Acetalization of carbonyl compounds catalyzed by acidic ionic liquid immobilized on silica gel

Jinmei Miao, Hui Wan, Yanbing Shao, Guofeng Guan *, Bin Xu

College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China

ARTICLE INFO

ABSTRACT

Imidazolium-silica heterogeneous catalyst (SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$) was prepared by immobilization of acidic ionic liquid 1-(propyl-3-sulfonate) imidazolium hydrosulfate ([(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$) on silica–gel using tetraethoxysilane (TEOS) as silica source in this study. The properties of the samples were characterized by FT-IR, SEM and TG/DSC. The results suggested that [(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ had been successfully immobilized on the surface of silica–gel and the immobilized ionic liquid catalyst SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ had good thermal stability. The original smooth surface of silica–gel was covered with [(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ and a rough surface of SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ was formed, but the size of particles had no obvious change. Moreover, SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ exhibited high catalytic activity for a series of acetalization and could be recovered easily. After reused for 10 times in the synthesis of benzaldehyde ethanediol acetal, the catalyst could still give satisfactory catalytic activity.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Acetalization of carbonyl compounds with alcohols to form acetals was one of the most useful methods for protecting carbonyl compounds in organic synthesis. Conventionally, this reaction was carried out in the presence of a protonic acid catalyst such as sulfuric acid or hydrochloric acid. Although these homogeneous acids showed satisfactory catalytic performance for this reaction, they caused the problems of tedious purification process of the product, large amount of acidic wastes, corrosion of equipments, and severe environmental pollution [1–4]. All these disadvantages made acetalization inefficient and uneconomical. Therefore, there was an urgent need to develop environmentally friendly and high efficient catalysts for acetalization.

In recent years, ionic liquids as being environmental-friendly reaction media had attracted significant attention for their unique properties, such as high thermal stability, negligible vapor pressure, tunable acidity and selective dissolvability [5–10]. Acidic ionic liquids including the Lewis and the Brønsted ones had proved to be efficient catalysts for acetalization [1,11–14]. However, several drawbacks of ionic liquids, such as unendurable viscosity, high cost, tedious purification procedure of the product and requirements of long reaction time for acetalization, restricted their widespread practical applications [15,16].

In order to solve these problems mentioned above, immobilized ionic liquid catalysts combining the advantageous characteristics of ionic liquids, inorganic acids and solid acids had been proposed [17]. In 2007, Sugimura et al. [18] investigated the copolymerization of 1-vinylimidazolium based acidic ionic liquid with styrene and its use as effective and reusable catalyst for acetal formation under mild reaction condition. In 2009, this research group further investigated the immobilization of metal chlorides on imidazolium-styrene copolymer [19]. The catalyst (GaCl$_3$) was demonstrated to be an efficient heterogeneous catalyst for acetalization. Recently, a novel nano-solid acid catalyst [20] was prepared by a facile two-step preparation procedure. It possessed an excellent performance for acetalization of the carbonyl under mild reaction conditions, and could be reusable without significant loss in catalytic activity. In all the literatures reported above, styrene or Fe$_3$O$_4$ were used as solid supports. Silica–gel was one of the most commonly used inorganic supports. It could be synthesized easily in a controllable way by hydrolysis of TEOS [21]. And the produced mesoporous silica–gel possessed the excellent characteristics of stable mesoporous structure, high surface area, controllable pore size, and good mechanical strength and thermal stability. These excellent characteristics made the produced mesoporous silica–gel an attractive solid support for the preparation of immobilized ionic liquid catalyst [22–24]. However, there were few studies about the preparation of silica-supported acidic ionic liquid catalyst using TEOS as silica source and its application for acetalization. And the preparation of immobilized Brønsted acidic ionic liquid [(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ by chemical covalent bond, to our knowledge, was still absent from the literature.

* Corresponding author. Tel.: +86 25 8358 7198.
E-mail addresses: guangf@njut.edu.cn, njutggf@163.com (G. Guan).
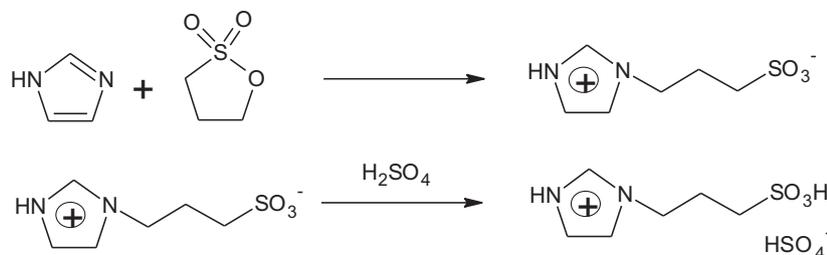
Scheme 1. Preparation of [(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$.
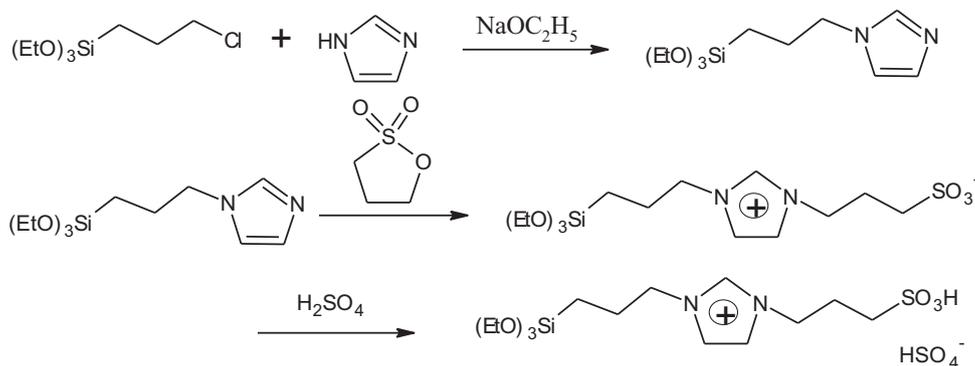
Scheme 2. Preparation of ClPTES-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$.
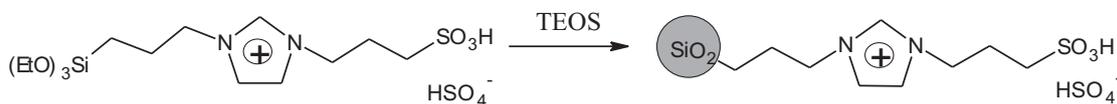
Scheme 3. Preparation of SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$.

In this study, we reported our efforts at exploring silica-supported Brønsted acidic ionic liquid catalyst SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ using TEOS as silica source. FT-IR, SEM and TG/DSC were employed to characterize the properties of samples. Moreover, the catalytic activity and reusability performance of the immobilized ionic liquid catalyst used for acetalization were also examined.

2. Experimental

2.1. Chemical reagents

Imidazole (99%), 1,3-propane-sultone (99%), 3-chloropropyltriethoxysilane (ClPTES, 98.8%), EO$_{20}$PO$_{70}$EO$_{20}$ (P123, Aldrich), TEOS, ether and other chemicals (AR grade) were commercially available and used without further purification.

2.2. Preparation of ionic liquid [(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$

First, imidazole (6.8 g) was dissolved in ethanol (100 mL), and equal-molar 1,3-propane-sultone was slowly added. The mixture was stirred at room temperature for 24 h and filtered to get the white precipitate. Subsequently, the product was washed with ethanol for several times and dried in vacuum at 60 °C for 6 h. Second, the formed solid was dissolved in water, and equal-molar sulfuric acid was slowly dropped. After the dropping was finished, the mixture was heated up to 60 °C gradually and then stirred for 12 h [25]. Finally, the formed colorless liquid was washed with ether for 3 times and dried in vacuum at 50 °C for 12 h (Scheme 1).

2.3. Preparation of ClPTES-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$

Imidazole (6.8 g) and sodium ethoxide (6.8 g) were dissolved in ethanol (100 mL), and the mixture was stirred at 70 °C for 8 h to give sodium imidazole [26]. Subsequently, ClPTES (24.05 g) was added drop-wise and the mixture was refluxed for 12 h under N$_2$ atmosphere. The formed orange suspension was filtered to remove NaCl precipitate from the solution [27]. The solvent was removed by rotatory evaporation under reduced pressure and an yellowish oil containing N-(3-propyltrimethoxysilane)imidazole was obtained.

1,3-Propane-sultone (12.2 g) was slowly added into the solution of equal-molar N-(3-propyltrimethoxysilane)imidazole and ethanol (100 mL). The mixture was stirred at 50 °C for 8 h and ethanol was removed by rotatory evaporation under reduced pressure. Then H$_2$SO$_4$ was added drop-wise. The solution was stirred at 60 °C for another 12 h. Finally, the formed ClPTES-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ was washed with ether for 3 times and dried in vacuum at 50 °C for 5 h (Scheme 2).

2.4. Preparation of immobilized ionic liquid catalyst SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$

[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$-functionalized silica–gel was synthesized with the molar ratio of the mixture as follows: 4 TEOS:xClPTES-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$:0.027 P123:16.2 HCl:100 H$_2$O, with x = 0.125, 0.25, 0.375, 0.5. In a typical synthesis, P123 (1.58 g) was dissolved in H$_2$O (18.0 g) and HCl (5.89 g). After TEOS (8.32 g) was added and pre-hydrolyzed for 1.5 h at 45 °C, ClPTES modified Brønsted acidic ionic liquid (2.46 g, x = 0.5) was added successively. Then the mixture was carried out at

Table 1
Catalytic performance of various catalysts for acetalization of benzaldehyde and ethanediol.[a]

Entry	x	Reaction temperature (°C)	Yield (%)[b]
1	0.125	60	85.3
2	0.25	60	89.4
3	0.375	60	90.2
4	0.5	60	96.8
5	0.5	50	93.0
6	0.5	70	93.5

[a] Benzaldehyde (70 mmol), ethanediol (126 mmol), catalyst (0.61 g, 4% of the total mass of benzaldehyde and ethanediol), cyclohexane (8 mL), 110 °C, 1.5 h.

[b] Yield was achieved by GC analysis.

different temperatures for a certain time to form the final product. The whole process was operated under N_2 atmosphere. The precipitate was filtered, subsequently washed with acetone, ether and ethanol, and then refluxed in ethanol for 24 h to remove the template P123. Finally, the formed immobilized acidic ionic liquid was dried in vacuum at 60 °C for 6 h (Scheme 3).

2.5. Characterization

Fourier transform infrared (FT-IR) spectra of the samples in the range of 400–4000 cm^{-1} were carried out on a Thermo Nicolet 870 spectrophotometer with anhydrous KBr as standard. Scanning electron microscope (SEM) QUANTA200 (FEI, Holland) was employed to characterize the average diameters and surface morphologies of silica–gel and SG-[$(CH_2)_3SO_3H$-HIM]HSO$_4$. The thermal properties were examined by a NETZSCH STA 409PC thermo gravimetric and differential scanning calorimetry (TG/DSC) analyzer with a heating rate of 10 °C per minute under a dynamic N_2 atmosphere and the temperature was ranging from 35 °C to 800 °C.
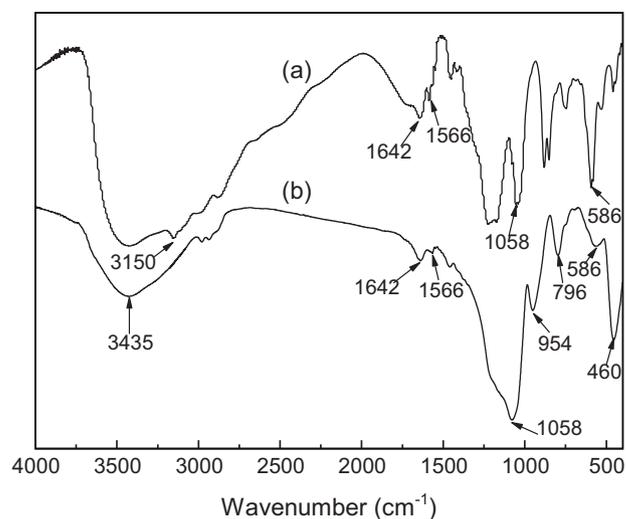
Fig. 1. FT-IR spectra of [$(CH_2)_3SO_3H$-HIM]HSO$_4$ (a), and SG-[$(CH_2)_3SO_3H$-HIM]HSO$_4$ (b).

2.6. Acetalization and analysis

Taking the acetalization of benzaldehyde with ethanediol as an example, the typical procedure was performed as follows: benzaldehyde (7.42 g, 70 mmol), ethanediol (7.81 g, 126 mmol), catalyst (0.61 g, 4% of the total mass of benzaldehyde and ethanediol), and cyclohexane (8 mL, as a water-carrying agent) were charged successively into a 250 mL round bottom flask with a reflux condenser, a water segregator and a magnetic stirrer. Then the reaction was allowed to proceed at desired temperature for 1.5 h. All the reactions were analyzed using a gas chromatograph
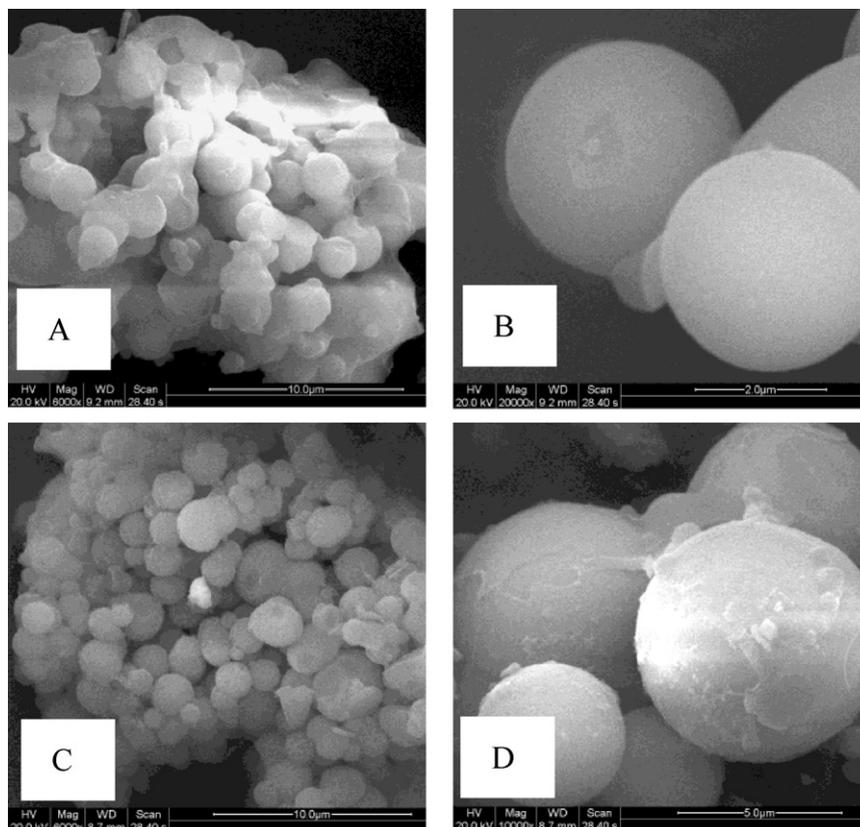
Fig. 2. The whole and magnified SEM images of silica–gel (A and B), and SG-[$(CH_2)_3SO_3H$-HIM]HSO$_4$ (C and D).
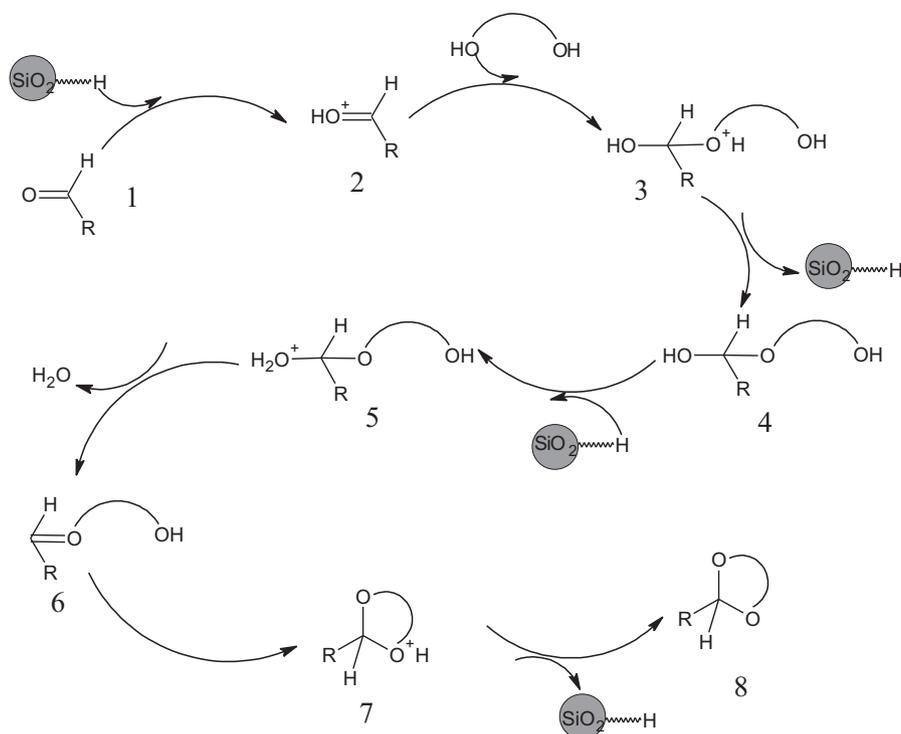
Scheme 4. Mechanism of acetalization over SG-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$.

equipped with an FID detector (SP6800A, SE-54 capillary column 30 m × 0.25 mm × 0.3 μm). The same procedures were carried out for the other acetalization of aldehydes by alcohols.

In a recycling experiment, SG-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ was recovered by decantation, and collected for catalytic reusability test after dried under 100 °C for 2 h. The procedures for recycling experiment were the same as described above.

3. Results and discussion

3.1. Catalytic performance of catalysts prepared under different conditions

In order to obtain the appropriate preparation conditions for SG-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$, effects of molar ratio of IL to TEOS and reaction temperature on catalytic performance of catalysts were investigated in the acetalization of benzaldehyde and ethanediol. The results were shown in Table 1. The more ClPTES-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ was added, the higher yield of benzaldehyde ethanediol acetal was obtained (Table 1, entries 1–4). When x increased up to 0.5, the high yield of 96.8% was achieved. It was unnecessary to further increase the amount of ionic liquid. With a rise in temperature (Table 1, entries 4 and 5), the molecular movement was intensified and the collision probability between silica–gel and ClPTES-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ increased correspondingly. However, a further increase of temperature (Table 1, entries 4 and 6) also enhanced the collision of ClPTES-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ itself which led to a decrease in the yield of benzaldehyde ethanediol acetal [28]. Next, the catalyst (Table 1, entry 4) was characterized as follows.

3.2. Catalyst characterization

3.2.1. FT-IR

To confirm the immobilization of active component $[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ on the support silica–gel, FT-IR spectroscopic studies were carried out. First, the characteristic peaks of $[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ around 586 cm^{-1}, 1642 cm^{-1}, 1566 cm^{-1} and 1058 cm^{-1} could be clearly observed in Fig. 1a and b. They were ascribed to C–H, C=C, C=N stretching vibrations of the imidazole ring [29], and S=O symmetric stretching vibrations of the –SO$_3$H group, respectively [30,31]. The band at 3150 cm^{-1} was assigned to N–H stretching vibration of $[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ [32]. Meanwhile, typical peaks of Si–O–Si of SG-$[(CH_2)_3SO_3H\text{-}$ HIM]HSO$_4$ could be observed around 460 cm^{-1}, 769 cm^{-1} and 954 cm^{-1} in Fig. 1b. And the band at 3435 cm^{-1} was assigned to the O–H of physical adsorbed water. However, the peak of N–H at 3150 cm^{-1} of $[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ which existed in Fig. 1a totally disappeared in the spectrum of SG-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ in Fig. 1b. This observation suggested that $[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ had been immobilized on silica–gel by chemical covalent bond via the route shown above.

3.2.2. SEM

Fig. 2 shows the average diameters and surface morphologies of silica–gel and SG-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$. It was seen that the spherical silica–gel particles were agglomerated together and in the size of 2–5 μm (Fig. 2A). After the immobilization of ionic liquid, the size of the obtained SG-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ had no obvious change (Fig. 2C). At a high magnification, the surface of silica–gel was rather smooth (Fig. 2B). However, it was found that the surface of SG-$[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ was much rough (Fig. 2D). This finding demonstrated that ionic liquid $[(CH_2)_3SO_3H\text{-HIM}]HSO_4$ had been immobilized on the surface of silica–gel.

3.2.3. TG/DSC

As shown in Fig. 3, TG/DSC analysis was employed to investigate the thermal stability of the chemically modified silica–gel since the observed weight loss was associated with the loss of the organic components attached to the surface.

The small amount of weight loss within 200 °C in Fig. 3a was attributed to the desorption of physical adsorbed water and

Table 2
Acetalization of different aldehydes and alcohols in SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$.[a]

Entry	Aldehydes	Alcohols	Time (h)	Yield (%)[b]	Selectivity (%)[c]
1	Benzaldehyde	Ethanediol	1.5	95.2	100
2	Benzaldehyde	1,2-Propanediol	2	93.0	100
3	Benzaldehyde	1,4-Butanediol	3	87.1	100
4	Benzaldehyde	Neopentyl glycol	1	98.5	100
5	Furfural	Ethanediol	3	85.0	100
6	Furfural	1,2-Propanediol	1.5	95.9	100
7	Furfural	Neopentyl glycol	0.5	97.4	100
8	Phenylacetaldehyde	Ethanediol	2.5	98.4	100
9	Phenylacetaldehyde	1,4-Butanediol	2.5	94.1	100

[a] Aldehyde (70 mmol), alcohol (126 mmol), catalyst (4% of the total mass of aldehyde and alcohol), cyclohexane (8 mL), 110 °C.
[b] Yield was achieved by GC analysis.
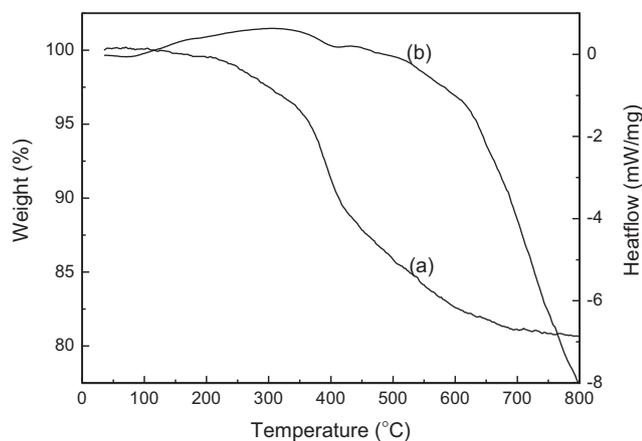[c] Selectivity for acetal.

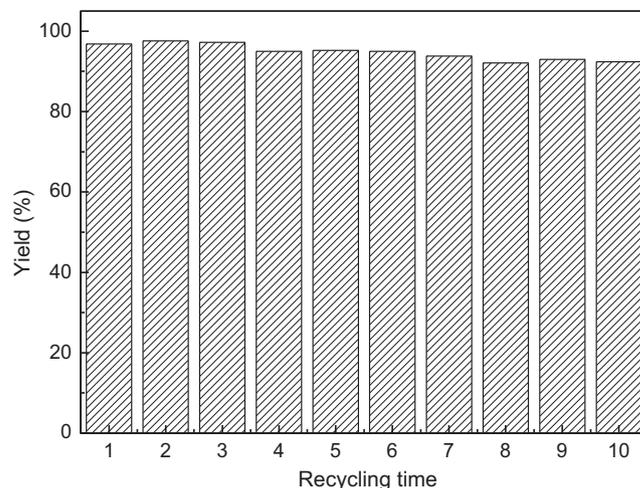

Fig. 3. TG (a)/DSC (b) patterns of silica–gel SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$.

Fig. 4. Recycling of SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ for the synthesis of benzaldehyde ethanediol acetal.

residual solvent. Correspondingly, an obvious endothermic peak appeared around 70 °C in Fig. 3b. When the temperature further increased to 350 °C, the weight of SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ decreased rapidly. The reason might be that the organic components of ionic liquid and the propyl of ClPTES separated from the surface of silica–gel. Correspondingly, endothermic peaks at 410 °C appeared. Finally, it was observed that the chemically modified silica–gel exhibited good thermal stability under 350 °C and the residual weight of SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ was about 80% around 700 °C.

3.3. Catalytic activity of SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ for acetalization

In order to investigate the scope and limitation of SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ as catalyst for acetalization, different aldehydes and alcohols as the reactants were also tested and the results were summarized in Table 2. It could be found that SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ could give high catalytic activity for acetalization. Good to excellent yields ranging from 85.0% to 98.5% were obtained in all systems under investigation. And it should be pointed out here that selectivities to the desired products were all 100% over SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$.

The reusability of SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ was evaluated in the acetalization of benzaldehyde and ethanediol. The results were shown in Fig. 4. It was apparent that SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ showed good reusability for the reaction. The catalyst could be reused for 10 times without significant loss of catalytic activity.

3.4. Mechanism for acetalization

In the present work, the possible mechanism for acetalization of aldehydes with alcohols over SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ was consistent with the reported ones [11,14]. As shown in Scheme 4, in the first step, the carbonyl group of aldehyde 1 took a proton from the immobilized ionic liquid catalyst. The protonated carbonyl group 2 was activated for nucleophilic addition of O atom of the alcohol. After deprotonation, the hemiacetal 4 was formed. Then the hemiacetal 4 was protonated again. After loss of water, the oxonium ion 6 was formed. It accepted a second alcohol hydroxyl group to form 7 and subsequent deprotonation gave the acetal 8.

4. Conclusion

The immobilized acidic ionic liquid catalyst SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ was prepared and applied in acetalization of aldehydes with alcohols in this study. After characterization, it was found that [(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ had been successfully immobilized on the surface of silica–gel by chemical covalent bond and the immobilized ionic liquid catalyst had good thermal stability. The original smooth surface of silica–gel was covered with [(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ and a rough surface of SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ was formed, but the size of particles had no obvious change. SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ showed good catalytic performance for a series of acetalization. Satisfactory yields of 81.0–98.5% were achieved under appropriate reaction conditions. The immobilized ionic liquid catalyst could be recovered easily and reused for 10 times for the synthesis of benzaldehyde ethanediol acetal without significant loss of catalytic activity. In conclusion, the immobilized

ionic liquid catalyst SG-[(CH$_2$)$_3$SO$_3$H-HIM]HSO$_4$ prepared in this study was proved to be an excellent recyclable heterogeneous catalyst for the synthesis of acetals and showed potential application in industry.

References

[1] Y.Y. Wang, D. Jiang, L.Y. Dai, Catal. Commun. 9 (2008) 2475–2480.
[2] B. Wang, Y.L. Gua, G.Y. Song, T. Yang, L.M. Yang, J.S. Suo, J. Mol. Catal. A: Chem. 233 (2005) 121–126.
[3] N. Gupta, Sonu, G.L. Kad, J. Singh, Catal. Commun. 8 (2007) 1323–1328.
[4] D. Fang, K. Gong, Q.R. Shi, Z.L. Liu, Catal. Commun. 8 (2007) 1463–1466.
[5] F. Shi, Q.H. Zhang, D.M. Li, Y.Q. Deng, Chem. Eur. J. 11 (2005) 5279–5288.
[6] C. Romero, S. Baldelli, J. Phys. Chem. B 110 (2006) 6213–6223.
[7] T. Welton, Coord. Chem. Rev. 248 (2004) 2459–2477.
[8] J.F. Brennecke, E.J. Maginn, AIChE J. 47 (2001) 2384–2389.
[9] O.B. Helene, M. Lionel, J. Mol. Catal. A: Chem. 182–183 (2002) 419–437.
[10] K.N. Marsh, J.A. Boxall, R. Lichtenthaler, Fluid Phase Equilibr. 219 (2004) 93–98.
[11] F. Zhang, D.Q. Xu, B.Y. Liu, S.P. Luo, W.L. Yang, Z.Y. Xu, Chin. J. Catal. 26 (2005) 815–818.
[12] H.H. Wu, F. Yang, P. Cui, J. Tang, M.Y. He, Tetrahedron Lett. 45 (2004) 4963–4965.
[13] Z.Y. Duan, Y.L. Gu, Y.Q. Deng, Catal. Commun. 7 (2006) 651–656.
[14] J. Zhang, S.H. Bao, J.G. Yang, Chin. Sci. Bull. 54 (2009) 3958–3964.
[15] S. Sahoo, P. Kumar, F. Lefebvre, S.B. Halligudi, Appl. Catal. A 354 (2009) 17–25.
[16] L.L. Zhu, Y.H. Liu, J. Chen, Ind. Eng. Chem. Res. 48 (2009) 3261–3267.
[17] W. Chen, Y.Y. Zhang, L.B. Zhu, J.B. Lan, R.G. Xie, J.S. You, J. Am. Chem. Soc. 129 (2007) 13879–13886.
[18] R. Sugimura, K. Qiao, D. Tomida, C. Yokoyama, Catal. Commun. 8 (2007) 770–772.
[19] Q.X. Bao, K. Qiao, D. Tomida, C. Yokoyama, Catal. Commun. 10 (2009) 1625–1628.
[20] P. Wang, A.G. Kong, W.J. Wang, H.Y. Zhu, Y.K. Shan, Catal. Lett. 135 (2010) 159–164.
[21] Y. Yamada, K. Qiao, Q.X. Bao, D. Tomida, D. Nagao, M. Konno, C. Yokoyama, Catal. Commun. 11 (2009) 227–231.
[22] J.N. Li, L.N. Wang, T. Qi, Y. Zhou, C.H. Liu, J.L. Chu, Y. Zhang, Micropor. Mesopor. Mater. 110 (2008) 442–450.
[23] Sujandi, E.A. Prasetyanto, D.S. Han, S.C. Lee, S.E. Park, Catal. Today 141 (2009) 374–377.
[24] J.N. Li, T. Qi, L.N. Wang, C.H. Liu, Y. Zhang, Mater. Lett. 61 (2007) 3197–3200.
[25] D. Jiang, Y.Y. Wang, M. Tu, L.Y. Dai, React. Kinet. Catal. Lett. 95 (2008) 265–271.
[26] H.Z. Zhi, C.X. Lü, Q. Zhang, J. Luo, Chem. Commun. (2009) 2878–2880.
[27] A. Šurca Vuk, V. Jovanovski, A. Pollet-Villard, I. Jerman, B. Orel, Sol. Energy Mater. Sol. C 92 (2008) 126–135.
[28] K. Guo, Q.F. An, M.T. Li, G. Li, Jingxi Shiyou Huagong. 26 (2009) 60–65.
[29] K. Qiao, H. Hagiwara, C. Yokoyama, J. Mol. Catal. A: Chem. 246 (2006) 65–69.
[30] Z.J. Xu, H. Wan, J.M. Miao, M.J. Han, C. Yao, G.F. Guan, J. Mol. Catal. A: Chem. 332 (2010) 152–157.
[31] J.M. Miao, H. Wan, G.F. Guan, Catal. Commun. 12 (2011) 353–356.
[32] Y.H. Shan, J.H. Deng, F.R. Lin, M.H. Lu, S.S. Li, Chin. J. Appl. Chem. 26 (2009) 1428–1434.