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YAL SOCIETY CHEMISTRY

## Journal Name

### ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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# Facile synthesis of furfuryl ethyl ether in high yield via reductive etherification of furfural in ethanol over Pd/C under mild conditions

Yun Wang, Qianqian Cui, Yejun Guan\* and Peng Wu

The one-pot synthesis of furfuryl ethyl ethyl (FEE) over Pd nanoparticles supported on TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and active carbon via catalytic reductive etherification of furfural in ethanol was systematically studied. Pd supported on SiO<sub>2</sub>, TiO<sub>2</sub> and active carbon are all active for this novel process under mild reaction conditions, with Pd/C showing the highest selectivity to FEE. The effects of palladium loading, reaction temperature, hydrogen pressure on the activity and selectivity of Pd/C have been investigated in detail. The results demonstrate that suitable Pd amount, low reaction temperature about 60 °C, and low H<sub>2</sub> pressure about 0.3 MPa are favorable to the formation of desired ether product. Under the optimized conditions, unprecedented high yield up to 81% of FEE was firstly obtained with the major by-products being furfuryl alcohol and 2-methyltetrahydrofuran. Compared with the conventional hydrogenation-etherification route via furfural alcohol as reaction intermediate, the reductive etherification shows significant advantage in product yield because of its much lower reaction temperature

#### Introduction

Due to the fast depletion of fossil fuels and environmental concerns about climate change, paradigm change from fossil to biomass resources for the manufacture of commodity and fine chemicals will become inevitable in the near future<sup>1-3</sup>. However, platform compounds obtained from biomass contain high oxygen content; hence, many catalytic processes i.e., hydrogenation, dehydration, decarboxylation, esterification, etherification, acetalization, and C-C coupling have been developed for selectively tailoring their oxygen content to achieve the desired chemicals and fuels<sup>4-10</sup>. Among these processes, etherification is one of the promising means for the production of oxygenated fuels, as it reduces the amount of hygroscopic alcohol groups, and increases both the energy content and cetane number<sup>11,12</sup>. Several ether productions obtained from platform compounds has been recently reported, eg., ethyl-4-ethoxy pentanoate<sup>13</sup>, ethylene glycol ethers<sup>15</sup>, ether<sup>14</sup>, glycerol 5-(ethoxymethyl)furfan-2carbaldehyde<sup>16-21</sup>, isosorbide tert-butyl ethers<sup>22</sup> and  $\beta$ -Citronellene ethers<sup>23</sup>.

Furfural (FF) as one of the platform molecules can be transformed to a variety of value-added chemicals and fuels

such as furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (TFA), 2-methylfuran (MF), 2-methyl tetrahydrofuran (MTF), furan and tetrahydrofuran (THF). Recently, another kind of furfural derivatives, furfuryl ethers, has attracted wide attention because it is one of the promising components of gasoline due to their high stability and high octane numbers<sup>24-28</sup>. The current production of furfuryl ethers generally includes two routes (Scheme1): one is a two-step process (a), wherein furfural is firstly hydrogenated to FA, which then undergoes etherification with alcohols. This route requires a bifunctional hydrogenation catalyst and a strong Bronsted acid catalyst. Lange and co-workers disclosed the production of furfuryl ethyl ether (FEE) by etherification of FA using zeolites, with FEE yield of 50 mol% at 80% furfural conversion using the HZSM-5 zeolite at 125 °C<sup>24,29</sup>. Further increase of FEE yield is a challenge task in route (a). As the etherification normally requires high reaction temperature (>100 °C), under such reaction conditions ring opening of furan-group of FEE inevitably takes place resulting in the formation of levunic acid or its esters<sup>30,31</sup>.



Route (b): reductive etherification

<sup>&</sup>lt;sup>a.</sup> Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, North Zhongshan Road 3663, Shanghai, China.

<sup>+</sup> Dr. Yejun Guan. Email: yjguan@chem.ecnu.edu.cn.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Scheme 1: Reaction parthways for the synthesis of furfuryl ethyl ether from fufural in ethanol.

Another strategy called reductive etherification (b), allows for the synthesis of ethers from an alcohol and an aldehyde substrate in one-step<sup>32</sup>. This methodology has been found to be very selective for the etherification of some commonly seen carbonyl compounds such as cyclohexanone, octanal, benzaldehyde, and etc. under hydrogen atmosphere<sup>33-41</sup>. However, few reports have been made in the synthesis of furfural-derived ethers by this robust way<sup>27,28</sup>. Recently, a maximum selectivity of 77% of furfuryl methyl ether (FME) has been noted on palladium charcoal catalysts under high hydrogen pressure (5 MPa) at about 100 °C<sup>27</sup>. Compared with the hydrogenation-etherification process, the reductive etherification path occurs at relatively lower temperature therefore inhibiting the decomposition of produced ether. In this study, we found that high yield synthesis of furfuryl ethyl ether (FEE) via reductive etherification of furfural in ethanol could be achieved under even more mild conditions. e.g., H<sub>2</sub> pressure as low as 0.3 MPa and temperature close to 60 °C. Under this reaction conditions, the decomposition of FEE is completely inhibited therefore high yield of 81% FEE was obtained on 0.7 wt.% Pd/C catalyst. The detailed kinetics results suggest that the Pd loading, reaction temperature together with hydrogen pressure all govern the FEE yield by tuning the competition between hydrogenation and hydrogenolysis activity of PdH hydride species.

#### **Results and discussion**

#### **Catalyst characterization**

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The structural properties of the supported Pd catalysts, including BET specific surface area (SSA) and total pore volume (V<sub>total</sub>) are summarized in Table 1. The surface areas of active carbon supported Pd (Pd/C) catalyst are all close to 1300 m<sup>2</sup>  $g^{-1}$ . With the Pd loading increasing from 0.3 to 1.4 wt.%, the surface area slightly decreased. The surface area of Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/SiO<sub>2</sub>, and Pd/TiO<sub>2</sub> is 204, 174.5, and 53 m<sup>2</sup> g<sup>-1</sup>, respectively. Figure 1 shows the XRD patterns of the as-prepared Pd catalysts. No diffraction peaks due to Pd nanoparticles are visible for the 0.7Pd/TiO<sub>2</sub>, 0.9Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/C catalysts, meaning that Pd is highly dispersed on these supports at loadings less than 1.5 wt%. The high dispersion of Pd on TiO<sub>2</sub> and  $Al_2O_3$  is likely due to the strong interaction between Pd and TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> surface. For Pd/C catalyst, the high surface area unambiguously benefits the loading of Pd species. By contrast, weak diffraction peak at 40° is observed for 0.8Pd/SiO<sub>2</sub> catalyst (JCPDS [46-1043]), suggesting the presence of larger Pd particles on SiO<sub>2</sub> because of the weak interaction between Pd species and silica surface.

We further measured the particle size and metal dispersion of palladium on active carbon by TEM and CO chemisorption, respectively. Typical TEM images of the supported Pd catalysts are shown in Figure 2. Narrow distribution of palladium particle size (1–9 nm) was obtained for all catalysts. Figs.2a–c shows the images of Pd/C with various Pd loading (from 0.3 to

1.4 wt.%). The average particle size of palladium in 0.3Pd/C, 0.7Pd/C and 1.4Pd/C according to TEM analysis is 6.4, 3.6 and 3.0 nm, respectively. For 0.3Pd/C, we see few Pd nanoparticles less than 2 nm in TEM. Figs.2d-f show the images of 0.8 Pd/SiO<sub>2</sub>, 0.9 Pd/Al<sub>2</sub>O<sub>3</sub>, and 0.7 Pd/TiO<sub>2</sub>, respectively. The average Pd particle size of 0.8 Pd/SiO<sub>2</sub>, 0.9 Pd/Al<sub>2</sub>O<sub>3</sub> and 0.7 Pd/TiO<sub>2</sub> is estimated to be 7.1, 3.1 and 4.7 nm, respectively. Serious aggregation of Pd nanoparticles on SiO<sub>2</sub> is noticed, which is consistent with the XRD diffraction that Pd/SiO<sub>2</sub> has the largest Pd particle size. The CO chemisorption results are also listed in Table 1. The Pd dispersion for 0.3Pd/C, 0.7Pd/C and 1.4Pd/C is 11%, 35%, and 40%, respectively. This trend is consistent with the TEM analysis. For oxides supported Pd catalysts, the Pd dispersion showed distinct results. 0.9Pd/Al<sub>2</sub>O<sub>3</sub> catalyst gave a dispersion of 31%, while 0.8Pd/SiO<sub>2</sub> and 0.7Pd/TiO<sub>2</sub> both showed lower dispersion about 6%. This very low Pd dispersion on SiO<sub>2</sub> and TiO<sub>2</sub> has been found previously and might be due to a support effect<sup>42</sup>.

#### Table 1. Structural properties of supported Pd catalysts

Catalyst	Pd <sup>ª</sup> (wt.%)	SSA <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	$V_{total}^{c}$ ( cm <sup>3</sup> g <sup>-1</sup> )	D <sup>d</sup> (%)	d <sub>TEM</sub> e (nm)
0.3Pd/C	0.29	1340	0.95	11	6.4
0.7Pd/C	0.68	1335	0.91	35	3.6
1.4Pd/C	1.4	1295	0.87	40	3.0
0.7Pd/TiO₂	0.7	53	0.40	6	4.7
$0.9Pd/AI_2O_3$	0.91	204	0.48	31	3.1
0.8Pd/SiO <sub>2</sub>	0.79	174	1.44	6	7.1

a Determined by ICP-AES. b Calculated using BET method. c Calculated from the adsorption capacity at  $P/P_0$  of 0.99. d According to pulse CO chemisorption. e Determined by TEM



Fig. 1 XRD patterns of supported Pd catalysts.

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Figure 2 TEM images of different Pd catalysts. a) 0.3Pd/C; b) 0.7Pd/C; c) 1.4Pd/C; d)  $0.8Pd/SiO_2$ ; e)  $0.9Pd/Al_2O_3$ ; f)  $0.7Pd/TiO_2$ .

#### Reductive etherification activity of Pd/C catalysts

Table 2 shows the catalytic performance of Pd/C catalysts in reductive etherification of furfural in ethanol in terms of furfural conversion and product distribution. As an initial study, we started the reaction at 60  $^{\circ}$ C and 0.3 MPa H<sub>2</sub> pressure. For each experiment, 10 mL of 0.24 M furfural in ethanol solution and 100 mg catalyst was used. After reaction Table 2. Reductive etherification of furfural with ethanol on different catalysts<sup>a</sup>

for 2 h. the reaction mixtures were withdrawn and analysed. Furfural conversion over 0.3, 0.7, and 1.4 Pd/C catalysts (Table 2, Entries 1-3) are 77, 98, and 100%, respectively. The three catalysts showed distinct product distribution. For 0.3Pd/C, the predominant product was 2-(diethoxymethyl)furan (DOF), with selectivity of 78%. The mass spectra of some of the products were shown in Fig. S1. The rest products were furfuryl ethyl ether (FEE, Sel. 15%) and furfuryl alcohol (FA, Sel. 7%). For 0.7Pd/C, the dominating product was FEE with selectivity of 83%. Other by-products included FA (10%), DOF (4%) and tetrahydrofurfuryl alcohol (TFA, 3%). For 1.4Pd/C, the major products contained 50% of FEE, 38% of FA and 6% of TFA. It should be noted that by decreasing the catalyst amount of 1.4Pd/C from 100 mg to 20 mg while keeping the rest reaction conditions unchanged, the FEE selectivity could be increased from 50% to 70%. This result can be explained by the similar particle size distribution of 0.7Pd/C and 1.4Pd/C. We may conclude that by using suitable furfural/Pd ratio, the Pd/C catalysts with particle size around 3 nm may selectively catalyse the formation of FEE.

Entry Catalyst	Cataluat	Conv.%	Sel.%							
	Catalyst		FEE	DOF	FA	TFA	DOTF	TFF	MTF	TFEE
1	0.3Pd/C	77	15	78	7					
2	0.7Pd/C	98	83	4	10	3				
3	1.4Pd/C	100	50		38	6		1	3	2
4	0.8Pd/SiO <sub>2</sub>	86	19	63	2		11	5		
5	$0.9Pd/Al_2O_3$	98		11	5	34	16	34		
6	0.7Pd/TiO₂	98	55	3	25	2	10			
7	0.7Pd/C <sup>b</sup>	100	76		8		6			
8	0.7Pd/C <sup>c</sup>	35				70			30	
9	0.7Pd/C <sup>d</sup>	0								

<sup>a</sup> Reaction conditions: 10 mL of 0.24 M furfural (FF) ethanol solution; 60 °C; 0.3 MPa H<sub>2</sub>; 100 mg catalyst; 2 h. FEE: Furfuryl ethyl ether ; DOF: 2-(diethoxymethyl)furan; FA: furfuryl alcohol; TFA: tetrahydrofurfuryl alcohol; DOTF: 2-(diethoxymethyl)tetrahydrofuran ; TFF: tetrahydrofurfural; MTF: 2-methyltetrahydrofuran; TFEE: tetrahydrofurfuryl ethyl ether .

<sup>b</sup> DOF as reactants.

<sup>c</sup>Reactant: Furfuryl alcohol

 $^{
m d}$  Reaction conditions: 10 mL of 0.24 M furfural (FF) ethanol solution; 60  $^{
m o}$ C; 0.5 MPa N<sub>2</sub>; 100 mg catalyst; 2 h.

#### Reductive etherification of furfural over Pd/Oxides

For comparison, the reductive etherification of furfural over oxide (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>) supported Pd catalysts was also investigated and the results are shown in Table 2, entries 4-6. Pd catalysts supported on three oxides all showed very high furfural conversion (>86%). For 0.8Pd/SiO<sub>2</sub>, 63% selectivity of 2-(diethoxymethyl)furan (DOF) was observed and 19% selectivity of furfuryl ethyl ether (FEE) was noticed. Previous report has shown that Pd/SiO<sub>2</sub> catalyst was active for the etherification of 2-methylpentanal though with much higher loading (16 wt.%) and at temperature above 125  $^{\circ}C^{40}$ .

Meanwhile, total hydrogenation of DOF and furfural also took place on this catalyst leading to the formation of 2-(diethoxymethyl)tetrahydrofuran (DOTF) and tetrahydrofurfural (TFF), respectively. No FEE was found for 0.9Pd/Al<sub>2</sub>O<sub>3</sub> catalyst and the products were mainly consisted of FA, TFA, DOTF and TFF. These products were formed via the partial or total hydrogenation of furfural, pointing to the hydrogenation nature of Pd species on alumina. In the case of 0.7Pd/TiO<sub>2</sub> catalyst, a 55% selectivity of FEE was noticed. The other main by-product was FA (Sel. 25%).

# Effects of reaction temperature, $H_2$ pressure on the reductive etherification activity of 0.7Pd/C catalyst

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DOI: 10.1039/C7GC03887A

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The above mentioned results unambiguously demonstrate that Pd/C catalyst showed unique performance in converting furfural to furfuryl ethyl ether (FEE) via reductive etherification. We next investigated the effect of reaction parameters on the activity of Pd/C catalyst. 0.7Pd/C was chosen because it showed the highest FEE yield among the catalysts studied. In these studies, the reactions were conducted under 0.5 MPa H<sub>2</sub> pressure at temperatures of 40, 60, or 80 °C for 2 h (Figure 3). 0.7Pd/C catalyst showed very high furfural conversion at all temperatures following the order of 80 °C (100%) > 60 °C (98%) > 40°C (85%). When the reaction was conducted at lower temperature (40 °C), the selectivity of FEE was 21%, while DOF was found to be the predominant product with 60% selectivity. This result means that the Pd/C catalyst is very active for DOF formation at low reaction temperature. Increasing the reaction temperature to 60 °C, 71% selectivity to FEE was observed along with the disappearance of DOF. This phenomenon suggests that the FEE was mainly formed via the hydrogenolysis of DOF under elevated temperature. Further increasing the reaction temperature to 80 °C, the selectivity to FEE decreased to 19% and the byproducts were consisted of hydrogenation compounds such as FA (23%), TFA (10%) and DOTF (25%). This result clearly emphases that Pd/C is highly active for the hydrogenation of both C=O and furan ring at higher temperatures. We conclude that the reductive etherification of furfural in ethanol occurs at very narrow reaction temperature window on Pd/C catalyst, i.e. higher than 40 °C and lower than 80 °C. It should be noted that under this reaction condition, neither levulinic acid nor ethyl levulinate was observed because the reaction temperature was not high enough for the decomposition of FEE. In this regard, reductive etherification shows remarkable advantage leading to the high yield synthesis of FEE compared with conventional hydrogenationetherification route.









We next investigated the effect of H<sub>2</sub> pressure on the ether (FEE) yield at 60 °C and the results are shown in Figure 4. Under 0.1 MPa H<sub>2</sub>, 73% conversion of furfural is obtained, and the selectivity of FEE is only 17% with DOF (Sel. 81%) as the dominant by-product. high selectivity of 83% to FEE is achieved with 98% conversion of furfural under 0.3 MPa H<sub>2</sub>. The overall FEE yield at 0.5 MPa (70%) is lower than that (83%) operated under 0.3 MPa. As the H<sub>2</sub> pressure further increasing to 0.8 MPa, full conversion of furfural was observed while the selectivity to FEE is only 4% and the main by-product is found to be TFA (54%). Apparently, higher H<sub>2</sub> pressure favours the C=O and furan hydrogenation reaction pathways, and therefore relatively low hydrogen pressure is preferred for the synthesis of desired ether product. Taking into account of the above results, one can clearly see that several reactions including acetalization, hydrogenolysis, and deep hydrogenation are all involved in the reductive etherification process. The selectivity to FEE is mainly determined by the competition between hydrogenolysis and hydrogenation. In principle, higher Pd loading, higher reaction temperature and higher H<sub>2</sub> pressure favours the deep hydrogenation pathways, therefore lowering the overall furfuryl ethyl ether yield. It should also be mentioned that over-reduction of FEE may also take place on 0.7Pd/C catalyst. We have tested the activity of 0.7Pd/C for FEE hydrogenation by using FEE/ethanol solution as starting reagent at 60 °C and 0.3 MPa H<sub>2</sub>. After reaction for 2 h, FEE was fully converted, with 75% selectivity towards tetrahydrofurfuryl ethyl ether 75% FEE and the rest product was mainly 2-methyl tetrahydrofuran (Table S1). The hydrogenation of FEE was hardly perturbed in presence of furfural or furfuryl alcohol over 0.7Pd/C (Table S1).

#### Reaction mechanism and kinetics study

The above results have highlighted the importance of 2-(diethoxymethyl)furan DOF formation in the reductive etherification. To understand the furfuryl ethyl ether formation mechanism in more detail, we have followed the reaction progress carefully on various Pd/C catalysts, namely, 0.7Pd/C and 1.4Pd/C. Figure 5A shows the furfural conversion and product distribution during the reaction course over Page 5 of 9

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0.7Pd/C at 60 °C and 0.3 MPa H<sub>2</sub> pressure. After reaction for 5 min, 70 % of furfural conversion was already observed with DOF yield of 61% and FA yield of 8%, suggesting that acetalization of furfural with ethanol to DOF proceeds very fast (Scheme 2). As the reaction further going on, the yield of furfuryl ethyl ether increased, and the yield of DOF decreased simultaneously. After 2 h reaction, almost no DOF was detected, and the yield of furfuryl ethyl ether reached 81%. To check whether DOF can serve as the precursor of furfuryl ethyl ether, the hydrogenolysis of commercially purchased DOF substrate was tested over 0.7Pd/C under the same condition (60 °C, 0.3MPa H<sub>2</sub>). The result (Table 2, entry 7) shows that DOF is highly reactive towards furfuryl ethyl ether (yield of 76%), firmly suggesting that the furfuryl ethyl ether is formed by the hydrogenolysis of DOF, which is consistent with the previous findings as observed in the synthesis of other ethers<sup>35,37</sup>. It should be noted that presence of tiny amount of water will significantly inhibit the production of DOF and furfuryl ethyl ether. When 100 µL deionized water was introduced, the 0.7Pd/C catalyst gave FEE yield of 7%, with 65% selectivity toward FA and other hydrogenation byproducts (see ESI Table S1). When FA is used as the substrate (Table 2, entry 8), no FEE was formed under otherwise the same conditions. We therefore safely conclude that DOF formed in furfural/ethanol solution via the acetalization is the precursor of FEE.



Fig. 5 Furfural (FF) conversion and products distribution as a function of reaction time for the reductive etherification of FF in ethanol over 0.7Pd/C (A) and 1.4Pd/C (B). Reaction conditions:10 mL of 0.24 M FF ethanol solution; 60  $^{\circ}$ C;0.3 MPa H<sub>2</sub>; 100 mg catalyst.

Figure 5B also shows the product distribution with time on stream over 1.4Pd/C at 60 °C and 0.3 MPa H<sub>2</sub> pressure. For the first 5 min, 1.4Pd/C gave furfural conversion of 41% with DOF yield of 16%. The other predominant product was FA with yield of 23%. It can be seen that after reaction for 5 min, the yield of furfuryl ethyl ether (FEE) is as low as 2%. As the reaction going on, the yield of both FA and FEE increased, and the yield of DOF went through a maximum for a 15-min reaction time, then decreased. Complete conversion of furfural was achieved after 60 min reaction, with FEE yield of 52% and FA yield of 41%. We hypothesize that the FA is produced by direct

hydrogenation of furfural, which is a competitive reaction with the acetalization. Moreover, the furfural conversion rate for 1.4Pd/C when hydrogenation occurs is much lower than that for 0.7Pd/C when acetalization takes place dominantly at the beginning of the reaction. This phenomenon again points to the importance of DOF formation as an intermediate for the production of furfuryl ethyl ether.



Scheme 2. Reaction pathways during the reductive etherification of furfural (FF) in ethanol over supported Pd catalysts.

The acetalization in general is a typical acid-catalyzed reaction. Solid Bronsted acids such as zeolites or soluble Lewis acids are both active for this reaction<sup>43,44</sup>. By contrast, the true active centre for the acetalization reaction in reductive etherification is still under debating. One assumption is that the acid sites on active carbon can catalyse the acetalization as observed for the acetalization of 1-butanol and octanal at 100 °C<sup>37</sup>. However, this possibility can be excluded in our study. We carried out the reaction under 0.5 MPa N<sub>2</sub> under otherwise the same reaction conditions (Table 2, entry 9). No reaction was seen at all, meaning that the support acidity is not strong enough for the acetalization at 60 °C. Another assumption is that the acetalization is likely ascribed to the palladium hydride formed in  $H_2$  atmosphere<sup>34, 45</sup>. The formation of palladium hydride in aqueous solution on supported Pd catalysts have been extensively studied<sup>46, 47</sup>. Certain forms of these hydrides have been proposed to be to some extent protonic in character, which can catalyse several reactions usually catalysed with protonic catalysts<sup>48</sup>. We noticed that furfuryl ethyl ether always formed along with DOF over the catalysts being selective for furfuryl ethyl ether synthesis (Table 2) in this study, namely, Pd/SiO<sub>2</sub>, Pd/TiO<sub>2</sub>, and Pd/C. We therefore may conclude that Pd hydrides on  $Pd/Al_2O_3$ ,  $Pd/SiO_2$ , Pd/TiO<sub>2</sub>, and Pd/C are all active for the acetalization reaction, whereas with different activity. The difference in acetalization activity can be explained by that PdH species may show support-dependent protonic character.

It has been shown that the nature of support or Pd loading may significantly affect the catalytic role of Pd hydride formed on it<sup>48,49</sup>. To elucidate the effect of Pd loading on hydrogenolysis and hydrogenation, we tested the catalytic performances of 0.7Pd/C and 1.4Pd/C under H<sub>2</sub> by using DOF directly as a starting reactant. We followed the DOF

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conversion and products distribution during the reaction course and results are shown in Figure 6. For 0.7Pd/C (Figure 6A), DOF conversion of 97% was achieved with FEE yield of 53% as main product. For 1.4Pd/C (Figure 6B), one can see that after reaction for 30 min, full conversion of furfural was achieved with tetrahydrofurfuryl ethyl ether (TFEE) (yield of 50%) and DOTF (yield of 31%) as the dominant by-product, and no furfuryl ethyl ether is detected. These results unambiguously suggest that higher Pd content on 1.4Pd/C prefers to catalyze the deep hydrogenation of furfuryl ethyl ether and DOF to TFEE and DOTF, respectively. When decreasing the amount of 1.4Pd/C catalyst used to 20 mg, the FEE yield was increased to 71%. Hence we conclude that the ability of Pd hydride towards hydrogenation or hydrogenolysis is likely associated with the reaction conditions employed, which affect the hydrogen dissociation and adsorption energy of surface H species. In general, low H<sub>2</sub> pressure and lower reaction temperature benefits to the hydrogenolysis reaction pathway. This result is different from the furfuryl methyl ether synthesis over Pd/C in methanol as reported by Pizzi et al.<sup>27</sup>, wherein high H<sub>2</sub> pressure up to 5 MPa was used. We surmise that the nature of solvent may also play an important role. We have done preliminary study on solvent effect on the ether yield by using methanol and 1-propanol as solvent. The results shows in Table S2 clearly shows that only 18% and 41% yield towards ethers were obtained in methanol and 1-propanol, respectively. In general the alcoholic solvent may affect the catalytic performance or substrate adsorption on Pd nanoparticles. Further study on the solvent effect on the reductive etherification performance need deeper investigation.



Fig. 6 2-(diethoxymethyl)furan (DOF) conversion and products distribution as a function of reaction time over 0.7Pd/C (A) and 1.4Pd/C(B). Reaction conditions: 10 mL of 0.24 M DOF ethanol solution; 60  $^{\circ}$ C; 0.3 MPa H<sub>2</sub>; 100 mg catalyst.



Fig. 7 Reusability of 0.7Pd/C catalyst for reductive etherification of furfural. Reaction conditions:10 mL of 0.24 M furfural/ethanol solution; 60  $^{\circ}$ C; 0.3 MPa H<sub>2</sub>; 100 mg catalyst, 2 h.

#### **Catalyst reusability**

Given the excellent performance of 0.7Pd/C in the synthesis of furfuryl ethyl ether, its reusability is also of interest from the viewpoint of practical application. We have tested the reusability of 0.7Pd/C catalyst and the results are shown in Figure 7. We found that the furfural conversion over this catalyst decreased slightly within 4 consecutive runs. It should be noticed that the selectivity of furfuryl ethyl ether (FEE) decreased remarkably from 83% to 55% after 4 runs, and the selectivity of FA increased from 10% to 38% simultaneously. Two possible reasons may be responsible for this selectivity decline. First the nature of PdH changed after several runs, which led to the lost in hydrogenolysis activity to some extent while the hydrogenation activity was enhanced. Theoretical studies on the electronic property and catalytic mechanism of PdH under hydrogen atmosphere will help understanding this complex behaviour. Second, the deposited carboneous species may alter the hydrophilicity of the carbon surface, which may change the hydrogenation and hydrogenolysis reaction pathway. Further study on improving the stability of this catalyst is ongoing.

#### Experimental

#### Materials.

Palladium (II) chloride (99.9%, J&K Chemical), TiO<sub>2</sub> (Anatase, Acros) and active carbon (surface area about 1300 m<sup>2</sup>/g, STREM Chemicals) were purchased from J&K Chemical Ltd. The SiO<sub>2</sub> support was Evonik Degussa Aerosil<sup>®</sup> 200 with surface area of 208 m<sup>2</sup>g<sup>-1</sup>.

#### **Preparation of catalysts**

Pd/C samples were prepared by a typical deposition– precipitation–reduction method<sup>50</sup>. In a typical preparation, 0.5 g of active carbon was dispersed in H<sub>2</sub>O (60 mL) with stirring. 0.116 mL of H<sub>2</sub>PdCl<sub>4</sub> aqueous solution (21.512  $g_{Pd}$  L<sup>-1</sup>) was added to the mixture, and then the mixture was stirred for 3 h. The final pH value of the suspension was adjusted to 10 by

DOI: 10.1039/C7GC03887A

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adding NaOH solution (1M). Then, NaBH<sub>4</sub> aqueous solution (NaBH<sub>4</sub>/Pd = 15, molar ratio) was added into the suspension and the mixture was stirred for another 0.5 h allowing for the full reduction of Pd<sup>2+</sup> species. Thus obtained catalyst was dried at 110 °C overnight. The Pd loading was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES). The samples were denoted as xPd/C (x = 0.3, 0.7, and 1.4 in wt.%). For comparison, Pd supported on some commonly used oxides were also prepared by the same method, namely, 0.8Pd/SiO<sub>2</sub>, 0.7Pd/TiO<sub>2</sub> and 0.9Pd/Al<sub>2</sub>O<sub>3</sub>.

#### Materials Characterizations

The power X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu Ka radiation ( $\lambda$ = 1.5405 Å) operated at 35 kV and 25 mA. Nitrogen adsorption-desorption isotherms at -196 °C were obtained on BELSORP-Max equipment. Prior to the measurement, the samples were first degassed at 300 °C under vacuum for 6 h. Specific surface areas (SSA) were calculated according to the BET method using five relative pressure points in the relative pressure range of 0.05-0.30. Micropore volume (Vmicro) was obtained by the t-plot method. Transmission electron microscopy (TEM) images were taken on a FEI Tecnai G<sup>2</sup> F30 microscope operating at 300 kV. The average Pd particle size was calculated by  $d_{TEM} = (\sum n_i d_i^3)/(\sum n_i d_i^2)$  by measuring at least 100 particles<sup>51</sup>. Pulse CO chemisorption was performed on a Micromeritics AutoChem 2910 to determine the metal dispersion of the reduced catalysts. Prior to measurement, the catalyst was reduced in a flow of 80 mL/min 10 vol.% H<sub>2</sub> in Ar at 80 °C for 2h and then cooled to 40 °C by flushing He for 2 h. Afterwards, CO gas pluses (5 vol.% in He) were introduced in a flow of 110 mL/min. The gas phase CO concentration was followed by thermal conductivity detector (TCD). The Pd loading was quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. About 25 mg catalysts were digested using 5 mL of aqua regia. The obtained solutions were diluted with deionized water to the desired Pd concentration.

#### **Catalytic tests**

The reductive etherification of furfural was conducted in a Teflon-lined (60 mL) steel batch reactor. No pretreatment on the catalysts was conducted prior to each reaction. The reactor was charged with 9.8 mL of ethanol, 0.2 mL of furfural and 100 mg of catalyst, and the mixture was stirred under 0.1-0.5 MPa H<sub>2</sub> pressure at 40-80 °C. After reaction for desired period, the H<sub>2</sub> was released and the liquid was diluted with ethanol before analysis. The products were analyzed with flame ionization detector (FID) and capillary column of DB-FFAP (30 m length and 0.25 mm internal diameter). The mass spectra of some products were recorded on Shimadzu GCMS-QP2010SE equipped with Rxi-5Sil MS column (30 m\*0.25 mm\*0.25 um).

#### Conclusions

In summary, we have demonstrated the successful synthesis of furfuryl ethyl ether from furfural and ethanol via reductive

etherification, which involves the acetalization/hydrogenolysis pathways in one-pot. A high yield of 81% furfuryl ethyl ether was achieved over 0.7 wt.% Pd/C under mild reaction conditions, i.e., 60 °C and 0.3 MPa H<sub>2</sub>. The remarkable advantage of this strategy compared with previous hydrogenation/etherification process lies in that much lower reaction temperature is required in this route thus preventing the sequential decomposition of furfuryl ethyl ether to other by-products such as levulinic acid or its esters. Detailed kinetics study suggests that 2-(diethoxymethyl)furan is the key intermediate, the formation of which is likely catalysed by the palladium hydride formed in situ. The hydrogenolysis of 2-(diethoxymethyl)furan will lead to the formation of ether, while this desirable reaction pathway competes with hydrogenation reactions that lead to the formation of furfural alcohol, tetrahydrofurfural alcohol and other saturated compounds. To achieve high yield of ether, a balanced protonic and hydrogenolysis activity of palladium hydride is required, which is highly related to the Pd loading, reaction temperatures and hydrogen pressure.

#### **Conflicts of interest**

There are no conflicts to declare.

#### Acknowledgements

We acknowledge the financial support from China Ministry of Science and Technology under contract of 2016YFA0202804 and the National Natural Science Foundation of China (Grant Nos. 21773067, 21533002).

#### Notes and references

- C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning and K. Egeblad, ChemSusChem, 2008, 1, 283.
- 2 M. Besson, P. Gallezot and C. Pinel, Chem. Rev., 2014, 114, 1827.
- 3 R. A. Sheldon, Catal. Today, 2011, 167, 3.
- 4 R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba and M. López Granados, Energy Environ. Sci., 2016, 9, 1144.
- 5 A. M. Robinson, J. E. Hensley and J. W. Medlin, ACS Catal., 2016, 6, 5026.
- 6 K.Yan, G. Wu, T. Lafleur and C. Jarvis, Renewable Sustainable Energy Rev., 2014, 38, 663.
- 7 L. Faba, E. Díaz and S. Ordóñez, Renewable Sustainable Energy Rev., 2015, 51, 273.
- 8 Y. Nakagawa, M. Tamura and K. Tomishige, ACS Catal., 2013, 3, 2655.
- 9 A. Bohre, S. Dutta, B. Saha and M. M. Abu-Omar, ACS Sustainable Chem. Eng., 2015, 3, 1263.
- 10 X. Hu, R. J. M. Westerhof, L. Wu, D. Dong and C.-Z. Li, Green Chem., 2015, 17, 219.
- 11 R. S. Karinen, A. O. I. Krause, K. Ekman, M. Sundell and R. Peltonen, Stud. Surf. Sci. Catal., 2000, 130, 3411.
- 12 W. Leitner, J. Klankermayer, S. Pischinger, H. Pitsch and K. Kohse-Hoinghaus, Angew. Chem., Int. Ed., 2017, 56, 5412.
- 13 Y. Wang, P. Zhang, G. Huang, Q. Yuan, Y. Guan and P. Wu, ACS Sustainable Chem. Eng., 2017, 5, 6645.
- 14 W. Yu, F. Lu, Q. Huang, R. Lu, S. Chen and J. Xu, Green Chem., 2017, 19, 3327.

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DOI: 10.1039/C7GC03887A

- 15 A. M. Ruppert, A. N. Parvulescu, M. Arias, P. J. C. Hausoul, P. C. A. Bruijnincx, R. J. M. K. Gebbink and B. M. Weckhuysen, J. Catal., 2009, 268, 251.
- 16 G. J. M. Gruter, US Patent 2010/0212217, 2010.
- 17 H. Wang, T. Deng, Y. Wang, Y. Qi, X. Hou and Y. Zhu, Bioresource Technol., 2013, 136, 394.
- 18 Z. Yuan, Z. Zhang, J. Zheng and J. Lin, Fuel, 2015, 150, 236.
- 19 Z. Wang and Q. Chen, Green Chem., 2016, 18, 5884.
- 20 P. Lanzafame, K. Barbera, S. Perathoner, G. Centi, A. Aloise, M. Migliori, A. Macario, J. B. Nagy and G. Giordano, J. Catal., 2015, 330, 558.
- 21 B. Xiang, Y. Wang, T. Qi, H.-Q. Yang and C.-W. Hu, J. Catal., 2017, 352, 586.
- 22 M. Rose, K. Thenert, R. Pfützenreuter and R. Palkovits, Catal. Sci. Technol., 2013, 3, 938.
- 23 S. Radhakrishnan, P. J. Goossens, P. C. Magusin, S. P. Sree, C. Detavernier, E. Breynaert, C. Martineau, F. Taulelle and J. A. Martens, J. Am. Chem. Soc., 2016, 138, 2802.
- 24 R. J. Haan and J.-P. Lange, US Patent 2011/0035991 A1, 2011.
- 25 E. R. Sacia, M. Balakrishnan and A. T. Bell, J. Catal., 2014, 313, 70.
- 26 D. Padovan, A. Al-Nayili and C. Hammond, Green Chem., 2017, 19, 2846.
- 27 R. Pizzi, R.-J. van Putten, H. Brust, S. Perathoner, G. Centi and J. van der Waal, Catalysts, 2015, 5, 2244.
- 28 M. Balakrishnan, E. R. Sacia and A. T. Bell, Green Chem., 2012, 14, 1626.
- 29 P. J. Lange, E. van der Heide, J. van Buijtenen and R. Price, ChemSusChem, 2012, 5, 150.
- 30 G. M. Gonzalez Maldonado, R. S. Assary, J. Dumesic and L. A. Curtiss, Energy Environ. Sci., 2012, 5, 8990.
- 31 V. E. Tarabanko, M. Y. Chernyak, I. L. Simakova, K. L. Kaigorodov, Y. N. Bezborodov and N. F. Orlovskaya, Russ. J. Appl. Chem., 2016, 88, 1778.
- 32 M. J. Climent, A. Corma, and S. Iborra, Chem. Rev., 2011, 111, 1072.
- 33 W. L. Howard and J. H. Brown, J. Org. Chem., 1961, 26, 1026.
- 34 S. Nishimura and T. Itaya, Chem. Commun., 1967, 232, 422.
- 35 V. Bethmont, F. Fache and M. Lemaire, Tetrahedron Lett., 1995, 36, 4235.
- 36 M. P. Doyle, D. J. DeBruyn and D. A. Kooistra, J. Am. Chem. Soc.,1972, 94, 3659.
- 37 V. Bethmont, C. Montassier and P. Marecot, J. Mol. Catal. A: Chem., 2000, 152, 133.
- 38 S. S. Mochalov, A. N. Fedotov, E. V. rofimova and N. S. Zefirov, Russ. J. Org. Chem., 2016, 52, 503.
- 39 Y. Fujii, H. Furugaki, E. Tamura, S. Yano and K. Kita, Bull. Chem. Soc. Jpn., 2005, 78, 456.
- 40 T. T. Pham, S. P. Crossley, T. Sooknoi, L. L. Lobban, D. E. Resasco and R. G. Mallinson, Appl. Catal. A: Gen., 2010, 379, 135.
- 41 M. Bakos, A. Gyomore, A. Domjan and T. Soos, Angew. Chem., Int. Ed., 2017, 56, 5217.
- 42 P. Weerachawanasak, O. Mekasuwandumrong, M. Arai, S.-I. Fujita, P. Praserthdam and J. Panpranot, J. Catal., 2009, 262, 199.
- 43 J. M. Rubio-Caballero, S. Saravanamurugan, P. Maireles-Torres, and A. Riisager, Catal. Today, 2014, 234, 233
- 44 B. L. Wegenhar, S. Liu, M. Thom, D. Stanley, and M. M. Abu-Omar, ACS Catal. 2012, 2, 2524
- 45 J.-I. Ishiyama, K. Esashika, Y. Senda and S. Imaizumi, Nippon Kagaku Kaishi, 1988, 1988, 126.
- 46 A. Valcarcel, F. Morfin, L. Piccolo, J. Catal. 2009, 263, 315
- 47 Z. A. Chase, J. L. Fulton, D. M. Camaioni, D. Mei, M. Balasubramanian, V.-T. Pham, C. Zhao, R. S. Weber, Y. Wang, and J. A. Lercher, J. Phys. Chem. C 2013, 117, 17603
- 48 L. Cerveny, Chem. Eng. Comm. 1989, 83, 31

- 49 M. A. Kulagina, P. A. Simonov, E. Yu. Gerasimov, R. I. Kvon, A. V. Romanenko, Colloids and Surfaces A: Physicohemical and Engineering Aspects, 2017, 526, 29
- 50 P. Zhang, Q. Yuan, L. Chen, T. Xue, Y. Guan and P. Wu, RSC Adv., 2016, 6, 65377.
- 51 J. M. M. Tengco, Y. K. Lugo-José, J. R. Monnier and J. R. Regalbuto, Catal. Today, 2015, 246, 9.

**8** | J. Name., 2012, **00**, 1-3



Furfuryl ethyl ether (FEE) was synthesized from furfural via reductive etherification in 81% yield over Pd/C catalyst under mild conditions.