

# Towards understanding the reaction pathway in vapour phase hydrogenation of furfural to 2-methylfuran

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## Abstract

The reactivity of furfural and its reaction intermediates is separately investigated in a fixed-bed reactor over a commercial catalyst (C<sub>1</sub>: Cu/Zn/Al/Ca/Na = 59:33:6:1:1, atomic ratio) and a self-made multicomponent one (C<sub>2</sub>: Cu/Cr/Ni/Zn/Fe = 43:45:8:3:1, atomic ratio). Some interesting results are obtained in this work. Firstly, both furfural and furfuryl alcohol can eliminate carbon monoxide to produce furan. Secondly, tetrahydrofuran and 2-methyltetrahydrofuran are all very stable, and *n*-butanol mainly derives from furan rather than tetrahydrofuran. Thirdly, 2-pentanone, 2-methyltetrahydrofuran, 1-pentanol and 2-pentanol are all the hydrogenation products of 2-methylfuran. Finally, with C<sub>2</sub> catalyst containing the Ni element, the main reaction product of tetrahydrofurfuryl alcohol is tetrahydrofuran, while  $\delta$ -valerolactone is the main product with C<sub>1</sub> one. This work has unified some conflicting mechanisms and discussed the origin of some interesting products, which is important to understand the mechanism and reaction pathway of furfural hydrogenation, and to provide an instruction for the design of new catalytic formulations.

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**Keywords:** Furfural; Hydrogenation; 2-Methylfuran; Reaction pathway; Vapour phase

## 1. Introduction

Furfural is a versatile compound in the fragrance industry, and the vapour phase hydrogenation of furfural is commonly used to produce 2-methylfuran, furfuryl alcohol and tetrahydrofuran [1,2]. 2-Methylfuran is an important intermediate in fine chemical industrial practices, which is mainly used for the synthesis of crysanthemate pesticides, perfume intermediates and chloroquine lateral chains in medical intermediates [3–5]. Furfuryl alcohol is mainly used for the production of dark thermostatic resins resistant to acids, bases and various solvents; liquid resins for galvanic bath-tube, and resins used for strengthening ceramics. It is also widely used as a solvent, e.g. phenolic resins or pigments of low solubility [2]. Tetrahydrofuran is mainly used as raw material for spandex fibers and polyurethane elastomers,

and as a solvent (it is a strong dissolving agent for both synthetic and natural resins) [6].

Many researchers [1,2,7–11] have reported some important results on the vapour phase hydrogenation of furfural, and recently we have developed a coupling process to synthesis 2-methylfuran and  $\gamma$ -butyrolactone simultaneously, in which the hydrogenation of furfural and the dehydrogenation of 1,4-butanadiol are combined at the same reactor [3–5]. However, furfural produces not only the desired products, but also many by-products of carbon monoxide, *n*-butanol, ethanol, pentanol, pentanone and so on both in the single process and the coupling one. Given the fact that the potential for enhancement of selectivity of the desired products by concentrating on the composition of catalysts as well as the operating conditions for the furfural hydrogenation [1–5,7–11] appears more or less limited, considerable effort should also be made into the reaction mechanism and the true origin of by-products. However, there are few experimental data reported in the open literature on the reaction pathway of vapour phase hydrogenation of furfural. In

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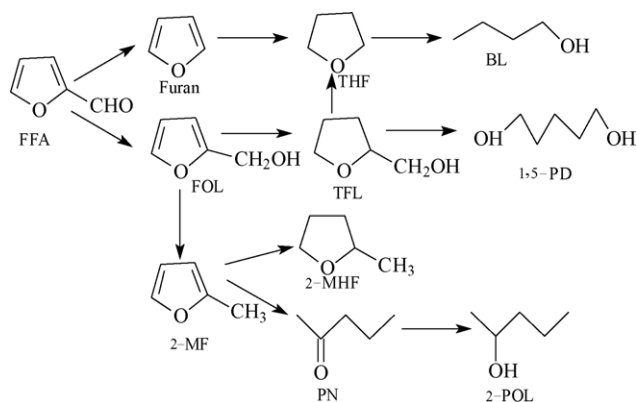


Fig. 1. Reaction pathway proposed in the literature for furfural hydrogenation. FFA, furfural; THF, tetrahydrofuran; BL, *n*-butanol; FOL, furfuryl alcohol; TFL, tetrahydrofurfuryl alcohol; 1,5-PD, 1,5-pentanediol; PN, 2-pentanone; 2-MHF, 2-methyltetrahydrofuran; 2-MF, 2-methylfuran; 2-PL, 2-pentanol.

addition, the debates about the origin of some by-products, such as *n*-butanol, carbon monoxide and ethanol, still exist. Fig. 1 illustrates the reaction pathway generally proposed for vapour phase hydrogenation of furfural [2,12–15], which is not comprehensive and contains some conflicting points.

In previous papers, some results on the behaviour of furfural and its reaction intermediates (such as, furfuryl alcohol, 2-methylfuran, tetrahydrofurfuryl alcohol) over Ni-Cu or Fe-Cu alloy catalysts are reported [12–15]. However, the alloy catalyst is unable to apply in industrial practices because of its serious deactivation phenomena. Cu-Cr catalyst has been successfully utilized for the hydrogenation reaction of furfural in practices [5,7], which exhibits excellent yield of 2-MF and long life. Cu-Zn catalyst is also an industrial catalyst for hydrogenation and has been traditionally used for methanol synthesis [16–21]. Recently, it has been used for the hydrogenation process other than methanol synthesis, and shows good performance [22,23]. During 2003–2004, we have successfully used the Cu-Zn catalyst for the hydrogenation of furfural [3,4].

The aim of this work is to unify some conflicting mechanisms, discuss the origin of some products, such as *n*-butanol, carbon monoxide and ethanol, and provide an instruction for the design of new catalytic formulations. In order to obtain general data, a commercial Cu-Zn catalyst ( $C_1$ ) and a self-made multicomponent Cu-Cr one ( $C_2$ ) are used. The two catalysts have been investigated in reaction conditions of industrial interest, which do not show any scale-up problems or deactivation phenomena with increasing time-on-stream. The reactivity of furfural and its main intermediates is separately investigated over the two catalysts to shed light on the reaction mechanism of furfural hydrogenation.

## 2. Experimental

### 2.1. Preparation of catalysts

The atomic compositions of the commercial catalyst ( $C_1$ ) and of the self-made multicomponent one ( $C_2$ ) were Cu/Zn/Al/Ca/Na = 59:33:6:1:1 and Cu/Cr/Ni/Zn/Fe = 43:45:8:3:1

(atomic ratio), respectively.  $C_2$  was prepared via the coprecipitation method. In a typical preparation procedure, a solution of mixed  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_3$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Fe}(\text{NO}_3)_3$  (1 M of total metal ions) was used as metal precursors, with a 1 M  $(\text{NH}_4)_2\text{CO}_3$  solution added as the precipitating agent. The flow rates of the two solutions were adjusted to give a constant pH of about 6.0. After precipitation, the suspension was maintained at 45 °C for 4 h to complete the aging step. The precipitate was washed, dried at 100–110 °C for 12 h and then calcined at 350 °C for 4 h in air atmosphere.

### 2.2. Catalytic test

The two fresh catalysts were shaped with a pressure of 40 MPa by a tablet machine and then crushed to 20–40 mesh. The catalytic tests were carried out in a tubular fixed-bed reactor (length of 500 mm and i.d. of 12 mm). Before the reaction, 5.0 g of catalyst packed in reactor was activated in situ at atmospheric pressure in a flow of  $\text{H}_2/\text{N}_2$  (5:95, v/v) stream, and the temperature was progressively increased from ambient temperature to 270 °C. After reduction, the gas flow was switched to pure hydrogen. The reactants were pumped to a vapourizer, mixed with pure hydrogen and then introduced into the reactor. The liquid products in the ice trap were identified with a GC/MS (GC6890A/5973MSD, HP, USA), and the contents were determined by an Agilent 6890N (Agilent, HP) equipped with a flame ionization detector (FID) and a J&W DB-WAX 30 m × 0.32 mm capillary column. The gaseous products were determined by a SP-2000 gas chromatograph (Ruihong Analyser Co., Shandong, PR China) equipped with a flame ionization detector (FID) and a column (3.0 mm × 2.0 m) filled with Chromosorb 101, and a GC-920 gas chromatograph (Shanghai Analyser Co., PR China) equipped with a thermal conductivity detector (TCD) and a 13 × molecular sieve packed column (3.0 mm × 1.5 m).

## 3. Results and discussion

### 3.1. Reactivity of furfural and furfuryl alcohol

As shown in Table 1, the two catalysts are all active in the hydrogenation of furfural, exhibiting nearly complete conversion in the range of 200–300 °C.  $C_1$  catalyst has better yield of 2-methylfuran than  $C_2$  catalyst, with a maximum yield (87.0%) at 250 °C. There are some results [24–27] concerning the production of furan by decarbonylation of furfural over Pd or Pt-based catalysts. Literature [12] reported that Ni-Cu alloy catalyst exhibited high selectivity of furfural to furan when the temperature was over 200 °C. Furan is also produced over the Cu-based catalysts in this work, furthermore,  $C_2$  catalyst produces more furan than  $C_1$  one probably because of containing Ni element.

The conversion of furfuryl alcohol with the two catalysts is over 96% from 220 to 300 °C (Table 2). The yield of 2-methylfuran with  $C_1$  catalyst is also higher than  $C_2$  one, and  $C_2$  catalyst also produces more furan than  $C_1$  one. References [14,28] reported that tetrahydrofurfuryl alcohol could eliminate carbon monoxide and hydrogen to produce tetrahydrofuran

Table 1  
Catalytic data for the test of furfural hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	T (°C)	Conversion (%)	Yield (%)								
			2-MF	Furan	2-MHF	THF	PN	PL	BL	FOL	Others
C <sub>1</sub>	200	99.4	66.1	0.1	0.3	–	0.3	2.5	0.4	19.6	10.1
	220	99.6	70.9	0.1	0.3	–	0.3	3.5	0.8	10.3	13.4
	250	99.7	87.0	0.1	0.4	–	2.2	1.0	0.3	5.0	3.7
	270	99.8	82.2	0.2	0.4	–	5.4	1.8	0.2	4.1	5.5
	300	99.7	77.6	0.3	0.2	0.4	5.8	8.0	0.9	1.5	5.0
C <sub>2</sub>	200	99.6	67.0	21.5	4.2	–	0.5	0.8	1.3	3.0	1.3
	220	99.2	57.2	21.3	5.2	–	0.9	0.8	1.7	8.1	4.0
	250	99.6	36.1	24.8	4.1	0.7	12.4	3.2	6.9	6.3	5.1
	270	99.6	15.5	22.5	2.6	1.1	24.7	4.9	11.4	2.6	14.3
	300	99.9	7.5	4.6	2.3	1.0	27.8	4.9	5.1	1.9	44.8

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.3 h<sup>-1</sup>, H<sub>2</sub>:furfural = 25 (molar ratio). 2-MF, 2-methylfuran; 2-MHF, 2-methyltetrahydrofuran; THF, tetrahydrofuran; PN, 2-pentanone; PL, 1-pentanol + 2-pentanol; BL, *n*-butanol; FOL, furfuryl alcohol.

Table 2  
Catalytic data for the test of furfuryl alcohol hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	T (°C)	Conversion (%)	Yield (%)							
			2-MF	Furan	2-MHF	THF	PN	PL	BL	Others
C <sub>1</sub>	200	84.4	70.2	0.2	0.1	–	–	2.3	0.5	11.1
	220	98.3	92.3	0.3	0.3	–	0.8	1.1	0.1	3.4
	250	98.1	92.7	0.5	0.3	–	1.2	0.7	0.2	2.5
	270	96.1	84.2	1.0	0.2	–	1.7	1.6	0.3	7.1
	300	97.8	78.8	2.4	0.4	0.2	5.1	3.7	1.2	6.0
C <sub>2</sub>	200	96.6	70.9	18.6	4.0	0.1	0.4	0.1	0.5	2.0
	220	96.8	59.8	22.5	5.1	0.1	2.0	1.5	3.4	2.4
	250	99.1	49.7	35.2	2.5	0.5	3.7	0.9	3.0	3.6
	270	97.2	43.0	28.7	1.9	0.4	7.3	3.5	8.5	3.9
	300	97.8	15.4	31.3	2.2	1.6	7.6	1.9	9.6	28.2

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.3 h<sup>-1</sup>, H<sub>2</sub>:furfuryl alcohol = 25 (molar ratio).

over Ni-based catalyst. According to this idea, furfuryl alcohol can also eliminate carbon monoxide and hydrogen to produce furan.

In this work, carbon monoxide is detected in the gaseous products in reactions of both furfural and furfuryl alcohol, and it is in approximately equimolecular portion with furan. Therefore, furan comes from not only furfural but also furfuryl alcohol. In our recent work [29], we have pointed out that the carbon monoxide content accumulated in the recycling tail gas system can suppress the activity of Cu-based catalyst, which is a great disadvantage for the formation of desired products. For this reason to enhance the performances of catalysts or develop new catalysts, it will be very important to control the capacity to favour the decarbonylation reaction.

### 3.2. Reactivity of *n*-butanol, furan and tetrahydrofuran

The hydrogenation of *n*-butanol leads to the formation with good yield of *n*-butanal (Table 3), which takes place notwithstanding the large excess of hydrogen present. It is reported that *n*-butanal can give rise to high amounts of ethanol (by hydrogenolysis) over Cu-Cr catalyst [6]. In this work, ethanol is also detected in the products, furthermore, the Cu-Cr catalyst

(C<sub>2</sub>) exhibits higher yield than the Cu-Zn catalyst (C<sub>1</sub>), with formation of ethanol. Therefore, it is concluded that ethanol also derives from *n*-butanal in this experiment.

With both catalysts, the hydrogenation of furan (Table 4) is characterized by relatively high conversion values. The main products are *n*-butanol, *n*-butanal, tetrahydrofuran, ethanol and hydrocarbon.

Table 3  
Catalytic data for the test of *n*-butanol hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	T (°C)	Conversion (%)	Yield (%)			
			BA	EL	HC	Others
C <sub>1</sub>	220	4.2	4.1	–	0.1	–
	250	9.7	9.3	–	0.4	–
	270	17.0	15.2	–	1.8	–
	300	34.1	25.3	0.1	8.7	–
C <sub>2</sub>	220	11.1	3.5	0.5	7.1	–
	250	56.5	2.5	0.5	53.5	–
	270	98.8	0.6	0.1	97.6	0.5
	300	98.8	0.3	0.1	98.3	0.1

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.2 h<sup>-1</sup>, H<sub>2</sub>:*n*-butanol = 15 (molar ratio). BA, *n*-butanal; EL, ethanol; HC, hydrocarbon.

Table 4  
Catalytic data for the test of furan hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	T (°C)	Conversion (%)	Yield (%)						
			THF	BA	BL	EL	HC	Others	
C <sub>1</sub>	220	16.8	0.1	3.4	9.3	-	1.9	2.1	
	250	28.4	0.2	4.2	17.2	-	6.1	0.7	
	270	39.1	0.4	4.5	23.2	0.1	9.1	1.8	
	300	83.7	0.8	9.7	31.2	0.1	37.0	4.9	
C <sub>2</sub>	220	64.7	16.2	3.6	18.6	0.5	24.6	1.2	
	250	96.9	11.4	2.3	39.4	0.3	40.7	2.8	
	270	96.3	4.5	0.8	8.4	0.1	82.2	0.3	
	300	99.7	0.7	0.1	8.1	0.1	90.5	0.2	

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.1 h<sup>-1</sup>, H<sub>2</sub>:furan = 35 (molar ratio).

Table 5  
Catalytic data for the test of tetrahydrofuran hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	T (°C)	Conversion (%)	Yield (%)			
			BL	BA	HC	Others
C <sub>1</sub>	220	0.4	0.1	-	0.1	0.2
	250	1.1	0.2	-	0.7	0.2
	270	2.7	0.1	0.1	2.4	0.1
	300	9.6	0.1	0.1	9.2	0.2
C <sub>2</sub>	220	0.4	0.1	0.1	0.1	0.1
	250	1.3	0.2	0.1	1.0	-
	270	2.9	0.4	-	2.5	-
	300	7.9	0.4	-	7.5	-

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.2 h<sup>-1</sup>, H<sub>2</sub>:tetrahydrofuran = 20 (molar ratio).

As shown in Table 5, tetrahydrofuran is very stable (from 220 to 300 °C) with low yield of *n*-butanol and *n*-butanal, and there is a trace of ethanol in the products. The previous researchers [2,30] thought that the *n*-butanol mainly came from tetrahydrofuran. However, the good yield of *n*-butanol (Table 4) and the high stability of tetrahydrofuran (Table 5) indicate that *n*-butanol mainly comes from furan rather than tetrahydrofuran.

Literature [6] reported that the hydrogenation of tetrahydrofuran over two Cu-Cr catalysts (from 245 to 275 °C) was characterized by low conversion values, with the formation mainly

of ethanol, while *n*-butanol was never detected. Furthermore, it was mentioned in the same literature that *n*-butanal could give rise to high amount of ethanol by hydrogenolysis reaction. In this work, tetrahydrofuran is also very stable with low yield of *n*-butanol and *n*-butanal, and there is a trace of ethanol (Table 5). So, it is thought that *n*-butanal may be the intermediate of tetrahydrofuran to ethanol and *n*-butanol, namely, tetrahydrofuran may hydrogenate to produce little *n*-butanal firstly and then *n*-butanal gives rise to ethanol by relatively high conversion over the two Cu-Cr catalysts in literature [6]. The Cu-Cr catalysts exhibit higher selectivity of ethanol than that of *n*-butanol,

Table 6  
Catalytic data for the test of 2-methylfuran hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	T (°C)	Conversion (%)	Yield (%)					
			PN	2-MHF	1-PL	2-PL	HC	Others
C <sub>1</sub>	126	1.9	1.4	0.1	-	-	0.4	-
	220	33.3	15.8	0.2	7.4	8.1	0.9	0.9
	250	36.4	20.9	0.3	5.5	6.0	2.7	1.0
	270	63.4	41.6	0.3	5.5	7.0	5.9	3.1
	300	84.6	45.2	0.2	3.6	6.2	23.7	5.7
C <sub>2</sub>	220	72.8	38.6	8.8	2.8	20.5	1.9	0.2
	250	91.7	56.6	5.1	0.7	24.9	3.6	0.8
	270	95.9	52.7	2.7	0.3	14.2	9.6	16.4
	300	97.5	22.4	0.7	0.3	3.0	23.9	47.2

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.2 h<sup>-1</sup>, H<sub>2</sub>:2-methylfuran = 20 (molar ratio). 1-PL, 1-pentanol.

and it may be that *n*-butanol is too little to detect with gas chromatograph equipped with packed column. The catalysts in this experiment exhibit higher selectivity of *n*-butanol than that of ethanol.

### 3.3. Reactivity of 2-methylfuran, 2-methyltetrahydrofuran, 2-pentanone and 2-pentanol

There are several standpoints about the hydrogenation products of 2-methylfuran. Wilson [15] thought that 2-methyltetrahydrofuran, 2-pentanone and 2-pentanol were the hydrogenation products of 2-methylfuran over Ni-based catalyst. Adkins [31] obtained 2-methyltetrahydrofuran, 1-pentanol and 2-pentanol in the hydrogenation of 2-methylfuran at 200 °C over Cu-Cr catalyst. 2-Pentanone, 2-methyltetrahydrofuran, 1-pentanol and 2-pentanol are all the hydrogenation products of 2-methylfuran, and 2-pentanone and pentanol are main products in Table 6. This results indicate that ring fission is easier than ring saturation over the Cu-based catalysts. Literature [15] showed that the chief hydrogenation product of 2-methylfuran was 2-methyltetrahydrofuran (86% yield) at 100 °C over Ni-based catalyst, but when the temperature was raised, the quantity decreased and 2-pentanone appeared in increasing amounts attaining a maximum (75% yield) at about 185 °C. Along with the 2-pentanone, a small quantity of its reduction product, 2-pentanol, was also formed. In this work, the conversion of 2-methylfuran is low (about 2%) over C<sub>1</sub> catalyst below 200 °C, with the main formation of 2-pentanone, while 2-methyltetrahydrofuran is very little. As mentioned above, either 2-methyltetrahydrofuran or 2-pentanone can be the main product depending on catalysts and reaction conditions.

From 220 to 300 °C, the conversion of 2-methyltetrahydrofuran is low over the two catalysts, especially over C<sub>1</sub> one (Table 7). The main hydrogenation products of 2-methyltetrahydrofuran are 2-pentanone and hydrocarbon. These above results are in accordance with those of reference [31].

Table 8 presents the catalytic data for the test with 2-pentanone, and the hydrogenation products are 2-pentanol and hydrocarbon, etc. As shown in Table 9, 2-pentanol is characterized by relatively high dehydrogenation conversion values,

Table 7  
Catalytic data for the test of 2-methyltetrahydrofuran hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	<i>T</i> (°C)	Conversion (%)	Yield (%)		
			PN	HC	Others
C <sub>1</sub>	220	0.4	0.1	0.1	0.2
	250	0.6	0.2	0.2	0.2
	270	1.8	0.4	1.0	0.4
	300	4.3	0.5	3.4	0.4
C <sub>2</sub>	220	5.8	1.7	3.1	1.0
	250	18.4	4.7	12.4	1.3
	270	44.1	11.3	28.3	4.5
	300	60.7	8.8	47.3	4.6

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.2 h<sup>-1</sup>, H<sub>2</sub>:2-methyltetrahydrofuran = 30 (molar ratio).

Table 8  
Catalytic data for the test of 2-pentanone hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	<i>T</i> (°C)	Conversion (%)	Yield (%)		
			2-PL	HC	Others
C <sub>1</sub>	220	70.3	13.6	15.0	41.7
	250	73.8	5.2	45.1	23.5
	270	79.5	4.0	49.3	26.2
	300	86.4	1.9	77.5	7.0
C <sub>2</sub>	220	48.5	24.4	2.1	22.0
	250	54.9	19.7	6.3	28.9
	270	72.8	6.6	13.4	52.8
	300	87.2	1.9	39.7	45.6

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.2 h<sup>-1</sup>, H<sub>2</sub>:2-pentanone = 30 (molar ratio).

Table 9  
Catalytic data for the test of 2-pentanol hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	<i>T</i> (°C)	Conversion (%)	Yield (%)		
			PN	HC	Others
C <sub>1</sub>	220	71.6	65.3	5.6	0.7
	250	80.0	60.0	12.4	7.6
	270	91.2	47.1	24.2	19.9
	300	96.6	32.5	51.6	12.5
C <sub>2</sub>	220	76.4	47.9	5.5	23.0
	250	83.8	35.9	12.7	35.2
	270	95.8	24.0	22.2	49.6
	300	98.9	17.3	43.8	37.8

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.2 h<sup>-1</sup>, H<sub>2</sub>:2-pentanol = 30 (molar ratio).

which takes place notwithstanding the large excess of hydrogen present.

### 3.4. Reactivity of tetrahydrofurfuryl alcohol

References [14,28,32] reported that tetrahydrofurfuryl alcohol could eliminate the side chain with formation of tetrahydrofuran over Ni-Cu or Co-Cu alloy catalysts. With C<sub>2</sub> catalyst containing the Ni element, the main reaction product is tetrahydrofuran, while δ-valerolactone is the main product with C<sub>1</sub> one (Table 10). Now there is still no explicit clue to the origin of

Table 10  
Catalytic data for the test of tetrahydrofurfuryl alcohol hydrogenation with C<sub>1</sub> and C<sub>2</sub><sup>a</sup>

Catalyst	<i>T</i> (°C)	Conversion (%)	Yield (%)			
			THF	VL	HC	Others
C <sub>1</sub>	220	5.0	0.1	2.7	0.2	2.0
	270	30.5	0.2	26.4	0.2	3.7
	300	55.1	0.5	47.4	0.4	6.8
C <sub>2</sub>	220	23.5	16.6	3.5	0.1	3.3
	270	96.4	77.2	1.3	6.5	11.4
	300	99.5	60.0	0.9	34.3	4.3

<sup>a</sup> Reaction conditions: atmosphere, LHSV = 0.3 h<sup>-1</sup>, H<sub>2</sub>:tetrahydrofurfuryl alcohol = 25 (molar ratio). VL, δ-valerolactone.

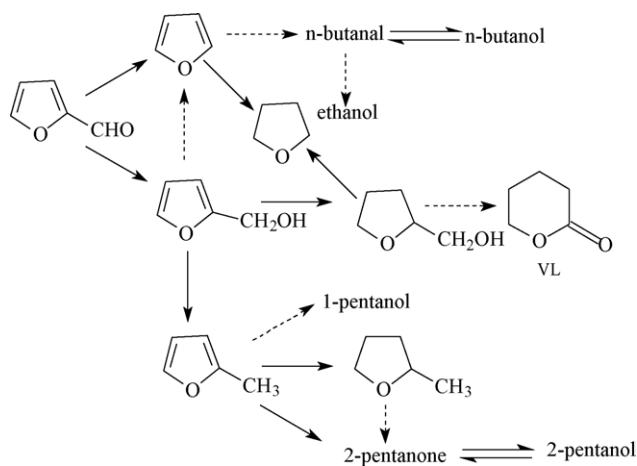


Fig. 2. Proper reaction pathway proposed for furfural hydrogenation. VL,  $\delta$ -valerolactone.

$\delta$ -valerolactone. Literature [2] reported that tetrahydrofurfuryl alcohol could hydrogenate to 1,5-pentanediol. In this work, there is a little of 1,5-pentanediol detected. Recently, we have reported some results on the dehydrogenation of 1,4-butanediol to produce  $\gamma$ -butyrolactone [3,4]. It is found that the conversion of 1,4-butanediol is nearly 100% over Cu-based catalyst. Applying this idea to the present work,  $\delta$ -valerolactone may come from the dehydrogenation of 1,5-pentanediol.

Therefore, on the basis of the results reported in this work and considering the existing literature, a proper pathway for the furfural hydrogenation in vapour phase over Cu-based catalyst is proposed (Fig. 2). The broken lines represent the difference points from Fig. 1.

#### 4. Conclusion

In summary, furfuryl alcohol can eliminate carbon monoxide to produce furan. *n*-Butanol mainly comes from furan rather than tetrahydrofuran. Depending on the catalysts and reaction conditions employed, 2-pentanone, 2-methyltetrahydrofuran, 1-pentanol and 2-pentanol are all the hydrogenation products of 2-methylfuran. 2-Methyltetrahydrofuran is very stable and the main hydrogenation products are 2-pentanone and hydrocarbon. With  $C_2$  catalyst containing the Ni element, the main reaction product of tetrahydrofurfuryl alcohol is tetrahydrofuran, while  $\delta$ -valerolactone is the main product with  $C_1$  one. These results are important to understand the mechanism and reaction pathway of furfural hydrogenation, and to supply an instruction for the design of new catalytic formulations.

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