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Short Communication

Liquid-phase dehydration of 1-phenylethanol to styrene over sulfonated D-glucose catalyst

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ABSTRACT

Dehydration of 1-phenylethanol to produce styrene has been studied in liquid phase without any solvent with carbon-based solid acid catalysts prepared in one step from renewable resources like D-glucose for the first time. The carbon-based catalyst shows higher styrene selectivity and lower activation energy than other solid acid catalysts that have been used so far, demonstrating that a carbon-based catalyst is very effective in producing styrene from 1-phenylethanol.

1. Introduction

Dehydration of alcohols [1] has been widely studied and used to produce organic intermediates including olefins, which are valuable intermediates because of their high activity and functionality. Dehydration has usually been carried out with acid catalysts such as mineral acids and solid acids. Various alcohols including methanol [2–5], butanol [6], hexanol [7] and sorbitol [8] have been converted into attractive intermediates using suitable catalysts.

Styrene (ST) is a very important raw material in the modern chemical industry since this chemical is widely used in the production of various polymers, copolymers, synthetic rubbers, plastics and resins, etc. [9]. Generally, ST is produced by two methods: one is a co-product of propylene oxide production and the other one is the dehydrogenation of ethylbenzene at high temperature using iron oxide catalysts in the presence of superheated steam [10–12]. Even though the direct production of ST from ethylbenzene is widely used, the process has a few shortcomings such as high energy consumption [9]. Around 15% of ST is produced by dehydration of 1-phenylethanol (PhE) which is obtained from a process called PO/SM (propylene oxide/styrene monomer) [13–16].

Dehydration of PhE has been commercially carried out at around 300 °C in a gas phase in the presence of solid acids like titania and alumina [15,16]. Recently, liquid-phase PhE dehydration has been studied using various catalysts like zeolites (H-ZSM-5 [13,16] mordenite [14,16] and H-Y [16]), alumina [15], polyoxometalate [16] and silica-alumina [16]. Liquid-phase dehydration is very attractive because energy consumption can be minimized due to low operation temperature. However, there have been only a few studies to develop suitable acid catalysts, especially solid acid catalysts, for ST from PhE in liquid phase. Solid acid catalysts are very promising and important because they are environment friendly, recyclable and can be separated easily. Inorganic-oxide solid acids such as zeolite and niobic acid or $AlPO_4$ are well studied solid acid catalysts [17,18]. However, these are reported to have low densities of effective acid sites [17,19]. On the other hand, ion-exchange resins such as Amberlyst and Nafion resins are also reported to be strong acid catalysts due to the presence of profuse sulfonic acid groups ($—SO_3H$). Nevertheless, these resins are expensive as well as exhibit low operational stability at high temperature [17]. Moreover, ZrO_2-based solids are attracting a great deal of attention in recent years and have been widely studied since they have high catalytic activity in important reactions [20–22]. However, they are comparatively costly and require high temperature calcinations both for synthesis as well as regeneration [17].

Recently, sulfonated carbonaceous materials have been reported as promising solid acids catalyst [23]. These types of solid acids are widely used in various reactions such as esterification or transesterification [17,24,25], alkylation, acetylation [26]. The generation of sulfonic acid groups on surfaces has been usually performed by treating carbonaceous materials with sulfuric acid [27] or oleum [28]. All of these solid-acid catalysts are synthesized in two steps. The carbonized materials are prepared in first step at high temperature (~450 °C) and sulfonation is carried out in the next step in harsh oxidation conditions. On the contrary, Wang et al. reported a one-step facile synthesis of a carbon-based solid acid catalyst recently [29].

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In this study, we adopted one-step synthesis of a carbon-based solid acid catalyst using D-glucose as the carbon source and H_2SO_4 as the sulfonating agent. So far, to the best of our knowledge, there have been no reports on the use of a carbon-based solid acid such as sulfonated D-glucose or sulfonated activated carbon in the dehydration of PhE. Moreover, the catalyst preparation is facile as well as cost effective due to the use of a very cheap and environment friendly carbon sources such as D-glucose. In this paper, the dehydration of PhE with carbon-based solid acid catalysts will be discussed.

2. Experimental

2.1. Material

D-glucose ($C_6H_{12}O_6$) and sulfuric acid (H_2SO_4, 95%) were purchased from DC Chemical Co. and OCI Chemical Co., respectively. 1-Phenylethanol (98%) and styrene (99%) were obtained from Sigma Aldrich. All the chemicals were used without further purification.

2.2. Catalyst preparation

Sulfonated carbonaceous solid acids were prepared to follow the reported method [29]. As a carbon source, D-glucose was used. Briefly, 2 g of D-glucose and 10 mL of concentrated H_2SO_4 were sealed into autoclaves and heated at 180 °C for 24 h in an electric oven. The obtained products were washed with hot deionized water (>80 °C) and filtered until no sulfate ion was detected in the filtrate and dried at 80 °C overnight in air. The samples were denoted as sulfonated D-glucose (S-Dg).

2.3. Catalyst characterization

The X-ray powder diffraction patterns were obtained with a diffractometer D2 Phaser (Bruker, with CuKα radiation, working at 30 kV and current 10 mA, 2θ range: 5 to 90, increment: 0.02 degree). FT-IR spectra were recorded over the range from 700 to 4000 cm^{-1} on a Jasco FTIR-4100 (ATR, maximum resolution: 0.9 cm^{-1}). Elemental analyses of the catalysts were done with an elemental analyzer (Thermo Fisher, Flash-2000) with a TCD detector. Nitrogen adsorption isotherms were obtained at −196 °C with a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation at 150 °C for 12 h. The thermal stability of the catalyst was examined with thermogravimetric analysis (TGA, SDT Q600V20.9 Build 20) under a flow of nitrogen at a heating rate of 10 °C/min. The acid density of S-Dg was determined by acid–base titration to follow previous reports [29,30].

2.4. General procedure for the dehydration of PhE to ST

The dehydration of PhE was carried out in the liquid phase using a round bottomed 100 mL three-neck flask equipped with a small rectification column and a water cooled condenser attached to a vacuum pump. For each batch of dehydration, the flask was loaded with 15 g of PhE and dipped in a hot oil bath for rapid heating to the reaction temperature and then 0.1 g catalyst was added to the PhE solution. The pressure of the reaction system was decreased (~0.8 bar) to remove the low boiling portion (water and ST). As the reaction proceeded, the distillate fraction containing water and ST was collected in a glass vessel. After a fixed reaction time, the reaction flask was removed from the oil bath and cooled to room temperature. The catalyst was separated from the residual slurry by centrifugation. The ST rich organic phase and residual slurry were mixed well and analyzed with a FID GC. Products like ST, diphenylethylether (DPEE) and heavy products were identified with authentic samples and GC-MS (Finnigan, MATGCQ).

To study the reusability of a catalyst, after each dehydration experiment, the used catalyst was regenerated in two steps with washing using acetone for several times followed by heating in a muffle furnace at 200 °C for 4 h. In each cycle, the dehydration was carried out at 180 °C for 90 min while the other reaction parameters were the same as described above.

3. Results and discussion

3.1. Characterization of the catalyst

The S-Dg sample has a broad and very weak XRD pattern (shown in Fig. 1(a)), confirming the S-Dg is still amorphous and far from the graphitic carbon [17,29]. The FT-IR spectra of the S-Dg and D-glucose samples are shown in Fig. 1(b). The strong peak at around 1712 cm^{-1} and the weak peak at around 1207 cm^{-1} could be typically assigned to the stretching modes of the SO_3H groups, which are regarded as "active sites" of this catalyst [17]. Again, the absorption bands at 1060 cm^{-1} and 1033 cm^{-1} are attributed to SO_3^- stretching and O S O stretching modes [30]. The supporting Fig. 3 shows thermogravimetric analysis (TGA) result of S-Dg. The first weight loss up to 127 °C may be for the removal of adsorbed water. After that, the sample weight remained almost constant from 127 °C to 289 °C, but showed a rapid weight loss between 289 and 417 °C. The rapid weight loss may be due to the decomposition of $—SO_3H$ group [17]. The total and strong ($—SO_3H$) acid site densities of S-Dg were determined by acid–base titration using 0.01 M NaOH solution [29,30]. The total acid density was 2.53 mmol/g, which is comparatively higher than the sulfur contents measured by elemental analysis. This high value is probably due to the generation of high concentration of —OH and —COOH groups during the process of partial oxidation by concentrated sulfuric acid [29,30]. Again, the $—SO_3H$ density was 0.91 mmol/g which is comparable with the sulfur contents determined by elemental analysis.

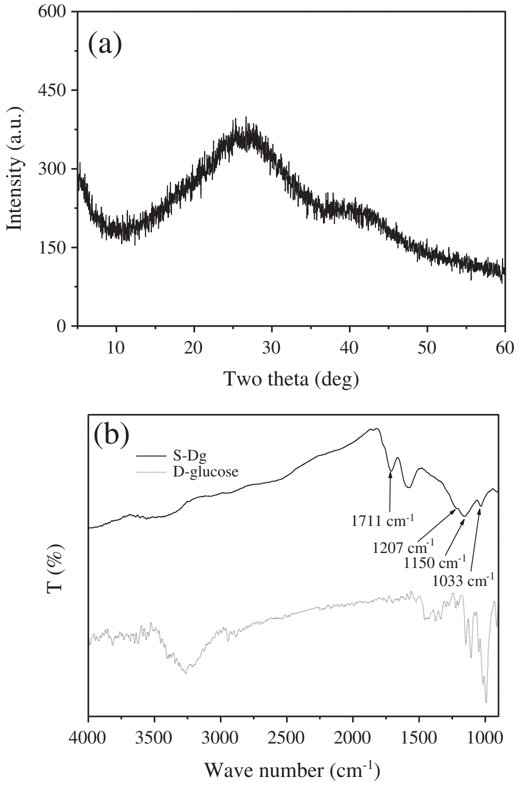

Fig. 1. (a) XRD pattern of S-Dg (b) FTIR analysis of D-glucose and S-Dg.

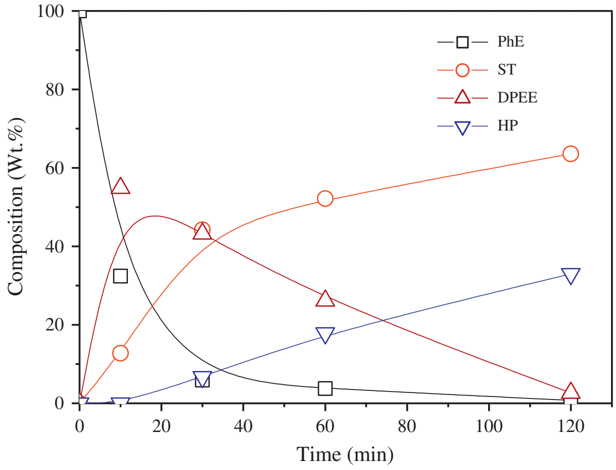

Fig. 2. Changes of the compositions of the reaction system depending on the reaction time in the presence of S-Dg.

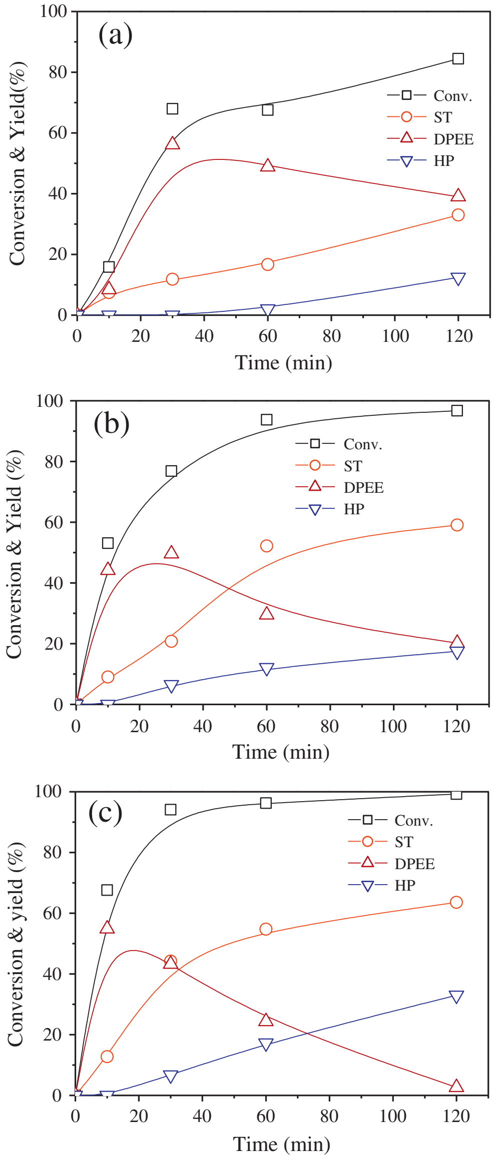

Fig. 3. Effect of reaction temperatures on the product yield and conversion for dehydration of PhE with S-Dg at pressure 0.8 bar; (a)160 °C (b)170 °C (c)180 °C.

3.2. Catalytic dehydration

Fig. 2 shows the changes in the compositions of the reaction system depending on the reaction time in the presence of S-Dg at 180 °C. It is clear, from the figure, that the main initial products in the dehydration of PhE over S-Dg are ST and DPEE. As the reaction proceeds, the ST selectivity increases (and DPEE selectivity decreases instead), and after 2 h, the selectivity is up to 64%. To the best of our knowledge, this is the best catalytic performance in ST selectivity in liquid phase dehydration of PhE to ST. Moreover, ST selectivity may be increased further using solvents in the reaction medium [13,31] even though solvents are not recommended in a reaction because of the environment and energy.

Fig. 3 shows the results of the dehydration of PhE over S-Dg at various temperatures. Both the conversion and ST selectivity increase with an increase in the reaction time up to 2 h. Generally, the conversion and ST selectivity also increase with increasing temperature and the best results are found at 180 °C. Fig. 4(a) shows the first order kinetic plots for the dehydration of PhE over S-Dg at various temperatures, showing the dehydration can be described with the first-order kinetic expression. The kinetic constant increases with an increase in temperature and the highest value is found at 180 °C. However, the kinetic constant of dehydration with S-Dg is much lower than that of the constant with Amberlyst-15 [31]. The lower reaction kinetic constant over S-Dg, compared with that over Amberlyst-15, may be explained by the sulfur contents. The sulfur contents of S-Dg and Amberlyst-15 are 0.35 mmol g^{-1} (Table 1) and 4.60 mmol g^{-1} [33], respectively. Since the active site of sulfonated catalysts is —SO_3H, catalytic activity usually depends on

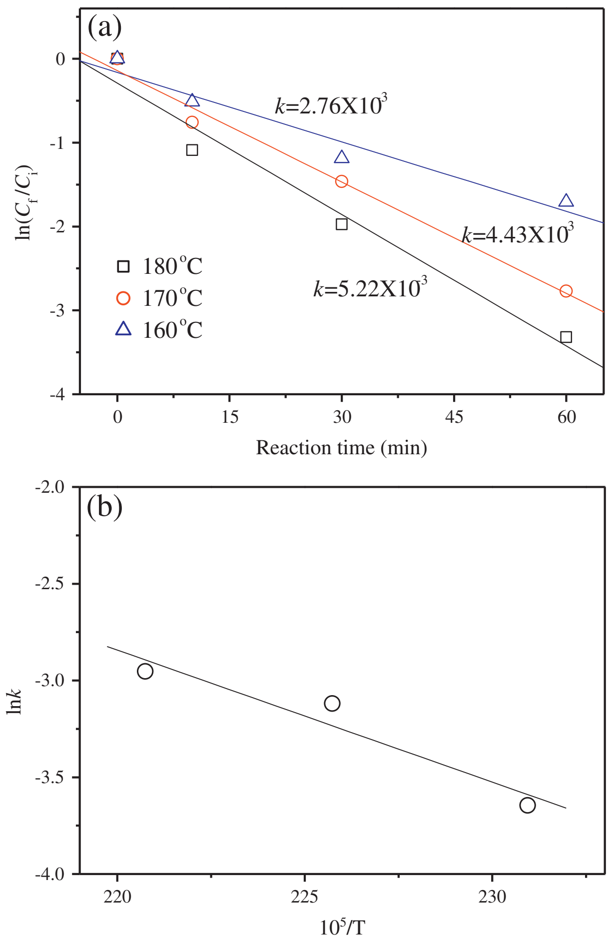

Fig. 4. (a) Plots to show the first order kinetics of the PhE dehydration over S-Dg at three different temperatures. The kinetic constants are also shown. (b) Arrhenius plot for the dehydration of PhE with S-Dg.

Table 1
Elemental composition and BET surface area of S-Dg.

Elements (wt.%)				BET surface area (m^2/g)
C	H	N	S	3.9
59.51	2.46	0	1.11[a]	

[a] 0.35 mmol/g.

the acid site or sulfur concentration [32]. Moreover, the surface area of S-Dg (3.9 m^2/g) is also lower than that of Amberlyst-15 (45 m^2/g). A low surface area of S-Dg may be another reason for a low kinetic constant because heterogeneous catalysis usually occurs on the surface rather than in bulk.

The activation energy is calculated from the Arrhenius equation or from a plot of ln$k$ vs. 1/T which is shown in Fig. 4(b). The calculated activation energy of dehydration over S-Dg is 56.7 kJ/mol and somewhat low compared with the energies observed with H-ZSM-5 and ALO-4 alumina catalysts (95.2 kJ/mol and 83.8 kJ/mol, respectively [13,34]). Even though further work is needed, the low activation energy observed in this study may suggest the effectiveness or high activity of the S-Dg catalyst per active site, which is in accordance with acid site densities determined by titrimetric analysis.

The reusability of the catalyst is of great importance for commercial feasibility; therefore, reusability tests of S-Dg were conducted, and the results are displayed in Supporting Fig. 1. The PhE conversions over the S-Dg catalyst in four cycles are all above 93%, representing a good reusability. The ST selectivity, however, decreases a bit with the number of recycles. The FTIR spectrum of the used catalyst (Supporting Fig. 2) shows the intact structure of the sulfonated group, which is the active site for acid catalysis. Generally, therefore, the S-Dg catalyst can be regarded as a reusable acid catalyst for ST production from PhE.

Two types of mechanisms for the dehydration of PhE over acidic catalysts have been described by different research groups [13–16,31,35]. Bertero et al. [13,14] and Romanova et al. [35] have suggested that DPEE can be converted into ST. On the contrary, Lange et al. [16] proposed that DPEE can be obtained from ST. The present study suggests that ST and DPEE are the primary products and HP is a secondary product since the primary and secondary products have non-zero and zero initial slopes, respectively [14,31]. Again, the concentration of DPEE shows a maximum and then decreases steadily with the progress of the reaction, suggesting that DPEE is an intermediate that can be converted into other products like ST or HP, which is in accordance with a previous report [31]. Moreover, it is known that olefins can be obtained from dimethylether in the methanol-to-olefin process [3,4]. Therefore, the DPEE, produced at the early stage of the reaction, may be converted into ST. GC-MS analysis shows that the HP is composed of carbon and hydrogen (chemical formula: $(C_6H_5)_4(CH)_6$; FW: 386). Therefore, HP may be mainly obtained from an oligomerization of ST.

4. Conclusion

Liquid phase dehydration of PhE to ST was carried out using carbon-based solid acid catalysts prepared form renewable resources like D-glucose for the first time. The catalysts were obtained facilely in one-step or carbonization and sulfonation were done simultaneously in one-pot synthesis. The S-Dg catalyst shows higher ST selectivity and lower activation energy than other solid acid catalysts that have been used so far, suggesting carbon-based catalysts are very effective in producing styrene.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.05.002.

References

[1] Á. Molnár, M. Bartók, Dehydration of Alcohols, in: R.A. Sheldon, H. van Bekkum (Eds.), Fine Chemicals through Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2001, pp. 295–307.
[2] Y.K. Lee, H.-J. Chae, S.-Y. Jeong, G. Seo, Applied Catalysis A: General 369 (2009) 60–66.
[3] D. Chen, K. Moljord, T. Fuglerud, A. Holmen, Microporous and Mesoporous Materials 29 (1999) 191–203.
[4] Y.-J. Lee, S.-C. Baek, K.-W. Jun, Applied Catalysis A: General 329 (2007) 130–136.
[5] S. Jiang, Y.K. Hwang, S.H. Jhung, J.-S. Chang, J.-S. Hwang, T. Cai, S.-E. Park, Chemistry Letters 33 (2004) 1048–1049.
[6] S. Delsarte, P. Grange, Applied Catalysis A: General 259 (2004) 269–279.
[7] E. Medina, R. Bringué, J. Tejero, M. Iborra, C. Fite, Applied Catalysis A: General 374 (2010) 41–47.
[8] N.A. Khan, D.K. Mishra, J.-S. Hwang, Y.-W. Kwak, S.H. Jhung, Research on Chemical Intermediates 37 (2011) 1231–1238.
[9] J.A. Maciá-Agulló, D. Cazorla-Amorós, A. Linares-Solano, U. Wild, D.S. Su, R. Schlögl, Catalysis Today 102–103 (2005) 248–253.
[10] F. Cavani, F. Trifiró, Applied Catalysis A: General 133 (1995) 219–239.
[11] J.-S. Chang, D.-Y. Hong, V.P. Vislovskiy, S.-E. Park, Catalysis Surveys from Asia 11 (2007) 59–69.
[12] M. Ji, G. Chen, J. Wang, X. Wang, T. Zhang, Catalysis Today 158 (2010) 464–469.
[13] N.M. Bertero, C.R. Apesteguía, A.J. Marchi, Catalysis Communications 10 (2009) 1339–1344.
[14] N.M. Bertero, C.R. Apesteguía, A.J. Marchi, Catalysis Communications 10 (2008) 261–265.
[15] J.-P. Lange, V. Otten, Industrial and Engineering Chemistry Research 46 (2007) 6899–6903.
[16] J.-P. Lange, V. Otten, Journal of Catalysis 238 (2006) 6–12.
[17] M.-H. Zong, Z.-Q. Duan, W.-Y. Lou, T.J. Smith, H. Wu, Green Chemistry 9 (2007) 434–437.
[18] J.M. Campelo, M. Jaraba, D. Luna, R. Luque, J.M. Marinas, A.A. Romero, Chemistry of Materials 15 (2003) 3352–3364.
[19] M.A. Harmer, W.E. Farneth, Q. Sun, Advanced Materials 10 (1998) 1255–1257.
[20] N. Lucas, A. Bordoloi, A.P. Amrute, P. Kasinathan, A. Vinu, W. Bohringer, J.C.Q. Fletcher, S.B. Halligudi, Applied Catalysis A: General 352 (2009) 74–80.
[21] S.M. Kumbar, S.B. Halligudi, Catalysis Communications 8 (2007) 800–806.
[22] J.S. Lee, J.W. Yoon, S.B. Halligudi, J.-S. Chang, S.H. Jhung, Applied Catalysis A: General 366 (2009) 299–303.
[23] R.J. White, V. Budarin, R. Luque, J.H. Clark, D.J. Macquarrie, Chemical Society Reviews 38 (2009) 3401–3418.
[24] R.A. Arancon, H.R. Barros Jr., A.M. Balu, C. Vargasc, R. Luque, Green Chemistry 13 (2011) 3162–3167.
[25] R. Luque, J.H. Clark, ChemCatChem 3 (2011) 594–597.
[26] R. Luque, V. Budarin, J.H. Clark, P. Shuttleworth, R.J. White, Catalysis Communications 12 (2011) 1471–1476.
[27] V.L. Budarin, J.H. Clark, R. Luque, D.J. Macquarrie, Chemical Communications (2007) 634–636.
[28] R. Xing, N. Liu, Y. Liu, H. Wu, Y. Jiang, L. Chen, M. He, P. Wu, Advanced Functional Materials 17 (2007) 2455–2461.
[29] B. Zhang, J. Ren, X. Liu, Y. Guo, Y. Guo, G. Lu, Y. Wang, Catalysis Communications 11 (2010) 629–632.
[30] J. Wang, W. Xu, J. Ren, X. Liu, G. Lu, Y. Wang, Green Chemistry 13 (2011) 2678–2681.
[31] N.A. Khan, J.-S. Hwang, S.H. Jhung, Bulletin of the Korean Chemical Society 32 (2011) 1327–1330.
[32] J.T. Yu, A.M. Dehkhoda, N. Ellis, Energy & Fuels 25 (2011) 337–344.
[33] X.-Y. Liu, M. Huang, H.-L. Ma, Z.-Q. Zhang, J.-M. Gao, Y.-L. Zhu, X.-J. Han, X.-Y. Guo, Molecules 15 (2010) 7188–7196.
[34] T. Takahashi, T. Kai, M. Tashiro, Canadian Journal of Chemical Engineering 66 (1988) 433–437.
[35] R.G. Romanova, A.A. Lamberov, I.G. Shmelev, Kinetics and Catalysis 45 (2004) 422–428.