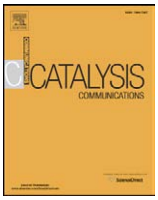
Catalysis Communications 12 (2011) 353–356

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom



Short Communication

Synthesis of immobilized Brønsted acidic ionic liquid on silica gel as heterogeneous catalyst for esterification

Jinmei Miao, Hui Wan, Guofeng Guan *

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

ARTICLE INFO

Article history:
Received 31 August 2010
Received in revised form 18 October 2010
Accepted 20 October 2010
Available online 28 October 2010

Keywords:
Esterification
Immobilized ionic liquid
Silica gel
1-Vinylimidazole

ABSTRACT

The Brønsted acidic ionic liquid 1-(propyl-3-sulfonate) vinylimidazolium hydrogen sulfate ([$(CH_2)_3SO_3$HVIm]HSO_4) was immobilized on the silica gel using tetraethoxysilane (TEOS) as silica source. The properties of samples were characterized by FT-IR, elemental analysis and TG. The results showed that [$(CH_2)_3SO_3$HVIm]HSO_4 had been successfully immobilized onto the silica gel, and the immobilized ionic liquid catalyst (IL/silica gel) had good thermal stability. Moreover, the IL/silica gel exhibited high catalytic activity for a series of esterification and could be separated from the reaction mixture easily. It also remained satisfactory catalytic activity for the synthesis of *n*-Butyl acetate after 7 times recycling.

1. Introduction

Esters ranging from aliphatic to aromatic were important organic compounds. They were generally used as plasticizers, solvents, perfumes and also as precursors for pharmaceuticals, agrochemicals and fine chemicals [1]. Esters were usually obtained by the esterification of alcohols with carboxylic acids [2]. Conventionally, the esterification was carried out using inorganic liquid acids, solid acids or bio-enzymes as catalysts [3]. However, several disadvantages of these catalysts made this process inefficient and uneconomical. Inorganic acids could cause the problems of equipment corrosion and severe environmental pollution. Solid acids also suffered from several disadvantages such as high molecular weight/active-site ratios, extended reaction time, low thermal stability and rapid deactivation from coking [4,5]. And bio-enzymes were generally expensive for commercial use and difficult to recycle without any catalytic activity loss [6]. Therefore, great efforts towards the development of environmentally friendly catalysts with high catalytic activity had been made [7,8].

In recent years, ionic liquids had attracted significant attention as being environmental-friendly reaction media for their unique properties of high thermal stability, negligible vapor pressure, tunable acidity and selective dissolvability [9–14]. Though ionic liquids possessed such promising advantages, their widespread practical application was still hampered by several drawbacks: (i) high viscosity, which resulted in only a minor part of ionic liquids took part in the catalyzed reaction, (ii) homogeneous reaction, which was difficult for product separation and catalyst recovery, and (iii) consequently high cost for the use of relatively large amounts of ionic liquids [15,16]. Therefore, in order to solve these problems mentioned earlier, immobilized ionic liquid catalyst combining the advantageous characteristics of ionic liquids, inorganic acids and solid acids had been proposed [17].

Recently, many reports about the preparation of silica-based immobilized acidic ionic liquids catalysts had been published [18–22] and the catalysts were normally immobilized on the amorphous silica gel. Compared to the amorphous silica gel, the produced mesoporous silica using TEOS as silica source possessed the excellent characteristics such as stable mesoporous structure, high surface area, controllable pore size and a large amount of silanol group. These advantageous characteristics made mesoporous silica an attractive solid support in the field of catalysis and functional materials [23–25]. However, there were few studies about the preparation of immobilized Brønsted acidic ionic liquid catalyst using TEOS as silica source and its application for esterification.

Herein, we reported our efforts at exploring the immobilization of Brønsted acidic ionic liquid [$(CH_2)_3SO_3$HVIm]HSO_4 on silica gel using TEOS as silica source. The properties of samples were characterized by FT-IR, elemental analysis, and TG. And the catalytic activity and reusability performance of IL/silica gel used for esterification were also examined.

2. Experimental

2.1. Chemical reagents

1-vinylimidazole (>98%), 3-mercaptopropyltrimethoxysilane (MPS) (>98%), 1,3-propane-sultone (99%), 2,2-azo-bis-isobutyronitrile (AIBN,

---

* Corresponding author. Tel./fax: +86 25 8358 7198.
E-mail address: guangf@njut.edu.cn (G. Guan).

1566-7367/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2010.10.014

CP grade), $EO_{20}PO_{70}EO_{20}$ (P123, Aldrich), p-hydroquinone, TEOS, ether and other chemicals (AR grade) were commercially available and used without further purification.

2.2. Preparation of Brønsted acidic ionic liquid $[(CH_2)_3SO_3HVIm]HSO_4$

First, 1,3-propane-sultone (12.2 g) was slowly added to 1-vinylimidazole (9.4 g) and p-hydroquinone (0.044 g) in a 100 mL beaker at 0 °C. The mixture was stirred until it turned into solid totally. Then the formed solid was washed with ether for 3 times and dried in vacuum at 50 °C [19]. Second, the formed solid (21.6 g) was dissolved in 5 mL H_2O in a 250 mL round bottom flask, and equal-molar sulfuric acid was slowly dropped into the flask at 0 °C. After the dropping was finished, the mixture was heated up to 60 °C gradually and then stirred for 12 h [20]. Finally, the formed wine-colored liquid was washed with ether for 3 times and dried in vacuum at 50 °C for 5 h [Scheme 1].

2.3. Preparation of immobilized Brønsted acidic ionic liquid

First, P123 (1.58 g) was dissolved in H_2O (18.0 g) and HCl (5.89 g) at 45 °C. After TEOS (10.40 g) was added and pre-hydrolyzed for 1.5 h, MPS was added. The mixture was stirred at 60 °C for 6 h to form thiol-functionalized silica gel. Then, $[(CH_2)_3SO_3HVIm]HSO_4$ and AIBN (20% molar faction of $[(CH_2)_3SO_3HVIm]HSO_4$) were successively added and the reaction was carried out for another 30 h to form the final product. The whole process was operated under N_2 atmosphere. The product was filtered, subsequently washed with acetone, ether and ethanol, and then refluxed in ethanol for 24 h [26] to remove the template P123. Finally, the formed immobilized Brønsted ionic liquid was dried in vacuum at 60 °C for 6 h [Scheme 2].

2.4. 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. The loading amount of ionic liquid immobilized on the thiol-functionalized silica gel was determined by elemental analysis (Elementar Vario ELIII, Germany). The thermal properties were examined by a STA 409PC thermo gravimetric analyzer with a heating rate of 10 K per min under a dynamic N_2 atmosphere and the temperature was ranging from 25 °C to 800 °C.

2.5. Esterification and analysis

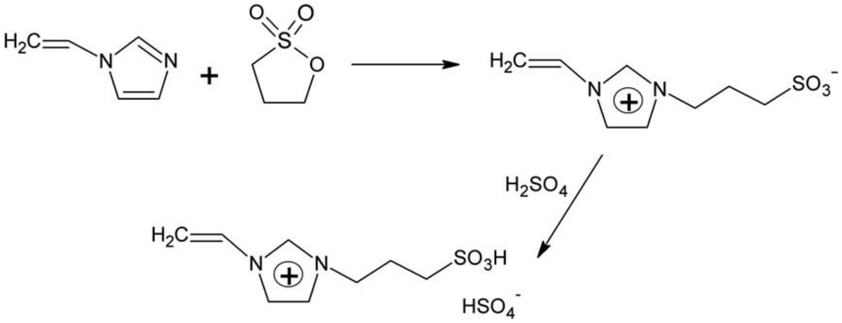
Taking the esterification of acetic acid with *n*-butanol as an example, the typical procedure was performed as follows: IL/silica gel (0.96 g, 8% of the total mass of *n*-butanol and acetic acid), acetic acid (4.80 g), *n*-butanol (7.12 g) and cyclohexane (8 mL, as a water-carrying agent) were charged 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 3 h. All the reactions were analyzed using a gas chromatograph 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 esterification of carboxylic acids by alcohols.

In a recycling experiment, IL/silica gel was recovered by vacuum filtration, and collected for catalytic reusability test without any disposal. The procedures for recycling experiment were the same as described earlier.

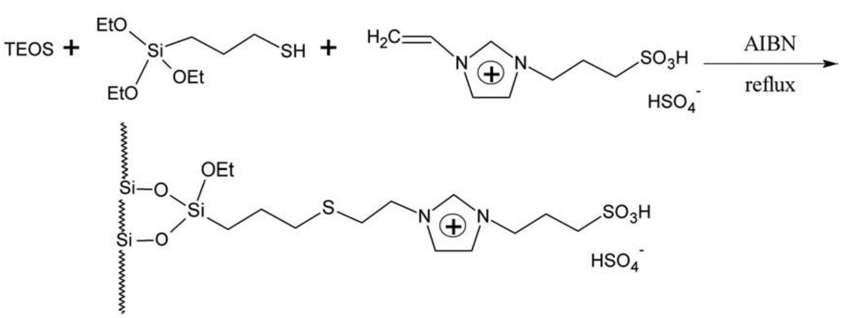
3. Results and discussion

3.1. Effect of molar ratio of IL to TEOS on catalytic performance of catalysts

In order to obtain the appropriate amount of IL, effect of molar ratio of IL to TEOS on catalytic performance of catalysts was investigated. The results were shown in Table 1. The more $[(CH_2)_3SO_3HVIm]HSO_4$ was added, the more loading amount of IL and the



Scheme 1. Preparation of $[(CH_2)_3SO_3HVIm]HSO_4$.



Scheme 2. Preparation of IL/silica gel.

Table 1
Effect of molar ratio of IL to TEOS on catalytic performance of catalysts[a]. $CH_3COOH + CH_3(CH_2)_3OH \rightarrow CH_3COO(CH_2)_3CH_3 + H_2O$.

Entry	IL:TEOS (mol/mol)	N (%)	Loading amout of IL (mmol/g)[b]	Yield (%)[c]
1	0.6	1.16	0.48	80.3
2	0.8	1.34	0.56	83.3
3	1	2.33	1.13	88.8
4	1.2	3.66	2.22	99.2

[a] *n*-Butanol (7.12 g); acetic acid (4.80 g); IL/silica gel (0.96 g); and cyclohexane (8.0 mL); 89 °C.
[b] Loading amount (mmol/g thiol-functionalized silica gel): $\frac{N\% / 128}{100 - N\% \times M / 28} \times 1000$, where M was the molecular weight of $[(CH_2)_3SO_3HVIm]HSO_4$, 314.
[c] Yield was achieved by GC analysis.

higher yield of *n*-butyl acetate were obtained. When the molar ratio of IL to TEOS increased up to 1.2, the high yield of 99.2% was achieved. It was unnecessary to further increase the amount of IL. Next, the catalyst (Table 1, entry 4) was characterized as follows.

3.2. Characterization

3.2.1. FT-IR

First, the characteristic peaks of $[(CH_2)_3SO_3HVIm]HSO_4$ around 1642 cm^{-1}, 1567 cm^{-1}, 3139 cm^{-1}, 1153 cm^{-1} and 1046 cm^{-1} could be clearly observed in Fig. 1a and b, which were ascribed to C═C, C═N, and C–H stretching vibrations of the imidazole ring [19], and S═O asymmetric and symmetric stretching vibrations of the $–SO_3H$ group, respectively. The bands at 1408 cm^{-1} in Fig. 1a and 3437 cm^{-1} in Fig. 1b were assigned to the end-group C═C shear vibration of $[(CH_2)_3SO_3HVIm]HSO_4$ [27] and the O–H of physical adsorbed water, respectively. Meanwhile, typical peaks of Si–O–Si and S–H of thiol-functionalized silica gel could be observed around 460 cm^{-1} and 2566 cm^{-1} in Fig. 1d. However, the peak of S–H and end-group C═C totally disappeared in Fig. 1b, which illustrated that $[(CH_2)_3SO_3HVIm]HSO_4$ ionic liquid was immobilized on silica gel by chemical covalent bond via the route shown in Scheme 1.

Second, comparing the FT-IR spectra in Fig. 1b and c, we could find that there were no significant changes. The result could explain the satisfactory catalytic activity given by the recycled catalyst (R-IL/silica gel).

3.2.2. TG

Thermal stability of samples was investigated by thermo gravimetric (TG) analysis, in which the observed weight loss was associated with the loss of the organic components attached to the silica gel. TG curves for silica gel, thiol-functionalized silica gel and IL/silica gel were shown in Fig. 2, respectively. As shown in Fig. 2a and b, small amount of weight loss within 200 °C was attributed completely to the loss of adsorbed water molecules as well as the condensation of silanol groups. However, the weight loss in Fig. 2c within 200 °C decreased significantly, which might be ascribed to the increased hydrophobicity of particle surface after immobilization of $[(CH_2)_3SO_3HVIm]HSO_4$ ionic liquid. Thiol-functionalized silica gel obtained after the chemical modification with trialkoxysilane showed a higher weight loss due to the loss of the mercaptopropyl moieties in Fig. 2b. After immobilization of ionic liquid, the weight loss in Fig. 2c increased again which was due to the further increased organic components on the silica gel. As shown in Fig. 2c, the solid catalyst IL/silica gel exhibited good thermal stability under 300 °C. The loading amount of IL of fresh catalyst was 2.22 mmol/g, and those of catalysts treated under 200 °C, 250 °C, and 300 °C were 2.07 mmol/g, 2.01 mmol/g and 1.92 mmol/g, respectively. The loading amounts of treated IL decreased slightly. The weight markedly decreased above 300 °C and organic components on the silica gel were decomposed completely around 700 °C.

3.3. Catalytic activities of different catalysts

In order to evaluate the catalytic activity of IL/silica gel, the same esterification of *n*-Butanol with acetic acid was carried out without any catalyst or with $[(CH_2)_3SO_3HVIm]HSO_4$ (mass of the active site of IL/silica gel) and IL/silica gel, respectively. It could be seen in Table 2 that without catalyst, the yield just could reach 23.0% (Table 2, entry 1) which was far lower than those catalyzed by $[(CH_2)_3SO_3HVIm]HSO_4$ and IL/silica gel (Table 2, entries 2 and 3). This result indicated that the esterification was hardly occurred without catalyst. In order to compare the catalytic activity of IL and IL/silica gel, we did kinetic experiments to get the activation energies of two reactions. The results showed that the activation energy of reaction catalyzed by IL/silica gel (38.2 kJ/mol) was a little higher than that catalyzed by its homogenous counterpart (33.9 kJ/mol). However, the heterogeneous IL/silica gel could be easily separated by vacuum filtration and reused. As shown in Fig. 3, catalytic performance of IL/silica gel could still achieve 88.7% after 7 times recycling. The loading amount of IL of

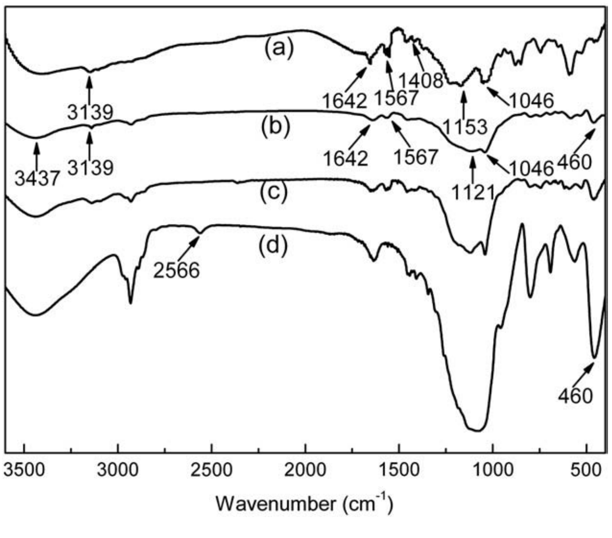


Fig. 1. FT-IR spectra of $[(CH_2)_3SO_3HVIm]HSO_4$ (a), IL/silica gel (b), R-IL/silica gel (c), and thiol-functionalized silica gel (d).

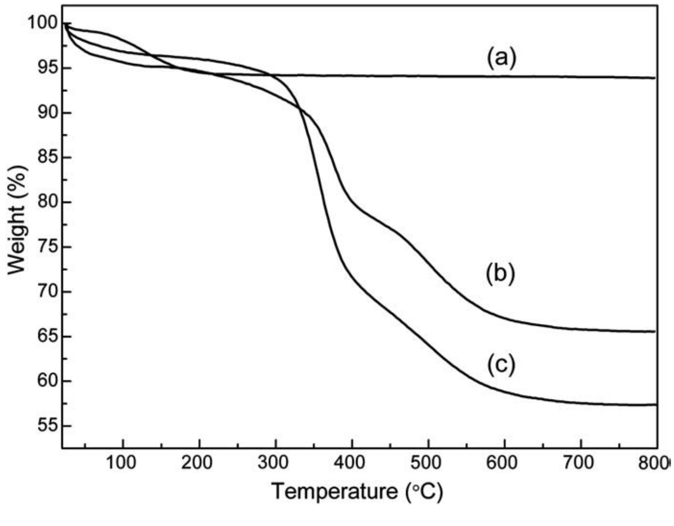


Fig. 2. Thermo gravimetric curves of silica gel (a), thiol-functionalized silica gel (b) and IL/silica gel (c).

Table 2
Esterification of *n*-Butanol and acetic acid under different conditions[a]. $CH_3COOH + CH_3(CH_2)_3OH \rightarrow CH_3COO(CH_2)_3CH_3 + H_2O$.

Entry	Catalysts	Temperature (°C)	Time (h)	Yield (%)[b]	Selectivity (%)[c]
1	–	89	3	23.0	100
2	IL			98.9	100
3	IL/silica gel			99.2	100

[a] *n*-Butanol (7.12 g); acetic acid (4.80 g); IL/silica gel (0.96 g); IL (0.39 g, mass of the active site of IL/silica gel); and cyclohexane (8.0 mL).
[b] Yield was achieved by GC analysis.
[c] Selectivity for ester.

catalyst used 7 times was 1.17 mmol/g. It was demonstrated that the decrease in catalytic activity was ascribed to the loss of ionic liquid.

3.4. Catalytic activity of IL/silica gel for esterification of other alcohols and carboxylic acids

In order to investigate the scope and limitation of IL/silica gel as catalyst for esterification, different alcohols and carboxylic acids as the reactants were also tested and the results were summarized in Table 3. It could be found that IL/silica gel could give very high catalytic activity for esterification. Good to excellent yields ranging from 84.1% to 99.4% with perfect selectivity for corresponding esters (100%) were obtained in all systems under investigation. The results showed that the yields of the long carbon chains carboxylic acids and primary alcohols were very satisfactory, and the length of carbon chains did not affect the yield significantly (Table 3, entries 1–6). Meanwhile, satisfactory results (Table 3, entries 8 and 9) of esterification of aromatic alcohol and carboxylic acids could also be obtained. Esterification of ethanol (Table 3, entry 7) gave lower yield compared with other alcohols due to its lower boiling point.

4. Conclusion

In conclusion, we reported a catalyst for esterification of alcohols with carboxylic acids by immobilization of $[(CH_2)_3SO_3HVIm]HSO_4$ on silica gel using TEOS as silica source. The immobilized ionic liquid catalyst showed good catalytic performance. Esterification of various alcohols and carboxylic acids could give satisfactory results of 84.1–99.4% under optimal reaction conditions. And it was demonstrated that the immobilized ionic liquid catalyst could offer practical convenience in product separation and be a recyclable solid catalyst with a higher catalytic performance than that of pure ionic liquid system. Satisfactory catalytic activity 88.7% could still been kept after the catalyst was recycled for 7 times for the synthesis of *n*-Butyl acetate. Thus, the immobilized ionic liquid catalyst in this study was proved to be a stable, efficient, reusable and potential catalyst for the synthesis of carboxylic esters.

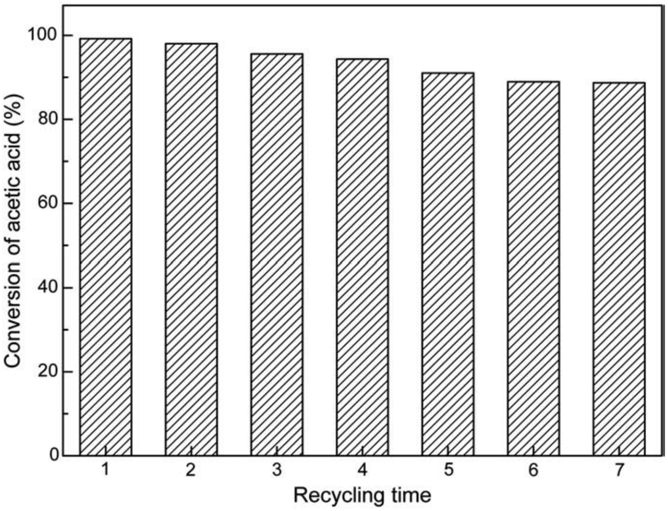


Fig. 3. Recycling of IL/silica gel for the synthesis of *n*-Butyl acetate.

Table 3
Esterification of different alcohols and carboxylic acids in IL/silica gel[a]. $R-COOH + R'-OH \xrightarrow{\text{IL/silica gel}} R-COO-R' + H_2O$.

Entry	R	R′	Temperature (°C)	Time (h)	Yield (%)[b]	Selectivity (%)[c]
1	CH_3	n-C_4H_9	89	3	99.2	100
2	CH_3	$CH_3(CH_2)_5$	95		99.4	100
3	CH_3	$CH_3(CH_2)_3(C_2H_5)CHCH_2$	94		98.6	100
4	CH_3	$CH_3(CH_2)_3OCH_2CH_2$	93		99.0	100
5	$CH_3(CH_2)_2$	n-C_4H_9	93		86.3	100
6	CH_3CH_2	S-C_4H_9	88		92.2	100
7	CH_3	C_2H_5	71		84.1	100
8	CH_3CH_2	$C_6H_5CH_2$	88		93.4	100
9	CH_3	$C_6H_5CH_2$	90		98.5	100

[a] Alcohol (96 mmol); carboxylic acid (80 mmol); IL/silica gel (8 wt.%); and cyclohexane (8.0 mL).
[b] Yield was achieved by GC analysis.
[c] Selectivity for ester.

References

[1] P.W. Greene, P.G.M. Wuts, Protective Groups in Organic Chemistry, Wiley, New York, 1999, (Chapter 5).
[2] T. Joseph, S. Sahoo, S.B. Halligudi, J. Mol, Catal. A Chem. 234 (2005) 107–110.
[3] H.E. Hoydonckx, D.E. De Vos, S.A. Chavan, P.A. Jacobs, Top. Catal. 27 (2004) 83–96.
[4] D. Fang, X.L. Zhou, Z.W. Ye, Z.L. Liu, Ind. Eng. Chem. Res. 45 (2006) 7982–7984.
[5] A.C. Cole, J.L. Jensen, I. Ntai, K.T. Tran, K.J. Weaver, D.C. Forbes, et al., J. Am. Chem. Soc. 124 (2002) 5962–5963.
[6] Z.J. Wei, F.J. Li, H.B. Xing, S.G. Deng, Q.L. Ren, Korean J. Chem. Eng. 26 (2009) 666–672.
[7] W.J. Wang, L.L. Shao, W.P. Cheng, J.G. Yang, M.Y. He, Catal. Commun. 9 (2008) 337–341.
[8] Q. Wu, H. Chen, M.H. Han, D.Z. Wang, J.F. Wang, Ind. Eng. Chem. Res. 46 (2007) 7955–7960.
[9] F. Shi, Q.H. Zhang, D.M. Li, Y.Q. Deng, Chem. Eur. J. 11 (2005) 5279–5288.
[10] C. Romero, S. Baldelli, J. Phys, Chem. B 110 (2006) 6213–6223.
[11] T. Welton, Coord. Chem. Rev. 248 (2004) 2459–2477.
[12] J.F. Brennecke, E.J. Maginn, AIChE J. 47 (2001) 2384–2389.
[13] O.B. Helene, M. Lionel, J. Mol, Catal. A Chem. 182–183 (2002) 419–437.
[14] K.N. Marsh, J.A. Boxall, R. Lichtenthaler, Fluid Phase Equilib. 219 (2004) 93–98.
[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] M.H. Valkenberg, C. DeCastro, W.F. Holderich, Top. Catal. 4 (2001) 139–144.
[19] K. Qiao, H. Hagiwara, C. Yokoyama, J. Mol, Catal. A Chem. 246 (2006) 65–69.
[20] G.J. Wang, N.Y. Yu, L. Peng, R. Tan, H.H. Zhao, D.H. Yin, et al., Catal. Lett. 123 (2008) 252–258.
[21] J.S. Zhang, H. Wan, G.F. Guan, Chem. React. Eng. Technol. 24 (2008) 503–508.
[22] H. Wan, J.S. Zhang, G.F. Guan, Pet. Technol. 38 (2009) 134–138.
[23] J.N. Li, L.N. Wang, T. Qi, Y. Zhou, C.H. Liu, J.L. Chu, et al., Micropor. Mesopor. Mat. 110 (2008) 442–450.
[24] E.A. Sujandi, D.S. Prasetyanto, S.C. Han, S.E. Lee, Park, Catal. Today 141 (2009) 374–377.
[25] J.N. Li, T. Qi, L.N. Wang, C.H. Liu, Y. Zhang, Mater. Lett. 61 (2007) 3197–3200.
[26] Y. Liu, J.J. Peng, S.R. Zhai, J.Y. Li, J.J. Mao, M.J. Li, et al., Eur. J. Inorg. Chem. 2006 (2006) 2947–2949.
[27] S.L. Zhang, D.N. Yi, T.M. Wu, Infrared Spectroscopy and New Technology, China, 1993, Chapter 4.