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Selective oxidation of furfural in a bi-phasic system with homogeneous acid catalyst

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ABSTRACT

The selective catalytic oxidation of furfural to 2(5H)-furanone, succinic acid (SA) and maleic acid (MA) was studied. Under optimized conditions, furfural was oxidized to 2(5H)-furanone with a yield of 60–62% in an aqueous/organic bi-phasic system using 1,2-dichloroethane or ethyl acetate as the solvent and formic acid as the catalyst, while the total yield of SA and MA was 15–20%. Compared with other homogeneous and heterogeneous acid catalysts, formic acid gave a much higher selectivity to 2(5H)-furanone because it reacted with hydrogen peroxide to generate performic acid that had a strong oxidizing nature and good solubility in both the aqueous and organic phases. The solvent had a significant influence on the product distribution. A simplified reaction network was established to quantitatively analyze the solvent effect based on the reaction rate constants. In the homogeneous system, the yield of 2(5H)-furanone decreased while the yield of SA increased with an increasing dielectric constant of the solvent. The formic acid/furfural molar ratio, reaction temperature and furfural concentration were optimized for the selective oxidation of furfural to 2(5H)-furanone in the bi-phasic reaction system.

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1. Introduction

With increasing consumption of energy and diminishing supply of fossil fuels, substantial interest has been devoted to search for renewable energy resources in the world. In this respect, biomass, which is renewable, environmental-friendly, abundant and widespread, is considered to be an ideal substitute for traditional fossil fuels [1–4]. In recent years, various catalytic conversion strategies have been developed for the conversion of biomass to bio-based platform compounds, which can be further converted to a wide range of target products [5–9]. Among these renewable platform compounds, furfural, produced by hydrolysis and dehydration of xylan contained in hemicellulose, is one of the most important building blocks for bio-refinery [10-12]. Catalytic oxidation has been used to convert furfural to many chemical intermediates and end products, including furanone, furoic acid, fumaric acid (FA), succinic acid (SA) and maleic acid (MA) [6,13-18]. Most of the current studies focus on the selective oxidation of furfural to diacids or acid anhydrides, especially to SA, MA and maleic anhydride. However, the studies on the oxidation of furfural to 2(5H)-furanone are very limited.

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Furanone can be synthesized by deoxygenation of substituted butanoic acids at high temperature, transformation of hydroxybutyrolactones with acids or amines, hydrolysis of 2-methoxyfuran and cyclocarbonylation of terminal alkynols in the presence of palladium [19–22]. Nevertheless, the above methods are deficient owing to their expensive reagents, complicated processes, extreme reaction conditions and low yield. Currently, 2(5H)-furanone is mainly produced by furfural oxidation. Badovskay [23] reported the oxidation of furfural to 2(5H)-furanone with a yield of 25% by autocatalysis, and the yield was not significantly improved in the presence of Mo (VI) or Cr (VI). Cao et al. [13]. found that when the autocatalytic oxidation of furfural was carried out in a bi-phasic system using dichloroethane as the solvent, a 37% yield of 2(5H)furanone was obtained, however the reaction time was longer than 10 hours. Poskonin [24] reported the synthesis of 2(5H)-furanone from furfural in water using niobium (V) acetate tetrahydrate as the catalyst and hydrogen peroxide as the oxidant, but more than 80 hours were needed to obtain a 60% vield. Despite decades of study, problems with furfural oxidation to 2(5H)-furanone still exist in the moderate yield (30-50%), long reaction time and the use of chlorinated solvents. The main utility of 2(5H)-furanone at present is limited to the intermediate for the synthesis of biologically active natural products [25].

2(5H)-Furanone is an ideal material for the production of lactones and diols in terms of its chemical structure. In our previous

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X. Li et al. / Catalysis Today xxx (2015) xxx-xxx

work, 2(5H)-furanone was hydrogenated to γ -butyrolactone (GBL) with a high yield using supported metal catalysts [26]. The use of 2(5H)-furanone as the intermediate for the conversion of furfural to C4 lactones and diols can improve the atom economy of the conversion path and reduce the cost caused by harsh conditions, in comparison with other biomass-derived intermediates like diacids and acid anhydrides. Thus, the highly selective oxidation of furfural to 2(5H)-furanone can provide a better approach to produce C4 lactones and diols from furfural, which have been widely used in the fields of medicine, chemical, plastics, electric and others [27,28]. Hydrogen peroxide is usually used as the oxidant for furfural oxidation to 2(5H)-furanone, because the non-catalytic polymerization of furfural is severe when furfural interacts with molecular oxygen [29]. The control of selectivity is a great challenge for furfural oxidation to 2(5H)-furanone, as many side reactions including noncatalytic polymerization, oxidation to diacids and deep oxidation may occur.

In this work, different acid catalysts were evaluated for the oxidation of furfural to 2(5H)-furanone in both the bi-phasic and homogeneous systems. A simplified reaction network was established, and the reaction rate constants and apparent activation energies were calculated to analyze the solvent effect. The solvent effect was investigated in homogeneous, bi-phasic and tri-phasic systems using a variety of solvents with different polarities. The product distribution was correlated with the solvent property to guide the selection of solvent for improved yield of 2(5H)-furanone. Additionally, the effects of the formic acid/furfural molar ratio, reaction temperature and furfural concentration were studied in detail.

2. Materials and methods

2.1. Materials

Methanol, tetrahydrofuran, tetrachloromethane, benzene, toluene, cyclohexane, iso-octane, *n*-heptane, ethyl acetate, sulfuric acid (98%), phosphoric acid (85%) and sodium sulfate were all of analytical grade and purchased from Beijing Chemical Works. Isopropanol (SCR Beijing, 99.5%), 1,2-dichloroethane (J&K Chemical, 99%), γ -butyrolactone (Xiya Reagent, 99%), formic acid (SCR Beijing, 88%) and hydrogen peroxide (Beijing Modern Oriental Fine Chemistry Co., Ltd., 30%) were purchased. The above reagents were used without further purification. Furfural (SCR Beijing, 99%) was purified by vacuum distillation before use. The strong acid ion exchange resin Amberlyst-15 was purchased from Aladdin Industrial Corporation, and ZrTiO₄ was prepared according to the literature [30]. The corresponding precursors were co-precipitated to synthesize Ti(OH)₄–Zr(OH)₄, and this hydroxide was calcined at 923 K to obtain ZrTiO₄.

2.2. Oxidation reaction

2.2.1. Oxidation of furfural

All the furfural oxidation reactions were carried out in a threenecked flask of 50 mL, equipped with a condenser to reduce volatilization loss of the solvent. An oil bath was used to control the reaction temperature. In a typical experiment, 10 mL of solvent, 1.5 mL of distilled water, 4.0 g of furfural, 4.0 g of sodium sulfate and an appropriate amount of acid catalyst were added to the flask and heated to the reaction temperature. When the reaction mixture reached the set temperature, 10 mL of hydrogen peroxide (30%) was added to the reactor dropwise during the first hour while stirring. The reaction mixture was sampled and analyzed by a gas chromatograph (GC) and a high performance liquid chromatograph (HPLC).

2.2.2. Oxidation of 2(5H)-furanone

The oxidation of 2(5H)-furanone was carried out in a similar apparatus to that for the oxidation of furfural. For each experiment, 4.0 g of 2(5H)-furanone was dissolved in 10 mL of 1,2dichloroethane, then 1.5 mL of formic acid and 1.5 mL of distilled water were added to the mixture. When the reaction temperature reached the set value, 10 mL of hydrogen peroxide was added dropwise to the mixture during the first hour while stirring. The reaction mixture was sampled and analyzed by GC and HPLC.

2.3. Analytical methods

Gas chromatograph (GC 7900 II, Techcomp Instrument Company) equipped with a super-wax capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.5 \mu \text{m}$) and an FID detector was used to analyze the contents of furfural and 2(5H)-furanone in the reaction mixture. The diacids including SA and MA were analyzed with a Shimazu 10 AT–VP HPLC equipped with a C18 column ($150 \text{ mm} \times 4.6 \text{ mm}$) and a UV detector. For HPLC measurement, the samples were diluted 500 times with distilled water; The mobile phase was methanol with distilled water (3/97, v/v) containing KH₂PO₄ (0.02 mol/L), and its pH was adjusted to 2.75 by H₃PO₄; The flow rate was fixed at 1.0 mL/min and the temperature of the column was kept at 303 K; The injection volume was 20 μ L.

The conversion of furfural and the selectivity and yield of products are calculated as follows:

Furfural conversion (%) =
$$\frac{\left(n_{\rm fur}^0 - n_{\rm fur}\right)}{n_{\rm fur}^0} \times 100$$
 (1)

Productselectivity(%) =
$$\frac{n_{\text{pro}}}{\left(n_{\text{fur}}^0 - n_{\text{fur}}\right)} \times 100$$
 (2)

Productyield(%) =
$$\frac{n_{\text{pro}}}{n_{\text{fur}}^0} \times 100$$
 (3)

where n_{fur}^0 is the initial mole quantity of furfural loaded into the reactor, and n_{fur} and n_{pro} are the moles of furfural and products, respectively. The mole quantity of each component n_i in the homogeneous system and bi-phasic system was calculated based on Eq. (4) and Eq. (5), respectively:

$$n_{\rm i} = C_{\rm i} \times V \tag{4}$$

where C_i is the concentration of the component measured by GC or HPLC, and V is the volume of the reaction mixture at a given time.

$$n_{i} = C_{i,aq} \times V_{aq} + C_{i,or} \times V_{or}$$
(5)

where $C_{i,aq}$ and $C_{i,or}$ refer to the concentration of the component in the aqueous and organic phases, respectively, and V_{aq} and V_{or} refer to the volume of the aqueous and organic phases at a given time, respectively.

3. Results and discussion

3.1. Homogeneous and heterogeneous acid catalysts

The furfural oxidation reaction was first studied in a bi-phasic system with 1,2-dichloroethane as the solvent and in a homogeneous system with methanol as the solvent, focusing on the effect of acid catalysts. The results are shown in Fig. 1. Among the selected homogeneous catalysts, formic acid had the best performance for furfural oxidation to 2(5H)-furanone in both the bi-phasic and homogeneous systems. The yield of 2(5H)-furanone reached 60.3% in the bi-phasic system, while it decreased to 13.1% in the homogeneous system. When inorganic acid, H₃PO₄ or H₂SO₄, was used as the catalyst, the yield of 2(5H)-furanone was lower than 10% in both the bi-phasic and homogeneous systems. For heterogeneous

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2

X. Li et al. / Catalysis Today xxx (2015) xxx-xxx



Fig. 1. Yield of 2(5H)-furanone using homogeneous and heterogeneous acids.

catalysts, Amberlyst-15 with strong acidity was tested considering its proven capability of converting furfural to C4 diacids [18], and ZrTiO₄ with moderate acid sites was chosen because of its catalytic activities for aldehyde oxidation [30]. The yield of 2(5H)-furanone over ZrTiO₄ (7.6% in the bi-phasic system and 10.2% in the homogeneous system) was similar to that over Amberlyst-15 (5.1% in the bi-phasic system and 9.0% in the homogeneous system).

Fig. 2 compares the catalytic mechanism of formic acid with that of the other selected catalysts in the bi-phasic system and homogeneous system. When formic acid was used as the catalyst in the bi-phasic system, it reacted with hydrogen peroxide to generate performic acid, which was the real active oxidant and soluble in the organic phase. Then performic acid transferred from the aqueous phase to the organic phase and reacted with furfural to form 2(5H)furanone following the proposed reaction pathway A (Scheme 1) [31]. Furfural and 2(5H)-furanone mainly existed in the organic phase, thus their direct contact with hydrogen peroxide and deep oxidation were effectively reduced. The water soluble byproducts, such as succinic acid (SA, 12.0%) and maleic acid (MA, 6.3%), were in the aqueous phase. The strong oxidizing nature and good solubility in both aqueous and organic phases of performic acid contributed to the better performance of formic acid [32]. When the reaction was carried out in the homogeneous system with methanol as the solvent, the yield of 2(5H)-furanone significantly decreased and more SA was formed. The reason was that the effective concentration of perfomic acid decreased due to the esterification of formic acid with methanol occurring under the reaction conditions. In addition, furfural also reacted with hydrogen peroxide directly in the presence of H⁺ following the reaction pathway B, contributing to an increased yield of SA. When other catalysts were used in the bi-phasic system, the oxidation reaction occurred in the aqueous phase and the organic phase served as a reservoir to gradually release the reactant furfural via phase equilibrium. Meanwhile, the non-catalytic polymerization of furfural occurred in the organic phase, and the color turned brown gradually. Consequently, the direct oxidation with hydrogen peroxide in the aqueous phase and the severe polymerization of furfural in the organic phase resulted in a much lower yield of 2(5H)-furanone. When inorganic acids or solid acids were used in the homogeneous system, the polymerization of furfural was slowed down. The concentration of furfural in the homogeneous system was lower than that in the organic phase of the bi-phasic system. With the assumption that furfural oxidation reaction is first-order and furfural polymerization reaction is second-order, the decrease of the concentration of furfural can promote the ratio of oxidation reaction to polymerization reaction. In the homogeneous system, the produced 2(5H)-furanone, SA and MA were easier to be further oxidized to small molecular acids as secondary byproducts.

3.2. Effect of formic acid/furfural molar ratio

The effect of formic acid/furfural molar ratio was studied in the bi-phasic system with 1,2-dichloroethane as the solvent at 333 K. The furfural conversion, selectivity to 2(5H)-furanone and selectivity to SA and MA are shown in Fig. 3. As a function of the reaction time. The reaction rate of furfural significantly increased with an increasing amount of formic acid. For example, the reaction time required for complete conversion of furfural was 180 min at a formic acid/furfural molar ratio of 0.8, and was only 60 min at a molar ratio of 2.0. With an increasing amount of formic acid, the concentration of performic acid increased and the mass transfer rate of this active oxidant from the aqueous phase to the organic phase also increased. As a result, the furfural oxidation was enhanced in the organic phase. During the reaction, the selectivity to 2(5H)-furanone first increased and then decreased. The highest selectivity to 2(5H)-furanone (62.3%) was obtained at a formic acid/furfural molar ratio of 0.8 and furfural conversion of 96.9%. Note that the selectivity to 2(5H)-furanone slightly decreased in the later stage of the reaction due to deep oxidation. The selectivity to diacids (SA and MA) decreased gradually during the reaction, as small molecular byproducts were formed.

Fig. 4 shows the influence of the formic acid/furfural molar ratio on the final yields of 2(5H)-furanone and diacids. With an increasing amount of formic acid, the yield of diacids monotonically increased, while the yield of 2(5H)-furanone first increased and then decreased. The highest yield of 2(5H)-furanone was obtained at a formic acid/furfural molar ratio of 0.8. At a low amount of formic acid, the catalytic oxidation of furfural was very slow and the non-catalytic polymerization decreased the yield of 2(5H)-furanone. However, a high amount of formic acid may accelerate side reactions such as deep oxidation of the produced organics.

3.3. Reaction network

To further analyze the oxidation reaction of furfural, a simplified reaction network is proposed, as shown in Scheme 2. This reaction network consists of the following four Reactions: (1) oxidation of furfural to 2(5H)-furanone, (2) further oxidation of 2(5H)-furanone to diacids including SA and MA, (3) direct conversion of furfural to diacids, and (4) deep oxidation of the produced diacids to some small molecular acids like malic acid, lactic acid and propionic acid. In the bi-phasic system, the concentration of performic acid in the organic phase is assumed to be constant, while the concentration of hydrogen peroxide in the aqueous phase is considerably excessive with respect to the dissolved organic compound. In the homogeneous system, the concentration of hydrogen peroxide is hypothesized to be unchanged considering that hydrogen peroxide is continuously added during the reaction. For simplicity, all the reactions in Scheme 2 are considered to be irreversible firstorder with respect to the organic reactant. The mass balance of each component leads to Eqs. (6)-(9).

$$\frac{dC_{F1}}{dt} = -k_1 C_{F1} - k_3 C_{F1} \tag{6}$$

$$\frac{dC_{F2}}{dt} = k_1 C_{F1} - k_2 C_{F2} \tag{7}$$

$$\frac{dC_{F3}}{dt} = k_2 C_{F2} + k_3 C_{F1} - k_4 C_{F3}$$
(8)

$$\frac{\mathrm{d}C_{\mathrm{F4}}}{\mathrm{d}t} = k_4 C_{\mathrm{F3}} \tag{9}$$

3

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4

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X. Li et al. / Catalysis Today xxx (2015) xxx-xxx







Fig. 2. Catalytic mechanism of acid catalysts in bi-phasic system and homogeneous system.



Scheme 1. Illustration of the proposed reaction pathways for furfural oxidation. Pathway A: furfural is transformed into 2-formyloxyfuran via Baeyer–Villiger rearrangement at first. Then 2-formyloxyfuran is hydrolyzed to 2-hydroxyfuran and its tautomers, 2(5H)-furanone and 2(3H)-furanone, which can be further oxidized to maleic acid and succinic acid, respectively. Pathway B: the furan ring of furfural is opened to form a dienol which is ketonised into diketo aldehyde. The diketo aldehyde is then oxidized to succinic acid by hydrogen peroxide.



Scheme 2. The reaction network for furfural oxidation.

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X. Li et al. / Catalysis Today xxx (2015) xxx-xxx



Fig. 3. Furfural oxidation with different formic acid/furfural molar ratios, (a) conversion of furfural,(b) selectivity to 2(5H)-furanone, and (c) selectivity to diacids.

where k_1 , k_2 , k_3 and k_4 are the reaction rate constants and C_{F1} , C_{F2} , C_{F3} and C_{F4} are the concentrations (mol/mL) of furfural, 2(5H)-furanone, diacids and secondary byproducts, respectively. The reaction rate of each component was obtained from derivation of its concentration-time curve. Then the reaction rate constants were calculated by solving Eqs. (6)–(9).

Using 1,2-dichloroethane as the solvent and formic acid as the catalyst, the reaction rate constants k_1 , k_2 and k_3 were estimated



Fig. 4. Effect of formic acid/furfural molar ratio on the final yields of 2(5H)-furanone and diacids.

Table 1

Reaction rate constants and apparent activation energies based on the proposed reaction network in the bi-phasic system.

Entry	$k(10^{-2} \min^{-1})$	<i>T</i> (K)			E _a (kJ/mol)
		323	333	343	
1	k_1	1.36	1.86	3.63	45.1
2	k_2	0.18	0.40	0.61	55.8
3 ^b	k2'	0.25	0.48	0.69	46.9
4	k_3	1.23	1.66	2.15	25.7

^aReaction conditions: 1,2-dichloroethane (10 mL), furfural (4.0 g), sodium sulfate (4.0 g), H₂O₂ (30%, 10 mL), distilled water (1.5 mL), formic acid (88%, 1.5 mL), 3 h. ^bThe reaction rate constant $k_{2'}$ and apparent activation energy $E_{a2'}$ were calculated based on the experimental data of the oxidation of 2(5H)-furanone.



Fig. 5. Arrhenius plots of -ln(k) versus 1/T.

for the bi-phasic system. In this case, the temperature range of 323–343 K was used for collecting the kinetics data, because the loss of solvent could not be neglected at a higher temperature while the non-catalytic polymerization was severe at a lower temperature. The results are listed in Table 1. For the same temperature, the reaction rate constants followed the trend of $k_1 > k_3 > k_2$, and k_3 was three to five times larger than k_2 , indicating that diacids were mainly formed via the direct conversion of furfural rather than the oxidation of 2(5H)-furanone. Fig. 5 demonstrates the Arrhenius plots of -ln(k) versus 1/T, showing a good linear relationship.

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The apparent activation energies E_{a1} , E_{a2} and E_{a3} were calculated from the slope of the Arrhenius plots. The activation energy for furfural oxidation to 2(5H)-furanone (E_{a1} , 45.1 kJ/mol) was higher than that for furfural oxidation to diacids (E_{a3} , 25.7 kJ/mol), therefore increasing temperature was beneficial to improve the yield of 2(5H)-furanone. However, the yield of 2(5H)-furanone slightly decreased with a further increase in the reaction temperature, because E_{a2} (55.8 kJ/mol) was even higher than E_{a1} . To verify the reliability of the proposed reaction network, the oxidation of 2(5H)furanone was also carried out under the same conditions. The results showed that the reaction rate constant $k_{2'}$ and apparent activation energy $E_{a2'}$ directly determined from 2(5H)-furanone oxidation reaction were very similar to those calculated based on the proposed reaction network.

3.4. Solvent effect

The solvent had a strong effect on the furfural oxidation reaction [26], therefore a variety of solvents were investigated using formic acid as the catalyst at 333 K. When nonpolar solvents such as cyclohexane, iso-octane and *n*-heptane were used, a tri-phasic reaction system consisting of an aqueous phase with little furfural, an organic phase with a low concentration of furfural and another organic phase rich in furfural was formed. Formic acid and performic acid existed in all the three phases. In such a tri-phasic system, the yield of 2(5H)-furanone was lower than 10%, and the organic phase rich in furfural became brown gradually. The addition of a nonpolar solvent like cyclohexane, iso-octane and *n*-heptane cannot dilute furfural, so the polymerization of furfural phase was still severe. In addition, the formation of the second organic phase decreased the concentration of performic acid in the furfural phase, thus reduced the reaction efficiency of furfural oxidation.

When other solvents such as ethyl acetate, 1,2-dichloroethane, tetrachloromethane, benzene and toluene were introduced, a biphasic system was formed. In this system, the performic acid was formed in the aqueous phase and transferred to the organic phase, where furfural was oxidized to 2(5H)-furanone by performic acid. The product distributions with different solvents are shown in Fig. 6(a). When using 1,2-dichloroethane as the solvent, the yield of 2(5H)-furanone was 60.3%, and the yields of MA and SA were 12.0% and 6.3%, respectively. Ethyl acetate with lower toxicity was found to be an ideal substitute for the toxic solvent 1,2-dichloroethane, giving 61.5%, 6.7% and 8.5% yields of 2(5H)-furanone, MA and SA, respectively. With the utilization of another chlorinated solvent, tetrachloromethane, a 40.2% yield of 2(5H)-furanone was obtained. In contrast, when benzene and toluene were used as the solvent, the yield of 2(5H)-furanone was only 8.9% and 12.2%, respectively. A possible reason for these low yields was that the interaction of furan ring with benzene ring promoted the polymerization of furfural. With different weak polar solvents, the yields of MA and SA were 5-15%, which was less dependent on the solvent, because the direct oxidation of furfural to diacids mainly occurred in the aqueous phase.

The solvent effect on furfural oxidation was also studied in the homogeneous system using methanol, isopropanol, tetrahydrofuran (THF) and GBL as solvents. As shown in Fig. 6(b), SA was the major product and the product distribution strongly depended on the solvent. The highest yield of SA was 38.3% with GBL as the solvent, and the yield of SA decreased with the decreasing dielectric constant of the solvent. The highest yield of MA (17.3%) was also obtained with GBL, and the yield of MA was 10.0–12.0% with the other three solvents. When THF was used as the solvent, an 18.2% yield of 2(5H)-furanone was obtained, while methanol, isopropanol and GBL gave similar yields of 2(5H)-furanone (13.1%, 11.3% and 12.8%, respectively). The total yield of 2(5H)-furanone and diacids (68.4% in GBL) in the homogeneous system was lower than that in



Fig. 6. Product yields with different solvents, (a) in the bi-phasic system and (b) in the homogeneous system.

Table 2

Reaction rate constants based on the proposed reaction network in the homogeneous system.

Entry	Solvent	ε	<i>k</i> (10 ⁻² n	k (10 ⁻² min ⁻¹)				
			k_1	k ₂	k_3	k_4		
1	Methanol	33	1.26	0.35	2.58	0.89		
2	Isopropanol	19	1.37	0.30	2.37	1.59		
3	THF	8	1.60	0.39	2.12	1.10		
4	GBL	39	1.00	0.38	3.73	0.92		

 a Reaction conditions: solvent (10 mL), furfural (4.0 g), sodium sulfate (4.0 g), H_2O_2 (30%, 10 mL), distilled water (1.5 mL), formic acid (88%, 1.5 mL), 333 K, 3 h.

the bi-phasic system with 1,2-dichloroethane or ethyl acetate as the solvent. In the homogeneous system, the products were easier to be excessively oxidized to small molecular acids. The incomplete carbon balance was caused by the formation of some GC and HPLC-silent products via deep oxidation or polymerization.

The reaction rate constants were calculated for the homogeneous system to quantify the solvent effect. The results are summarized in Table 2. It can be seen that the values of k_2 were similar with different solvents, but k_1 and k_3 strongly depended on the solvent. The polarity of the solvent, which can be described by the dielectric constant, is an important factor for the influence of solvent. As shown in Fig. 7, when the dielectric constant increased from 8 of THF to 39 of GBL, the reaction rate constant k_3 increased

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X. Li et al. / Catalysis Today xxx (2015) xxx-xxx



Fig. 7. Correlation of reaction rate constants with dielectric constant of the solvents.

from 0.0212 min^{-1} to 0.0373 min^{-1} , while the reaction rate constant k_1 decreased from 0.0160 min^{-1} to 0.0100 min^{-1} . It indicates that increasing polarity of the solvent promotes the direct conversion of furfural to diacids and decreases the oxidation of furfural to 2(5H)-furanone. This is consistent with the experimental results that a higher yield of SA was obtained using a solvent with a larger dielectric constant.

3.5. Effect of reaction temperature

The influence of the reaction temperature on furfural oxidation was investigated in the bi-phasic system using 1,2-dichloroethane as the solvent with a formic acid/furfural molar ratio of 0.8. As shown in Fig. 8(a), the conversion of furfural increased with increasing reaction temperature. When the reaction temperature increased from 313 K to 333 K, the yield of 2(5H)-furanone significantly increased from 9.0% to 60.3%, whereas a slight decrease was observed when the reaction temperature further increased to 343 K. In particular, the yield of 2(5H)-furanone increased from 34.9% at 323 K to 60.3% at 333 K. The non-catalytic polymerization of furfural was the main reaction under a lower temperature, until the reaction temperature reached a certain value to promote the catalytic oxidation of furfural. The slight decrease of the 2(5H)-furanone yield at 343 K was probably caused by the fast decomposition of hydrogen peroxide and reduced stability of performic acid. The yield of diacids only slightly changed with the reaction temperature. The total yield of 2(5H)-furanone, SA and MA increased from 29.5% at 313 K to 86.4% at 333 K. For the bi-phasic system using ethyl acetate as the solvent, the reaction temperature varied in the range of 313-339 K, considering that the boiling point of ethyl acetate is lower than that of 1,2-dichloroethane. As shown in Fig. 8(b), the conversion of furfural and the yield of 2(5H)furanone increased with increasing reaction temperature, while the yield of diacids was nearly unchanged. At the same reaction temperature, the yield of 2(5H)-furanone in the bi-phasic system using ethyl acetate as the solvent was higher while the yield of diacids was lower than that using 1,2-dichloroethane as the solvent.

3.6. Effect of furfural concentration

To investigate the influence of furfural concentration, the oxidation reaction was carried out with different initial concentrations of furfural at 333 K in the bi-phasic systems using 1,2-dichloroethane, ethyl acetate and toluene as solvents. The formic acid/furfural molar ratio was maintained at 0.8. It can be seen from Fig. 9 that the yield of 2(5H)-furanone was almost unchanged when





Fig. 8. Effect of reaction temperature on furfural oxidation in the bi-phasic system (a) with 1,2-dichloroethane as the solvent, and (b) with ethyl acetate as the solvent.



Fig. 9. Yield of 2(5H)-furanone with different initial furfural concentrations.

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X. Li et al. / Catalysis Today xxx (2015) xxx-xxx

1,2-dichloroethane or ethyl acetate was used as the solvent. When toluene was used as the solvent, however, the yield of 2(5H)-furanone decreased gradually with increasing concentration of furfural, which aggravated the second-order polymerization reaction in the presence of benzene ring.

4. Conclusions

The selective oxidation of furfural to 2(5H)-furanone was studied using hydrogen peroxide as the oxidant and acid as the catalyst. Formic acid showed the best catalytic performance for furfural oxidation to 2(5H)-furanone when the reaction was carried out in a bi-phasic system using 1,2-dichloroethane or ethyl acetate as the solvent, giving a 60-62% yield of 2(5H)-furanone. The catalytic mechanism of formic acid in comparison with other acid catalysts in both homogeneous and bi-phasic systems was explained in detail. The good solubility in the organic phase and the strong oxidizing nature of performic acid, which was the real active oxidant generated from formic acid and hydrogen peroxide, contributed to the better performance of formic acid. The formation of a biphasic system using 1,2-dichloroethane or ethyl acetate as the solvent was beneficial for the selective oxidation of furfural to 2(5H)-furanone, while the oxidation to diacids and polymerization of furfural were the dominant reactions in the homogeneous system and tri-phasic system, respectively. To further discuss the solvent effect, a simplified reaction network was established. In the homogeneous system, the yield of SA increased gradually, while the yield of 2(5H)-furanone first increased and then decreased with an increasing dielectric constant of the solvent. Additionally, the reaction conditions were studied in the bi-phasic system, showing that the optimum reaction temperature was 333 K and formic acid/furfural molar ratio was 0.8.

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8