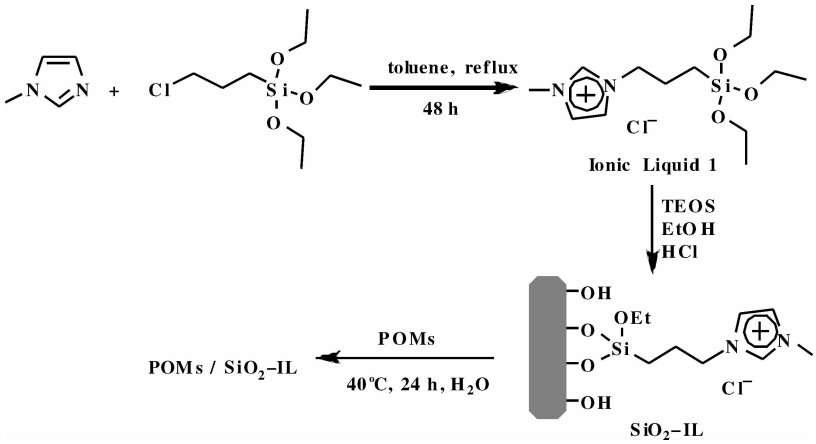
there unique properties, including low volatility, high polarity, and thermal stability over a wide temperature range, as well as tunability of their acidity and solubility [15-16]. Supported ionic liquid catalysis is a concept that combined the advantages of ionic liquid phase with heterogeneous support[17], which not only reduce the required amounts of ionic liquid but also facilitate catalyst recovery. Venturello type POM $\{PO_4[WO(O_2)_2]_4\}^{3-}$[18] and Prandi type POM $[W_2O_3(O_2)_4(H_2O)]^{2-}$[19] had been successfully immobilized on ionic liquid modified support as catalysts with H_2O_2. Here, we present a supported ionic liquid catalysis system for alcohol oxidation with 30 % aqueous H_2O_2 catalyzed by POMs ($[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, and $[PMo_{12}O_{40}]^{3-}$) immobilized on ionic liquid functionalized SiO_2 (POMs/SiO_2-IL). POMs were immobilized on the modified SiO_2 (SiO_2-IL) by anion exchange via a simple preparation procedure under mild conditions. Furthermore, recycling and reusing of the catalyst were demonstrated, which make the system economical friendly.



Scheme 1 Preparation of POMs/ SiO_2-IL

1 Experimental

1.1 Chemicals and instruments

N-methylimidazole was redistilled before use. All the other chemicals (AR grade) were commercially available and used without further purification. NMR spectra were recorded on an INOVA-400 spectrometer. Elemental analyses (EA) were performed on an Elementar VARIO EL cube. Fourier transform infrared (FTIR) spectra were recorded at room temperature on powdered samples using the KBr wafer technique in a Nicolet Nexus 870 FTIR spectrometer. Spectra were recorded with a resolution of 4 cm^{-1}. The X-ray powder diffraction (XRD) of the samples was carried out on a PANalytical X'pert Pro diffractometer using nickel filtered Cu Kα radiation with a scanning angle (2θ) of 15-80°, a scanning speed of 2°/min, and a voltage and current of 40 kV and 30 mA. X-ray photoelectron spectra (XPS) were obtained using a VG ESCALAB 210 spectrometer equipped with a Mg Kα X-ray radiation source ($h\upsilon$ = 1253.6 eV) and a hemispherical electron analyzer. The spectra were recorded in the constant pass energy mode with a value of 20 eV, and all binding energies were calibrated using the C1s peak at 285.0 eV as the reference. The BET surface area measurements were performed on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature.

1.2 Catalyst preparation

1.2.1 Preparation of ionic liquids functionalized SiO_2 (SiO_2-IL) [20, 21]

1-Methylimidazole (4.51 g, 55 mmol) was dissolved in 50 mL of dry toluene, 3-chloropyltriethoxysilane (12.05 g, 50 mmol) was added to the solution and the mixture was refluxed for 48 h under an argon atmosphere. After reaction, two phases rapidly formed, with the slightly yellow colored ionic liquid at the bottom and toluene at the top. The phases were then separated and the ionic liquid was washed three times with 20 mL toluene. After drying under vacuum at 60 C for 24 h, ionic liquid 1-(triethoxysilypropyl)-

3-methylimidazolium chloride (Ionic Liquid 1) was obtained with a honey-like consistency at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.59 (s, 1H, NCHN), 7.71 (s, 1H, NCHCH), 7.40 (s, 1H, NCHCH), 4.32-4.36 (t, J = 7.2 Hz, 2H, CH_2N), 4.15 (s, 3H, NCH_3), 3.79-3.85 (q, J = 14.0 Hz, 6H, OCH_2), 1.99-2.03 (m, 2H, $CH_2CH_2CH_2$), 1.20-1.24 (t, J = 7.0 Hz, 9H, CH_3CH_2O), 0.59-0.63 ppm (t, J = 8.0 Hz, 2H, $SiCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0 (NCN), 123.6 (NCH), 121.7 (CHN), 58.6 (OCH_2), 51.7 (NCH_2), 36.5 (NCH_3), 24.4 ($CH_2CH_2CH_2$), 18.4 (CH_3CH_2), 7.9 ppm ($SiCH_2$).

Afterwards, Ionic Liquid 1 (3.23 g, 10 mmol) was dissolved in 10 mL of ethanol, and TEOS (10.42 g, 50 mmol) was added, after the mixture was stirred at 60 C for about 30 minutes, 4.2 ml hydrochloride acid solution (0.4 mol/L) was added dropwise under vigorous stirring. Stirring was continued for about 3 h, then stopped and a transparent gel formed gradually. After the gel was aged for at 60 C for 12 h, it was subjected to a vacuum at 80 C for 5 h to remove the volatile component. The resulting solid containing 1-propyl-3-methylimidazolium chloride ionic liquid (denoted as SiO_2-IL) was triturated to about 100-200 μm in diameter. The nitrogen content of SiO_2-IL was found to be 5.09 % (1.82 mmol/g) by elemental analysis of nitrogen.

1.2.2 Preparation of polyoxometalates immobilized on SiO_2-IL

$H_3PW_{12}O_{40}$ (HPW, 3.0 g) was dissolved in distilled water and heated to 40 C. Then 3 g of SiO_2-IL was added to this solution, and the mixture was vigorously stirred at this temperature for 48 h. The resulting product was washed with a large amount of water until the washings become neutral and dried in the vacuum to afford 4.6 g final product (denoted as PW/SiO_2-IL). The loading amount of $H_3PW_{12}O_{40}$ was about 120 $\mu mol \cdot g^{-1}$.

SiW/SiO_2-IL and PMo/SiO_2-IL were prepared in a similar method to that mentioned above, and the loading amount of $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ were 86 $\mu mol \cdot g^{-1}$ and 95 $\mu mol \cdot g^{-1}$ respectively.

1.2.3 Preparation of $[C_4mim]_3PW_{12}O_{40}$ [22]

Equal molar amounts of chlorobutane and 1-methylimidazole were refluxed at 70℃ for 72 h with stirring until two phases formed. The top phase, containing unreacted starting material, was decanted and washed three times with ethyl acetate. The crude product was then recrystallized three times from acetate and acetonitrile, after dried under vacuum at for 24 h, $[C_4mim][Cl]$ was obtained as a white solid at room temperature. $[C_4mim]^+$ salt of $[PW_{12}O_{40}]^{3-}$ was precipitated from water solution of $H_3PW_{12}O_{40}$ by the addition of excess $[C_4mim][Cl]$. The white solid was collected, wash thoroughly with water and dried. ^{1}H NMR (400 MHz, [D_6] DMSO): δ = 9.10 (s, 1H, NCHN), 7.76 (s, 1H, NCHCH), 7.70 (s, 1H, NCHCH), 4.15-4.18 (t, J = 7.2 Hz, 2H, CH_2N), 3.89 (s, 3H, NCH_3), 1.74-1.80 (q, CH_2), 1.22-1.32 (q, CH_2), 0.89-0.93 ppm (t, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4 (NCN), 123.6 (NCH), 122.2 (CHN), 48.4 (NCH_2), 35.7 (NCH_3), 31.3 (CH_2), 18.8 (CH_2), 13.2 ppm (CH_3).

1.3 Typical reaction procedure

A 25-mL round-bottom flask equipped with a magnetic stirring bar and a reflux condenser was charged with 0.14 g catalyst, 5 mmol of substrate, 15 mmol H_2O_2 (30 % aqueous solution) and 3 mL of MeCN. The mixture was kept at 90 C for 12 h and then cooled to room temperature, 3 mL ethyl ether was added and stirred for 5 minutes. The organic and aqueous phases were collected, after decomposition of the excess amount of H_2O_2 with MnO_2, the products were dried over anhydrous Na_2SO_4. The qualitative analyses of the oxidation products were determined by GC-MS (HP 6890/5973), and quantitative analyses were performed on GC (Agilent 6820) with a flame ionization detector, N_2 carrier gas, and dodecane was used as the internal reference.

2 Results and discussion

2.1 Characterization of the catalyst

Three kinds of POMs ($[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$ and $[PMo_{12}O_{40}]^{3-}$) were immobiled on SiO_2-IL

successfully by ion exchange (Scheme 1) under benign condition. Then the catalysts were characterized by FT-IR and XRD and XPS.

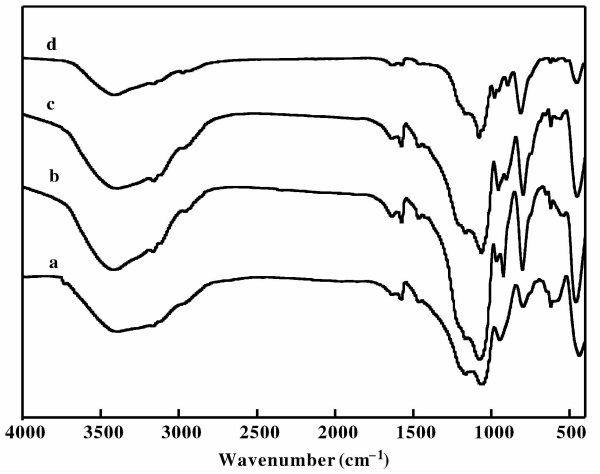


Fig. 1 FTIR spectra of (a) SiO_2-IL, (b) SiW/SiO_2-IL, (c) PMo/SiO_2-IL, and (d) PW/SiO_2-IL

FTIR spectra (Fig. 1) shows the absorption bands of SiO_2 at 1 060 (υ_{as} υSi-O-Si), 940 (υSi-OH), 800 (υ_s Si-O-Si), 440 cm^{-1} (δSi-O-Si)[23], and the characteristic bands of the parent imidazole salt at 3 160 (υCH), 2 950 (υ_{as} CH_2), 2 850 (υ_s CH_2), and 1 570 cm^{-1} (υC = N), which confirm the surface anchor between ionic liquid and SiO_2. After the immobilization of POMs on SiO_2-IL, four characteristic bands in the 700 – 1 100 cm^{-1} range are clearly observed. Take PW/SiO_2-IL as an example, spectrum at 1 080 (υ_{as} P-O_a), 980 (υ_{as} W = O_d), 890 (υ_{as} W-O_b-W), and 810 cm^{-1} (υ_{as} W-O_c-W)[24] are the characteristic bands of Keggin-type polyoxometalate. The characteristic bands of SiW/SiO_2-IL and PMo/SiO_2-IL are similar to that of PW/SiO_2-IL mentioned above, indicating that POMs had been successfully immobilized on ionic liquid functionalized SiO_2 (SiO_2-IL) without structural damage. XPS analysis also confirmed the structural integrity of POMs after immobilization. The 2p level binding energy of the P atom presents in PW/SiO_2-IL is 134.4 eV, which is consistent with that in HPW (134.5 eV). While the binding energy of Si and P atom in SiW/SiO_2-IL and PMo/SiO_2-IL, is 103.3 eV and 134.0 eV respectively.

The XRD patterns of PW samples are show in Fig. 2. The characteristic peaks of bulk HPW are observed at 2θ of 10.3°, 20.6°, 25.6° and 34.5°. After supported by impregnation method, HPW may aggregate on the surface of the support[25], however, the characteristic peaks of HPW disappeared after immobilizing on SiO_2-IL. This demonstrates that no HPW crystal phase was observed and HPW was finely dispersed on the SiO_2-IL carrier. And this also demonstrates that the introduction of ionic liquid enhanced the dispersion of HPW.

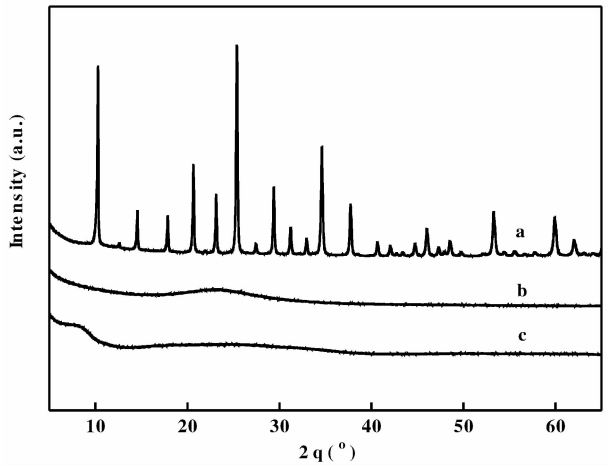


Fig. 2 XRD patterns of (a) HPW; (b) SiO2-IL and (c) PW/ SiO2-IL

2.2 The catalytic oxidation of alcohols

The catalytic activities of the three POMs/SiO_2-IL catalysts were evaluated in the oxidation of cyclohexanol with H_2O_2 at 90 ℃ and $[C_4mim]_3PW$ was also investigated for a comparison between heterogeneous and homogeneous catalysis systems. The results are given in table 1 (Entries 1-5). Compared with bare SiO_2-IL, all these catalysts have better catalytic activities for the oxidation of cyclohexanol. It's no surprise that PW/SiO_2-IL exhibited the highest activity. However, it's even better than $[C_4mim]_3PW$ when the reaction was homogeneously performed.

These results encouraged us further explore the effect of different reaction conditions on alcohol oxidation using PW/SiO_2-IL as the catalyst. Effect of the catalyst amount on cyclohexanol oxidation is shown in table 1 (Entries 4, 6-8). Reactions were conducted with different catalyst loadings which ranged from 0.1 g

to 0.16 g at 90 ℃ with 1∶3 (alcohol∶H_2O_2) molar ratio for 12 h. The yield of cyclohexone increased with the increase in the amount of the catalyst. Quantitative conversion of cyclohexanol was achieved (100%) when only 0.14 g (0.34 mol% based on PW) PW/SiO_2-IL was used. Further increase of the catalyst loading has no inhibiting effect on cyclohexone yield, thus, we use 0.14 g PW/SiO_2-IL for further studies.

Table 1 Effect of catalyst and amount on the oxidation of cyclohexanol with H_2O_2

Entry	Catalyst	Amount of Catalyst (g)	Yield[a] (%)
1	SiO_2-IL	0.10	22
2	SiW/SiO_2-IL	0.14	40
3	PMo/SiO_2-IL	0.13	36
4	PW/SiO_2-IL	0.10	91
5	$[C_4mim]_3PW$	0.056	45
6	PW/SiO_2-IL	0.12	96
7	PW/SiO_2-IL	0.14	100
8	PW/SiO_2-IL	0.16	100

Reaction conditions: substrate 5 mmol; H_2O_2 15 mmol; 12 h, MeCN 3.0 mL. [a]GC yield.

In order to optimize the reaction condition, the influence of molar ratio of the reactants, reaction temperature and reaction time were studied and the results are shown in Table 2. Effect of reaction temperature was studied firstly. Little ketone was obtained at 50 ℃, ketone yield increased with increasing temperature to 70-90 ℃ (75-100%). It is obvious that ketone yield increased when the reaction time is prolonged (Entries 3, 7-9). Then the effect of different molar ratios of H_2O_2 to alcohol was studied (Entries 3 6). The results indicate that the yield was improved while increasing the amount of H_2O_2 because the excess of one of the reactants makes the equilibrium shifting towards the products side. Based on these experiments, we can conclude that the maximum cyclohexone yield can be obtained at 90 ℃ and 12 h with the molar ratios of H_2O_2 to alcohol is 3.

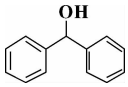
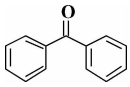
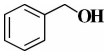
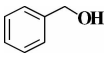
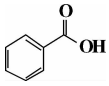
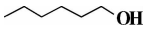
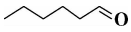
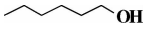
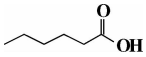
Table 2 Effect of different reaction conditions on the oxidation of cyclohexanol with H_2O_2

Entry	Temp. (℃)	Time (h)	H_2O_2/Sub.	Yield[a] (%)
1	70	12	3.0	75
2	80	12	3.0	89
3	90	12	3.0	100
4	90	12	2.5	97
5	90	12	2.0	92
6	90	12	1.5	87
7	90	8	3.0	91
8	90	10	3.0	96
9	90	14	3.0	100

Reaction conditions: substrate 5 mmol, PW/SiO_2-IL (0.14 g, 0.34 mol % based on PW); MeCN 3.0 mL. [a] GC yield.

Moreover, the oxidation of other alcohols using PW/SiO_2-IL was studied. As it is shown in Table 3, secondary alcohols oxidized to the corresponding ketones in high yield. It can be seen that linear alcohols were slightly less active than cyclohexanol (Entries 1-5), for 2-propanol, 2-butanol, 2-Pentanol and 3-pentanol, the yields were 98 %, 99%, 93 % and 96 %, respectively. Because aromatic alcohols were more reactive than aliphatic alcohols, the yields of acetophenone (Entry 6) and benzophenone (Entry 7) were 100% with only 1.5 equivalent H_2O_2. Interestingly, the oxidation of benzyl alcohol with 1.5 equivalents H_2O_2 afforded benzaldehyde with nearly 80 % yield; when increasing the amount of H_2O_2 to 3.0 equivalent, the main product turns out to be benzylacid (Entries 8, 9). Thus, different products can be obtained by adding different amounts of H_2O_2. For the oxidation of primary aliphatic alcohol, 1-hexanol, the main product was hexanoic acid, no matter how many H_2O_2 was added (Entries 10, 11).

Table 3 Result of oxidation of different alcohols with H_2O_2 catalyzed by PW/SiO_2-IL

Entry	Substrate	H_2O_2/ Substrate[a]	Product	Conversion (%)	Yield[b] (%)
1		3		100	100
2		3		98	98
3		3		99	99
4		3		93	93
5		3		96	96
6		1.5		100	100
7		1.5		100	100
8		1.5		85	78
9		3		100	80
10		1.5		28	10
11		3		55	46

Reaction conditions: substrate (5 mmol) and PW/SiO_2-IL (0.14 g, 0.34 mol % based on PW) were stirred at 90 ℃ for 12 h in MeCN (3 mL). [a]Molar ratio. [b]GC yield

The easy and convenient recovery of a catalyst system is very important for any catalytic reaction. After completion of the reaction, 3 mL ethyl ether was added and stirred for 5 minutes.

Then the reaction mixture was standing for a while or centrifuged and the organic and aqueous phases were collected, leaving the catalyst precipitated at the bottom. The heterogeneous catalyst was washed with ethyl ether and dried under vacuum ready for reuse. Then the reaction flask was recharged with fresh substrate and oxidant and the reaction was continued for 7 cycles with good yields (Table 4).

Table 4 Recyclability of PW/SiO_2-IL on the oxidation of cyclohexanol with H_2O_2

Run	1	2	3	4	5	6	7	8
Yield (%)	99.5	99.8	99.7	93.1	85.3	80	76.5	70.1

Reaction conditions: substrate (5 mmol); H_2O_2 (15 mmol); PW/SiO_2-IL (0.14 g); 90 ℃; 12 h; MeCN (3 mL). GC yield

The FTIR spectra of the fresh and recovered PW/SiO_2-IL catalyst are very similar (Fig. 3), which suggest the structure stability of the catalyst. The strong peak at 1080 cm^{-1} was assigned to P-O stretching vibration. Peaks at 980, 890 and 810 cm^{-1} suggest the presence of W = O and W-O-W. However, the recovered catalyst shows two new peaks at 560 (υ_{as} W-O-O)[19] and 850 cm^{-1} (υ W-O-O covered by W-O-W vibrations), which were the characteristic spectra of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (PW_4), indicating $[PW_{12}O_{40}]^{3-}$ (PW_{12}) was firstly degraded to Peroxy species PW_4 in the presence of excess H_2O_2[26] and PW_4 was the active species for alcohol oxidation. After each run of the former four cycles, the reaction mixture was monitored by ^{31}P NMR. Interestingly, no ^{31}P signals were found due to the low containing of PW species in the reaction mixture, thus ionic liquid may have an effect on inhibiting the loss of PW species. However, after the reaction mixture of the first four cycles was mixed and then concentrated under reduced pressure, ^{31}P NMR spectra was clearly obtained (Fig. 4). $[C_4mim]_3PW_{12}O_{40}$ shows a signal peak at δ = -14.39 ppm, and the reaction mixture shows a new peak at δ = 0.77 ppm due to the formation of PW_4[12], together with the peak of PW_{12} at δ = -14.56 ppm, and this was in accordance with the FTIR data. On the other hand, the ^{31}P NMR spectra confirmed the loss of catalyst, which causes the decrease of cyclohexone yield (from 100 % to 70 %).

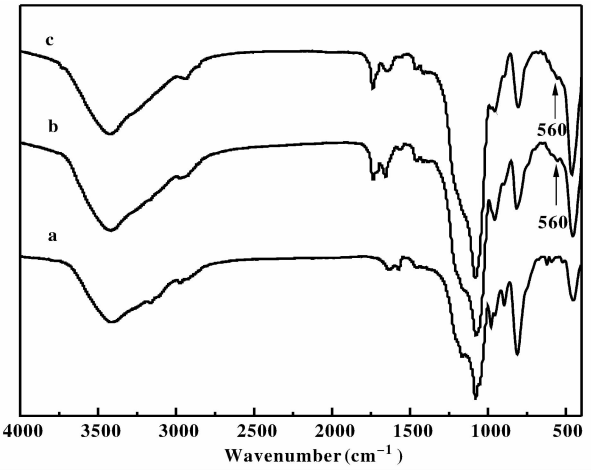


Fig. 3 FTIR spectra of (a) fresh-PW/SiO_2-IL, (b) used1-PW/SiO_2-IL; (c) used8-PW/SiO_2-IL

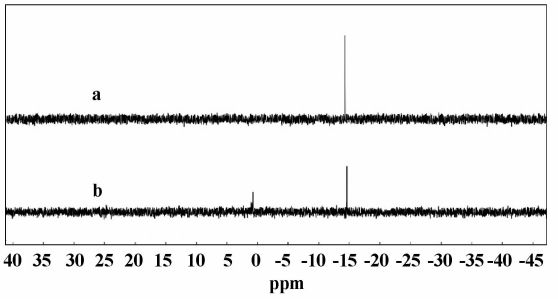


Fig. 4 The ^{31}P NMR spectra of (a) $[C_4mim]_3PW_{12}O_{40}$ and (b) the combined reaction mixture in CD_3CN.

3 Conclusion

In summary, ionic liquid functionalized SiO_2 was prepared through sol-gel method conveniently, then three kinds of commercially available POMs were immobilized on the functionalized SiO_2 as supported ionic liquid catalysis for alcohol oxidation with 30 % aqueous H_2O_2. PW/SiO_2-IL shows the best activity and was capable of oxidizing a series of alcohols to the desired product with high yield. During the oxidation process, the active species was PW_4 and ionic liquid may have an effect on inhibiting the loss of PW species. Furthermore, the catalyst can be conveniently recovered and used for 8 times with good yields.

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基于杂多酸的负载离子液相催化在醇氧化中的应用

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摘 要: 采用溶胶-凝胶法制备的离子液体功能化的二氧化硅对于杂多酸是一种可行的载体, 三种商用杂多酸成功的负载在离子液体功能化的二氧化硅上作为醇氧化的催化剂. 利用 FTIR、XRD、XPS 对该种负载离子液相催化剂进行了表征. 基于磷钨酸的负载离子液相催化剂活性最好, 高产率(大部分 > 93 %)的得到了相应的羰基化合物. 且该催化剂经过简单的过滤即可回收, 重复使用七次效果较好.

关键词: 杂多酸; 负载离子液相催化; 醇氧化; 双氧水