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PAPER

## Selective conversion of furfuryl alcohol to 1,2-pentanediol over a Ru/MnO<sub>x</sub> catalyst in aqueous phase

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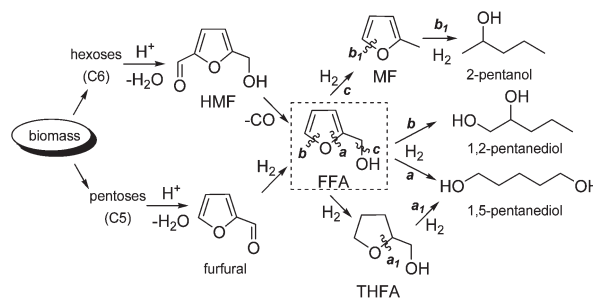
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The aqueous-phase hydrogenolysis of furfuryl alcohol (FFA) to 1,2-pentanediol (1,2-PeD) was carried out on a series of supported Ru catalysts and MnO<sub>x</sub> supported Pt, Pd and Rh catalysts. The Ru/MnO<sub>x</sub> catalysts showed high selectivity for 1,2-PeD, while the Pd and Rh catalysts displayed high selectivity for tetrahydrofurfuryl alcohol. The function of MnO<sub>x</sub>, the effects of solvent, temperature, H<sub>2</sub> pressure and reaction time were further investigated. The support MnO<sub>x</sub> in the Ru/MnO<sub>x</sub> catalysts not only suppressed the polymerization of the FFA, but also enhanced the 1,2-PeD selectivity. Low pressure and high temperature favoured the generation of 1,2-PeD, and water significantly enhanced the reaction rate. At 150 °C, 1.5 MPa, the yield of 1,2-PeD was up to 42.1% over the Ru/MnO<sub>x</sub> catalyst. The proposed mechanism for FFA hydrogenolysis in aqueous medium over the Ru/MnO<sub>x</sub> catalyst is suggested to occur via a partially hydrogenated intermediate.

### Introduction

Biomass, the sustainable source of energy and organic carbon, has the potential to displace non-renewable fossil resources in the production of chemicals and liquid transportation fuels.<sup>1,2</sup> To utilize the biomass effectively, efficient technologies are need for the selective tailoring oxygen content and functionality of the biomass-derived raw materials.<sup>3</sup> The main components are C5 and C6 sugars in biomass feed stock, and C6 sugars are more versatile and widely available. Furfural is already produced on an industrial scale from pentose sugars *via* acidic hydrolysis, and the vast majority of furfural is industrially converted into furfuryl alcohol (FFA).<sup>1,2,4,5</sup> Recently, Geilen *et al.*<sup>6</sup> have obtained FFA by a highly selective catalytic decarbonylation of 5-(hydroxymethyl)furfural (HMF), which can be obtained through catalytic processes from hexoses or even cellulose. Given that FFA can be generated from both furfural and HMF, it seems attractive to establish a process network to produce valuable chemicals by using FFA as the platform chemical (Scheme 1).

Selective hydrogenation and hydrogenolysis are considered to be the most effective methods for conversion of furan compounds to valuable chemicals.<sup>7,8</sup> Generally, the selective hydrogenation of a furan ring is easier to realize under mild conditions. For instance, the selectivity of tetrahydrofurfuryl alcohol (THFA) was higher than 97% in the liquid-phase hydrogenation of FFA over the supported Ni or Ru catalyst.<sup>9,10</sup> On the



**Scheme 1** Pathways for the production of diols from biomass.

contrary, harsh reaction conditions are required in the furan ring hydrogenolysis to synthesis of polyols, such as 1,2-pentanediol (1,2-PeD) and 1,5-pentanediol (1,5-PeD) from FFA.

1,2-PeD, which is currently produced from non-renewable petroleum resources *via* a costly multistep process involving selective oxidation of pentene to pentene oxide and subsequent hydrolysis,<sup>11</sup> is widely used as a monomer of polyesters and the key intermediate of low-toxic microbicides. Adkins *et al.* reported that 1,2-PeD (yield = 40%) and 1,5-PeD (30%) can be formed by hydrogenolysis of FFA over the CuCr<sub>2</sub>O<sub>4</sub> catalyst at 175 °C, 10–15 MPa.<sup>12,13</sup> Although the use of chromium in the catalysts may result in severe environmental pollution, it is still an alternative route to produce valuable diols from sustainable bio-derived furan compounds. Recently, Lu *et al.*<sup>14</sup> have developed a Pt/Co<sub>2</sub>AlO<sub>4</sub> catalyst to convert furfural to 1,5-PeD and 1,2-PeD by the hydrogenolysis of intermediate FFA at 140 °C, 1.5 MPa in an alcohol solvent, but the obtained yield of 1,2-PeD was only 16%. It still a challenge to perform selective hydrogenolysis of FFA to 1,2-PeD at mild conditions.

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Water, which is an environmentally friendly, safe and high heat capacity solvent, has been reported to be a good medium for the hydrogenation/hydrogenolysis of bio-derived compounds, such as polyols,<sup>15–18</sup> organic acids<sup>19,20</sup> and carbohydrates.<sup>21</sup> Koso *et al.*<sup>22,23</sup> have also developed the  $\text{ReO}_x$  and  $\text{MoO}_x$  modified  $\text{Rh}/\text{SiO}_2$  catalysts for the aqueous phase hydrogenolysis of THFA to produce 1,5-PeD with high selectivity (>94%) at 120 °C, 8 MPa. Then, the direct reductive upgrading of furan compounds in an aqueous medium using metal catalysts under mild conditions offers a new attractive alternative route. However, unlike the saturated tetrahydrofuran ring of THFA, the furan ring was unstable and easily polymerized in the aqueous system. Insoluble polymers were inevitably generated in the production or conversion of furfural, HMF and other furan compounds in the aqueous phase.<sup>24–27</sup> These polymers lead to a number of problems, including catalyst deactivation and low yield of target product in heterogeneous catalysis. Therefore, it is necessary to develop some water tolerant catalysts, which can suppress furan polymerization in the aqueous phase.

In this work, we have tried to develop a method for the aqueous phase hydrogenolysis of FFA to produce 1,2-PeD. The effects of supports on the catalytic performance of Ru catalysts were examined. The supports include  $\text{MnO}_x$ ,  $\text{MgO}$ ,  $\text{MgAlO}_4$ , NaY zeolite (NaY), active carbon (AC),  $\text{ZrO}_2$  and  $\text{TiO}_2$ , with a wide range of acid–base properties. A series of other supported noble metal catalysts (Pt, Pd, Rh) were also studied to compare the influence of metal nature. Besides, the function of  $\text{MnO}_x$  and water, and the effects of reaction parameters were also investigated and discussed. Moreover, the conversion of other furan compounds over the Ru/ $\text{MnO}_x$  catalyst was tested, which may help to shed light on the possible reaction mechanism for the FFA hydrogenolysis.

## Experimental

### Catalyst preparation and reaction tests

The  $\text{MnO}_x$  support was prepared by co-precipitation method using the 0.5 M manganese nitrate aqueous solution and 0.5 M  $\text{Na}_2\text{CO}_3$  aqueous solution at 80 °C and pH 9. The precipitate was aged for 2 h at 80 °C, and then separated by filtration and washed with hot distilled water to remove the traces sodium. The obtained precipitate was dried in static air at 120 °C for 12 h followed by calcination at 500 °C for 5 h. The  $\text{MgO}$  and  $\text{MgAlO}_4$  supports were also prepared by the same co-precipitation method.

The Ru/ $\text{MnO}_x$  catalyst was prepared by incipient wetness impregnation of  $\text{MnO}_x$  with an aqueous solution of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (37.5 wt% Ru, Shaaxi Kaida Chemical Engineering Co. Ltd, China) for 12 h. After that, the resulting powders were dried at 120 °C overnight, and then calcined in air at 500 °C for 5 h. The content of ruthenium in the supported catalysts is 4 wt%. The same method was used in the preparation of 4 wt% Ru/ $\text{TiO}_2$ , Ru/ $\text{ZrO}_2$  and Ru/AC, using  $\text{TiO}_2$ ,  $\text{ZrO}_2$  (Jiangsu Qianye Co., Ltd, China) and active carbon (AC,  $S_{\text{BET}} = 1091 \text{ m}^2 \text{ g}^{-1}$ , Liyang Zhuxi Carbon Co., Ltd, China) as supports, respectively. Other  $\text{MnO}_x$  supported noble metal catalysts, 4 wt% Pd/ $\text{MnO}_x$ , Pt/ $\text{MnO}_x$ , and Rh/ $\text{MnO}_x$ , were prepared by a similar method with aqueous solutions of  $\text{Pd}(\text{NO}_3)_2$ ,  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ ,  $\text{Rh}(\text{NO}_3)_3$  (Shaaxi Kaida Chemical Engineering Co., Ltd, China) as precursor, respectively. The Ru metal particles ( $\text{Ru}^0$ ) were

prepared by dissolving the  $\text{MnO}_x$  support of the reduced the Ru/ $\text{MnO}_x$  catalyst with a hydrochloric acid solution. The obtained black sample was repeatedly centrifuged and washed with distilled water until no  $\text{Cl}^-$  was detected in the wash water by  $\text{AgNO}_3$  test. The  $\text{CuCr}_2\text{O}_4$  catalyst was prepared according to the procedure in the literature.<sup>12</sup>

All the catalysts were used in powder form with granule size of <100 mesh. Prior to each test, the samples were pre-reduced in an  $\text{H}_2$  flow at 200 °C for 3 h. Catalytic tests were performed in a 100 mL stainless steel autoclave at a stirring speed of 600 rpm. In a typical run, 40 g of 10 wt% furfuryl alcohol (Shanghai Jin Shan Ting Xin Chemical Reagent) aqueous solution, 0.2 g pre-reduced catalyst (reduced at 200 °C) were introduced into the autoclave. Afterwards, the reactor was purged with  $\text{H}_2$  (>99.99%, Jinan Deyang Special Gas Co. Ltd, China) three times and pressurized to 0.5 MPa, and then heated to 150 °C. When the temperature was stable, the  $\text{H}_2$  pressure was increased to 1.5 MPa and regulated by a pressure controller. The experiment was rapidly stopped by using an ice-bath to cool down, and all gases were collected in a gas bag. The autoclave contents were transferred to vials, and the catalysts were separated by centrifugation and filtration. For comparison, the hydrogenation/hydrogenolysis of other furan compounds, such as furan, tetrahydrofuran (Sinopharm Chemical Reagent Co. Ltd, China), 2,3-dihydrofuran (Tokyo Chemical Industry Co, Ltd, Japan) and 2-methylfuran (Alfa Aesar), were also studied over the Ru/ $\text{MnO}_x$  catalyst.

The liquid reaction products were analyzed by a GC-950 gas chromatograph (Shanghai Haixin chromatogram analysis Co., Ltd, China) equipped with a flame ionization detector (FID) and a capillary column (J&W DB-WAX, 30 m  $\times$  0.32 mm). The gas was analyzed by GC (models 6890N and 4890D, Agilent). The conversion and selectivity were determined based on the area normalization method. The content of 1,2-pentanediol and tetrahydrofurfuryl alcohol was also tested by the internal standard method using 1-hexanol or 1,4-butanediol as an internal standard. The results calculated by the two methods were consistent. All the products were identified by GC/MS (GC6890N/5973MSD, Agilent, USA) equipped with a capillary chromatographic column (J&W DB-WAX: 30 m  $\times$  0.32 mm).

### Characterization of catalysts

$\text{N}_2$  physisorption isotherms were measured at –196 °C with a Micromeritics ASAP 2500 sorption analyzer. The sample was degassed under vacuum at 90 °C for 1 h and 120 °C for 8 h prior to the measurement. X-ray diffraction (XRD) patterns of the samples were measured on a Bruker D2 PHASER Diffractometer equipped with  $\text{Cu K}\alpha$  radiation. Transmission electron microscopy (TEM) was taken for determination of the particle size using equipment (JEM-2100; UHR) operated at 200 kV. The average particle size ( $d_s$ ) was calculated by  $\sum n_i d_i^3 / \sum n_i d_i^2$  ( $d_i$ , particle size;  $n_i$ , number of particles with  $d_i$ ).

## Results and discussion

### Catalyst characterization

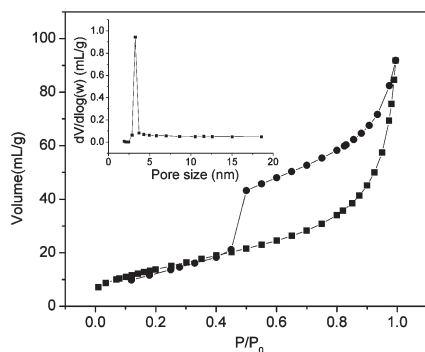
The BET surface area of the Ru/ $\text{MnO}_x$  catalyst after reaction was  $52.5 \text{ m}^2 \text{ g}^{-1}$ . The nitrogen adsorption–desorption measurements

for the catalyst showed a type IV isotherm typical of lamelleted mesoporous materials (pore width between 3–4 nm) (Fig. 1).

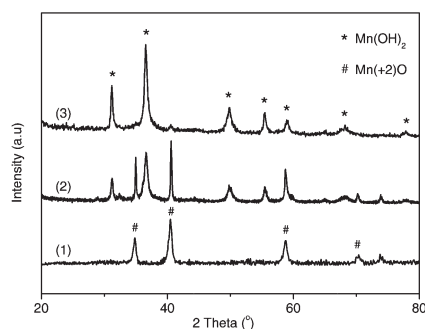
Fig. 2 shows the X-ray diffraction (XRD) patterns of Ru/MnO<sub>x</sub> and Ru<sup>0</sup> + MnO<sub>x</sub>. The peaks at 18.7°, 31.3°, 36.6°, 49.9°, 55.3°, 58.9° are assigned to Mn(OH)<sub>2</sub> (Pyrochroite, PDF#18-0787), while the peaks at 34.9°, 40.5°, 58.7° and 70.2° are assigned to Mn(+2)O (Manganosite, PDF#07-0230). Before reaction, the reduced Ru/MnO<sub>x</sub> catalyst only showed the peaks of Mn(+2)O. The peaks of Mn(OH)<sub>2</sub> were observed for the Ru/MnO<sub>x</sub> catalyst after reaction. Both peaks of Mn(OH)<sub>2</sub> and Mn(+2)O were observed in the pattern of the used Ru<sup>0</sup> + MnO<sub>x</sub> catalyst. The peaks of Ru species were not observed in the tested catalysts, which may be due to the low loading of Ru (4 wt%) or the high dispersion of Ru species. In fact, the HRTEM results confirmed the good dispersion. Fig. 3(A) and (B) show HRTEM images of the Ru/MnO<sub>x</sub> catalyst and the Ru<sup>0</sup> catalyst after reaction in the water medium, respectively. The average particle size of Ru particles in both catalysts was determined to be 3.0 nm.

### Furfuryl alcohol conversion over different catalysts

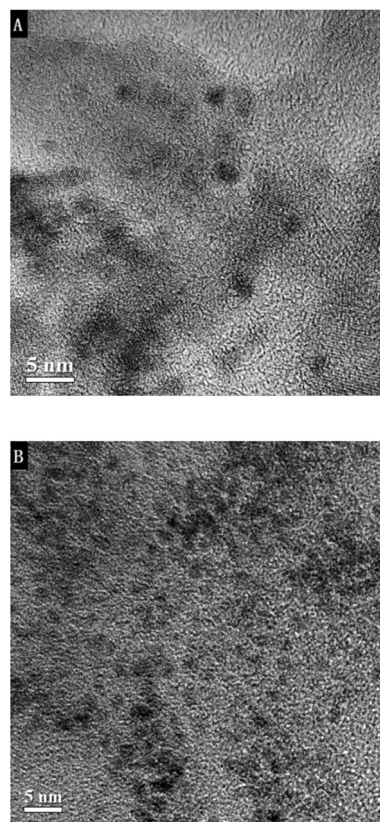
While the Ru-based catalysts<sup>28–30</sup> and Cu-based catalysts<sup>31</sup> were well known to be active in the aqueous phase hydrogenolysis of biomass-derived polyols, the Ru/AC (active carbon), Ru/TiO<sub>2</sub>, Ru/ZrO<sub>2</sub> and CuCr<sub>2</sub>O<sub>4</sub> catalysts showed a low yield of 1,2-PeD in FFA conversion due to the high yield of a brown gelatinous polymer (Table 1). Choura *et al.*<sup>32</sup> have shown that the



**Fig. 1** N<sub>2</sub> physisorption isotherm and pore size distribution of the used Ru/MnO<sub>x</sub> catalyst.



**Fig. 2** XRD patterns of the catalysts. (1) Ru/MnO<sub>x</sub> after reduction, (2) Ru<sup>0</sup> + MnO<sub>x</sub> after reaction, (3) Ru/MnO<sub>x</sub> after reaction.



**Fig. 3** TEM images of the catalysts after reaction (A) Ru/MnO<sub>x</sub>, (B) Ru<sup>0</sup>.

polycondensation of FFA was catalyzed by a Lewis-acid catalyst even at low temperature (0 °C), and a rise in reaction temperature can induce a corresponding increase in the polymer yield. According to our previous result, the Ru/AC catalyst has some weak acid sites,<sup>33</sup> which may catalyze the polymerization. However, a high yield of polymer was observed in the blank test without the addition of catalyst (Table 1, entry 9), indicating the instability of FFA in the aqueous phase. Cheng and Tseng<sup>34</sup> have found that the presence of protonic acids promote the polymerization of FA in aqueous phase. Therefore, the H<sub>3</sub>O<sup>+</sup> generated from the hot water may catalyze FFA polymerization.

By contrast with the above catalysts, the Ru/MnO<sub>x</sub> catalyst showed a higher yield of 1,2-PeD (20%, Table 1, entry 1), and THFA was the only competitive product at 120 °C and 6 MPa. In addition, the polymerization of FFA was not observed. According to the XRD results, the support of the used Ru/MnO<sub>x</sub> catalyst is Mn(OH)<sub>2</sub>, which is a water-insoluble base.<sup>35</sup> Therefore, the basic support may inhibit the polymerization of FFA. For this reason, the basic MgO, MgAlO<sub>4</sub> and NaY zeolite supported Ru catalysts were also tested, and the results revealed the suppression of FFA polymerization. For the Ru/MgO catalyst and Ru/NaY catalyst, the selectivity of 1,2-PeD was low with a high selectivity for the byproducts. The Ru/MgAlO<sub>4</sub> catalyst showed a low selectivity for the byproducts, but the 1,2-PeD selectivity was lower than that over the Ru/MnO<sub>x</sub> catalyst.

Since the MnO<sub>x</sub> has shown a good performance in inhibiting the FFA polymerization, the performance of other noble metals,

**Table 1** Furfuryl alcohol conversion over different catalysts<sup>a</sup>

Entry	Catalysts	<i>p</i> MPa	Conv. (%)	Selectivity (%)		
				1,2-PeD	THFA	Others
1	Ru/MnO <sub>x</sub>	6	99.9	20.0	78.7	1.3
2	Ru/MgO	6	62.5	12.8	76.8	10.4
3	Ru/MgAlO <sub>4</sub>	6	99.9	14.7	84.4	0.9
4	Ru/NaY	6	99.7	15.8	77.0	7.2
5	Ru/AC	6	99.8	0.2	2.1	97.7
6	Ru/TiO <sub>2</sub>	6	99.5	1.0	3.5	95.5
7	Ru/ZrO <sub>2</sub>	6	99.7	0.2	1.6	98.2
8	CuCr <sub>2</sub> O <sub>4</sub>	6	100.0	0.2	0.2	99.6
9	Blank <sup>b</sup>	6	100.0	0.0	0.0	100.0
10	Ru/MnO <sub>x</sub>	3	99.6	24.4	73.7	1.9
11	MnO <sub>x</sub> <sup>c</sup>	3	1.1	0.0	0.0	100.0
12	Pt/MnO <sub>x</sub>	3	1.2	25.0	50.0	25.0
13	Pd/MnO <sub>x</sub>	3	45.6	0.3	99.7	0.0
14	Rh/MnO <sub>x</sub>	3	32.0	1.6	95.9	2.5

<sup>a</sup> Furfuryl alcohol 4 g, catalyst 0.2 g, H<sub>2</sub>O 36 g, 120 °C, 4 h. <sup>b</sup> Furfuryl alcohol 4 g, in absence catalyst, H<sub>2</sub>O 36 g, 120 °C, 4 h. <sup>c</sup> Furfuryl alcohol 4 g, MnO<sub>x</sub> 0.2 g (after reduction 400 °C), H<sub>2</sub>O 36 g, 120 °C, 4 h.

such as Pd, Rh, Pt, supported on MnO<sub>x</sub> were also investigated (Table 1, entries 12–14). The Pt/MnO<sub>x</sub> catalyst showed similar 1,2-PeD selectivity as the Ru/MnO<sub>x</sub> catalyst, but the FFA conversion was only 1.2%. For the Pd/MnO<sub>x</sub> catalyst and the Rh/MnO<sub>x</sub> catalyst, the main product was THFA (sel. > 95.9%), which is generated through the C=C bond hydrogenation. In addition, the MnO<sub>x</sub> itself exhibited a low reaction activity with no 1,2-PeD formation. Thus, Ru is an essential metal for the production of 1,2-PeD via C–O bond hydrogenolysis of FFA, and the selectivity of 1,2-PeD depends on the nature of metals.

The adsorption configuration of the furan compound on the single crystal of different metals may provide insights into the mechanism of furan-ring decomposition. Density functional theory (DFT) calculations indicated that the parallel adsorbed furan rings of furan,<sup>36</sup> furfural<sup>37</sup> or FFA<sup>38</sup> on Pd(111) are energetically advantageous. This parallel adsorbed FFA on a Pd surface may be rapidly undergoing the hydrogenation of the C=C bond to generate THFA in the presence of active hydrogen species. However, the results from high resolution electron energy loss spectroscopy (HREELS)<sup>39</sup> revealed that, besides the parallel adsorbed species, there is also a tilted adsorbed species from furan bonding with one of its  $\alpha$ -C to the surface of Ru(001). Similar tilted species might relate to the generation of 1,2-PeD.

### The function of MnO<sub>x</sub> and Ru in furfuryl alcohol conversion

To further investigate the role of MnO<sub>x</sub> in 1,2-PeD formation, the Ru<sup>0</sup> and Ru<sup>0</sup> + MnO<sub>x</sub> physical mixture catalysts were also tested (Table 2). All the reactions were conducted at 120 °C, 3 MPa with 1,2-PeD and THFA as the main products. The Ru<sup>0</sup> catalyst was prepared by dissolving the support of the reduced Ru/MnO<sub>x</sub> catalyst in a hydrochloric acid solution. The TEM results showed that the average particle size of the Ru<sup>0</sup> catalyst was the same as that on the Ru/MnO<sub>x</sub> catalyst after reaction (Fig. 3). Thus, the size effect of the Ru particles can be neglected. The

**Table 2** Furfuryl alcohol conversion over different Ru catalysts<sup>a</sup>

Entry	Catalysts	Conv. (%)	Selectivity (%)		
			1,2-PeD	THFA	Others
1	Ru/MnO <sub>x</sub>	94.7	24.4	73.7	1.9
2 <sup>b</sup>	Ru <sup>0</sup>	90.5	16.6	82.5	0.9
3 <sup>c</sup>	Ru <sup>0</sup> + MnO <sub>x</sub>	82.2	22.6	76.2	1.2

<sup>a</sup> Furfuryl alcohol 4 g, Ru/MnO<sub>x</sub> 0.2 g, H<sub>2</sub>O 36 g, 120 °C, 3 MPa, 4 h. <sup>b</sup> Furfuryl alcohol 4 g, Ru<sup>0</sup> 0.008 g, KOH 0.023 g, H<sub>2</sub>O 36 g, 120 °C, 3 MPa, 4 h. <sup>c</sup> Furfuryl alcohol 4 g, Ru<sup>0</sup> 0.008 g, MnO<sub>x</sub> 0.2 g (reduced at 400 °C), H<sub>2</sub>O 36 g, 120 °C, 3 MPa, 4 h.

Ru<sup>0</sup> catalyst exhibited a similar activity to the Ru/MnO<sub>x</sub> catalyst, but the 1,2-PeD selectivity was decreased from 24.4% to 16.6%. Interestingly, it was increased to 22.6% by the addition of MnO<sub>x</sub> (Table 2, entry 3). The above results confirmed that the Ru metal provides the major active sites for the generation of 1,2-PeD from FFA, which is enhanced by the addition of MnO<sub>x</sub>.

The MnO<sub>x</sub> may promote the generation of 1,2-PeD by stabilizing the hydrogenolysis intermediate of FFA. Tomishige *et al.* have reported that the ReO<sub>x</sub> or MoO<sub>x</sub> modified Rh/SiO<sub>2</sub> catalyst can effectively open the tetrahydrofuran ring of THFA to produce 1,5-PeD.<sup>22,23</sup> Chia *et al.* have confirmed the bifunctional nature of the Rh–ReO<sub>x</sub> catalyst, which facilitates the selective hydrogenolysis of C–O bonds of THFA to produce 1,5-PeD via acid-catalyzed ring-opening coupled with metal-catalyzed hydrogenation.<sup>40</sup> However, the selectivity of 1,5-PeD was low (<1%) over the Ru/MnO<sub>x</sub> catalyst for FFA conversion, and the support was alkaline oxide Mn(OH)<sub>2</sub> after aqueous phase reaction (XRD, Fig. 2). Therefore, the generation of 1,2-PeD from FFA is not due to synergy of the acid sites and metal sites. Furthermore, the CoO<sub>x</sub> modified Pt/Al<sub>2</sub>O<sub>3</sub> catalyst has shown good performance in breaking the C–O bond of FFA to produce 1,5-pentane-diol.<sup>14</sup> The CoO<sub>x</sub> (Co<sup>3+</sup> ions) are responsible for the adsorption of the C=C bond and the opening of the furan ring, while Pt works for the following hydrogenation. Analogously, MnO<sub>x</sub> may play the similar role to adsorb a C=C bond of the aromatic ring to inhibit the full hydrogenation of the furan ring. In fact, MnO<sub>x</sub> can improve the selectivity and yield of cyclohexene in the partial hydrogenation of benzene over the Ru-based catalyst.<sup>41</sup> Therefore, a partially hydrogenated species, which is stabilized by MnO<sub>x</sub>, might be the intermediate to the formation of 1,2-PeD from FFA.

### Influence of the solvent in furfuryl alcohol conversion over the Ru/MnO<sub>x</sub> catalyst

The nature of the solvent had a dramatic effect on the rate and selectivity of the 1,2-PeD (Table 3). In aqueous phase, high FFA conversion and 1,2-PeD selectivity were observed. However, the reaction rate of FFA was rather low in the alcohol, THF or 1,4-dioxane. Thus, water is a good medium for the FFA conversion. We also performed the reaction in the absence of any solvent, but the reaction rate was also remarkably low. Besides, the selectivity to 1,2-PeD (20.5%) was a little lower than the

result in the aqueous phase (24.4%). These results suggest that the water contributes to the increase in catalytic activity.

It has been reported that water can enhance the reaction rate in the metal catalyzed hydrogenation and hydrogenolysis reactions. The reaction rate of glycerol<sup>42</sup> or THFA<sup>23</sup> hydrogenolysis over the Rh–ReO<sub>x</sub>/SiO<sub>2</sub> catalyst in other solvents, such as 1,4-dioxane, was much lower than that in water, which may be due to the formation of Re–OH species. The similar hydroxide species were largely generated for the Ru/MnO<sub>x</sub> catalyst in the aqueous phase. Before the reaction, only the XRD peaks of Mn(+2)O were observed for the reduced Ru/MnO<sub>x</sub> catalyst. After contact with water, the Mn(+2)O transformed to Mn(OH)<sub>2</sub>, which is a layered crystalline material built from the edge-sharing of Mn(OH)<sub>6</sub><sup>4–</sup> octahedral clusters.<sup>43,44</sup> The Mn–OH species in the Ru/MnO<sub>x</sub> catalyst might be the active sites as the Re–OH species in the Rh–ReO<sub>x</sub> catalyst, which promote the hydrogenolysis of THFA by interacting with the hydroxide of THFA.<sup>45</sup> However, almost no conversion of THFA was observed over the Ru/MnO<sub>x</sub> catalyst (Table 5, entry 3), indicating the generation of Mn–OH species is secondary in the increasing of the reaction rate. The other possible explanation might lie in that the proton of water (H<sup>+</sup>) could favour the cleavage of the metal–carbon bond through reductive elimination.<sup>46</sup> Once the adsorbed intermediate of the products were formed on the active sites of metal (in the form of Ru–C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>), the desorption rate may be enhanced in the presence of H<sup>+</sup>.<sup>47</sup>

**Table 3** Effect of solvent on furfuryl alcohol conversion over the Ru/MnO<sub>x</sub> catalyst<sup>a</sup>

Solvent	Reaction rate mmol (g Cat h) <sup>-1</sup>	Conv. (%)	Selectivity (%)		
			1,2-PeD	THFA	Others
Water	50.8	99.6	24.4	73.7	1.9
Alcohol	2.2	4.4	13	77.8	9.2
THF	0.1	0.1	—	—	—
Dioxane	1.6	3.1	9.6	12.9	77.5
— <sup>b</sup>	1.7	10.0	20.5	71.7	7.8

<sup>a</sup> Furfuryl alcohol 4 g, Ru/MnO<sub>x</sub> 0.2 g, H<sub>2</sub>O 36 g, 120 °C, 3 MPa, 4 h.  
<sup>b</sup> Furfuryl alcohol 40 g, Ru/MnO<sub>x</sub> 1.0 g, 120 °C, 3 MPa, 24 h.

### Influence of reaction temperature and H<sub>2</sub> pressure on furfuryl alcohol conversion over the Ru/MnO<sub>x</sub> catalyst

The influence of reaction temperature on the conversion of FFA was investigated over the Ru/MnO<sub>x</sub> catalyst at 3 MPa in aqueous phase (Table 4). The selectivity of THFA was 99.8% at 60 °C, indicating low activation energy for FFA hydrogenation. At 120 °C, the selectivity of 1,2-PeD was increased to 24.4%. As temperature was further raised from 120 °C to 150 °C, the selectivity of 1,2-PeD increased from 24.4% to 34.3%. Therefore, the generation of 1,2-PeD is favorable at high temperature. However, the 1,2-PeD selectivity was decreased to 33.3% at 160 °C due to the generation of more by-product. On the contrary, the selectivity of THFA was sharply decreased with an increasing in temperature. When the temperature was raised above 150 °C, the 2-(hydroxymethyl)-tetrahydrofuran-2-ol (D), which was the hydrolysis product of 2,3-dehydrofurfuryl alcohol (A2, Scheme 2), was generated in high yield (>10%). So the optimal reaction temperature for FFA conversion over the Ru/MnO<sub>x</sub> catalyst to 1,2-PeD is 150 °C.

Table 4 also shows the influence of the hydrogen pressure in FFA conversion. When the pressure decreased from 3.0 MPa to 1.5 MPa, the FFA conversion decreased, and the selectivity of 1,2-PeD increased from 33.3% to 41.4%. Correspondingly, the selectivity of THFA was decreased from 48.6% to 41.6%. However, the reaction rate was quite low at 1 MPa, and the selectivity of 1,2-PeD was decreased to 38.5% due to the formation of byproducts.















According to above results, both the low hydrogen pressure and the high temperature favor the generation of 1,2-PeD from FFA. The low hydrogen pressure can result in the decrease of hydrogen concentration in the aqueous phase, which also happened with the temperature increasing.<sup>48</sup> Chen *et al.*<sup>9</sup> and Tike *et al.*<sup>10</sup> have shown that a high hydrogen pressure enhances the reaction rate of FFA hydrogenation to produce THFA. On the contrary, the low hydrogen concentration in the aqueous phase inhibited the hydrogenation rate of FFA to THFA and may cause the high yield of partially hydrogenated intermediates. On the other side, the initial adsorption structure of FFA may be changed with the temperature and modify the production selectivity. Xu *et al.*<sup>39</sup> have found that the parallel adsorbed species of furan over the Ru(001) surface can be transformed to the

**Table 4** Effect of reaction temperature and pressure in the hydrogenation/hydrogenolysis of furfuryl alcohol over the Ru/MnO<sub>x</sub> catalyst<sup>a</sup>

Entry	T (°C)	p (MPa)	Conv. (%)	Selectivity (%)				
				1,2-PeD	THFA	D	1,4-PeD	Others
1 <sup>b</sup>	60	3	91.3	0.2	99.8	0.0	0.0	0.0
2	120	3	99.6	24.4	73.7	0.2	0.4	1.3
3	130	3	99.7	24.9	72.3	0.3	0.9	1.6
4	140	3	99.9	31.9	60.0	1.7	1.6	4.8
5	150	3	100.0	34.3	48.6	2.7	2.1	12.3
6	160	3	100.0	33.3	38.1	13.5	1.6	13.5
7	150	2	100.0	37.5	47.8	3.5	3.2	8.0
8	150	1.5	89.2	41.4	41.6	3.5	3.8	9.7
9 <sup>c</sup>	150	1	95.1	38.5	21.9	8.7	5.2	25.7

<sup>a</sup> Furfuryl alcohol (4 g), catalyst (0.2 g), H<sub>2</sub>O (36 g), 4 h. <sup>b</sup> Furfuryl alcohol (4 g), catalyst (0.2 g), H<sub>2</sub>O (36 g), 12 h. <sup>c</sup> Furfuryl alcohol (4 g), catalyst (0.2 g), H<sub>2</sub>O (36 g), 24 h.

**Table 5** The conversion of furan compounds over the Ru/MnO<sub>x</sub> catalyst<sup>a</sup>

Entry	Reactant	Conv. (%)	Selectivity (%)		
			A	B	
			1,2-PeD	THFA	
					
1	 FA	99.6	24.4	73.7	—
2	 THFA	1.3	0.0	—	—
3 <sup>b</sup>	 THFA	3.5	8.2	—	—
			2-PeOH	MTHF	—
					
4	 MF	99.4	16.0	68.8	—
			BuOH	THF	BDO
					
5	 THF	6.2	4.1	—	17.5
6	 DHF	97.0	6.7	34.1	53.3
7	 Furan	98.4	2.5	79.5	10.1

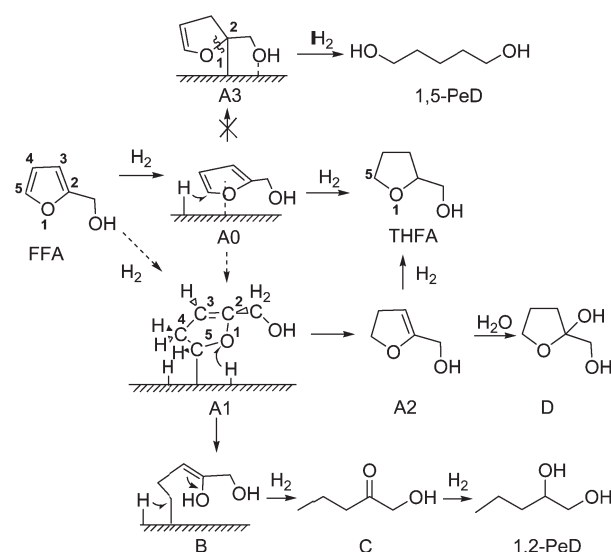
<sup>a</sup> Reactant 4 g, catalyst 0.2 g, H<sub>2</sub>O 36 g, 120 °C, 3 MPa, 4 h. <sup>b</sup> Reactant 4 g, catalyst 0.2 g, H<sub>2</sub>O 36 g, 160 °C, 3 MPa, 4 h. **A** = C–O bond hydrogenolysis. **B** = C=C bond hydrogenation. 2-PeOH = 2-pentanol. MTHF = 2-methyltetrahydrofuran. BuOH = *n*-butanol. BDO = 1,4-butanediol.

tilted species with the increasing of the temperature. The tilted species of furan ring of FFA are probably undergoing partial hydrogenation to generate A1 (Scheme 2), which might be an intermediate in the production of 1,2-PeD.

#### Product formation during furfuryl alcohol hydrogenolysis over the Ru/MnO<sub>x</sub> catalyst as a function of the reaction time

The time dependence of FFA hydrogenolysis/hydrogenation over the Ru/MnO<sub>x</sub> catalyst was used to investigate reaction pathways.

Fig. 4A displays the effect of reaction time on the conversion of FFA over the Ru/MnO<sub>x</sub> catalyst at 120 °C and 6 MPa, and only 1,2-PeD and THFA were observed. The conversion of FFA increased with the reaction time and reached 100% after 2 h. However, the molar ratio of 1,2-PeD/THFA was nearly constant with time (1/4). The direct conversion of THFA was also carried out over the Ru/MnO<sub>x</sub> catalyst at 120 °C and 160 °C (Table 5, entries 2, 3), and low conversion of THFA was observed. This is consistent with previous reports that the hydrogenolysis of

**Scheme 2** Reaction pathways in the hydrogenolysis/hydrogenation of furfuryl alcohol over the Ru/MnO<sub>x</sub> catalyst in the aqueous phase.

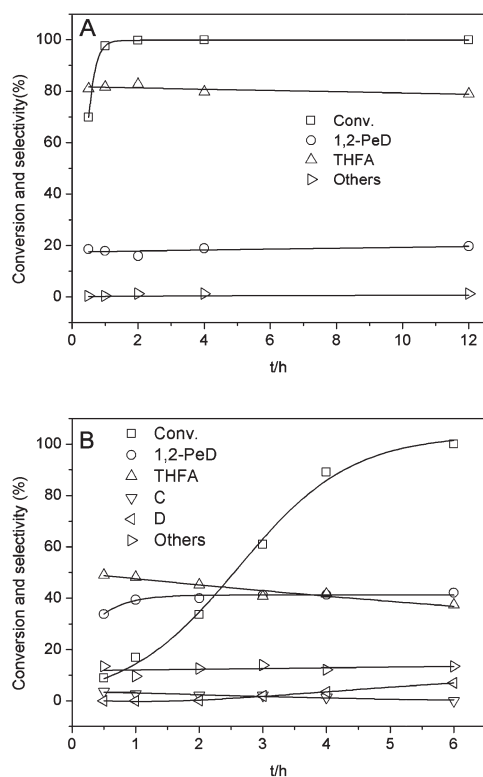
THFA is not easy under mild conditions.<sup>12–14</sup> Therefore, 1,2-PeD cannot be generated from THFA, but is the parallel product from FFA.

Fig. 4B displays the effect of reaction time on the conversion of FFA over the Ru/MnO<sub>x</sub> catalyst at 150 °C and 1.5 MPa. The full conversion of FFA was observed at 6 h. The selectivity of 1,2-PeD was gradually increased to 42.1% after 6 h, while the selectivity of 1-hydroxy-2-pentanone (C, Scheme 2) was decreased to zero. In fact, C can be easily hydrogenated to 1,2-PeD. On the other side, the selectivity of THFA was linearly decreased with the reaction time. Since only the selectivity of 2-(hydroxymethyl)-tetrahydrofuran-2-ol (D) was significantly increased with the reaction time, the decrease of THFA selectivity might be due to the formation of D. Traces of 2,3-dihydrofurfuryl alcohol (A2, not shown), which might be the intermediate to form THFA and D, was also detected during the conversion of FA. Thus, D is another parallel product from FFA.

#### The conversion of furan compounds over the Ru/MnO<sub>x</sub> catalyst

The hydrogenation of other furan compounds, such as 2-methylfuran (MF), tetrahydrofuran (THF), 2,3-dihydrofuran (DHF) and furan, were also investigated over the Ru/MnO<sub>x</sub> catalyst (Table 5). The conversion of THF was remarkably low, similar to the low reactivity of THFA. Both DHF and furan showed low activity of C–O bond hydrogenolysis to produce 1-butanol (BuOH), and the presence of water favored the generation of 1,4-butanediol (BDO) from 2,3-dihydrofuran through a hydrolysis and subsequent hydrogenation process. These results agreed with the suggestion of Belskii and Shuikin<sup>7</sup> that the intermediate in the hydrogenolysis of the furan ring is not the dihydrofurans and tetrahydrofurans, but might be a surface-adsorbed complex.

The furan and MF have the similar furan ring structure as FA. However, the selectivity of C–O hydrogenolysis products was decreased with 1,2-PeD (from FFA, 24.4%) > 2-PeOH (from MF, 16.0%) > *n*-BuOH (from furan, 2.5%) (Table 5, entries 1, 4



**Fig. 4** Effect of the reaction time on the conversion of furfuryl alcohol over the Ru/MnO<sub>x</sub> catalyst at (A) 120 °C, 6 MPa, (B) 150 °C, 1.5 MPa.

and 7). This is consistent with the previous DFT result that functional groups of the furan ring strongly influences the reaction pathways for furan ring-opening.<sup>38</sup> Here, the larger functional group adjacent to the ether-oxygen of the furan ring favors the C–O bond hydrogenolysis.

### Reaction network and proposed mechanism

On the basis of the experimental results in this work and existing literature, a proper reaction mechanism for the hydrogenolysis of FFA was proposed, which suggested that 1,2-PeD is not generated from the dihydrofurans and tetrahydrofurans, but might be originated from a partially hydrogenated species (Scheme 2). Although the generation of 1,2-PeD from THFA is essentially irreversible due to the large negative  $\Delta G$  values,<sup>45</sup> the low conversion of THFA over the Ru/MnO<sub>x</sub> catalyst suggested that the 1,2-PeD is the parallel product of THFA in the conversion of FFA. Therefore, THFA and 1,2-PeD are generated through different pathways. According to the DFT results in previous research,<sup>36–39</sup> two initial adsorption species, the parallel and tilted adsorbed species, may be responsible for the formation of the two products. As shown in Scheme 2, the parallel adsorbed species (A0) may be rapidly undergoing hydrogenation to produce THFA, while the tilted adsorbed species of FFA may generate the key intermediate (A1) through semi-hydrogenation of the C<sup>4</sup>=C<sup>5</sup> bond of FFA. Then, A1 is chemisorbed on the metal surface by forming the C<sup>5</sup>–metal bond, similar to the intermediate in the metal catalyzed ring-opening of cyclic ethers (2-methyltetrahydrofuran).<sup>40</sup> The C<sup>5</sup>–O<sup>1</sup> bond of A1 further

undergoes hydrogenolysis to produce C, which can be hydrogenated to 1,2-PeD. In fact, the p– $\pi$  conjugation between the p-orbital of O<sup>1</sup> atom and  $\pi$  orbital of the C<sup>2</sup>=C<sup>3</sup> bond can remarkably weaken the C<sup>5</sup>–O<sup>1</sup> bond of A1, which may facilitate the hydrogenolysis of the C<sup>5</sup>–O<sup>1</sup> bond. Without the presence of the C=C bond, the C–O bond in the saturated tetrahydrofuran ring is stable and does not easily undergo hydrogenolysis under mild conditions. This can explain the low activity of THF and THFA over the Ru/MnO<sub>x</sub> catalyst.

The substituent group on the furan ring favored the hydrogenolysis of furan ring, which may be due to the steric effects. Pang and Medlin<sup>38</sup> showed that the methyl group of MF was repelled by the surface of Pd(111). Similarly, the methylol group (–CH<sub>2</sub>OH) of FFA may be repelled by the Ru surface and inhibit the full hydrogenation of the furan ring to generate THFA. Compared to MF and furan, the highest selectivity of C–O bond hydrogenolysis product from FFA is obtained due to the larger –CH<sub>2</sub>OH group, which has a bigger steric hindrance. Furthermore, the steric hindrance of the group can prevent the semi-hydrogenation of the C<sup>2</sup>=C<sup>3</sup> bond of FFA to form A3, which might be an intermediate to generate 1,5-PeD. Therefore, little 1,5-PeD was observed over the Ru/MnO<sub>x</sub> catalyst.

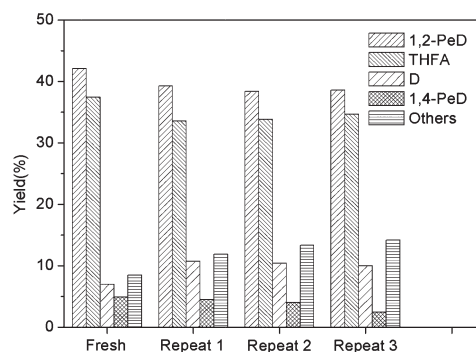
The Mn(+2) in the catalyst promoted the generation 1,2-PeD. This may due to the stabilization A1 by forming an adduct with the Mn ion, which weakens the interaction of the double bond of A1 with the d orbital of Ru to suppress the generation of THFA. A similar explanation has been proposed to explain the doping effect of the Zn ions in the partial hydrogenation of benzene to cyclohexene.<sup>49</sup> At high temperature (>140 °C), however, A1 can easily convert to A2, which is unstable and easily generates D through hydrolysis in aqueous phase.

### Catalyst recycling in furfuryl alcohol conversion

The recyclability of the Ru/MnO<sub>x</sub> catalyst was investigated by reusing the catalyst in four consecutive runs at 150 °C, 1.5 MPa. Prior to each reuse of the catalyst, the reaction crude was allowed to settle down, and the supernatant was removed from the reactor. A fresh charge of reactant was then added to the reactor and the subsequent run was continued. In the first run, the yield of 1,2-PeD reached 42.1% at 150 °C and 1.5 MPa, which is higher than the reported CuCr<sub>2</sub>O<sub>4</sub> at 175 °C, 15 MPa in FFA conversion, and 2.5 times higher than Pt/Co<sub>2</sub>AlO<sub>4</sub> in furfural conversion at 150 °C, 1.5 MPa. A marginal decrease in 1,2-PeD selectivity from 42.1 to 38.6% after four consecutive runs could be due to the further hydrogenolysis of 1,2-PeD and the generation of D (Fig. 5).

### Conclusion

In summary, a Ru/MnO<sub>x</sub> catalyst was developed to produce highly value-added chemicals, including 1,2-PeD and THFA from FFA *via* aqueous phase hydrogenolysis/hydrogenation. High temperature and low pressure is favorable for the generation of 1,2-PeD, and the water promotes the reaction rate. A high yield of 1,2-PeD was obtained (42.1%) over the Ru/MnO<sub>x</sub> catalyst at 150 °C, 1.5 MPa, which was the highest value reported under mild condition so far. The MnO<sub>x</sub> in the form of



**Fig. 5** Reuse of the Ru/MnO<sub>x</sub> catalyst in the conversion of furfuryl alcohol. Reaction conditions: furfuryl alcohol 4 g, catalyst 0.2 g, H<sub>2</sub>O 36 g, 150 °C, 1.5 MPa.

Mn(OH)<sub>2</sub> not only inhibited the polymerization of FFA in the aqueous phase but also promoted the generation of 1,2-PeD. In addition, 1,2-PeD was suggested to be formed from FFA via a partially hydrogenated species (A1) over the Ru/MnO<sub>x</sub> catalyst. However, only the parallel adsorbed species is favorable over the Pd or Rh catalyst, which may account for the remarkable high selectivity for THFA. These results are important to understand the mechanism and reaction pathway for the hydrogenolysis of biomass-derived furan compounds in the aqueous phase, and provide guidance for the design of new catalytic formulations.

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