Catalysis Communications 42 (2013) 125–128

Contents lists available at ScienceDirect

Catalysis Communications

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

Short Communication

A heteropolyacid-based ionic liquid as a thermoregulated and environmentally friendly catalyst in esterification reaction under microwave assistance

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ARTICLE INFO

Article history:
Received 6 June 2013
Received in revised form 8 August 2013
Accepted 13 August 2013
Available online 27 August 2013

Keywords:
Heteropolyacids
Ionic liquid
Esterification
Microwave
Biodiesel

ABSTRACT

A new kind of heteropolyacid (HPA) ionic liquid $[(CH_3)_3NCH_2CH_2OH]H_2PW_{12}O_{40}$ (ChH_2PW) has been synthesized using choline chloride and $H_3PW_{12}O_{40}$ (HPW) as precursors. The catalyst exhibited a novel switchable property based on temperature. The separation of the catalyst would be explored by simply decreasing reaction temperature without appreciable loss. Excellent conversions (97%) for esterification have been obtained under microwave-accelerated conditions.

1. Introduction

Biodiesel, a mixture of the mono-alkyl esters from esterification of fatty acid or transesterification of triglyceride molecules, is alternative to conventional diesel fuel [1–3]. The routine procedure for biodiesel production is esterification of free fatty acids (FFAs) and transesterification of triglycerides [4,5] with short chain alcohols catalyzed by base or acid catalysts [5–7]. Heterogeneous acid-catalyzed processes can be applied to produce biodiesel from low-cost raw materials with high amount of FFAs. By now, many approaches involving acid catalysis had been developed [8,9]. Compared to homogeneous catalysis, solid acid catalysts have served as important functional materials for green and recyclable catalysts.

Heteropolyacids (HPAs) and their salts have been reported as promising heterogeneous catalysts for esterification [10–15]. Wang Jun's group [16] designed acidic ionic liquid (IL) functional HPAs and acted as a "reaction-induced self-separating catalyst" for esterification. By now, a series of HPA-IL hybrids had been employed as catalysts for esterification and transesterification [9,17]. Nevertheless, more attention needs to be paid for designing new kinds of HPA ILs for esterification or transesterification. Compared to the most ILs, choline chloride (ChCl) exhibits less expensive, low toxic to humans, environmentally friendly and non-flammable characters [18], which has been used in the conversion of carbohydrates into 5-hydroxymethylfurfural [19,20]. The combination of ChCl with Lewis acids had been investigated in o-acetylation of cellulose and monosaccharides [21]. As we were preparing our manuscript, Zhang's group [22] reported a series of chorine IL catalysts, which were applied in biodiesel production as efficient base catalysts. Therefore, it is beneficial to replace expensive ILs with choline for sustainable synthesis of biodiesel.

To our knowledge, there is no report on the combination of ChCl with HPAs on esterification. Microwave assisted synthesis of biodiesel showed amazing accelerations, higher yields and high selectivity [23–25]. Therefore, we explored an alternative to fulfill esterification of FFAs catalyzed by ChCl functionalized HPA catalyst under microwaves. Its competitive advantages are (1) thermoregulated catalysis. It could be used as a homogeneous catalyst in enhancement of temperature. When temperature decreases, it precipitated and could be recycled, just like a heterogeneous system. Thus, this catalyst combines the advantages of homogeneous and heterogeneous catalysis resulting in easy handling of the catalyst; (2) First example of a highly efficient use of a ChCl functionalized HPA catalyst; (3) Providing hydrophobic surroundings leading to water-tolerant property availability; (4) Very

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http://dx.doi.org/10.1016/j.catcom.2013.08.014

efficient for the conversion of long chain FFAs; (5) The use of microwave irradiation instead of conventional heating.

2. Experimental

2.1. Preparation of the catalysts

$H_3PW_{12}O_{40}6H_2O$ was synthesized by the reported paper [26]. ChCl (0.467 g, 3.34 mmol) was added to the solution of HPW (10 g, 3.34 mmol) in 20 mL of distilled water with stirring at room temperature for 8 h. A white precipitate was formed and washed with distilled water, recrystallized twice by CH_3CN and dried at 60 °C and then gave a white product $[(CH_3)_3NCH_2CH_2OH]H_2PW_{12}O_{40}$ (ChH_2PW) with the yield of 71.2%. $[(CH_3)_3NCH_2CH_2OH]_2HPW_{12}O_{40}$ abbreviated as $(Ch)_2HPW$ was prepared by the similar procedure with the molar ratio of ChCl to $H_3PW_{12}O_{40}$ as 2:1. $[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$ ($CTAH_2PW$) was prepared by the previous report [27].

2.2. Esterification reaction

Esterification reactions were carried out in the presence of ChH_2PW at different reaction conditions. This reaction mixture was then irradiated by microwave (A 2450 MHz microwave generator) under reflux (65 °C) for the specified reaction time. After the esterification reaction completed, the upper layer were esters and the excess alcohol and the lower layer was the catalyst, which was recovered by decantation and washing with methanol and removing water under a vacuum at 60 °C for further use. The mixture was concentrated using a rotary evaporator to remove the excess alcohol. The conversion of free fatty acid into ester was calculated by measuring the acid value of the product and the yield of ester was detected by gas chromatography (GC).

3. Results and discussion

3.1. Catalyst characterization

The FT-IR spectrum of ChH_2PW was given in Fig. S1a. The four bands at 1080, 978, 893 and 808 cm^{-1} are due to $v_{as}(P–O_a)$, $v_{as}(W–O_d)$, $v_{as}(W–O_b)$ and $v_{as}(W–O_c)$, respectively, corresponding to the characteristic bands of Keggin structure [18]. It indicated that the catalyst well retained the Keggin structure after the organic cation replaced the proton in HPW. The peaks at 3519, 3037 and 1471 cm^{-1} were attributed to C–H, and C–N, respectively, showing the existence of the organic group.

The X-ray diffraction pattern was used to confirm the structure of ChH_2PW. Compared with pure HPW, ChH_2PW shows the similar diffraction peaks (Fig. S2) at 10°, 15–18°, 21–27° and 30–40° (JCPDS no. 76-1815). This result indicates the original structure of HPW being attained after forming HPAs.

The ^{31}P MAS NMR spectrum of ChH_2PW (Fig. S3) shows one peak at $\delta = -16.2$ ppm, whereas $H_3PW_{12}O_{40}\cdot 6H_2O$ gives peak at −15.6 ppm. The shift of ^{31}P MAS NMR is attributed to the introduction of organic cations into HPW, which could confirm the formation of ChH_2PW and no physical mixture of ChCl and $PW_{12}O_{40}^{3-}$.

The transmission electron microscopy (TEM) image (Fig. 1) shows that the catalyst consists of irregular particles with sizes from 10 to 20 nm. The result of energy-dispersive X-ray (EDX) measurement suggested the molar ratio of C:P:W = 5:1:12, giving the formula as $[(CH_3)_3NCH_2CH_2OH]H_2PW_{12}O_{40}$. These results demonstrate the formation of ChH_2PW (Scheme S1). Also, the elemental analyses of Ch_2HPW are: W, 72.8; P, 1.11; C, 2.10; H, 0.65; and N, 0.55%, respectively.

The formation of micellar assembly of ChH_2PW had been determined using specific conductivity to define the critical micelle concentration (CMC) of ChH_2PW (Fig. S4). It gave nearly a portion of two straight lines with break points of specific conductivity versus concentration plot [28]. Therefore, ChH_2PW is a kind of amphiphilic molecules, which could form micellar assembly in water or polar-solvent.

The Brønsted acidity of ChH_2PW was determined by titration [29]. The acidity capacity of ChH_2PW is about 0.62 mmol/g, which is lower than that of HPW (1.79 mmol/g), but higher than that of ChCl (0.02 mmol/g). This could be attributed to the organic fragment instead of the proton of $H_3PW_{12}O_{40}$.

3.2. The catalytic activity of ChH_2PW

In esterification of palmitic acid and methanol by microwave assistance, different catalysts gave various performances, while the catalytic activity (Fig. 2) was in the range of HPW ~ ChH_2PW > ChCl. HPW as a homogeneous catalyst, presented the conversion of 98.5% and TOF of 47.2 h^{-1}. ChH_2PW exhibited the similar performance as homogeneous HPW. This result is very important that there are only a few successful examples at present, in which the catalytic activity of heterogeneous HPAs is comparable to those of the homogeneous analogs [30]. Compared to other HPAs supported on silica, our results showed the higher activity with lower usage of methanol and short reaction time [31] due to the unique properties of ChH_2PW.

The higher activity of ChH_2PW comes from the acid center of $H_2PW_{12}O_{40}^{-}$ and thermoregulated property of choline functionalized

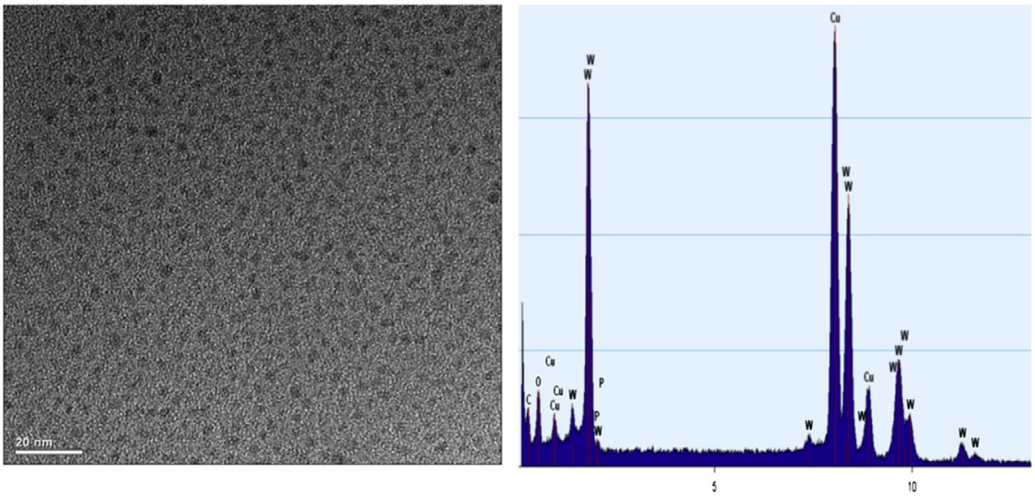

Fig. 1. The TEM image (left) and EDX pattern (right) of ChH_2PW.

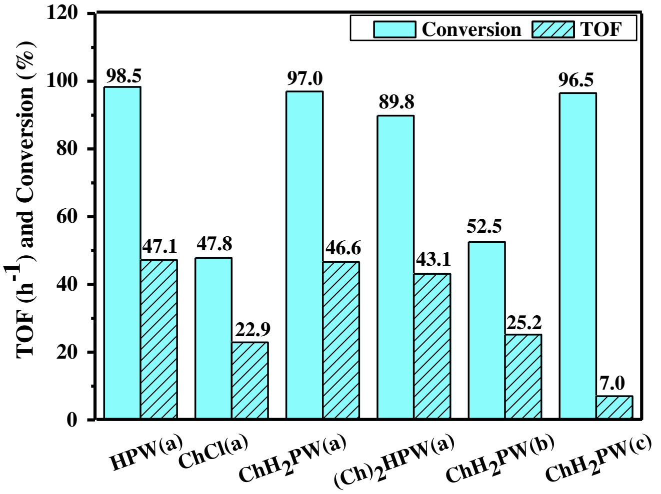

Fig. 2. Esterification of palmitic acid with different catalysts. Reaction conditions: palmitic acid 0.02 mol, the molar ratio of methanol/acid/catalyst 520:40:1, 50 min, 65 °C, (a) microwave irradiation, 50 min; (b) conventional heating, 50 min; (c) conventional heating, 5.5 h.

HPA (Fig. 3). It can be seen that before the reaction, ChH_2PW decanted to the bottom of the reactor to form heterogeneous one with methanol (Fig. 3a). With an increase in temperature to 65 °C, ChH_2PW dispersed around methanol phase (Fig. 3b). The morphology of this form was tested by TEM (Fig. 1), showing that ChH_2PW assembles as micellar spheres with size around nanometers. In addition, the formation of micellar assembly in methanol at 65 °C had been confirmed by the CMC test. Therefore, choline functionalized HPAs could act as a temperature-responsive catalyst in this reaction. The catalytic activity of ChH_2PW could be enhanced and exhibited a high conversion of 97%, which is close to that of HPW. After the reaction, with a decrease in temperature to the room temperature, the catalyst precipitated from the mixture to be separated for reuse. In addition, microwave assistance (97% for 50 min) is more available for esterification and can reduce reaction time compared to the conventional heating (96.5% for 5.5 h and 52.5% for 50 min). Therefore, microwave assistance could promote the reaction and shorten the reaction time.

Another purpose of this work is to seek a heterogeneous acid catalyst to fulfill esterification of FFAs in crude feedstocks containing water. The presence of water could promote the reverse reaction, therefore the effect of water on catalytic activity had been done by adding some excess water to the mixture. It can be seen that the conversion was related to water content (Fig. 4). When water content was below 0.2%, the conversion was reduced to 72.8%, but the conversion was significantly reduced to 1.46% for 1% of water. This result is comparable to the other solid HPA catalyst $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [32] and higher than H_2SO_4 [33] and SO_4^{2-}/ZrO_2 [34]. The reason is that ChH_2PW is composed of choline hydrophobic tail and a HPA hydrophilic head group, whose hydrophobic tail would help water molecules be eliminated from the catalytic sites. Compared to the other amphiphilic HPA molecules such as $CTAH_2PW$ (CTA represents cetyltrimethyl ammonium), the longer organic groups led to higher water-tolerance.

The influence of chain length of acid and alcohol on esterification with ChH_2PW had been checked. The conversions for different alcohols (methanol, ethanol, and butanol) are shown in Fig. S5. The type of alcohols affects the reaction very obviously, which is perhaps because of the different dissociation degree of three alcohols. It is known that for alcohols, the acidity decreased as the alkyl group substitution increased [35] resulting in weak dissociation degree. Therefore, methanol can be easier to form alkoxide ions compared with other alcohols, which is helpful for esterification. Therefore, the different acids reacting with methanol give the highest conversion compared to other alcohols and the different lengths of acid did not show significant influence on esterification. As a heterogeneous acid catalyst, ChH_2PW could form micellar assembly in methanol during the reaction. The acid sites from HPAs are fixed on the surface of the assembly, and the palmitic acid molecules are easy to access to the catalytic sites. Therefore, no steric effects were observed in esterification of different carboxylic acids.

Main parameters affecting esterification were investigated in Fig. S6. The optimism reaction conditions are the molar ratio of methanol/acid/catalyst 520:40:1, reaction time 50 min and temperature 65 °C.

As for heterogeneous catalysts, their regeneration is the most important parameter in application. This thermoregulated ChH_2PW can be easily achieved by decreasing the temperature (Fig. 3c). The catalytic activity remains efficient after six runs, showing only a slight decrease in activity (Fig. 5). The leaching of ChH_2PW was about 1.1 wt.% for each cycle. And the total amount of ChH_2PW leaching through six runs is 6.5% of the starting amount. In order to determine the leaching of ChH_2PW, the UV–vis spectroscopy of the sample in methanol was done. The two characteristic bands at 221 nm and 260 nm could be seen corresponding to the charge transfer of oxygen to tungsten, indicating that ChH_2PW dissolved in methanol with Keggin structure. It can be concluded that the leaching of ChH_2PW was attributed to the dissolution in methanol during the reaction. The IR spectrum of ChH_2PW

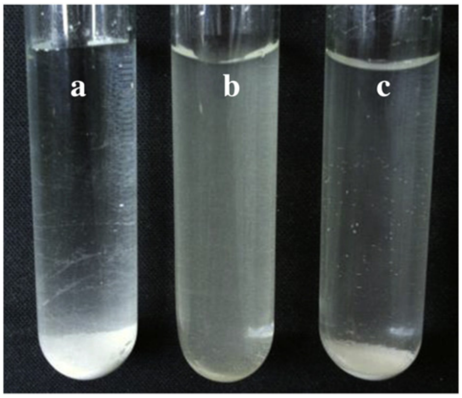

Fig. 3. Photographs of the esterification of palmitic acid and methanol over ChH_2PW. (a) Before the reaction; (b) homogeneous mixture during the reaction; (c) after the reaction.

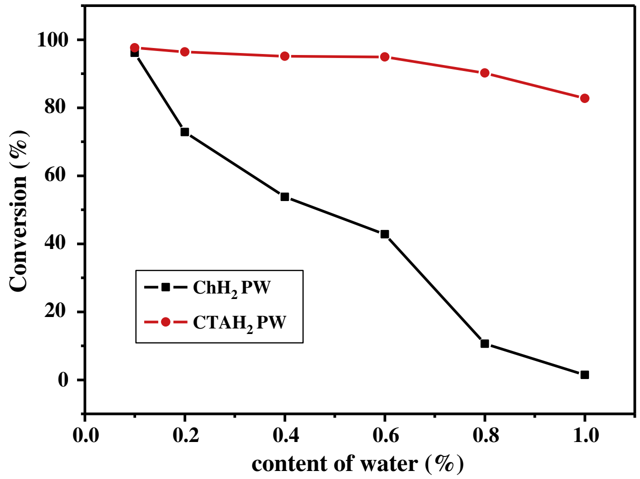

Fig. 4. Effect of water on the esterification. Reaction conditions: palmitic acid 0.02 mol, the molar ratio of methanol/acid/catalyst 520:40:1, 50 min, 65 °C.

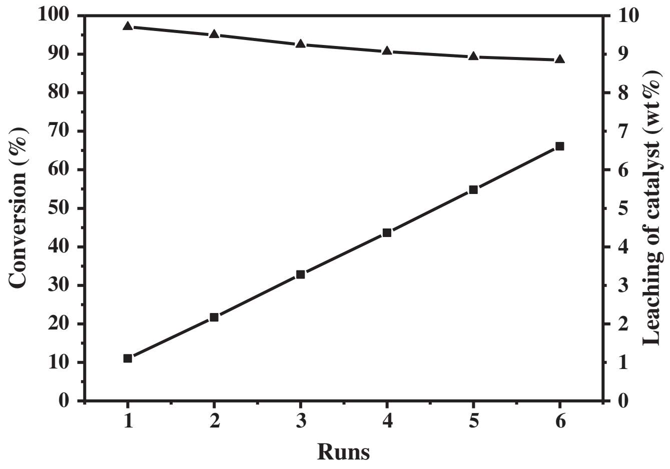

Fig. 5. The reuse of the catalyst (palmitic acid 0.02 mol, the molar ratio of methanol/acid/catalyst 520:40:1, 50 min, 65 °C).

after esterification (Fig. S1b) confirmed that the catalyst maintained its Keggin structure. In addition, the nature of ChH_2PW had been tested. ChH_2PW was in contact with palmitic acid at 65 °C during 50 min and afterwards the solid was separated from the liquid phase by decantation; then, methanol was added to the liquid phase and the reaction was monitored during 50 min. The conversion was only 20.3%. The compared experiment had been done, while the catalyst was in contact with methanol in similar condition then reacted with palmitic acid. The conversion was about 21.1%. From the above result, ChH_2PW was confirmed as a heterogeneous one with a little leaching amount.

4. Conclusions

ChH_2PW had been fabricated by ChCl and HPW which results in nonconventional IL HPAs. It was used as a “temperature controlled self-separation catalyst” for esterification and made the recovery and reuse very convenient. Microwave assistance greatly shortened the reaction time and was successfully contributed to esterification with high efficiency. It is an important result switching from homogeneous to heterogeneous catalysis system.

Acknowledgments

The work was supported by the National Natural Science Foundation of China (51078066 and 20871026) and the project of Jilin Provincial Science and Technology Department (20086035, 20100416, and 201105001).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.08.014.

References

[1] M.E. Borges, L. Díaz, Renew. Sustain. Energy Rev. 16 (2012) 2839–2849.
[2] T.M. Mata, I.R.B.G. Sousa, S.S. Vieira, N.S. Caetano, Energy Fuel 26 (2012) 3034–3041.
[3] A. Talebian-Kiakalaieh, N.A.S. Amin, H. Mazaheri, Appl. Energy 104 (2013) 683–710.
[4] W. Chen, P. Yin, H. Chen, Z. Wang, Ind. Eng. Chem. Res. 51 (2012) 5402–5407.
[5] B. Zhen, H. Li, Q. Jiao, Y. Li, Q. Wu, Y. Zhang, Ind. Eng. Chem. Res. 51 (2012) 10374–10380.
[6] A. Baig, F.T.T. Ng, Energy Fuel 24 (2010) 4712–4720.
[7] G.W. Tan Zillillah, Z. Li, Green Chem. 14 (2012) 3077–3086.
[8] A. Patel, N. Narkhede, Energy Fuel 26 (2012) 6025–6032.
[9] H. Li, Y. Qiao, L. Hua, Z. Hou, B. Feng, Z. Pan, Y. Hu, X. Wang, X. Zhao, Y. Yu, ChemCatChem 2 (2010) 1165–1170.
[10] W.H. Zhang, Y. Leng, D.R. Zhu, Y.J. Wu, J. Wang, Catal. Commun. 11 (2009) 151–154.
[11] C.F. Oliveira, L.M. Dezaneti, F.A.C. Garcia, J.L. de Macedo, J.A. Dias, S.C.L. Dias, K.S.P. Alvim, Appl. Catal. A Gen. 372 (2010) 153–161.
[12] Y. Leng, J. Wang, D.R. Zhu, Y.J. Wu, P.P. Zhao, J. Mol. Catal. A Chem. 313 (2009) 1–6.
[13] L.H. Wee, S.R. Bajpe, N. Janssens, I. Hermans, K. Houthoofd, C.E.A. Kirschhock, J.A. Martens, Chem. Commun. 46 (2010) 8186–8188.
[14] L.L. Xu, Y.H. Wang, X. Yang, X.D. Yu, Y.H. Guo, Green Chem. 11 (2009) 314–317.
[15] V. Brahmkhatri, A. Patel, Appl. Catal. A Gen. 403 (2011) 161–172.
[16] Y. Leng, J. Wang, D.R. Zhu, X.Q. Ren, H.Q. Ge, L. Shen, Angew. Chem. Int. Edit. 48 (2009) 168–171.
[17] Y. Qiao, Z. Hou, Curr. Org. Chem. 13 (2009) 1347–1365.
[18] F. Ilgen, D. Ott, D. Kralisch, C. Reil, A. Palmbergera, B. König, Green Chem. 11 (2009) 1948–1954.
[19] S.Q. Hu, Z.F. Zhang, Y.X. Zhou, J.L. Song, H.L. Fan, B.X. Han, Green Chem. 11 (2009) 873–877.
[20] F. Liu, J. Barrault, K.D. Oliveira Vigier, F. Jérôme, ChemSusChem 5 (2012) 1223–1240.
[21] A.P. Abbott, T.J. Bell, S. Handa, B. Stoddart, Green Chem. 7 (2005) 705–707.
[22] M.M. Fan, J.L. Huang, J. Yang, P.B. Zhang, Appl. Energy 108 (2013) 333–339.
[23] D. Kim, J. Choi, G.J. Kim, S.K. Seol, S. Jung, Bioresour. Technol. 102 (2011) 7229–7231.
[24] D. Kim, J. Choi, G.J. Kim, S.K. Seol, Y.C. Ha, M. Vijayan, S. Jung, B.H. Kim, G.D. Lee, S.S. Park, Bioresour. Technol. 102 (2011) 3639–3641.
[25] H. Zhang, J. Ding, Z. Zhao, Bioresour. Technol. 123 (2012) 72–77.
[26] R.C. Deltcheff, M. Fournier, R. Franck, R. Thouvenot, Inorg. Chem. 22 (1983) 207–216.
[27] M.X. Cheng, T. Shi, H.Y. Guan, S.T. Wang, X.H. Wang, Z.J. Jiang, Appl. Catal. B Environ. 107 (2011) 104–109.
[28] N. Nazir, M.S. Ahanger, A. Akbar, J. Dispers. Sci. Technol. 1 (2009) 51–55.
[29] L.N. Zhou, K. Liu, W.M. Hua, Y.H. Ying, Z. Gao, Chin. J. Catal. 30 (2009) 196–200.
[30] N. Mizuno, K. Kamata, Coord. Chem. Rev. 255 (2011) 2358–2370.
[31] B. Zhen, H.S. Li, Q.Z. Jiao, Y. Li, Q. Wu, Y.P. Zhang, Ind. Eng. Chem. Res. 51 (2012) 10374–10380.
[32] F. Chai, F.H. Cao, F.Y. Zhai, Y. Chen, X.H. Wang, Z.M. Su, Adv. Synth. Catal. 349 (2007) 1057–1065.
[33] D. Kusdiana, S. Saka, Bioresour. Technol. 91 (2004) 289–295.
[34] J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, P. Jenvanitpanjakul, Chem. Eng. J. 116 (2006) 61–66.
[35] J.A. Colucci, E.E. Borrero, F. Alape, J. Am. Oil Chem. Soc. 82 (2005) 525–530.