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A modified biphasic system for the dehydration of D-xylose into furfural using $SO_4^{2-}/TiO_2\text{-}ZrO_2/La^{3+}$ as a solid catalyst

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ABSTRACT

One of the most promising strategies for furfural production is to extract continually the target product from the aqueous solution utilizing organic solvents. With the aim to develop an ecologically viable catalytic pathway for furfural production without the addition of mineral acids, we presented a modified biphasic system using a solid acid ($SO_4^{2-}/TiO_2\text{-}ZrO_2/La^{3+}$) as catalyst for producing furfural from xylose. Different kinds of aprotic organic solvents (DMSO, DMF and DMI) in water phase and 2-butanol in organic phase (MIBK) were investigated as reaction media. Furfural yield and xylose conversion efficiency were dependent on the amounts of aprotic organic solvents and 2-butanol, the solid/liquid ratio, and the volume ratio of the organic phase and the aqueous phase as well as the reaction temperature and time. As a result, DMI showed the best performance on improving furfural yield during the furfural production. 3563.3 μmol of furfural/g of xylose with 97.9% xylose conversion efficiency was obtained after 12 h at 180 °C when the volume ratios of water to DMI and MIBK to 2-butanol were 8:2 and 7:3, respectively.

1. Introduction

Interests to explore abundant and renewable biomass as a promising alternative of chemicals and energy have recently arisen due to the diminishing fossil fuel reserves and growing concerns about environmental issues [1,2]. Among various biomass-derived chemicals, furfural is a highly versatile and key derivative used as a starting material in the manufacture of a wide range of important non-petroleum-based chemicals, polymers as well as organic solvents [3]. There is no synthetic way for furfural production, it is industrially produced from pentose in lignocellulosic materials such as corncobs, oat hulls, cottonseed hull bran and so on, using mineral acids (H_2SO_4, HCl, etc.) as catalysts [4]. The potential drawbacks of the equipment corrosive and a large amount of waste produced are present when mineral acids are applied as catalysts. Thus furfural production is strongly hampered in many countries especially in EU and USA in the last few decades [5]. Therefore, it is essential to develop an economical process for the conversion of pentose into furfural under convenient conditions with high yield and selectivity.

Alternative investigations, which focus on the conversion of pentose into furfural by thermo-chemical processes, have already been implemented. Recent researches on furan manufacture processes involve the use of inorganic salts such as chlorine salts, metal oxides as well as solid acids instead of mineral acids as catalysts in monophasic systems (water, organic solvents or ionic liquids) [4,6]. The aqueous phase is favorable to the economic and environmental issue for furfural production industries, but the efficiency is very low due to the further rehydration of furfural in aqueous solution and the formation of oligomeric species resulted from consecutive condensation reactions between furfural with itself and with xylose [7,8]. Organic solvents, such as dimethylsulfoxide (DMSO) and dimethyl formamide (DMF), which favored the formation of furan compounds, have been proven to effectively depress side-reactions in the dehydration reactions of fructose and xylose [2,9–12]. Binder and Raines developed the *N*,*N*-dimethylacetamide/lithium chloride (DMA/LiCl) system for the conversion of cellulose into 5-hydroxymethylfurfural (HMF) under mild conditions (≤140 °C) [13]. However, monosaccharide, polysaccharide as well as biomass can be only dissolved in a few types of organic solvents to form a homogeneous system. Moreover, the use of organic solvents gives rise to environmental pollution, danger of explosion, and health hazards unless costly recycling

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procedures are used. Ionic liquids with desirable properties of negligible vapor pressures and high thermal stabilities, have been proven to be effective solvents in pentose dehydration [14,15]. Zhang et al. reported that 84.8% furfural yield from the dehydration of xylose was obtained when using $AlCl_3$ as a catalyst in [BMIM]Cl at 170 °C for 10 s under microwave irradiation, and the yields of furfural from corncob, grass and pine wood were in the range of 16.0–33.0% [4]. Zhang and Zhao demonstrated $CrCl_3$ could promote biomass (corn stalk, rice straw and pine wood) effectively to produce furfural in yields of 23.0–31.0% under microwave irradiation in ionic liquids [16]. However, the high cost of ionic liquids has kept them from being applied in a large-scale furfural production [2].

Intensive research endeavours have pursued the replacement of monophasic systems with biphasic systems (water/second organic or water/organic), in which high steam [17], nitrogen [18] as a second organic phase and methyl isobutyl ketone (MIBK) [19], dioxane [20], 4-methyl-2-pentanone [19] and toluene [21] as organic extraction solvents are often employed to extract continuously furfural from the aqueous phase once produced [22,23]. High steam and nitrogen, which can extract continuously furfural from the reaction system and form two water-furfural phases, were considered as new approaches in recent studies. However, expensive purification stages, safety issues and high installation cost inhibited their applications [18]. The organic layer serving as "storage" for the target product is crucial to maximize product yield. Zhang et al. used 1-butanol as an extraction solvent for the dehydration of D-xylose to furfural over MCM-41 as a catalyst [24]. The addition of organic solvents such as DMSO [19], cyclopentyl methyl ether (CPME) [8] as co-solvents to enhance the furfural yield by limiting undesired side reactions is also under studied. When the residence time of furfural in aqueous phase decreased, side reactions including the condensation of furfural and intermediates, resinification reactions, and fragmentation or decomposition reactions were thus minimized [8,25].

In order to restrain the side reaction and the formation of byproducts and to improve the furfural yield, an extraction solvent was applied in this study. MIBK has been proven to be an effective extraction solvent that can extract continuously furan compounds from water phase during the dehydration reaction of biomass [26,27]. Moreau et al. reported the dehydration reaction of xylose in a batch mode using H-faujasite and H-mordenite as catalysts at 170 °C using MIBK/water as the media and low xylose conversion was obtained [28]. However, poor partitioning of furfural into the organic phase and large energy expenditures limited its application [15]. High-boiling point organic solvents such as DMSO and DMF with water over mineral acids or solid acid catalysts had been investigated and had given promising results [29]. However, these homogeneous systems were not suitable for the generation of furfural production and necessitated energy-intensive isolation procedures [1]. Therefore, it is essential to add isolation procedures to the reaction system and change the solvent composition in the modified biphasic system for improving the target product yield in the dehydration of xylose.

The main objective of our work was to investigate a modified biphasic system using a solid acid ($SO_4^{2-}/TiO_2\text{-}ZrO_2/La^{3+}$) as catalyst for producing furfural from xylose. The influence of aprotic organic solvents like DMSO, DMF and 1,3-Dimethyl-2-imidazolidinone (DMI) in the aqueous phase and the impact of 2-buthanol in MIBK phase on furfural production were discussed. Furthermore, the reaction parameters such as the amounts of aprotic organic solvent and 2-butanol, the solid/liquid ratio, the volume ratio of the organic phase and the aqueous phase, the reaction temperature and time were investigated to optimize the reaction conditions. And a kinetic model for the dehydration of xylose in a modified biphasic system using $SO_4^{2-}/TiO_2\text{-}ZrO_2/1.0\,\text{wt\%-}La^{3+}$ as a solid acid catalyst was proposed.

2. Experimental

2.1. Materials

D-Xylose (≥99%), $ZrOCl_2 \cdot 8H_2O$, $TiCl_4$ and NH_4OH were purchased from Tianjin Kemiou Chemical Co. Ltd., (China). $La(NO_3)_3 \cdot 6H_2O$, DMSO, DMF, DMI, MIBK and 2-butanol were purchased from Aladdin (China). Furfural (≥99%) was provided by Guangzhou Chemical Reagent Factory (China). All reagents were used without any purification.

2.2. Preparation of $SO_4^{2-}/TiO_2\text{-}ZrO_2/1.0\,\text{wt\%-}La^{3+}$

$SO_4^{2-}/TiO_2\text{-}ZrO_2/1.0\,\text{wt\%-}La^{3+}$ was prepared by coprecipitation and impregnation methods [30,31]. $TiCl_4$ (0.04 mol) and $La(NO_3)_3 \cdot 6H_2O$ in a required stoichiometric ration of lanthanum (1.0 wt%) were added to $ZrOCl_2 \cdot 8H_2O$ (0.02 mol) solution slowly in an ice bath. Then the solution was adjusted to pH in the range of 9–10 with concentrated ammonia and aged for 24 h to form $Zr(OH)_4\text{-}Ti(OH)_4/La^{3+}$. The washed power was dried at 110 °C for 24 h to form $TiO_2\text{-}ZrO_2/La^{3+}$. Then $TiO_2\text{-}ZrO_2/La^{3+}$ was impregnated with 1.0-M H_2SO_4 at the proportion of 15 mL/g for 6 h. The solid product was dried at 110 °C for 12 h and calcined for 4 h at 550 °C to get the targeted catalyst.

2.3. Catalytic dehydration of xylose to furfural in a modified biphasic system

A 150-mL glass reactor was used to perform the xylose conversion reactions. In a typical procedure, xylose and catalyst were added in a reactor at a weight ratio of 2:1. Followed by the addition of water and organic solvents, the reaction mixtures were heated up to a desired temperature with a stirring rate of 450 rpm. After the required reaction time, the reactor was cooled down immediately in an ice bath and the products in organic phase as well as in water phase were filtrated with 0.22 μm filter membranes for high-performance liquid chromatography (HPLC), gas chromatography (GC), respectively.

2.4. Product analysis

Furfural in water phase was measured by HPLC (Aglient 1100 series with a reversed-phase C18 column) with a photodiode array detector at 277 nm based on the standard curves [32]. Samples were injected with a 10-μL loop and the column oven was set to 30 °C. A volume ratio of 0.1 wt% acetic acid aqueous solution to acetonitrile (85/15, v/v) was employed as a mobile phase with a flow rate of 1.0 mL/min.

Furfural in organic phase was determined by GC (Shimadzu 2010) equipped with a capillary column (DB-5). The injection and detector ports were maintained at 250 °C, while the column temperature was maintained initially at 40 °C for 6 min and then heated to 250 °C at a heating rate of 25 °C/min. Nitrogen was used as carrier gas.

Xylose in water phase was determined by HPLC system (Waters 2414) equipped with a refractive index detector and a Bio-rad Aminex® HPX-87H (300 mm × 7.8 mm) column. 5 mM of H_2SO_4 was employed as the eluent with a 0.5 mL/min flow rate at room temperature. Due to the isomerization of xylose can not be observed and xylose served as raw material, we use pentose peak area for calculation here.

Furfural yield and xylose conversion were defined by Eqs. (1) and (2):

$$\text{Furfural yield (mmol of furfural/g of xylose)} = \frac{\text{moles of furfural in the product}}{\text{initial xylose weight}} \qquad (1)$$

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$$\text{Conversion of xylose}\,(\%) = \frac{\text{initial xylose weight} - \text{remainig xylose weight}}{\text{initial xylose weight}} \times 100 \qquad (2)$$

3. Results and discussion

3.1. Influence of different modified biphasic systems on furfural yield and xylose conversion

Recently solid acid catalysts with good thermal and chemical stabilities have been attracted much attentions in biomass conversion. Zirconia-based and titanium-based solid acid SO_4^{2-}/TiO_2-ZrO_2/La^{3+} has emerged as an attractive alternative catalyst for a variety of organic transformations such as cracking, alkylation and isomerization reactions due to its strong acidity, high thermostability and high catalytic activity [33,34]. In our previous study, we found that SO_4^{2-}/TiO_2-ZrO_2/La^{3+} prepared showed high catalytic performance for xylose dehydration in the aquesou system under ultraviolet irradiation at low temperature. So this solid acid catalyst was used again in the dehydration of xylose in a biphasic system. Table 1 shows the dehydration of xylose in different reaction media. When the aqueous sytem was used in the dehydration of xylose (Table 1, entry 1), 46.1 μmol of furfural/g of xylose with 40.0% xylose conversion efficiency was obtained under 120 °C at a reaction time of 4 h. This may be attributed to a large amount of acidic sites on the surface of the prepared catalyst, which was comfirmed by NH_3-TPD and pyridine FT-IR (data not shown) [31,35]. Besides, the existing of La^{3+} loaded on the solid acid catalyst may enhance its catlytic performance by changing the chemical state of exterior atoms, thus strengthening the interaction of SO_4^{2-} and TiO_2-ZrO_2/1.0 wt%-La^{3+} and thereby increasing the number of effective active center of catalysts [36]. Although water was considered as a green solvent in many processes, it was apparently unable to enhance the dehydration reaction of xylose since the rehydration of furfural and the consecutive condensation reactions between furfural and intermediates of the xylose-to-furfural in aqueous solution [7,37].

Compared to the pure water system, water/MIBK as a biphasic system (Table 1, entry 2) yielded the relatively higher furfural yield and xylose conversion of 60.6 μmol of furfural/g of xylose and 49.2%, respectively, under the same reaction condition. This may be due to the higher solubility of furfural in MIBK phase than in water. When DMSO as a co-solvent was added in this aqueous phase, the biphasic system resulted in 409.7 μmol of furfural/g of xylose (entry 3), which was increased by 576.0% compared with the water/MIBK system. While no obvious difference occurred in xylose conversion efficiency. These results were consistent with the literature reported that DMSO can effectively depress side-reactions in dehydration reactions and increase the selectivity of furfural product [2]. However, the addition of 2-butanol as a co-solvent into the MIBK phase in the biphasic system had small impacts on the increasing of furfural yield as well as xylose conversion efficiency (Table 1, entry4).

To understand the influence of different types of polar aprotic solvents in water phase on xylose dehydration, DMSO, DMF and DMI were investigated in a modified biphasic system under the same reaction conditions (Table 1, entries 5–7). Clearly, the yield of furfural and the conversion efficiency of xylose were related to the types of polar aprotic solvents. The addition of DMSO, DMF and DMI to the aqueous phase of the biphasic system can greatly improves the furfural yield, especially for the DMI solvent. A more than fifteen-fold increase in furfural yield was achieved with DMI in comparison with the non-polar-aprotic system (Table 1, entry 4). However, xylose conversion efficiency increased relatively little, which indicated that DMI could greatly inhibit the unwanted side-reactions and thereby improve the furfural selectivity. From these observations, DMI is the most suitable auxiliary solvent along with the modified extracting solvents for the furfural production. This phenomenon demonstrated that the modified biphasic system was in favor of the generation of furfural, thus restrained the formation of byproducts and increased the selectivity of the main product.

3.2. Influence of the co-solvent amount in the modified biphasic system

The modified biphasic system mentioned above obviously improved the furfural yield and the xylose conversion efficiency, thus the influence of the amounts of the best co-solvents (DMI and 2-butanol) on the xylose dehydration is discussed in Fig. 1. The dehydration reaction was conducted in the xylose/catalyst weight ratio of 2:1 at 120 °C for 4 h, and the volume of water phase and organic phase was set to 30 mL, respectively. As shown in Fig. 1b, with a decrease of water/DMI volume ratio from 9:1 to 8:2, furfural yield remarkably increased from 581.4 μmol to 936.6 μmol from per gram of xylose. However, further decreasing the ratio, which meant increasing DMI content, led to the decrease in furfural yield, which was due to the reducing of extracting power of solvent [1]. In addition, along with promoting the percentage of DMI, the conversion efficiency of xylose sharply increased firstly and then leveled off. Thus the amount of DMI in aqueous phase of biphasic system had important impact on the dehydration of xylose, and the desirable water/DMI volume ratio was kept at 8:2.

Fig. 1b shows the furfural yield and xylose conversion efficiency as a function of MIBK/2-butnal volume ratio. There was no obvious change in the furfural yield and xylose conversion efficiency as the volume ratio of MIBK and 2-butanol decreased from 9:1 to 7:3. However, as the volume ratio decreased to 6:4, xylose conversion efficiency increased while furfural yield reduced quickly. This phenomenon was attributed to the accessibility of part of 2-butanol accessible to water phase, resulting in an increment of the solubility of furfural in water phase, thus leading to secondary reactions [1].

Table 1
Influence of the reaction media composition on furfural yield and xylose conversion efficiency.[a]

Entry	Solvents	Furfural yield (μmol of furfural/g of xylose)	Conversion (%)
1	Water	46.1	40.0
2	Water:MIBK (1:1)	60.6	49.2
3	(8:2 water:DMSO): MIBK	409.7	46.0
4	Water: (7:3 MIBK:2-butanol)	61.4	50.0
5	(8:2 water:DMSO):(7:3 MIBK:2-butanol)	717.8	60.8
6	(8:2 water:DMF):(7:3 MIBK:2-butanol)	541.4	63.4
7	(8:2 water:DMI):(7:3 MIBK:2-butanol)	936.6	56.1

[a] Reaction conditions: 120 °C, 4 h, 0.2 g xylose, 0.1 g SO_4^{2-}/TiO_2-ZrO_2/1.0 wt%-La^{3+}, $V_{(\text{water phase})} = V_{(\text{organic phase})} = 30$ mL.

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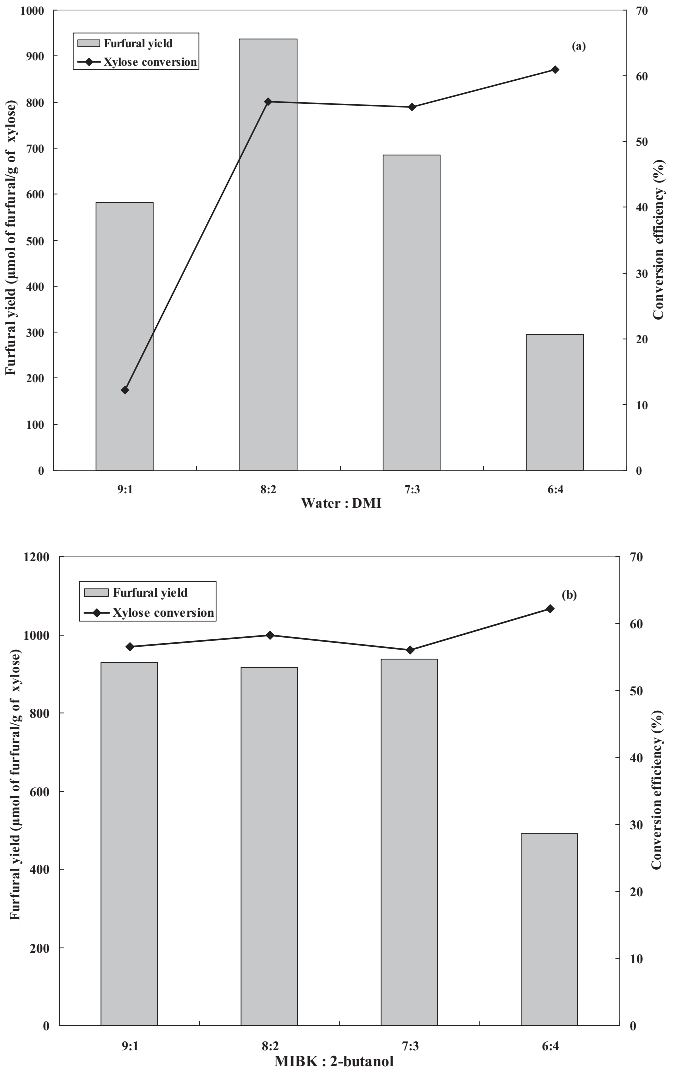

Fig. 1. Influence of the auxiliary amount in the modified biphasic system (a) MIBK:2-butanol = 7:3 (v/v); (b) water:DMI = 8:2 (v/v).

3.3. Influence of the xylose content in the modified biphasic system

Experiments were performed to investigate the effect of xylose content in the modified biphasic system on the furfural yield and conversion efficiency and the results are shown in Fig. 2. Treatments at five different ratios of xylose to water phase (1:200, 1:150, 1:100, 1:20 and 1:10, g/mL) were carried out at 120 °C in the presence of catalyst, and the reaction media was the aqueous phase of water–DMI (8:2, v/v) combined with the organic phase of MIBK–2-butanol (7:3, v/v). The highest furfural yield was 1234.2 μmol from per gram of xylose at 6 h when the ratio of xylose to the water phase was 1:150, but the value reduced with increasing xylose-loaded content. The losses of furfural yield in the higher xylose concentration was thought to be due to increasing the probability that xylose and furfural collide with each other to form humins [38]. However, the conversion efficiency of xylose was found to be mostly independent on the xylose concentration. The reaction time had a significant influence on xylose conversion efficiency at high ratios of 1:150 and 1:200. However, a small change in xylose conversion efficiency was observed in a low ratio rang of 1:10–1:100 although prolonging the reaction from 2 h to 12 h.

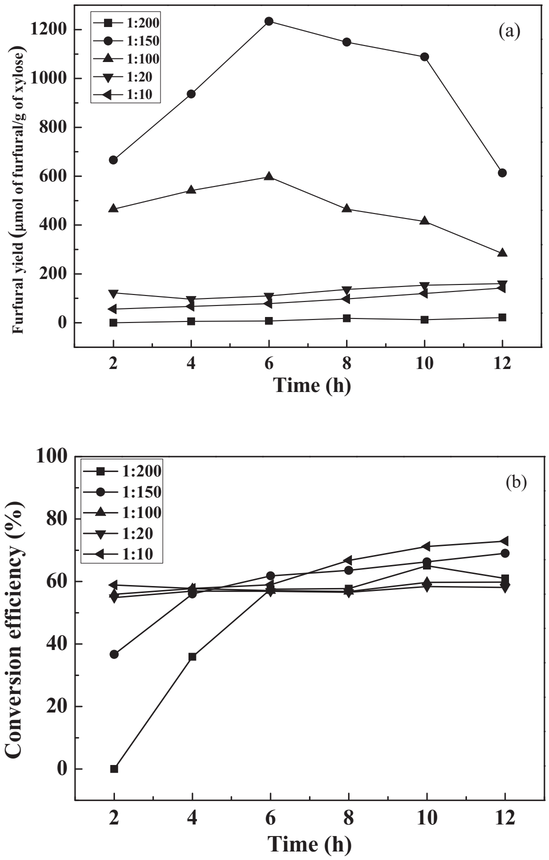

Fig. 2. Yields of furfural and the conversion efficiency of xylose with different xylose content in the modified biphasic system.

3.4. Influence of the volume ratio of water phase to organic phase

The volume ratio of water phase to organic phase has great influences on product distribution and should be carefully designed to enhance the extraction efficiency and product yield from the reaction system. Experiments with different volume ratios of the water phase to the organic phase were performed by employing $SO_4^{2-}/TiO_2\text{-}ZrO_2/1.0\,wt\%\text{-}La^{3+}$ as catalyst in a xylose to the water phase ratio of 1:150 at 120 °C for 6 h and the results are shown in Fig. 3. Highest furfural yield as well as xylose conversion efficiency were obtained when the volume ratio was 1:1 (v/v). Lower target product yield and xylose conversion efficiency were observed with larger amount of the water phase or the organic phase. As the amount of the water phase was higher than the organic phase, the rehydration rate of furfural increased. On the other hand, when larger amount of organic phase presented, the potential of forming humins was enhanced. Therefore, it was necessary to control the definite volume ratio, and a ratio of 1:1 was required at the dehydration of xylose in this modified biphasic system.

3.5. Influence of the reaction temperature and time

The effects of operation conditions (temperature and duration) with respect to the furfural yield and xylose conversion efficiency were examined in the optimized modified biphasic system discussed above, and the results are shown in Fig. 4. Experiments of the dehydration of xylose in the presence of $SO_4^{2-}/TiO_2\text{-}ZrO_2/1.0\,wt\%\text{-}La^{3+}$ were conducted at 120, 140, 160 and 180 °C in the time range of 0–12 h to study the influence of reaction temperature on furfural yield and xylose conversion.

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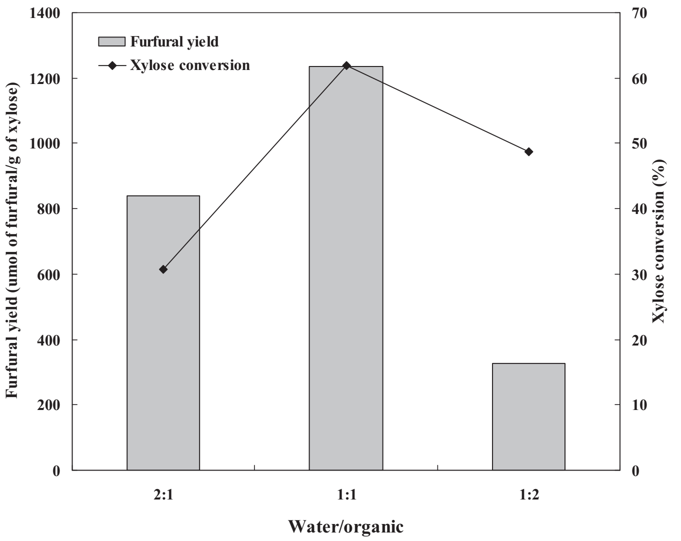

Fig. 3. Yields of furfural and the conversion efficiency of xylose with different volume ratios of water phase to organic phase.

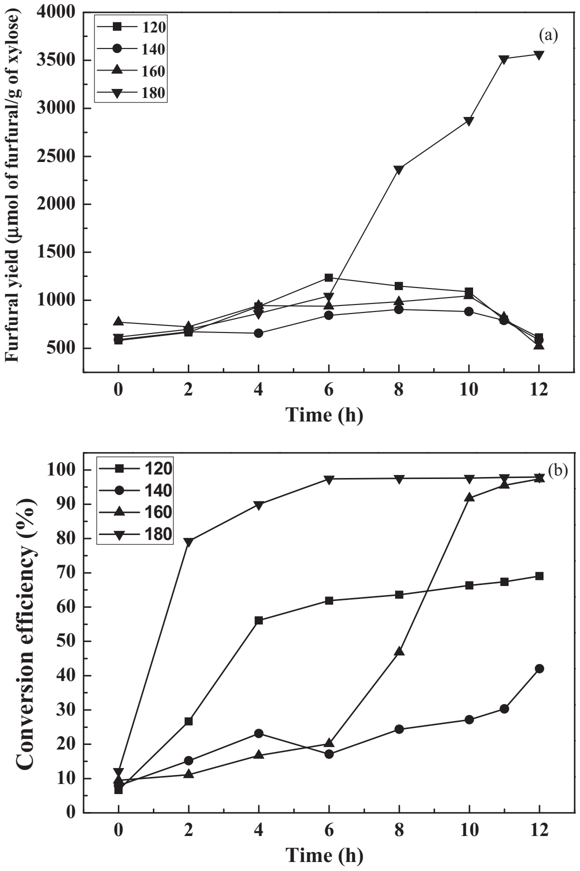

Fig. 4. Yields of furfural and the conversion efficiency of xylose in different reaction temperature in the modified biphasic system.

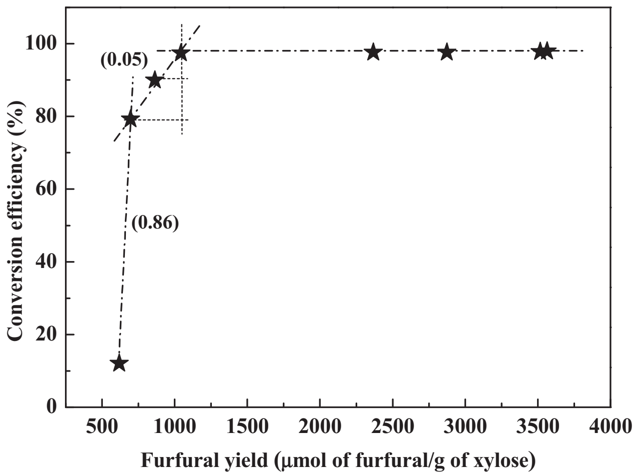

Fig. 5. Xylose conversion efficiency plotted against furfural yield at 180 °C.

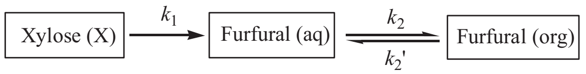

Fig. 6. Schematic diagram of the biphasic dehydration model.

As illustrated in Fig. 4a, similar furfural yields were obtained within 6 h at various reaction temperatures. When further prolonging the reaction time to 8 h, 2367.5 μmol of furfural/g of xylose was achieved at 180 °C, which was more than twice of that in 6 h. Moreover, higher furfural yield could be obtained with the prolongation of time to 12 h at 180 °C. This may be attributed to some sort of low activation of the catalysts within 6 h. Meanwhile, furfural yield decreased when the residence time further increased to 10 h below 180 °C, which may be attributed to long reaction periods without enough reaction energy promoted the yield-loss reactions and led to the formation of soluble degradation products and black insoluble solids [39,40].

The duration of the reaction had the remarkable impact on the xylose conversion efficiency in the temperature range of 120–180 °C (Fig. 4b). Prolonging the reaction time, the conversion efficiency of xylose increased gradually. However, this was not consistent well with the results of furfural yield discussed above. Below 180 °C, high conversion efficiency with low furfural yield indicated side reactions caused by the degradation process [41]. However, with prolonging the reaction time at 180 °C, higher furfural yield could be obtained with higher xylose conversion efficiency. Over $SO_4^{2-}/TiO_2\text{-}ZrO_2/1.0\,wt\%\text{-}La^{3+}$ catalyst, the same xylose conversion efficiency of more than 97.0% was achieved as increasing the reaction temperatures from 160 to 180 °C within the corresponding time of 12 and 16 h, respectively. This observations presented in Fig. 4 were consistent with the work of Weingarten et al. that the dehydration of xylose into furfural is a higher activation energy process compared to the furfural degradation process [23].

In order to understand the relationship between xylose conversion efficiency and furfural yield at 180 °C, xylose conversion efficiency plotted against furfural yield was made as illustrated in Fig. 5. The selective conversion of xylose into furfural was different at different reaction stages (0–2 h, 2–6 h and 6–12 h). In the first stage, the selectivity was the lowest with a highest gradient (0.86). While in the second stage, the gradient was much lower than the first stage, indicating that the selectivity of xylose to furfural was greatly enhanced during the second period. In the third stage, furfural yield increased significantly with similar xylose conversion efficiency, which suggested that fewer by-products were produced after 6 h at 180 °C.

A reaction scheme for the dehydration of xylose in the optimized modified biphasic system ((8:2 water:DMI):(7:3 MIBK:2-butanol)) was assumed as shown in Fig. 6. Liu reported that the dehydration of xylose in the biphasic system was first-order reaction [42]. Based on the experimental observation, detailed equations for the biphasic kinetic model are listed below:

$$\frac{d[X]}{dt} = -k_1[X] \tag{3}$$

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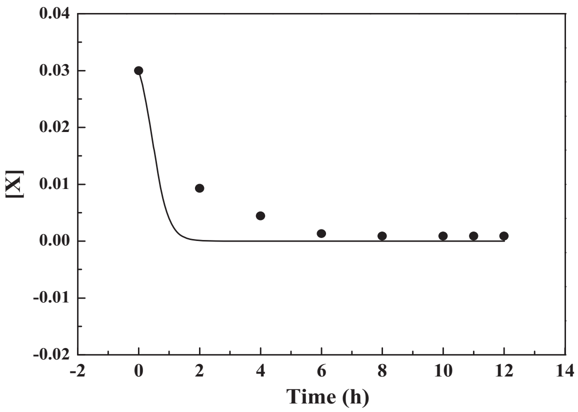

Fig. 7. Kinetic mode fit for xylose decomposition in the modified biphasic system model predicition (—), experimental data (●).

$$\frac{d[\mathrm{F}]\mathrm{aq}}{dt} = k_1[\mathrm{X}] - k_2[\mathrm{F}]\mathrm{aq} + k'_2[\mathrm{F}]\mathrm{org} \quad (4)$$

$$\frac{d[\mathrm{F}]\mathrm{org}}{dt} = k2[\mathrm{F}]\mathrm{aq} - k'_2[\mathrm{F}]\mathrm{org} \quad (5)$$

where [X] is the concentration of xylose (mol/L). Fig. 7 exhibits the biphasic model calculated by non-linear regression analyses. The model shows a good fit for xylose decomposition at 180 °C.

4. Conclusions

The present study clearly demonstrated that an efficient modified biphasic system for the dehydration of xylose into furfural using a solid acid ($SO_4{}^{2-}/TiO_2$-ZrO_2/1.0 wt%-La^{3+}) as catalyst. Aprotic organic solvents and 2-butanol were proven to be effective solvents to enhance the furfural yield and xylose conversion efficiency. 3563.3 μmol of furfural/g of xylose with 97.9% xylose conversion efficiency was obtained after 12 h at 180 °C in the modified biphasic system ((8:2 water:DMI):(7:3 MIBK:2-butanol)). Kinetic model results demonstrated that experimental data of xylose decomposition fits well with the prediction one. The next work is to investigate the dehydration of xylose using this solid acid catalyst in the modified biphasic system under microwave irradiation to improve furfural yield with higher selectivity within shorter reaction time. And the recycle ability of the catalyst will be detected by subjecting to calcination for the removal of the organic materials.

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References

[1] J.N. Chheda, Y. Román-Leshkov, J.A. Dumesic, Green Chemistry 9 (2007) 342–350.
[2] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith Jr., Green Chemistry 10 (2008) 799–805.
[3] J. Forstner, G. Unkelbach, E. Pindel, R. Schweppe, Chemie Ingenieur Technik 84 (2012) 503–508.
[4] L. Zhang, H. Yu, P. Wang, H. Dong, X. Peng, Bioresource Technology 130 (2013) 110–116.
[5] G. Marcotullio, W. De Jong, Green Chemistry 12 (2010) 1739–1746.
[6] V. Choudhary, S.H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N.S. Marinkovic, A.I. Frenkel, S.I. Sandler, D.G. Vlachos, Journal of the American Chemical Society 135 (2013) 3997–4006.
[7] A.S. Dias, S. Lima, D. Carriazo, V. Rives, M. Pillinger, A.A. Valente, Journal of Catalysis 244 (2006) 230–237.
[8] M. Campos Molina, R. Mariscal, M. Ojeda, M. López Granados, Bioresource Technology (2012) 321–327.
[9] E. Lam, E. Majid, A.C. Leung, J.H. Chong, K.A. Mahmoud, J.H. Luong, ChemSusChem 4 (2011) 535–541.
[10] A.S. Dias, M. Pillinger, A.A. Valente, Journal of Catalysis 229 (2005) 414–423.
[11] H. Zhu, Q. Cao, C. Li, X. Mu, Carbohydrate Research 346 (2011) 2016–2018.
[12] F. Wang, A.W. Shi, X.X. Qin, C.L. Liu, W.S. Dong, Carbohydrate Research 346 (2011) 982–985.
[13] J.B. Binder, R.T. Raines, Journal of the American Chemical Society 131 (2009) 1979–1985.
[14] J.C. Serrano-Ruiz, J.M. Campelo, M. Francavilla, A.A. Romero, R. Luque, C. Menéndez-Vázquez, A.B. García, E.J. García-Suárez, Catalysis Science & Technology 2 (2012) 1828–1832.
[15] D. Mercadier, L. Rigal, A. Gaset, J.P. Gorrichon, Journal of Chemical Technology and Biotechnology 31 (1981) 489–496.
[16] Z. Zhang, Z.K. Zhao, Bioresource Technology 101 (2010) 1111–1114.
[17] A.S. Mamman, J.M. Lee, Y.C. Kim, I.T. Hwang, N.J. Park, Y.K. Hwang, J.S. Chang, J.S. Hwang, Biofuels, Bioproducts and Biorefining 2 (2008) 438–454.
[18] I. Agirrezabal-Telleria, A. Larreategui, J. Requies, M. Güemez, P. Arias, Bioresource Technology 102 (2011) 7478–7485.
[19] Y. Román-Leshkov, J.N. Chheda, J.A. Dumesic, Science 312 (2006) 1933–1937.
[20] J.N. Chheda, J.A. Dumesic, Catalysis Today 123 (2007) 59–70.
[21] Y. Román-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Nature 447 (2007) 982–985.
[22] V. Ordomsky, J. Schouten, J. van der Schaaf, T. Nijhuis, Applied Catalysis A: General 451 (2012) 6–13.
[23] R. Weingarten, J. Cho, W.C. Conner Jr., G.W. Huber, Green Chemistry 12 (2010) 1423–1429.
[24] J. Zhang, J. Zhuang, L. Lin, S. Liu, Z. Zhang, Biomass and Bioenergy 39 (2012) 73–77.
[25] R. Carrasquillo-Flores, M. Käldström, F. Schüth, J.A. Dumesic, R. Rinaldi, ACS Catalysis 3 (2013) 993–997.
[26] H. Amiri, K. Karimi, S. Roodpeyma, Carbohydrate Research 345 (2010) 2133–2138.
[27] O. Yemis, G. Mazza, Bioresource Technology 109 (2012) 215–223.
[28] C. Moreau, R. Durand, D. Peyron, J. Duhamet, P. Rivalier, Industrial Crops and Products 7 (1998) 95–99.
[29] W. Dedsuksophon, K. Faungnawakij, V. Champreda, N. Laosiripojana, Bioresource Technology 102 (2011) 2040–2046.
[30] Y. Li, X.D. Zhang, L. Sun, J. Zhang, H.P. Xu, Applied Energy 87 (2010) 156–159.
[31] J. Zhang, L. Lin, S. Liu, Energy & Fuels 26 (2012) 4560–4567.
[32] S. Albalá-Hurtado, M.T. Veciana-Nogués, M. Izquierdo-Pulido, M.C. Vidal-Carou, Journal of Agricultural and Food Chemistry 45 (1997) 2128–2133.
[33] B.M. Reddy, M.K. Patil, P. Lakshmanan, Journal of Molecular Catalysis A: Chemical 256 (2006) 290–294.
[34] G. Lu, Applied Catalysis A: General 133 (1995) 11–18.
[35] E.I. Gürbüz, J.M.R. Gallo, D.M. Alonso, S.G. Wettstein, W.Y. Lim, J.A. Dumesic, Angewandte Chemie International Edition 52 (2013) 1270–1274.
[36] X. Shi, Y. Wu, H. Yi, G. Rui, P. Li, M. Yang, G. Wang, Energies 4 (2011) 669–684.
[37] F. Benvenuti, C. Carlini, P. Patrono, A.M. Raspolli Galletti, G. Sbrana, M.A. Massucci, P. Galli, Applied Catalysis A: General 193 (2000) 147–153.
[38] A.S. Dias, S. Lima, M. Pillinger, A.A. Valente, Catalysis Letters 114 (2007) 151–160.
[39] L. Zhang, H. Yu, P. Wang, Bioresource Technology 136 (2013) 515–521.
[40] M.J. Antal Jr., T. Leesomboon, W.S. Mok, G.N. Richards, Carbohydrate Research 217 (1991) 71–85.
[41] A.S. Amarasekara, C.C. Ebede, Bioresource Technology 100 (2009) 5301–5304.
[42] X. Liu, M. Lu, N. Ai, F. Yu, J. Ji, Industrial Crops and Products 38 (2012) 81–86.

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