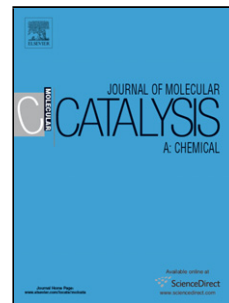


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Study on the reaction pathway in decarbonylation of biomass-derived 5-hydroxymethylfurfural over Pd-based catalyst

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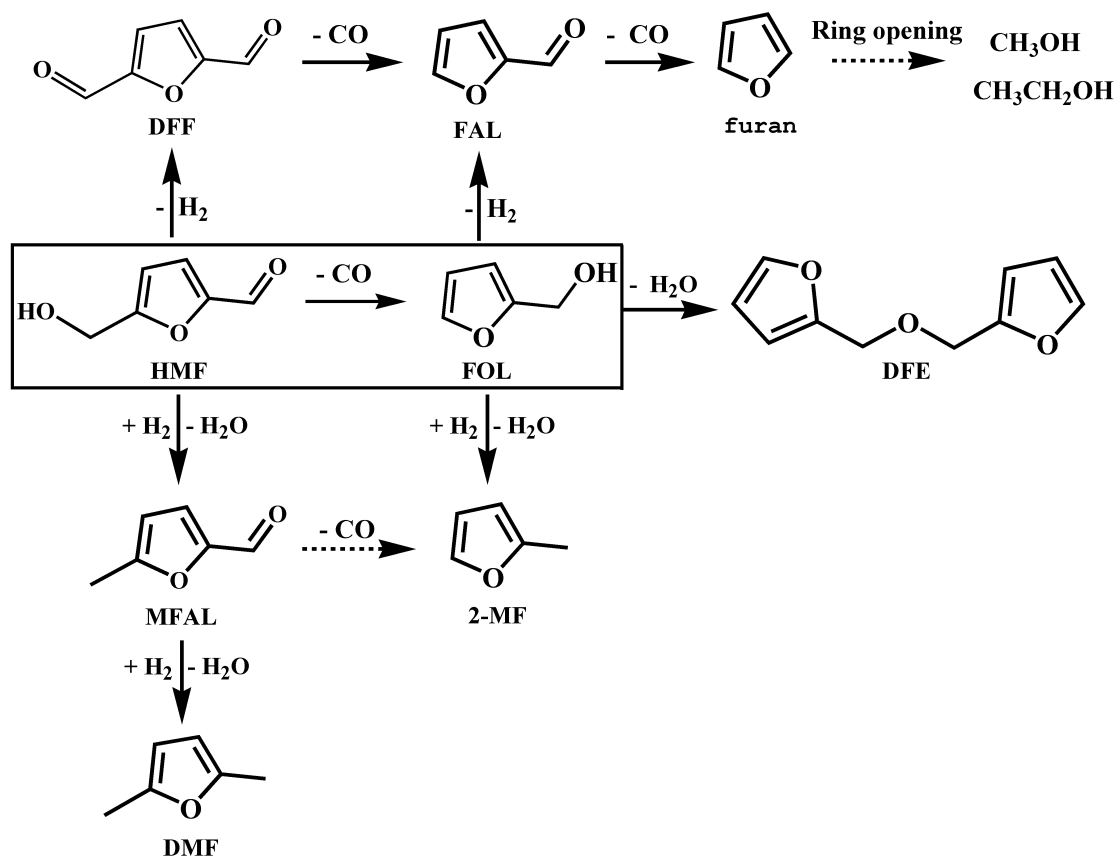
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Graphical abstract



Highlights

- An extensive product distribution is firstly examined in decarbonylation of HMF.
- The H₂ source was determined to be the hydroxymethyl dehydrogenation.
- The elimination path of -CH₂OH is sequential dehydrogenation and decarbonylation.
- The reactivity of the main intermediates was separately investigated.
- A comprehensive reaction pathway for HMF decarbonylation is proposed.

Abstract

An extensive product distribution is firstly examined in the process of 5-hydroxymethylfurfural (HMF) decarbonylation over Pd-based catalysts and some interesting results are obtained. The main side reactions are due to the high activity of the furan ring-branched hydroxymethyl, which could go through hydrogenolysis, dehydrogenation and etherification. The H₂ source was carefully explored and determined to be the hydroxymethyl dehydrogenation. The reactivity of the main intermediates was separately investigated and their evolution pathway was obtained. Noticeably, it is demonstrated that the elimination of the furanic ring-branched hydroxymethyl (in HMF or furfuryl alcohol) is completed by sequential dehydrogenation and decarbonylation via the intermediate of aldehyde (2, 5-diformylfuran or furfural). A comprehensive reaction pathway for HMF decarbonylation is proposed, which is significant for designing highly selective decarbonylation catalysts.

Keywords: 5-hydroxymethylfurfural; Decarbonylation; Reaction pathway; Pd

1. Introduction

Furfuryl alcohol (FOL) has been widely used for fine chemicals and polymer industries. The main applications of FOL are the production of thermostatic resins resistant to acids, bases and certain solvents; liquid resins for galvanic bath tub; synthetic fibers; farm chemicals; foundry binders; adhesives for plywood and furniture; also other fine chemical products such as Vitamin C and tetrahydrofurfuryl alcohol [1-5]. Presently, FOL is produced by hydrogenation of furfural (FAL). FAL and HMF, which are converted from Polymers of C₅ sugars and C₆ sugars respectively, are two important platform chemicals in the process of biomass conversion [6, 7]. The conversion technology of furfural has been already well

developed [7-11], while the production and application of HMF is limited to the development in its process chemistry. Decarbonylation of HMF to FOL provided another way to utilize the C₆ sugars.

The liquid-phase decarbonylation of HMF has been subjected to several studies which mainly focused on screening of catalysts or optimizing of the catalytic system, targeting a high decarbonylation yield [12-15]. Though an optimal FOL yield (94%) was obtained over an homogeneous compound [IrCl(cod)]₂PCy₃ [13] or heterogeneous Pd/SBA-15 [14], the byproducts was not analyzed in detail. Moreover, the high cost of the catalysts limits their application for large scale practices. Pd/Al₂O₃ has been widely used in the catalytic conversion, including hydrogenation [16-22] and hydrogenolysis [23] reactions, hydrodechlorination [24-27] reaction, oxidation [28-31] and reduction [32-34] reactions, reforming [35] and isomerization [36] reactions. Pd/Al₂O₃ exhibited high catalytic activity [29, 32, 37] and the strong metal-support interaction in Pd/Al₂O₃ leads to a good stability [26, 27]. The synergy of the metallic sites on Pd and the abundant Lewis acid sites on Al₂O₃ could induce high specific selectivity [35, 36]. Moreover, Pd/Al₂O₃ is available commercially [38], applicable for industrial practice. Noticeably, Pd/Al₂O₃ is efficient for decarbonylation reaction [39], but has not been used for HMF decarbonylation [12]. A clear understanding of the reaction mechanism and the origin of by-products are significantly important for the catalytic design for selectivity enhancement of the desired products. The reaction pathway in the process of HMF decarbonylation over Pd/Al₂O₃ was focused in this report.

Though the product distribution and the reaction pathway in the process of HMF decarbonylation has not been reported in the open literature, the reaction route of hydrogenation of HMF [40-42] and FAL [43-45] has been studied a lot and can provide some guidance. In the process of catalytic conversion of HMF to 2, 5-dimethylfuran (DMF), 5-methylfurfural (MFAL) is the necessary intermediate [40, 42, 46], which is similar with decarbonylation process. In previous works, some results on the behaviour of furfural hydrogenation and its intermediates (such as FOL, tetrahydrofurfuryl alcohol) over Cu-based catalysts were also reported [43, 47]. However, more reactions are involved and much behaviour of the intermediates evolution are different in the HMF decarbonylation. Furthermore, the transformation

path in HMF decarbonylation could also provide significant references for the conversion path of HMF or FAL into a series of value added furan-derived compounds through hydrogenation or oxidation reactions.

The aim of this work is to shed light on the product distribution and the reaction mechanism in the process of HMF decarbonylation, thus to provide an instruction for designing highly selective catalysts. The H₂ source was carefully explored and was determined to mainly from the dehydrogenation of the furan ring-branched hydroxymethyl, though with small amount of water gas shift reaction (WGS). Furthermore, the elimination mechanism of the furanic ring-branched hydroxymethyl was determined to be sequential dehydrogenation and decarbonylation via the intermediate of aldehyde. The evolution pathway of HMF and its main intermediates over Pd/Al₂O₃ was investigated detailedly and its applicability to Pd/C was also tested in order to obtain general results. As a result, the reaction pathway in the process of HMF decarbonylation was firstly proposed.

2. Experimental

2.1 Preparation of catalysts

Pd/ γ -Al₂O₃ and Pd/C were prepared by incipient wetness impregnation method. Firstly, the parent γ -Al₂O₃ or C powders were impregnated in aqueous solution of palladium nitrate for 5h. Then the precursors were dried at 80 °C for 16 h and calcinated at 400 °C for 2 h. The loading of Pd/Al₂O₃ and Pd/C is 1 wt%. The resulting catalysts were shaped by a tablet machine and crushed into granules of 20-40 mesh for activity test.

2.2 Characterization

The amount of H₂ adsorption on catalysts during reduction was approximately measured by thermal programmed desorption (TPD) of H₂ on Auto Chem. II 2920 equipment (Micromeritics, USA) with mass spectra. Prior to each measurement, 200 mg sample was reduced in situ by flowing H₂ at 200 °C for 2 h, cooling to 50 °C under continuous flow of H₂, and then purged with Ar for 0.5 h. TPD was conducted from 100 °C to 800 °C at a heat rate of 10 °C/min. Quantification was conducted by injecting a series of a certain amount of H₂, acquiring an standard curve and then comparing the measured peak area with the standard curve.

X-ray photoelectron spectroscopy (XPS) of calcined and reduced Pd/Al₂O₃ was measured on an AXIS ULTRA DLD (Kratos U. K.) spectrometer with Al K α radiation and a multichannel detector. The binding energies were calibrated with the C_{1s} peak at 284.6 eV as the reference.

TEM of reduced Pd/Al₂O₃ and used Pd/Al₂O₃ after reaction of HMF at 180 °C for 16h was performed with a field-emission transmission electron microscopy (FETEM, JEM-2011F) operating at 200 kv voltages. The pre-treated samples were suspended in ethanol with ultrasonic dispersion and deposited on copper grids amorphous carbon films. The average diameter of Pd nanoparticles was determined using the following equation [48].

$$d_{\text{Pd}} = \frac{\sum n_i \cdot d_i^3}{\sum n_i \cdot d_i^2}$$

2.3 Activity test

The catalytic tests were performed in a 50 ml stainless steel autoclave at a stirring speed of 300 rpm. Prior to reaction, the samples were reduced with pure H₂ flow at 200 °C for 2 h. In a typical run, the solvent (1, 4-dioxane), reactant and the catalysts were introduced into the autoclave. After purge with N₂ for several times, the reaction mixture was heated to 180 °C. After reaction, the autoclave was cooled down rapidly by ice-water bath. The gas was collected and analyzed by two GC (models 6890N, Agilent, USA) with a FID and a TCD detector respectively. The liquid was filtered and the mixture was analyzed by a GC (models 6890N, Agilent) equipped with a FID detector. The conversion and the selectivity were calculated by the area normalization method. The yield of FOL, 2-methylfuran (2-MF), FAL, 5-methylfurfural (MFAL) and HMF was also examined by an internal standard method with 1, 4-dioxane as the internal standard. The results calculated by the two methods were consistent.

3. Results and discussions

3.1 Reactivity of 5-hydroxymethylfurfural

XPS spectrum of Pd (3d_{3/2}, 3d_{5/2}) for calcined Pd/Al₂O₃ (Fig. 1) appears at 342.6 and 337.3 eV respectively, which is in good agreement with the values for Pd (II) state [49]. While the binding energy of 3d_{3/2} at 340.3 eV and 3d_{5/2} at 335.0 eV for reduced Pd/Al₂O₃ is consistent with the presence of zero-valence Pd [50]. It indicates that the

Pd-based catalysts could be reduced under the reduction conditions. Thus, it is considered that the Pd (0) species are proposed as responsible for the observed reactivity. The solvent was investigated previously and HMF exhibited good stability in 1, 4-dioxane [14]. Thus, 1, 4-dioxane was selected as the solvent to study the reaction mechanism in this work. Table 1 shows the conversion of HMF and products distribution in process of decarbonylation over Pd/Al₂O₃ and Pd/C. The two catalysts are all active for decarbonylation of HMF, exhibiting similar conversion values at 180 °C. Pd/C exhibits better selectivity of FOL than Pd/Al₂O₃ due to lower selectivity of difurfuryl ether (DFE) and polymers. This difference of selectivity may be derived from the different acidity of the two catalysts. An extensive product distribution was generated on the catalysts, which mainly falls into four categories: (1) furan ring-connecting DFE; (2) C₆ furan derivatives: 5-methylfurfural (MFAL), 2, 5-dimethylfuran (DMF) and 2, 5-diformylfuran (DFF); (3) C₅ furan derivatives: 2-methylfuran (2-MF), FAL and FOL; (4) C₄ furan. DFE indicates the etherification of FOL, as the acidic Al₂O₃ support could promote dehydration of hydroxyl group [51, 52]. On account of the carbon number, MFAL and DMF are deduced to from the hydrogenation/hydrogenolysis of HMF, while DFF demonstrates the dehydrogenation of hydroxymethyl in HMF. Generally, FAL and 2-MF indicates the cracking of one branched 'C-C' bond on the furan ring, while the appearance of furan demonstrates the cracking of the two branched 'C-C' (C2 and C5) in HMF. The selectivity of DFF is decreased with rising temperature and that of FAL and furan shows an adverse tendency. This indicates that FAL and furan could be produced by decarbonylation of DFF, as high temperature is in favour of decarbonylation. As a result, the first conversion step of HMF can be concluded as scheme 1. Pd/Al₂O₃ was reused for several times to investigate the deactivation for decarbonylation of HMF (Table S1). Though Pd/Al₂O₃ exhibits gradual deactivation, the products distribution is similar in these runs with decreased selectivity of side products. From TEM results showed in Fig. 2, the mean particle size of reduced Pd/Al₂O₃ is 5.3 nm, while it is increased to 6.6 nm after reaction, indicating slight sintering of palladium. This is consistent with the slight deactivation in stability results (Table S1).

3.2 The origins of hydrogen involved in the side reactions.

As quite amount of hydrogenation products are formed without external H₂, figuring out the H₂ source is the top priority to depict the reaction pathway. The H₂ might be derived from three ways: (1) WGS (Scheme 2(d)), (2) H₂ adsorbed on catalysts during reduction, and (3) dehydrogenation of the products. Trace water involved in WGS could be introduced by the dehydration step of hydrogenolysis, the moist biomass HMF or the solvent. The quantitative data of H₂ amount, including the consumption amount and the generation amount from the three sources in the process of HMF conversion (reactions in Table 1), is compared in Table 2. Assuming that FAL and furan were produced through dehydrogenation or sequential decarbonylation of the furan ring-branched hydroxymethyl, the H₂ amount generated from the pathway of dehydrogenation could be evaluated by the summing amount of DFF, FAL and furan. The H₂ amount produced through the WGS could be evaluated by the ratio of CO and CO₂ in the tail gas after decarbonylation of HMF. The H₂ amount adsorbed on the surface in the process of catalysts reduction could be approximately evaluated by the characterization of H₂-TPD. From the results in Table 2, it is evident that the H₂ amount from adsorption on catalyst and WGS is quite insufficient to involve in the hydrogenation side reactions for both catalysts. While the H₂ amount calculated from dehydrogenation could compensate for the insufficiency. This further verified that FAL and furan might be formed by the dehydrogenation route. It can be concluded that the dehydrogenation of the furan ring-branched hydroxymethyl is the main H₂ source, while the WGS and H₂ adsorption on the surface during the catalysts reduction also provide small amount of H₂.

3.3 Reactivity of furfural, furfuryl alcohol and 5-methylfurfural

FAL and FOL are used as model compounds to investigate the conversion pathways of the furan ring-branched -CHO and -CH₂OH respectively. Table 3 reports the catalytic data of tests with FAL over Pd/Al₂O₃ and Pd/C, which show similar product distribution at 180 °C. Furan is the main product, indicating that FAL goes mainly through decarbonylation. Besides, small amount of FOL and 2-MF are also produced, demonstrating the hydrogenation and the sequential hydrogenolysis path of FAL. The yield both of furan and 2-MF increases with the rise of temperature, as high temperature is beneficial to decarbonylation and hydrogenolysis. The H₂ involved in the hydrogenation/hydrogenolysis side reactions might mainly derive from WGS. H₂,

CO and CO₂ were all detected in the tail gas (Table S2), indicating the occurrence of WGS. It can be deduced that, similar with the main decarbonylation pathway of FAL, DFF mainly goes through decarbonylation as well. As a result, FAL can be produced by DFF decarbonylation. As DFF is the dehydrogenation product, the hydrogenation of the –CHO in DFF can be negligible. Therefore, the main reaction pathway of FAL and DFF can be described as Scheme 2(a).

The conversion of FOL (Table 4) is characterized by low conversion values with both catalysts, which show similar product distribution at 180 °C. The generation of 2-MF indicates the hydrogenolysis of FOL and the product DFE demonstrates the etherification of FOL. The higher yield both of 2-MF and DFE over Pd/Al₂O₃ than that over Pd/C may due to the stronger acidity of Pd/Al₂O₃. Besides, FAL and furan are also produced. The forming of FAL provides a direct evidence for the dehydrogenation pathway of FOL, which is similar with dehydrogenation of HMF to DFF. It can be concluded that FAL can come from DFF decarbonylation or FOL dehydrogenation. References have reported that tetrahydrofurfuryl alcohol [47] over Ni-based catalyst and FOL [43] over Cu-based catalyst can eliminate CO and H₂ to produce tetrahydrofuran and furan respectively. To make the elimination pathway of the branched –CH₂OH more clear, 0.2 MPa N₂ (RT) was used to make it possible to obtain the tail gas after reaction of FOL at 180 °C (Table 4). As a result, CO was detected (see Table S3) and is in approximately equimolecular portion with furan. Therefore, furan can be produced by sequential dehydrogenation and decarbonylation of FOL through the intermediate FAL. This is consistent with the dehydrogenation data in Table 2. The occurrence of WGS was also detected (Table S3), providing the H₂ source for hydrogenolysis of FOL. The conversion pathway of FOL can be described as Scheme 2(b).

In all the catalytic tests, MFAL (Table 5) gave rise to mainly 2-MF and small amount of furan and DMF. It is demonstrated that decarbonylation is the main pathway of MFAL. The formation of DMF indicates the sequential hydrogenation and hydrogenolysis path of the branched –CHO in MFAL. The H₂ involved in hydrogenolysis of MFAL might also mainly come from WGS (Table S4 see the tail gas composition). The main reaction pathway of MFAL can be described as Scheme 2(c). Conclusively, 2-MF can be generated both by MFAL decarbonylation and

hydrogenolysis of FOL. However, the concentration of MFAL is quite low when HMF is used as reactant and the H₂ involved in hydrogenolysis is mainly derived from dehydrogenation of the hydroxymethyl (Table 2). Therefore, 2-MF is probably mainly produced by FOL hydrogenolysis.

In all the tail gas composition (Table S1, Table S2 and Table S3), the percent of CO₂ with Pd/C is lower than that with Pd/Al₂O₃, indicating lower WGS activity of Pd/C. The amount of hydrogenolysis products on Pd/C is lower than that on Pd/Al₂O₃ for tests of FAL, FOL and MFAL (Table 3, Table 4, Table 5), because of both its lower acidity and lower WGS activity.

3.4 Reactivity of 2, 5-dimethylfuran, 2-methylfuran and furan

With both catalysts, DMF, 2-MF and furan (Table 6) are very stable, with low yield of lower weight molecules. The branched methyl in DMF and 2-MF could be break, while 2-MF also gave rise to trace FOL at higher temperature. The yield of methanol or ethanol in the tests of furan is higher than that in the test of DMF and 2-MF. On this basis, it may be hypothesized that methanol and ethanol is generated by ring-opening of furan.

On the basis of the experimental results in this work, a proper pathway of HMF decarbonylation is proposed in Scheme 3. The broken lines represent a minor pathway.

4. Conclusions

In summary, the versatile product distribution in HMF decarbonylation is resulted from the high activity of the hydroxymethyl in HMF or FOL. Moreover, dehydrogenation of the furan ring-branched hydroxymethyl makes the main H₂ source leading to hydrogenation/hydrogenolysis side reactions. The WGS reaction and H₂ adsorption on catalysts during reduction also provide small amount of H₂. The elimination of the furanic ring-branched hydroxymethyl (in HMF or FOL) is completed by sequential dehydrogenation and decarbonylation via the intermediate of

aldehyde (DFF or FAL). 2-MF is probably mainly derived from FOL hydrogenolysis. Etherification of FOL occurred only over the acidic Pd/Al₂O₃. The branched methyl in 2-MF and DMF can also be elimination at low conversion, and methanol is produced by ring-opening of furan. These results are helpful to understand the mechanism and reaction pathway of HMF decarbonylation, and to provide an instruction for design of new catalytic formulations.

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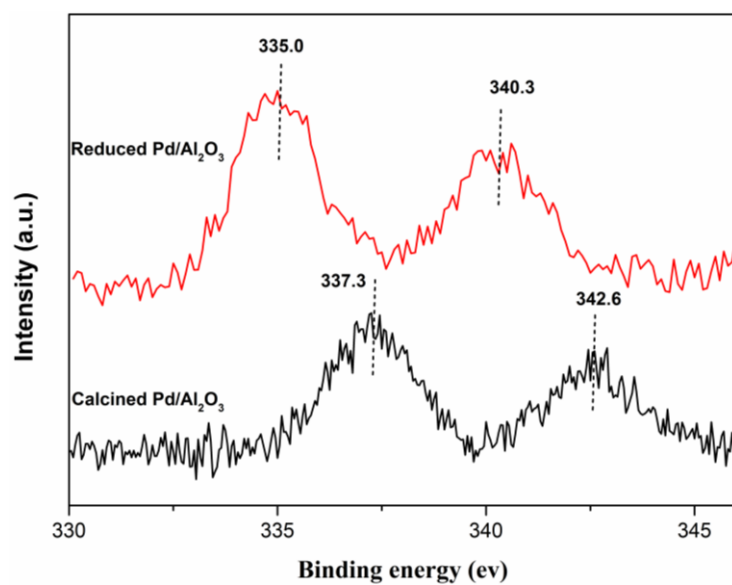


Fig. 1 XPS patterns of calcined and reduced Pd/Al₂O₃.

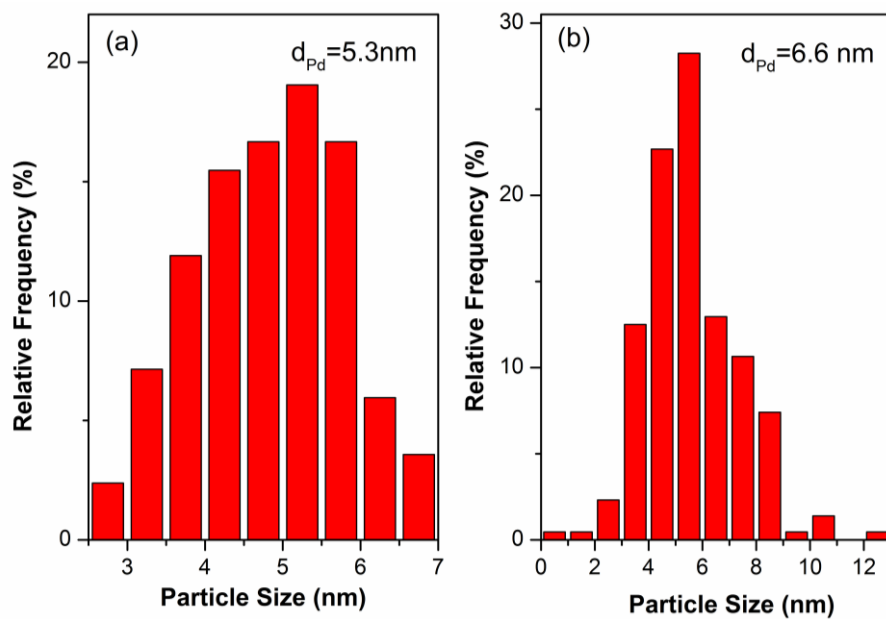
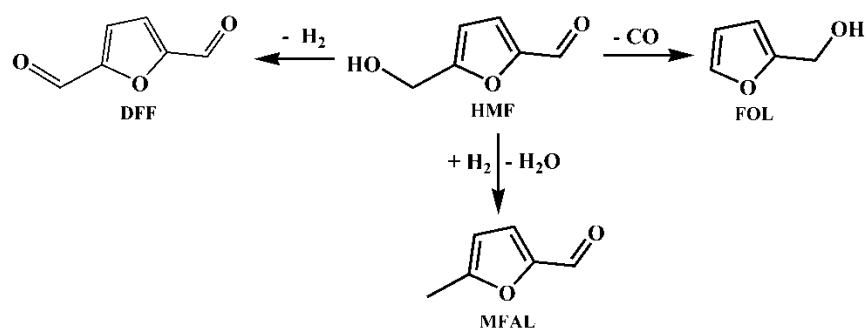
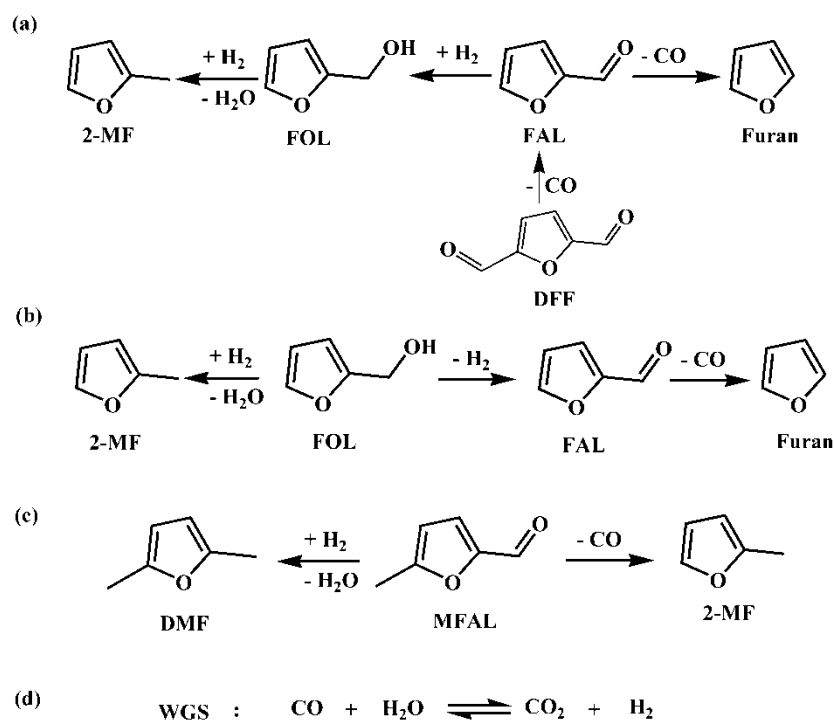


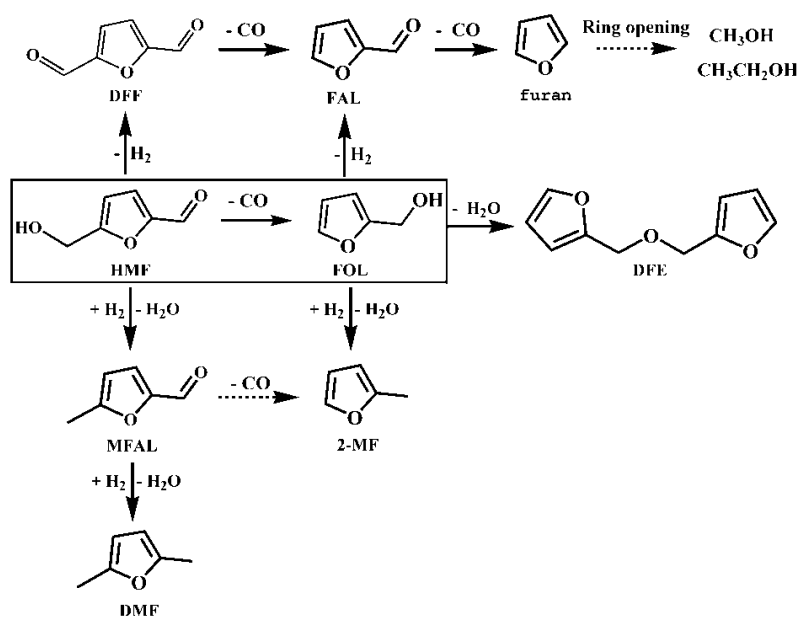
Fig. 2 Particle sizes of catalysts: (a) reduced Pd/Al₂O₃; (b) used Pd/Al₂O₃ after reaction of HMF at 180 °C for 16h.



Scheme 1. The evolution direction of HMF.



Scheme 2. The proposed reaction pathway for the intermediates.



Scheme 3. Proper reaction pathway proposed for HMF decarbonylation.

Table 1 Catalytic data for the tests of HMF decarbonylation.^a

T(°C)	Conv. (%)	Selectivity								
		FOL	DFE	FAL	fura n	DM F	MFA L	2- MF	DFE	Other s ^b
140	11.9	77.7	8.0	3.6	-	3.3	-	2.2	-	5.2
160	30.6	72.0	4.3	6.9	-	2.2	1.8	4.3	-	8.6
180	56.3	64.5	1.9	8.6	1.7	1.6	2.0	5.9	7.6	6.2
200	75.7	57.6	-	8.8	4.3	1.7	2.1	6.7	3.6	15.3
180 ^c	54.6	80.5	1.7	8.7	1.9	2.0	1.4	2.5	-	1.3

a Conditions: 1.2 g HMF, 25 g 1,4-dioxane, 0.25 g catalyst, N₂ atmospheric pressure (room temperature=RT), T=180 °C, t=16h.

b Others = methanol, ethanol (trace) and polymers.

c Catalyst: 1% Pd/C

HMF=5-hydroxymethylfurfural, FOL=furfuryl alcohol, DFF=2, 5-diformylfuran, FAL=furfural, DMF=2, 5-dimethylfuran, MFAL=5-methylfurfural, 2-MF=2-methylfuran, DFE= difurfuryl ether.

Table 2 Quantitative data of H₂ amount for reactions in Table 1.

Cat.	T (°C)	H ₂ /Hydrogenation ^a (mmol)	H ₂ /Dehydrogenatio ^b (mmol)	H ₂ /WGS ^c (mmol)	H ₂ /H ₂ -TPD ^d (mmol)
Pd/Al ₂ O ₃	140	0.14	0.13	0.066	0.012
	160	0.37	0.33	0.088	
	180	0.68	0.66	0.089	
	200	1.00	0.94	0.10	
Pd/C	180	0.51	0.64	0.048	0.010

^a H₂ involved in hydrogenation side reactions.

^b Calculated from the summing amount of DFF, FAL and furan.

^c Calculated based on the amount of CO and CO₂ in the tail gas.

^d Calculated from the quantitative data of H₂-TPD.

Table 3 Catalytic data for the tests of furfural.^a

Sample	T (°C)	Conv. (%)	Yield (%) ^b			
			fura	2-	FOL	others
	140	5.4	3.8	-	1.5	trace
Pd/Al ₂ O ₃	180	43.6	40.5	1.6	1.3	0.2
	200	78.6	75.1	2.4	1.0	0.4
Pd/C	180	40.1	39.5	0.2	0.2	0.3

a Conditions: 1.2 g FAL, 25 g 1,4-dioxane, 0.25 g catalyst, N₂ atmospheric pressure (RT), T=180 °C, t=16h.

b Others = methanol, ethanol (trace) and polymers.

FAL=furfural, 2-MF=2-methylfuran, FOL=furfuryl alcohol.

Table 4 Catalytic data for the tests of furfuryl alcohol.^a

Sample	T (°C)	Conv. (%)	Yield (%) ^b				
			fura	2-	FAL	DFE	others
Pd/Al ₂ O ₃	140	10.8	0.12	5.0	1.1	1.0	3.5
	180	9.3	2.7	3.3	0.5	2.4	-
	180 ^c	17.7	1.6	5.2	1.3	5.2	4.4
	200	25.1	5.0	10.8	0.9	3.5	5.0
Pd/C	180 ^c	7.5	2.2	2.0	3.4	-	trace

a Conditions: 1.2 g FOL, 25 g 1,4-dioxane, 0.25 g catalyst, N₂ atmospheric pressure (RT), T=180 °C, t=16h.

b others = methanol, ethanol (trace) and polymers.

c N₂:0.2 MPa (RT).

FOL=furfuryl alcohol, 2-MF=2-methylfuran, FAL=furfural, DFE= difurfuryl ether.

Table 5 Catalytic data for the tests of 5-methylfurfural.^a

Sample	T (°C)	Conv. (%)	Yield (%) ^b				
			fura	2-	FAL	DM	others
	140	5.1	-	4.5	-	0.6	-
Pd/Al ₂ O ₃	180	55.9	-	49.6	-	4.5	-
	200	83.2	0.8	78.3	1.30	2.7	0.2
Pd/C	180	53.5	1.7	50.8	-	0.9	0.1

a Conditions: 1.2 g MFAL, 25 g 1,4-dioxane, 0.25 g catalyst, N₂ atmospheric pressure (RT), T=180 °C, t=16h.

b others = methanol, ethanol (trace) and polymers.

MFAL=5-methylfurfural, 2-MF=2-methylfuran, FAL=furfural, DMF=2, 5-dimethylfuran.

Table 6 Catalytic data for the tests of 2, 5-dimethylfuran, 2-methylfuran and furan.^a

Feed	Cat.	T (°C)	Yield				
			Methanol	Ethanol	furan	2-MF	FOL
DMF	Pd/Al ₂ O ₃	140	trace	trace	0.2	trace	-
		180	trace	trace	0.2	0.1	-
	Pd/C	180	trace	trace	0.2	0.2	-
2-MF	Pd/Al ₂ O ₃	140	0.1	0.1	0.2	-	-
		180	trace	0.1	0.1	-	0.4
	Pd/C	180	trace	-	trace	-	0.2
furan	Pd/Al ₂ O ₃	140	0.3	trace	-	-	-
		180	1.0	0.2	-	-	-
	Pd/C	180	0.2	trace	-	-	-

a Conditions: 1.2 g substrate, 25 g 1,4-dioxane, 0.25 g catalyst, N₂ atmospheric pressure (RT), T=180 °C, t=16h.

DMF=2, 5-dimethylfuran, 2-MF=2-methylfuran, FOL=furfuryl alcohol.