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Application of Pyridinium Ionic Liquid as a Recyclable Catalyst for Acid-Catalyzed Transesterification of Jatropha Oil

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Abstract A series of pyridinium ionic liquids were synthesized and characterized. Acid-catalyzed transesterifications of Jatropha oil were carried out with these ionic liquids under mild reaction conditions. [BSPy]CF_3SO_3 showed the best catalytic activity and biphasic behavior in the proposed process. The products could simply be separated from the catalyst phase. The catalyst exhibited constant activity for seven successive cycles after being recycled.

Keywords Pyridinium ionic liquid · Transesterification · Esterification · Recyclable catalyst · Jatropha oil

1 Introduction

The transesterification of vegetable oil is one of the major industrial processes for the production of biodiesel. The fatty acid methyl ester (FAME), which is the main component of biodiesel fuel, is prepared through the transesterification of triglycerides (TGs) and the esterification of free fatty acids (FFAs) in the present of acid or base catalysts [1–4]. However, these catalysts cannot be readily recovered nor reused. Moreover, they have other disadvantages such as equipment corrosion, more byproducts, a tedious workup procedure, and difficult separation from the products. These disadvantages result in a series of environmental problems and reaction inefficiency. The use of lipases as biocatalysts for biodiesel production has been of great interest due to its environmental friendliness [5–7]. But some alcohols such as methanol deactivate the lipase to some extent and the enzyme stability is poor. Moreover, glycerol,which is a byproduct in the transesterification, easily adsorbs on the surface of the lipase and inhibits the enzyme activity. Although solid acid catalysts are widely used in these organic reactions because of their regenerative capacity, as well as the ability to eliminate corrosion while solving environmental and toxicity problems [8], some disadvantages such as low activity, easy deactivation and high mass-transfer resistance are the major limits for further application. Because of the detrimental effects of these catalysts, great efforts have been directed towards the benign development of environmentally friendly catalysts in the transesterification of vegetable oil.

The task specific ionic liquids (TSILs), which are environmentally friendly solvents and catalysts, have gained the attention of scholars from various fields due to their adjustable physical and chemical properties. They are non-flammable, exhibit negligible vapor pressure, as well as high catalytic acitivity and offer the potential for recyclability [9–11]. Since Cole etal. [12] designed a series of water-stable Brönsted acidic ionic liquids in 2002, many organic reactions involving esterification [13], nitration [14], and acetylation [15], have been performed with these task-specific ionic liquids, resulting in excellent yields and selectivity. All of these studies offer us the possibility of designing suitable catalysts for the appointed reaction.

Aiming to create an environmentally friendly procedure for the synthesis of biodiesel from Jatropha oil and an easy separation of catalyst from the product,we are especially interested in the application of pyridinium ionic liquids in the acid-catalyzed transesterificaiton and esterificaiton of Jatropha oil with high level FFA. The pyridinium ionic liquids are highly active [16], water-stable, nonvolatile,

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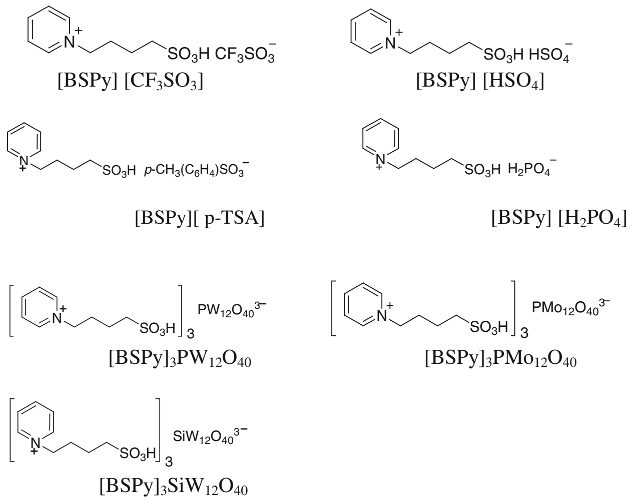


Scheme 1 Structures of pyridinium ionic liquids prepared and used in this paper

noncorrosive and immiscible with many organic solvents, which may further facilitate the reaction and make the separation of the product from the catalyst convenient. Moreover, a discussion of pyridinium ionic liquids as catalysts for the acid-catalyzed transesterification of Jatropha oil with high level FFA is still absent from the literature.

In this paper, several acidic ionic liquids with pyridinium cations (as shown in Scheme 1) were prepared and used in the process for the transesterification of jatropha oil. These ionic liquids were characterized by infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) and electrospray ionization mass spectrometry (ESI–MS). The temperature, reaction time, yields in the process and distribution of esters in the biphasic system were studied. Finally, the recycling performance of the pyridinium ionic liquid is examined.

2 Methods

2.1 Chemicals and Instruments

Pyridine (99%), 1,4-butane sultone (99%), trifluoromethane sulfonic acid (99%), phosphotungstic acid (AR),phosphomolybdic acid (AR) and other chemicals (AR) were commercially available and were used without further purification unless otherwise stated. NMR spectra were recorded on a BRUKER AV400 spectrometer in D_2O and were calibrated with tetramethylsilane (TMS) as the internal standard. IR measurements were performed on a Nicolet.510P FT-IR absorption spectrometer using KBr windows suitable for fourier transform infrared (FTIR) transmittance technology to form a liquid film. ESI–MS spectra were obtained on BRUKER Corporation Esquire HCT PLUS instrument. The quantitative analysis of the product was directly carried out by an Agilent 1100 HPLC using an ultraviolet detector and was determined by inner standard method. A Hypersil ODS (C_{18}) column (4.6 mm × 5 µm × 250 mm) was used and the mobile phase was chromatographic grade acetonitrile at a flow rate of 1.0 mL/min. The column temperature was 40 °C and the detection wavelength was 210 nm. The biodiesel samples were diluted with acetone (HPLC grade)

2.2 Preparation of TSILs with Pyridinium Cations

The TSILs with pyridinium cations were prepared in a procedure similar to the previous reported paper [17, 18]. The synthesis of [BSPy] was carried out under the following condition: pyridine was dissolved by stirring it with 1,4-butane sultone at 40 °C for 24 h. Then, the zwitterions ([BSPy]) formed as white solid. They were washed by ether three times to remove residual material and dried in a vacuum at 80 °C for 10 h. When the corresponding acid was liquid, equimolar of [BSPy] and acid solutions were mixed and stirred for 8 h at 80 °C. Then the combined solution was dried in a vacuum at 80 °C to remove water. Finally, the produced TSILs were washed repeatedly with diethyl ether to remove left over material and dried in a vacuum again.

When the corresponding acid was solid, such as *p*-toluenesulfonic acid hydrate (p-TSA·H_2O) or phosphotungstic acid ($H_3PW_{12}O_{40}$), the reaction was carried out with proper proportion of [BSPy] and an aqueous solution of acid, and then the mixture was stirred at 80 °C for 10 h, resulting in the formation of objective products. The resulting liquids were purified and dried in a similar procedure as proposed above. Finally, the TSILs were evaluated by IR measurement, NMR spectroscopy and ESI–MS. The spectral data was agreed with their structures showed in Scheme 1.

The spectral data for [BSPy] [CF_3SO_3]:FT-IR(KBr): 3072, 2949, 1637, 1493, 1339, 1170, 1030 cm^{-1}. ^1H NMR (400 MHz, D_2O, TMS): δ 1.68 (m, 2H), 2.05 (m, 2H), 2.88 (t, 2H, $J = 7.6$ Hz), 4.57 (t, 2H, $J = 7.2$ Hz), 4.71 (s, 2H), 7.99 (t, 2H, $J = 6.8$ Hz), 8.47 (t, 1H, $J = 7.2$ Hz), 8.76 (d, 2H, $J = 6.4$ Hz).^{13}C NMR (400 MHz, D_2O): δ 20.5, 27.8, 49.5, 60.7, 128.6, 145.1, 145.7. Positive-ion electrospray ionization mass spectrometry (ESI–MS) *m/z*: 216.5 ($BSPy^+$). Negative-ion electrospray ionization mass spectrometry (ESI–MS) *m/z*: 149.6 ($CF_3SO_3^-$).

The spectral data for [BSPy][HSO_4]: FT-IR(KBr):3072, 2951,1638,1492,1173,1036 cm^{-1}. ^1H NMR (400 MHz, D_2O, TMS):δ 1.62 (m, 2H), 2.03 (m, 2H), 2.80 (t, 2H, $J = 15.2$ Hz), 4.50 (t, 2H, $J = 14.8$ Hz), 4.70 (s, 2H), 7.90 (t, 2H, $J = 14.4$ Hz), 8.39 (t, 1H, $J = 1.2$ Hz), 8.69 (d, 2H, $J = 6.4$ Hz).^{13}C NMR (400 MHz, D_2O): δ 23.8, 32.4, 52.8, 64.2, 131.4, 146.8, 148.6. Positive-ion electrospray ionization mass spectrometry (ESI–MS) *m/z*: 216.4 ($BSPy^+$). Negative-ion electrospray ionization mass spectrometry (ESI–MS) *m/z*: 96.9 (HSO_4^-).

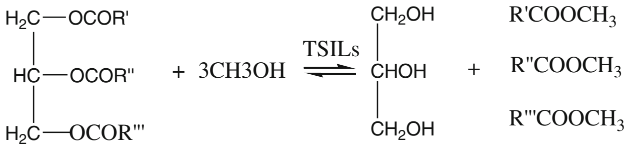
The spectral data for $[BSPy]_3$ $PW_{12}O_{40}$: FT-IR(KBr): 3070, 2948, 1636, 1491, 1170, 1035, 1080, 983, 893, 800 cm^{-1}. ^1H NMR (400 MHz, D_2O, TMS):δ 1.61 (m, 2H), 2.12 (m, 2H), 2.89 (t, 2H, $J = 15.2$ Hz), 4.51 (t, 2H, $J = 14.8$ Hz), 4.73 (s, 2H), 7.95 (t, 2H, $J = 14.4$ Hz), 8.41 (t, 1H, $J = 1.2$ Hz), 8.70 (d, 2H, $J = 6.4$ Hz).^{13}C NMR (400 MHz, D_2O): δ 21.8, 29.4, 51.2, 60.2, 128.4, 141.8, 145.6. Positive-ion electrospray ionization mass spectrometry (ESI–MS) *m/z*: 216.5 ($BSPy^+$). Negative-ion electrospray ionization mass spectrometry (ESI–MS) *m/z*: 959.08 ($PW_{12}O_{40}{}^{3-}$).

The spectral data for $[BSPy]_3PMo_{12}O_{40}$: FT-IR(KBr): 3073, 2947, 1632, 1493, 1171, 1032, 1041, 974, 917,789 cm^{-1}. ^1H NMR (400 MHz, D_2O, TMS):δ 1.58 (m, 2H), 2.01 (m, 2H), 2.78 (t, 2H, $J = 15.2$ Hz), 4.51 (t, 2H, $J = 14.8$ Hz), 4.71 (s, 2H), 7.92 (t, 2H, $J = 14.4$ Hz), 8.38 (t, 1H, $J = 1.2$ Hz), 8.72 (d, 2H, $J = 6.4$ Hz).^{13}C NMR (400 MHz, D_2O): δ 25.6, 33.2, 54.3, 62.2, 130.4, 145.8, 146.6. Positive-ion electrospray ionization mass spectrometry (ESI–MS) *m/z*: 216.4 ($BSPy^+$). Negative-ion electrospray ionization mass spectrometry (ESI–MS) *m/z*: 607.9 ($PMo_{12}O_{40}{}^{3-}$).

2.3 Preparation of Biodiesel from Jatropha Oil

The reaction was carried out in a 100 mL cylindrical stainless steel reactor, equipped with a thermostat, mechanical stirring and a sampling outlet. Jatropha oil, methanol and an ionic liquid catalyst with different molar ratios were quantitatively introduced into the reactor, successively. The reaction was allowed to proceed for 1–8 h with vigorous stirring and heating at the desired temperature. After the reaction, the mixture was placed for a few hours for the formation of two phases (Scheme 2). The upper phase mainly consisted of the produced methyl esters, and the lower phase contained the ionic liquid catalyst, water, excess methanol and a portion of the produced ester.

The sample of the upper layer was purified by filtration, water washing and distillation at 100 °C to remove the hydrophilic residue. The TG conversion and FAME yield were determined by HPLC analysis.



Scheme 2 Transesterification of Jatropha oil catalyzed by TSILs

2.4 Recycling Experiment

The ionic liquid phase was simply separated from the product by decantation and washed with ethyl acetate. The excess methanol and water were removed from the ionic liquid phase by atmospheric distillation at 100 °C. The crude glycerin was removed from the ionic liquid phase by vacuum distillation at a temperature range of 180–210 °C. Finally, the ionic liquid was directly reused in subsequent runs.

3 Results and Discussion

We first studied the effect of ionic liquids with different anions on the acid-catalyzed transesterification of Jatropha oil. The results are summarized in Table 1. It can be seen that little product could be detected when the reaction was heated at 100 °C for 8 h in the absence of ionic liquid (Table 1, entry 1), which indicated that the catalysts should be absolutely necessary for this reaction. $[BSPy][CF_3SO_3]$ shows the best catalytic performance among all the ionic liquids and the optimized reaction conditions went to entry 4 in Table 1. Other catalysts (entries 11–16) are shown to be less active under the optimized conditions.

The anion of an ionic liquid has a significant effect on its catalytic activity [17, 19], which is related to the Brönsted acidic strength of anion [20]. As an organically stronger acid, trifluoromethane sulfonic acid could ionize a proton rapidly because of the negative induction effect of fluorine atoms between the–CF_3 group and the–SO_3H group [21]. The proton combined with carbonyl group to form a carbocation intermediate, which reacted with methanol through nucleophilic substitution reaction and finally formed one molecular of diglyceride, FAME and a produced proton to catalyze the following reaction (Scheme 3). Therefore, as a stronger Brönsted-acidity ionic liquid, $[BSPy][CF_3SO_3]$ facilitates the acid-catalyzed transesterification.

On the other hand, the different partial immiscibility of obtained esters with the TSILs might also affect TSILs catalytic activity. The TSILs are miscible with water but partially immiscible with esters, which finally results in a biphasic system. Most of hydrophilic products remained in TSILs to form a heavy phase and most of the produced esters formed the light phase. As shown in Table 2, the distribution of esters between the two phases is variable in the different TSILs under the optimized condition. $[BSPy][CF_3SO_3]$ presents the best immiscibility with the produced esters, which facilitates the shifting of the esterification and transesterification equilibrium to the product side.

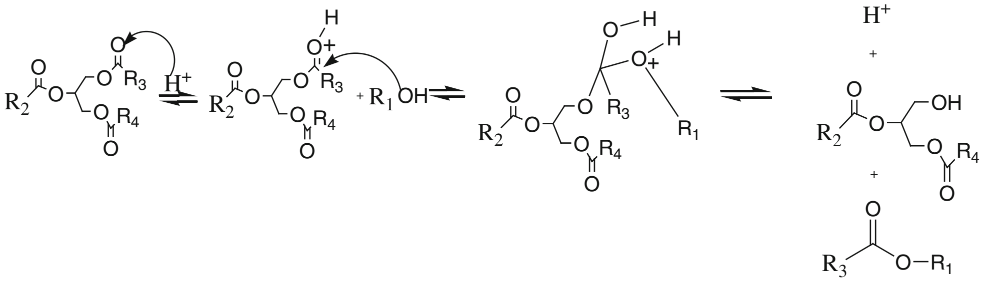
Since results were most favorable for $[BSPy][CF_3SO_3]$, different parameters including temperature, reaction time, FAME yield and TG conversion were carefully examined

Table 1 Effect of ionic liquids with different anions on the transesterification reaction

Entry	TSIL	Temperature (°C)	Molar ratio of oil/alcohol/TSIL	Time (h)	FAME yield[a] (%)	TG conversion (%)
1	–	100	1:10	8	1.5	3.2
2	[BSPy][CF_3SO_3]	100	1:10:0.05	8	70.5	90.2
3	[BSPy][CF_3SO_3]	100	1:10:0.10	6	85.6	95.1
4	[BSPy][CF_3SO_3]	100	1:10:0.12	5	92.0	99.1
5	[BSPy][CF_3SO_3]	100	1:10:0.12	8	90.3	96.5
6	[BSPy][CF_3SO_3]	100	1:10:0.15	5	90.8	99.2
7	[BSPy][CF_3SO_3]	100	1:10:0.18	5	91.5	99.3
8	[BSPy][CF_3SO_3]	90	1:10:0.12	6	86.2	99.1
9	[BSPy][CF_3SO_3]	90	1:10:0.12	8	88.3	97.5
10	[BSPy][CF_3SO_3]	80	1:10:0.12	6	83.3	99.0
11	[BSPy][CF_3SO_3]	80	1:10:0.12	8	88.0	96.9
12	[BSPy][HSO_4]	100	1:10:0.12	6	88.6	99.8
13	[BSPy][H_2PO_4]	100	1:10:0.12	5	30.3	71.2
14	[BSPy][*p*-TSA]	100	1:10:0.12	5	75.5	90.6
15	[BSPy]$_3PW_{12}O_{40}$	120	1:10:0.12	5	80.1	91.4
16	[BSPy]$_3PMo_{12}O_{40}$	120	1:10:0.12	5	80.3	91.3
17	[BSPy]$_3SiW_{12}O_{40}$	120	1:10:0.12	5	79.5	90.8

[a] Isolated yield and conversion were determined by HPLC using internal standard method

Scheme 3 Acid-catalyzed reaction mechanism for the transesterification of triglycerides



R_1,R_2,R_3:carbon chain of the fatty acids
R_4: alkyl group of the alcohol

Table 2 Distribution of esters in the biphasic system after reaction

Entry	TSIL	Fraction of produced esters		Total esters[a]
		Light phase	Heavy phase	
1	[BSPy][CF_3SO_3]	97.9	2.1	92.0
2	[BSPy][HSO_4]	96.8	3.2	83.6
3	[BSPy][p-TSA]	69.8	30.2	75.5
4	[BSPy][H_2PO_4]	50.6	49.4	30.3

After the esterification and transesterification of Jatropha oil with methanol, the reaction systems were biphasic. The produced esters in the light phase were isolated by decantation, and the esters dissolved in the heavy phase were extracted with ethyl acetate. Reaction conditions:molar ratio of oil/alcohol/catalyst 1:10:0.12, temperature 100 °C, time 5 h

[a] Isolated yields were determined by HPLC

(Table 1, entries 2–11). With a rise of temperature, the FAME yield and TG conversion reached a maximum of 92.0 and 99.1% at 100 °C for 5 h, respectively (entry 4). It can be noticed that the FAME yield increases with higher temperature and varies smoothly with enough reaction time (entries 4, 5, 9, 11). The use of [BSPy][CF_3SO_3] as a catalyst in the acid-catalyzed transesterification reduced the temperature compared with the previous work [16, 22, 23]. The higher acidity of the anion $CF_3SO_3^-$ should probably be responsible for its higher catalytic activity in this reaction. These results also indicated that increasing temperature is favorable to the improvement of catalyst activity and reaction rate, which is in agreement with the previous work [16].

It can also be found from entry 4, 5 that the TGs conversion was as high as 99.1% and slightly decreased as the FAME yield reached about 92.0%. Similar trend has been found from entries 8, 9 and entries 10, 11. As all of the reactions are reversible, some monoglycerides (MGs) and diglycerides (DGs) would form at the end of the reaction, and isomerization may occur, which results in the formation of some isomerized products. We had examined trace amounts of isomerized products by GC–MS during our experiment, which is in agreement with our supposition. In this work, the decrease in TG conversion with reaction time is supposed to be due to the inverse transesterification of MGs, DGs. And the existence of the isomerized products may reduce the FAME selectivity in TG transesterification slightly.

To investigate the reusability of [BSPy][CF_3SO_3] as an environmental friendly catalyst for the acid-catalyzed transesterification of Jatropha oils, we performed a series of recycling experiments. After the first reaction, water and excess methanol were easily removed by atmospheric distillation, glycerin was removed by vacuum distillation. The experimental results with and without removing glycerin were given in Fig 1. It was found that almost the same yields were obtained between the two experiments in the six successive trials. The FAME yield was not obviously affected by the recycling system without removing glycerin even in the sixth time, which may be due to the high thermodynamic constant of the reaction and the little amount of glycerin. Since the vacuum distillation to remove glycerin is a difficult separating process, it may be neglected in the six successive recycling experiments.

We also found that the yield decreased slightly without removing glycerin in the seventh run. In order to examine the reason of the decrease in the FAME yield, gas chromatography (GC) analysis for determining the free glycerin in the ionic liquid phase after six runs was performed using EN 14105 standard. After six cycling experiments, the ionic liquid phase was distillated under high vacuum pressure for a few hours and then analyzed by GC detection. No free glycerin was detected within the detection limits. And the ionic liquid [BSPy][CF_3SO_3] still present excellent yield in the seventh cycling experiment. In contrast, the experiment without removing glycerin showed poorer FAME yield.

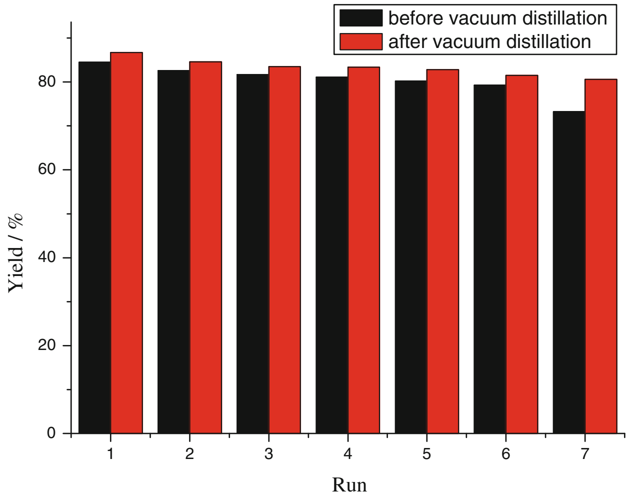


Fig. 1 Reusability of the ionic liquid [BSPy][CF_3SO_3]

Therefore, we can conclude that the catalytic activity of the ionic liquid was almost not changed after seven repeated times, the decrease in FAME yield may mainly result from the accumulative amount of glycerin in the seventh recycling experiment and the gradual lost of catalyst in the phase separation and decantation. The good reusability of [BSPy][CF_3SO_3] may be due to its molecular structure. The alkane sulfonic acid group is the constituent of the active sites, and it is covalently tethered to the cation of ionic liquid, which is not readily lost. Moreover, the electrostatic force between the cation and anion in ionic liquid is stronger than Vander Waals force. Therefore, the [BSPy][CF_3SO_3] presents more excellent stability and reusability than traditional molecular catalysts. We may conclude that it is a very promising recyclable catalyst for the acid-catalyzed transesterification of Jatropha oil.

4 Conclusion

In summary, some pyridinium ionic liquids were synthesized and [BSPy][CF_3SO_3] presents the best catalytic activity and biphasic behavior among these ionic liquids in the acid-catalyzed transesterificaiton of Jatropha oil. The product was easily separated from the catalyst with high conversion and good yield. Furthermore, the ionic liquid can be conveniently separated from the products and reused at least seven times without obvious change in the catalytic activity. Thus, the effect of the transesterification on the environment will be significantly reduced and the ionic liquid may be the suitable recyclable catalyst for the acid-catalyzed transesterification of Jatropha oil.

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References

1. Igor MN, Abdelhamid S (2008) Appl Catal A 339:45
2. Mohamad IAW, Ali OAS (2002) Bioresour Technol 85:253
3. Freedman B, Butterfield RO, Pryde EH (1986) J Am Oil Chem Soc 63:1375
4. Galen SJ, Mohanprasad DA, Eric DJ, Pratik MJ, Michael GJ (2004) Appl Catal A 257(2):213
5. Wu H, Zong MH, Lou WY (2004) Chin J Catal 25:903
6. Xu YY, Du W, Liu DH, Zeng J (2003) Biotechnol Lett 25:1239
7. Du W, Xu YY, Liu DH, Zeng J (2004) J Mol Catal B 30:125
8. Li Y, Zhang XD, Sun L, Zhang J, Xu HP (2010) Appl Energy 87:156
9. Kenneth SR (1997) J Chem Technol Biotechnol 68:351
10. Thomas W (1999) Chem Rev 99:2071
11. Wilkes JS (2002) Green Chem 4:73

12. Cole AC, Jensen JL, Ntai I, Tran KLT, Weaver KJ, Forbes DC, Davis JH (2002) J Am Chem Soc 124:5962
13. Gu YL, Shi F, Deng YQ (2004) J Mol Catal A 212:71
14. Qiao K, Hagiwara H, Yokoyama C (2006) J Mol Catal A 246:65
15. Wang WJ, Cheng WP, Shao LL, Yang JG (2008) Catal Lett 121:77
16. Wu Q, Chen H, Han MH, Wang DZ, Wang JF (2007) Ind Eng Chem Res 46:7958
17. Xing HB, Wang T, Zhou ZH, Dai YY (2007) J Mol Catal A 264:55
18. Leng Y, Wang J, Zhu DR, Ren XQ, Ge HQ, Shen L (2009) Angew Chem Int Ed 48:170
19. Pralhad AG, Gigi G, Jagannath D (2008) J Mol Catal A 279:183
20. Zhao YW, Long JX, Deng FG, Liu XF, Li Z, Xia CQ, Peng JJ (2009) Catal Commun 10:733
21. Bhardwaj RC, Enayetullah MA, Bockris JO'M (1990) J Electrochem Soc 137:2072
22. Han MH, Yi WL, Wu Q, Liu Y, Hong YC, Wang DC (2009) Bioresour Technol 100:2308
23. Kaewta S, Edgar L, Kanokwan N, James GG Jr (2009) Ind Eng Chem. Res 48:2810