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Efficient one-pot conversion of furfural into 2-methyltetrahydrofuran using non-precious metal catalysts

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ABSTRACT

2-methyltetrahydrofuran, a biomass-derived chemical, is an important solvent with broad applications in organic chemistry. In this study, one-pot conversion of furfural into 2-methyltetrahydrofuran over non-precious metal catalysts was achieved by two-stage packing in a single reactor. The first stage converted furfural into 2-methylfuran over Co-based catalysts, and the second stage converted 2-methylfuran into 2-methyltetrahydrofuran over Ni-based catalysts. In order to reveal the reaction pathway and mechanism of this process, the hydrogenation reactions of 2-methylfuran, furfuryl alcohol, and tetrahydrofurfuryl alcohol were also carefully investigated. It is discovered that the conversion of furfural into 2-methylfuran could be catalyzed by Lewis acid sites, which was confirmed by a correlation between 2-methylfuran production rate and Lewis acid site density. Also, a mechanism on the direct conversion of furfural into 2-methylfuran without forming furfuryl alcohol as the intermediate is proposed. The experimental results of 2-methylfuran, furfuryl alcohol, and tetrahydrofurfuryl alcohol hydrogenation/hydrodeoxygenation over various catalysts provided valuable information on the future design of 2-methyltetrahydrofuran catalyst.

1. Introduction

The huge consumption of fossil fuel in modern society has stimulated serious energy and environmental issues. In order to reduce the societal dependence on fossil fuels, research efforts are devoted to developing renewable resources as the replacement for fossil fuels. Lignocellulosic biomass stands out as a promising candidate in recent years. Lignocellulose from agricultural or forestry waste could be effectively converted into various energy resources or valuable chemicals. Among many biomass-derived chemicals, furfural is one of the most important biomass platform chemicals due to it high availability and high chemical versatility. Furfural is commercially produced through acid-catalyzed dehydration of xylan-type hemicellulose [1], and could be transformed into a number of useful chemicals such as furfuryl alcohol (FOL), 2-methylfuran (2MF), and cyclopentanone.

2-Methyltetrahydrofuran (2MTHF), an important derivative of furfural, is recently identified as a renewable solvent with broad applications in organic chemistry. As an aprotic ether solvent, 2MTHF possesses low miscibility with water, strong Lewis basicity and high stability in acid medium [2], making 2MTHF a better option than tetrahydrofuran or dichloromethane in a variety of organic reactions such as Grignard reactions and nucleophilic substitutions [3]. For instance, Aycock [2] found that yields of addition products from benzyl Grignard reagents prepared in 2-MTHF is nearly four times as in tetrahydrofuran. In addition to solvents, 2MTHF has shown potential as renewable fuel additive due to its better combustion properties compared to ethanol, including higher heating value, lower heat of vaporization, and lower solubility in water [4].

The potentials of 2MTHF as solvents or fuels have attracted researchers to study the production of 2MTHF. Several types of biomass resource have been used to produce 2MTHF, including levulinic acid [5–7], γ-valerolactone [8,9] and furfural [10,11]. Among them, due to the high availability of furfural, the production of 2MTHF from furfural is of great research value. The efficient production of 2MTHF from furfural would require two types of reactions and the corresponding catalysts: furfural hydrodeoxygenation to produce 2MF which could be achieved by Cu-based [12,13] or Co-based catalysts [14,15], and the subsequent 2MF hydrogenation to produce 2MTHF which was

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previously achieved by noble metal catalysts [10,11]. Poliakoff et al. [10] obtained a 82 % yield of 2MTHF with copper chromite and Pd/C in a two-reactor system, one reactor being 240 °C and another being 300 °C. Zhu et al. [11] obtained a 97 % yield of 2MTHF under atmospheric pressure using copper phyllosilicate and Pd/SiO_2 by two-stage packing in one reactor. Despite many potential applications of 2MTHF, researches focusing on the conversion of furfural into 2MTHF are still insufficient, leaving many important aspects unrevealed. Also, the performance and mechanism of non-precious metal catalysts in the conversion of furfural into 2MTHF have not been examined in the literature yet. According to our previous work [14], Co-based catalysts showed high selectivity in furfural hydrodeoxygenation to produce 2-methylfuran, while Ni-based catalysts showed high reactivity for furan ring hydrogenation. Therefore, it is anticipated that furfural could be transformed to 2MTHF with high yield if Co and Ni catalysts were utilized in sequence, achieving an efficient transformation of furfural into 2MTHF without non-precious metals.

In this work, the general strategy of transforming furfural into 2MTHF is to load two different types of catalysts into a single reactor with the uniform temperature. The first stage of catalyst would aim at converting furfural into 2MF, while the second stage of catalyst aiming at converting 2MF to 2MTHF. In this respect, the reaction of furfural hydrodeoxygenation to produce 2MF, and the subsequent 2MF hydrogenation over various catalysts will be studied separately. Cobalt and nickel catalysts supported on various oxides were prepared and loaded in the reactor to achieve high 2MTHF yield. To further explore the reaction mechanism in the reactor, furfuryl alcohol (FOL), 2-methylfuran (2MF), and tetrahydrofurfuryl alcohol (THFOL) were used as reactants and tested. By analyzing the distribution of products, a feasible strategy with a high yield of 2-methyltetrahydrofuran was proposed.

2. Experimental section

2.1. Catalyst synthesis

CeO_2 was prepared through the precipitation of cerium (III) nitrate hexahydrate (Innochem, 99.5 %). The precursor was dissolved in deionized water to form a 0.1 M solution and then the ammonium hydroxide aqueous solution was added dropwise to the solution with continuous stirring. The resulting precipitate was washed with deionized water and then dried overnight in an oven at 100 °C. The precursor was calcined in air at 500 °C for 4 h with a ramp rate of 5 °C/min. ZrO_2 were synthesized in a similar manner, using zirconium (IV) oxynitrate hydrate (Innochem, 99.9 %) as the precursor, and calcined under the same temperature profile. γ-Al_2O_3 was obtained by calcination of pseudo-boehmite at 550 °C for 4 h with a ramp rate of 2 °C/min in air. TiO_2 was prepared through the precipitation of titanium tetrachloride (Innochem, 99 %). Deionized water was added into the titanium tetrachloride solution to form a 0.1 M solution and then the 0.1 M urea solution was added dropwise to the solution with continuous stirring until the solution pH reached 6. The resulting precipitate was aged at room temperature for 30 min and then washed with deionized water and dried overnight in an oven at 120 °C. The powder was then calcined at 400 °C for 4 h with a ramp rate of 2 °C/min to obtain m-TiO_2. Commercial MgO (Acros, 98 %) and SiO_2 gel (Qingdao Haiyang, 99.9 %, 100–200 mesh) were used as the support.

All catalysts were synthesized using incipient wetness impregnation method. The certain amount of cobalt (II) nitrate hexahydrate (Sinopharm, 99 %) was dissolved in deionized water to form a 0.86 M $Co(NO_3)_2$ aqueous solution. The oxide support was then added. The solution of Ni precursor was prepared similarly using nickel (II) nitrate hexahydrate (Sinopharm, 99 %). After impregnation at room temperature for 6 h, all catalysts were dried in an oven at 90 °C overnight. Dried catalysts were calcined in air at 120 °C for 2 h and then calcined at 400 °C for 3 h both with a ramp rate of 2 °C/min.

2.2. Sample characterization studies

Powder x-ray diffraction (XRD) patterns of all samples were obtained on a Shimadazu XRD-7000 powder diffractometer after the reduction in pure H_2 of 20 mL/min at 500 °C for 3 h. Temperature programmed reduction (TPR) of all samples were detected by a CAM200 quadrupole mass spectrometer (InProcess Instruments). Typically, 100 mg of samples were loaded in a quartz tube put in the furnace. All catalysts were heated from room temperature to 800 °C with a heat rate of 5 °C/min in a flow of 10 vol% H_2/Ar (30 mL/min). Total acid sites were measured by temperature-programmed desorption of ammonia (NH_3-TPD) using the mass spectrometer. Pyridine adsorbed Fourier-transform infrared spectroscopy (FTIR) were used to characterized Brønsted and Lewis acidity.

2.3. Hydrogenation/hydrodeoxygenation reactions

Hydrogenation/hydrodeoxygenation reactions were carried out in a fixed-bed tubular reactor. Catalyst powders were loaded into the reactor tube between two layers of quartz wool and pre-reduced in pure hydrogen at 500 °C for 3 h with a flow rate of 42 mL/min. For the two-stage packing, a layer of quartz wool was placed between two stages. Reactants including furfural, furfuryl alcohol, 2-methylfuran and tetrahydrofurfuryl alcohol were pumped into the reactor using a HPLC pump at a flow rate of 0.03 mL/min. The liquid products of first 2 h were discarded and then collected every 50 min. All samples were analyzed by Agilent 7890B gas chromatography equipped with a HP-5 capillary column (30 m × 0.32 mm × 0.23 μm) and flame ionization detector (FID). The compositions of liquid products were calibrated by the internal standard method using decane as the inner standard. The carbon balance of every sample was calculated. The conversion and product selectivity were calculated using the following formulas:

$$\text{Conversion}=\frac{\text{Mole of raw material in product}}{\text{Mole of raw material in the feed}}$$

$$\text{Selectivity}=\frac{\text{Mole of specific in product}}{\text{Mole of all products}}$$

3. Results and discussion

3.1. Catalysts characterization

A series of Ni-based and Co-based catalysts supported on various support were synthesized. X-ray diffraction results of all samples after 3 h of H_2 reduction at 500 °C are shown in Fig. 1. For nickel-containing catalysts, peaks at 44.5° and 51.6°, corresponding to the metallic Ni (111) and (200) planes, respectively, were observed [16]. Cobalt samples exhibited characteristic diffraction peaks at 44.2° and 51.5°, corresponding to the metallic Co (111) and (200) crystal planes, respectively [17]. Characteristic diffraction peaks of CeO_2 at 33.1°, 47.6°, and 56.4° indicated the synthesized CeO_2 displayed the expected cubic structure [18]. For Co/ZrO_2, peaks at 31.5°, 34.1°, 35.3°, 50.1°, and 60.1° suggested that the synthesized ZrO_2 is monoclinic (m-ZrO_2), consistent with previous research [19]. For Ni/CeO_2, Co/CeO_2, and Co/MgO, diffraction peaks of the support (CeO_2 or MgO) are much stronger than diffraction peaks of the cobalt and nickel peaks, so that diffraction peaks of the metallic nickel and cobalt particles were almost invisible. For Co/Al_2O_3, the peak at 46.4° was also detected, which could be attributed to the irreducible cobalt aluminate [20]. Based on the XRD results, the absence of Ni oxides or Co oxides indicates that the reduction at 500 °C was sufficient to yield metallic particles, so the 500 °C reduction was conducted before the catalysts reactivity tests. Metal dispersions of all catalysts were calculated using Scherrer's equation and results were shown in Table 1.

The reducibility of all catalysts was evaluated using temperature

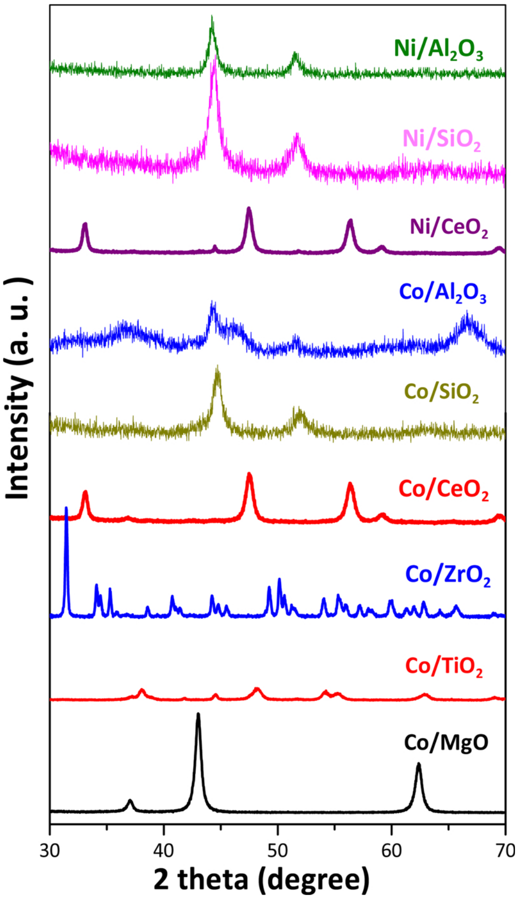


Fig. 1. X-ray diffractograms of all samples after reduction at 500 °C.

programmed reduction (TPR) results as shown in Fig. 2. Co/Al$_2$O$_3$ sample showed a sharp peak near 300 °C and a broad peak at 400–750 °C, corresponding to the reduction of Co$_3$O$_4$ to metallic cobalt and the reduction of cobalt aluminate, respectively [21]. Co/SiO$_2$ catalyst showed two sharp reduction peaks near 270 °C and 300 °C, which are assigned to the absorption peaks of Co$_3$O$_4$ to CoO and CoO to metallic cobalt, respectively [21]. Ni/Al$_2$O$_3$ displayed one broad H$_2$ consumption peak ranging from 400 °C to 750 °C, in good agreement with a previous research [22]. This peak could be regarded as the reduction peak for nickel aluminate rather than nickel oxide, because no diffraction peaks for nickel oxides were detected in XRD when reduced at 500 °C.

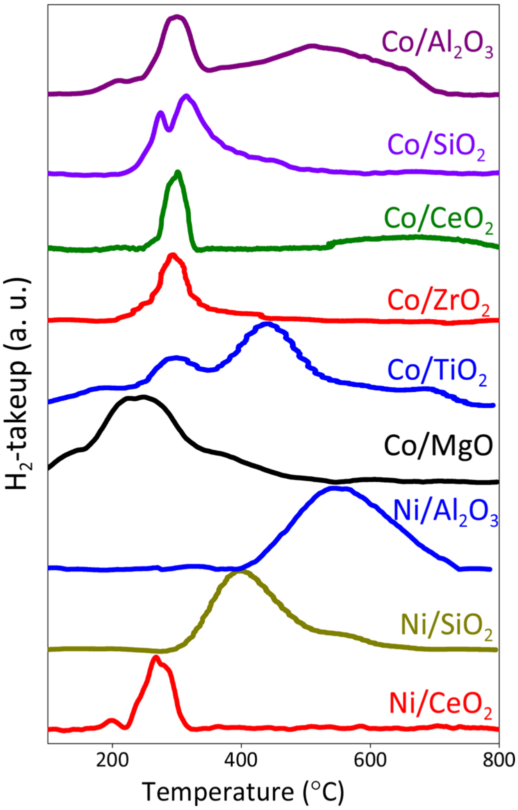


Fig. 2. Temperature programmed reduction (TPR) of all catalysts.

3.2. Furfural hydrodeoxygenation

In the first stage of the reactor, furfural is anticipated to be transformed into 2-methylfuran (2MF). Previous research results suggested that pressure is critical for conversion of furfural, while temperature is crucial for 2MF selectivity [14,23]. This is confirmed by trial tests of furfural hydrodeoxygenation of this study (Figure S1 – 3 of Supplementary Information). As shown in Figure S1 of Supplementary Information, in furfural hydrogenation over Co/SiO$_2$, increasing reaction temperature from 150 °C to 230 °C led to increased 2-methylfuran selectivity. In contrast, increasing temperature from 160 to 200 °C would lead to a decreased 2MTHF selectivity in 2MF hydrogenation over Ni/Al$_2$O$_3$ (Figure S3) due to more furan ring cleavage, in agreement with a previous study [24]. Reaction pressure is also crucial in furfural hydrogenation over Co/SiO$_2$, for 2MF selectivity increased about 4 times when the pressure increased from 0.1 MPa to 1 MPa (Figure S2).

Table 1
Hydrodeoxygenation of furfural with various catalysts at 1 MPa H$_2$ and 180 °C.[a]

Catalyst	Dispersion (%)	Conversion (%)	Selectivity (%)[b]						Carbon balance (%)
			2MF	FOL	Furan	THFOL	2MTHF	Others[c]	
Co/Al$_2$O$_3$	8.5	100	93.4	–	2.9	–	3.2	0.5	82.8
Co/SiO$_2$	6.5	91.2	67.7	3.0	6.4	0.2	4.8	18.0	89.6
Co/TiO$_2$	4.0	60.6	70.7	25.8	–	–	1.6	1.9	98.6
Co/CeO$_2$	5.7	65.3	44.1	49.2	4.1	–	0.9	1.7	100.2
Co/MgO	8.0	12.8	15.3	84.1	–	–	0.1	0.5	107.5
Co/ZrO$_2$	3.6	53.2	77.3	21.8	–	–	0.5	0.3	91.1
Ni/Al$_2$O$_3$	7.4	100	65.5	5.1	10.2	7.1	11.0	1.1	95.4
Ni/SiO$_2$	8.2	84.6	13.7	15.3	10.0	44.8	6.7	9.6	92.0
Ni/CeO$_2$	4.4	51.9	3.8	58.0	4.7	19.8	1.0	12.8	83.5

[a] Reaction conditions: catalyst = 2.1 g, furfural feed rate = 0.03 mL/min, H$_2$/furfural molar ratio = 8.4, weight hourly space velocity (WHSV) = 0.99 h^{-1}.

[b] Abbreviations: 2MF, 2-methylfuran; FOL, furfuryl alcohol; THFOL, tetrahydrofurfuryl alcohol; 2MTHF, 2-methytetrahydrofuran.

[c] Others include: tetrahydrofuran, 2-pentanone, 2-pentanol.

However, pressurizing the reactor too much might significantly increase the cost and risk during operation. Therefore, based on literature research [11,25] and trial test runs, reaction temperature of 180 °C and pressure of 1 MPa were used in this study. Furfural hydrodeoxygenation over various catalysts were shown in Table 1. All cobalt catalysts showed high selectivity toward 2MF except Co/MgO catalyst, while tetrahydrofurfuryl alcohol (THFOL) and furfuryl alcohol (FOL) were prominent over the supported nickel catalysts. Among all catalysts tested, Co/Al_2O_3 showed the highest 2MF yield of 93.4 %, as well as 3.2 % yield of 2MTHF. Other major side products were FOL, furan, THFOL, etc. Therefore, Co/Al_2O_3 was used as the catalyst of the first stage in the two-stage reactor.

Interestingly, Co catalysts supported on different oxides showed distinct 2MF yields. Since their metal dispersions calculated from XRD were similar as shown in Table 1, one plausible explanation for their yield difference is the support-induced effect. Vlachos et al. discussed the importance of Lewis acidity in the hydrogenolysis of furfural to 2MF over Ru oxide catalysts [26,27], which inspired this study to probe into the effect of support acidity on 2MF yield. Four typical Co catalysts with high 2MF yields were characterized by NH_3-TPD and in situ infrared spectra of adsorbed pyridine. As shown in Fig. 3, for all four catalysts, the adsorbed pyridine showed 4 peaks at 1450, 1488, 1538, and 1608 cm^{-1}, corresponding to pyridine adsorbed at different types of acid sites. Peaks at 1450 and 1608 cm^{-1} could be ascribed to pyridine adsorbed on the strong Lewis acid sites [28]. The peak at 1538 cm^{-1} was due to the protonated pyridine molecule on Brønsted acid sites [29]. The peak at 1488 cm^{-1} was the vibration mode of pyridine absorbed on both Brønsted and Lewis acid sites [29]. With increasing temperature, peak intensity decreased for all adsorption bands, indicating reduced amounts of both Brønsted and Lewis acid sites, in agreement with previous research [30]. The ratios of Brønsted to Lewis acid site concentration (B/L) were obtained by integrating the peak area at 1538 and 1450 cm^{-1}, corresponding to Brønsted and Lewis acid sites, respectively, and taking extinction coefficient into consideration (1.88 for Brønsted sites and 1.42 for Lewis sites) [28]. Combining this B/L ratio with the total acid site concentration measured by NH_3-TPD, the concentration of Brønsted and Lewis acid site could be calculated (Table 2). A particular case was observed with Co/CeO_2, which displayed no NH_3 desorption peak in NH_3-TPD, likely due to its low acid site concentration below detection limit. Therefore, the total acid sites and Lewis acidity was approximated to zero for Co/CeO_2.

Lewis acid sites were believed to play important role in the furfural conversion into 2MF [26,27,31], and this is confirmed in this study by the correlation between the 2MF production rate and the number of Lewis acid sites in Fig. 4. The near-linear relationship provides confirmative indication that Lewis acid sites directly participated in the formation of 2MF. The non-zero intercept at y-axis suggested that mechanisms to produce 2MF without the assist of Lewis acid sites might exist as well. In general, the Lewis acid sites on oxide support surface are coordinatively unsaturated cations, such as Co^{n+} or Al^{n+} in Co/Al_2O_3 [32]. These Lewis acid sites are highly electrophilic, which could interact strongly with the oxygen of the formyl group in furfural. We hypothesize that during the reaction the formyl-group oxygen is bonded to a Lewis acid site, followed by the addition of chemisorbed hydrogen atoms from adjacent metal sites to the carbonyl bond, ending in the scission of the C—O bond and the formation of 2MF [26].

According to this study, the efficient production of 2MF from furfural requires bifunctional catalysts possessing both Lewis acid sites and metal sites. Lewis acid sites could interact strongly with the formyl-group oxygen to facilitate its scission from furfural molecules. Metal sites not only provide adsorbed hydrogen atoms for carbonyl bond saturation but should also be relatively inactive to prevent the formation of side products such as furfuryl alcohol or furan. Metal catalysts such as nickel, copper or palladium have been showed previously [14,33,34] and in this study to display high reactivity in either carbonyl bond hydrogenation or decarbonylation, which would transform furfural into other products rather than 2MF. On the contrary, Co is less active in C═C or C═O bond saturation [35] but still able to provide adsorbed hydrogen atoms, which becomes a good choice for 2MF production. In this respect, the combination of abundant Lewis acid sites and a relatively less active metal component such as Co would be an important design principle for catalysts aiming at furfural conversion into 2MF.

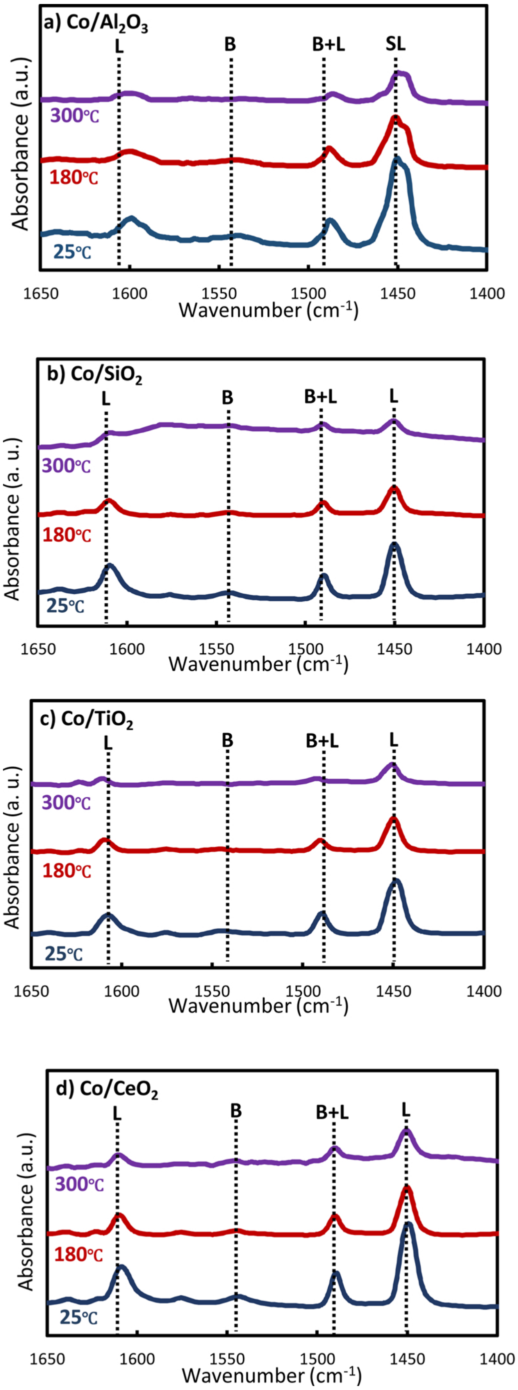


Fig. 3. Pyridine-adsorption FTIR spectra of a) Co/Al_2O_3, b) Co/SiO_2, c) Co/TiO_2 and d) Co/CeO_2 at 25 °C, 180 °C and 300 °C. Absorbance peaks characteristic of Lewis (L), and Brønsted (B) acid sites are indicated.

3.3. Mechanism study of furfural to 2MF

Although many researches focused on the direct conversion of furfural to 2MF, whether furfuryl alcohol is a necessary reaction

Table 2
The concentration of acid sites and the relative Brønsted and Lewis acidity ratio (B/L) of selected catalysts.

Catalyst	Total acid sites[a] (umol/g)	B/L[b]	Lewis acidity[c] (umol/g)
Co/Al_2O_3	466.8	0.110	420
Co/SiO_2	235.4	0.171	201
Co/TiO_2	101.7	0.078	94
Co/CeO_2	~0[d]	0.150	~0

[a] Determined by ammonia TPD.

[b] Determined based on the integral of peak area at 1538 cm^{-1} (Brønsted acidity) and peak area at 1450 cm^{-1} (Lewis acidity) in pyridine-probed FTIR with extinction coefficients taken into consideration [28].

[c] Calculated by multiplying the percentage of Lewis acidity (calculated from B/L ratio) by the total acid sites.

[d] No desorbed ammonium was detected.

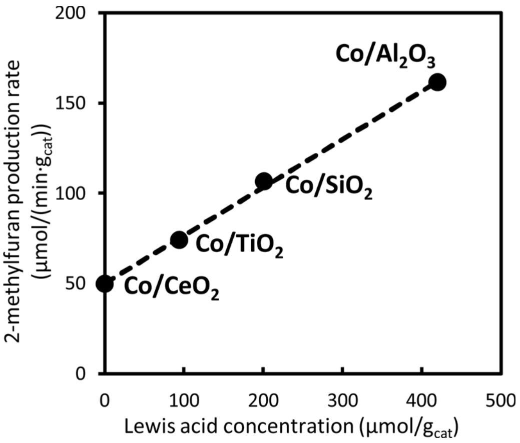


Fig. 4. The correlation of production of 2MF in furfural hydrodeoxygenation with respect to concentration of Lewis acid sites for selected catalysts.

Table 3
Hydrogenation of furfuryl alcohol (FOL) with various catalysts at 1 MPa H_2 and 180 °C.[a]

Catalyst	Conversion (%)	Selectivity (%)[b]					Carbon balance (%)
		2MF	THFOL	2MTHF	PL	Others[c]	
Co/Al_2O_3	62.8	88.8	–	11.2	–	–	95.5
Co/SiO_2	94.8	88.2	0.8	4.8	5.3	0.9	88.7
Co/CeO_2	76.2	94.5	–	1.6	2.0	1.9	89.5
Ni/Al_2O_3	100	0.2	85.5	11.9	–	2.4	81.8
Ni/SiO_2	100	3.1	77.3	17.3	0.9	1.4	86.3
Ni/CeO_2	61.8	3.2	84.3	2.5	–	10.0	98.9

[a] Reaction conditions: catalyst = 2.0 g, FOL feed rate = 0.03 mL/min, H_2/FOL molar ratio = 8.4, WHSV = 1.02 h^{-1}.

[b] Abbreviations: 2MF, 2-methylfuran; THFOL, tetrahydrofurfuryl alcohol; 2MTHF, 2-methytetrahydrofuran; PL, 2-pentanol.

[c] Other products include: tetrahydrofuran, 1-butanol, 2-pentanone, tetrahydropyran.

Table 4
Hydrogenation of 2-methylfuran (2MF) into 2-methyltetrahydrofuran (2MTHF) with various catalysts at 1 MPa H_2 and 180 °C.[a]

Catalyst	Conversion (%)	Selectivity (%)[b]					Carbon balance (%)
		2MTHF	Furan	PN	PL	Others[c]	
Co/Al_2O_3	94.3	38.7	5.9	4.2	51.2	–	74.9
Co/SiO_2	89.5	48.4	5.9	5	40.7	–	78.6
Co/CeO_2	70.6	36.9	7.9	9.4	45.7	0.1	86.9
Ni/Al_2O_3	81.3	91	2.9	3.7	1.8	0.6	81.0
Ni/SiO_2	89.9	91.2	1.9	2.6	4.3	–	85.0
Ni/CeO_2	88.8	75.3	4.8	9.3	8.8	1.8	95.4

[a] Reaction conditions: catalyst = 1.7 g, 2MF feed rate = 0.03 mL/min, H_2/2MF molar ratio = 8.4, WHSV = 0.96 h^{-1}.

[b] Abbreviations: 2MTHF, 2-methytetrahydrofuran; PN, 2-pentanone; PL, 2-pentanol.

[c] Others include: tetrahydrofuran, 2-butanol, tetrahydropyran.

intermediate in the transformation of furfural into 2MF has yet reached an agreement. It has been reported previously [23] that 2MF is formed in two consecutive steps, namely the hydrogenation of furfural to produce FOL and the subsequent hydrogenolysis of FOL to yield 2MF. On the other hand, reaction pathways of furfural conversion into 2MF without going through FOL were also proposed [36–38]. In order to clarify this question, the hydrogenation of furfuryl alcohol over 6 representative catalysts was studied and the result are shown in Table 3.

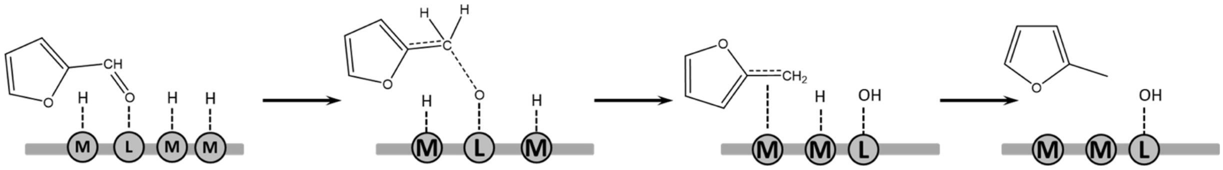
Compared with the 2MF selectivity from furfural hydrodeoxygenation in Table 1,4 out of 6 tested catalysts (Co/Al_2O_3, Ni/Al_2O_3, Ni/SiO_2, and Ni/CeO_2) showed much lower 2MF selectivity in FOL hydrodeoxygenation. This indicates the presence of a direct conversion pathway from furfural to 2MF without going through FOL as an intermediate, because the selectivity of 2MF in furfural hydrodeoxygenation should not be higher than 2MF selectivity in FOL hydrodeoxygenation under the assumption that all 2MF is formed via FOL.

It is highly probable that 2-methylfuran could be produced with different mechanisms in terms of whether FOL is formed as the necessary intermediate. Starting from furfural as the reactant, 2MF could be produced with the synergistic effect between metal sites and Lewis acid sites, without FOL formation as the intermediate. A plausible process for this mechanism inspired by a previous research [39] is proposed in this study and shown in Scheme 1. Furfural will adsorb on the surface with the formyl-group oxygen bonding to a Lewis acid sites. The carbonyl bond will be partially hydrogenated to form a methoxy intermediate. This methoxy intermediate is susceptible to the direct deoxygenation to form a methylene intermediate, as the formyl-group oxygen is strongly interacted with Lewis acid sites [26]. Afterwards, one more adsorbed hydrogen atoms were added to the deoxygenated intermediate, forming 2MF as the final product.

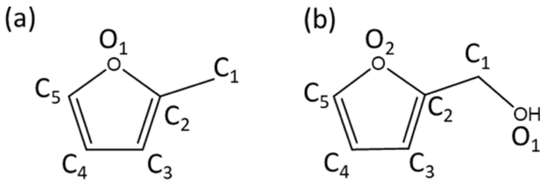
The reaction mechanism of 2MF formation will be different if furfuryl alcohol were either formed during the reaction or provided as the reactant. For this mechanism, furfuryl alcohol, acting as the precursor of 2MF, could also adsorbed on metal sites [23,40] or Lewis acid sites [26], with the hydroxy group interacting with the site. Adsorbed furfuryl alcohol is then dehydroxylated or dehydrated to form a methylene intermediate [23,40]. This methylene intermediate is later hydrogenated to form 2MF. Although this reaction pathway could also lead to the formation of 2MF, due to the high reactivity of FOL toward ring hydrogenation, a significant amount of THFOL rather than 2MF was produced, especially for Ni-based catalysts as shown in Table 3. Ni-based catalysts showed high tetrahydrofurfuryl alcohol selectivity, likely due to the strong affinity between nickel active sites and furan ring, facilitating ring hydrogenation [41]. Therefore, according to this research, in order to achieve high selectivity of 2MF or 2MTHF, the formation of FOL should be inhibited, as FOL could be readily hydrogenated or demethylated especially with Ni-based catalysts.

3.4. 2-Methylfuran hydrogenation

After furfural was converted into 2-methylfuran, the furan ring hydrogenation of 2-methylfuran is required to produce 2-methyltetrahydrofuran (2MTHF). The reactivity of 2-methylfuran hydrogenation over 3 Ni-based catalysts and 3 Co-based catalysts was shown in Table 4. When 2MF was used as feed for hydrogenation, Ni catalysts favored 2MTHF, while Co catalysts mainly produced 2-pentanol. This selectivity difference is likely due to the difference of the dominant adsorption configuration between Ni and Co metal surface. Nickel has



Scheme 1. Possible reaction pathway with Lewis acid sites during conversion of furfural into 2MF.



Scheme 2. Assignment of the carbon and oxygen atoms in (a) 2-methylfuran and (b) furfuryl alcohol.

been reported to have strong affinity with the furfural furan ring, adopting an adsorption mode in which the furan ring lies parallel to the metal surface and both C=C double bonds interact with metal surface [42]. With this adsorption geometry, adsorbed hydrogen will be able to hydrogenate C=C double bonds to produce ring hydrogenation products [23,41], namely 2MTHF in this study.

For Co-based catalysts, 2-pentanol was the major product in 2MF hydrogenation, with 2MTHF being the second most produced product. The presence of 2-pentanol unambiguously indicated a C_5-O_1 bond scission in 2MF (the assignment of the carbon and oxygen atoms in 2MF and FOL are shown in Scheme 2). This bond scission resembles the C—O bond scission in furfural transformation to 1,2-pentanediol, except that a methyl group is attached to the furan ring in 2MF rather than a formyl group as in furfural. In comparison, as can be seen in Table 3, the hydrogenation of FOL over Co catalysts generated mostly 2MF, with little 2-pentanol and 2-pentanone. No 1,2-pentanediol was detected in FOL hydrogenation over Co-based catalysts, suggesting the absence of FOL C_5-O_2 bond scission during reaction. From these experimental results, it could be deduced that FOL is much more inclined to C_1-O_1 bond scission than C_5-O_2 bond scission, perhaps due to a much lower activation energy of the former compared to the latter. As a result, FOL hydrogenation over Co catalysts showed absolute dominance in hydrodeoxygenation to produce 2MF over ring-opening reactions to produce 1,2-pentanediol. Once the hydroxy group in the side chain was removed, Co catalysts were able to break C_5—O_1 on the furan ring of 2MF. In literature, the production of 1,2-pentanediol was studied carefully, and few non-precious metal catalysts were reported. According to this research, Co-based catalysts showed potentials in transforming furfural derivatives into 1,2-pentanediol, if the hydrodeoxygenation of the side chain could be suppressed.

The highest 2MTHF selectivity among catalysts tested was about 91 % with Ni/SiO_2 and Ni/Al_2O_3, so these two catalysts were used as the catalyst of the second stage for the dual-stage reactor system. Main byproducts were cracking products, including furan, 2-butanol, 2-pentanol and 2-pentanone. It was previously reported that higher temperature will lead to lower 2MTHF selectivity for various metal catalysts [24], and it is thus believed that the 91 % 2MTHF selectivity obtained in this study could be improved further if the reaction temperature was decreased. However, regarding that furfural hydrodeoxygenation into 2MF is sensitive to temperature, 180 °C will still be used in the two-stage reactor. A separate reactor with a lower temperature for the second stage where 2MF is converted into 2MTHF would be both more selective and more energy-efficient (despite of the higher cost), and this would be the focus in future research if aiming at higher 2MTHF yields.

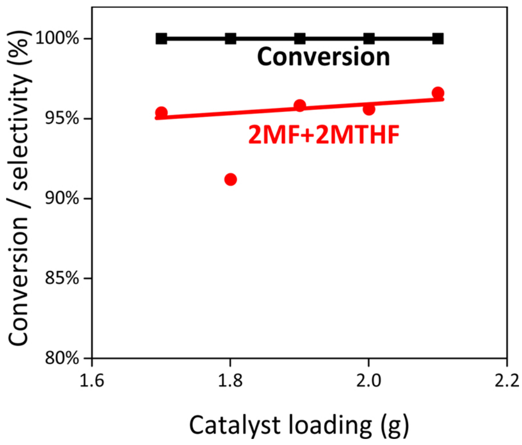


Fig. 5. Furfural conversion and selectivity of 2MF and 2MTHF combined in furfural hydrodeoxygenation at 1 MPa H_2 and 180 °C as a function of Co/Al_2O_3 loading amount. Reaction conditions: feed rate = 0.03 mL/min, H_2/furfural molar ratio = 8.4.

3.5. The effect of catalyst amount on conversion and selectivity

After examination of furfural and 2MF hydrogenation results, several catalysts were selected for the two-stage reactor converting furfural into 2MTHF. Co/SiO_2 would be used for the first stage, while Ni/SiO_2 and Ni/Al_2O_3 would be used in the second stage. In order to determine the catalyst loading for each stage of the reactor, the effect of catalyst loading amounts on conversion and selectivity was investigated. The results for furfural hydrodeoxygenation over Co/Al_2O_3 were shown in Fig. 5. For furfural hydrogenation, furfural conversion reached 100 % even at the catalyst loading amount of 1.7 g. Because Co catalysts were also active to hydrogenate 2MF further into 2MTHF, 2–4% of 2MHTF were also detected in the product stream. The selectivity of 2MF and 2MTHF combined maintained at around 95 % with increasing catalyst loading. The major byproducts were small amount of furfuryl alcohol (1–2 %) and furan (2–3 %). Since excess catalyst will not negatively affect the eventual 2MTHF yield, 2.5 g of Co/SiO_2 was used for the two-stage packing in the reactor to ensure the complete conversion of furfural.

Next, 2MF conversion and 2MTHF selectivity with respect to the catalyst amount in 2MF hydrogenation for the second stage were studied. Two catalysts, Ni/SiO_2 and Ni/Al_2O_3, were tested and results were shown in Fig. 6. Counterintuitively, the reaction did not achieve complete conversion of 2MF with increasing catalyst loading, but stabilized at 97 % for Ni/SiO_2 and 80 % for Ni/Al_2O_3. This coincides with a previous research from Zhu et al. on 2MF hydrogenation observing that 2MF conversion increased slowly with temperature and did not reach 100 % even at 300 °C [43]. Another research on 2MF also reported incomplete conversion of 2MF in 4 out of 5 catalysts tested [24]. It is speculated that the chemical equilibrium was the main factor limiting the full conversion of 2MF. However, due to the lack of necessary thermodynamic data, further efforts will be needed to verify this hypothesis. 2MTHF selectivity also decreased with increasing catalyst loading for both catalysts. Main byproducts include furan, 2-pentanol (PL), and 2-pentanone (PN). The decreased 2MTHF selectivity with increasing catalyst mass is likely due to the further transformation of

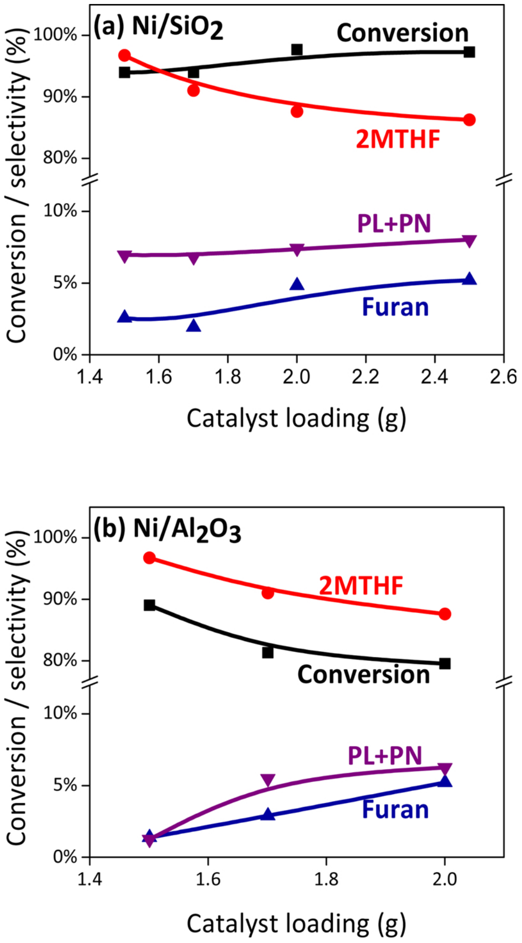


Fig. 6. 2MF conversion and 2MTHF selectivity in 2MF hydrogenation at 1 MPa H_2 and 180 °C as a function of (a) Ni/SiO_2 and (b) Ni/Al_2O_3 loading amount. Reaction conditions: feed rate = 0.03 mL/min, H_2/furfural molar ratio = 8.4.

2MTHF over an excessive amount of catalysts. Previous study indicated that 2MTHF could go through ring scission reactions and be converted into pentanone or hydrocarbons over metal catalysts [43]. Therefore, the catalyst amount of the second stage in the reactor should be controlled with caution to maximize the 2MTHF yield and avoid side products. After some trial tests, 2 g of Ni/SiO_2 and Ni/Al_2O_3 were used for the second stage in the reactor to obtain the highest 2MTHF yield.

3.6. One-pot synthesis of 2-methyltetrahydrofuran from furfural

The one-pot synthesis of 2MTHF from furfural was studied and the results were shown in Table 5. The conversion of furfural into 2MTHF requires two different catalyst function in sequence: furfural hydrodeoxygenation in the first stage and ring hydrogenation of 2MF in the second stage. An equally important requirement is that both catalysts are supposed to be highly selectively to their corresponding target products. Therefore, the conversion of furfural into 2MTHF will not be accomplished with a single catalyst. This is confirmed by loading 4.5 g of Co/Al_2O_3 or Ni/Al_2O_3 into the reactor, and the yield of 2MTHF is relatively low as shown in Table 5.

Since 2MTHF cannot be prepared through the furfural hydrodeoxygenation over a single catalyst, one-step conversion of furfural to 2MTHF was tested over dual solid catalysts based on two-stage packing reactor. By means of a two-stage packing, when Co/Al_2O_3 and Ni/Al_2O_3 were loaded into a single fixed-bed tubular reaction, an 87 % yield of 2MTHF was obtained. Although previous researches reported higher 2MTHF yields [10,11], to the best of authors' knowledge, this is the first research achieving the efficient production of 2MTHF from furfural using non-precious metal catalysts. 2MF was still present in the product stream at a noticeable amount after the two-stage reaction, likely due to the incomplete conversion of 2MF into 2MTHF in the second stage of the reactor as mentioned above. The major byproduct is 2-pentanol, which is due to the ring-opening function of catalysts. Besides, furfuryl alcohol, furan, tetrahydrofurfuryl alcohol were also detected as minor byproducts. The one-step conversion of furfural into 2MTHF using the two-stage packing saves additional energy or effort between two steps. Still, due to the intrinsic difference of two reactions, separate reactors with difference temperatures, pressures, etc. would be beneficial to further improve the 2MTHF yield although at a higher cost.

The stability of the two-stage catalyst system was also monitored. After the liquid sample of first two hours were discarded, the samples were collected and tested every 50 min at a WHSV of 0.46 h^{-1}, and the result is shown in Fig. 7. The reaction reached steady state at about 4 h after the furfural introduction. It is noticed that furfural conversion was maintained at 100 % throughout the test period, and 2MTHF yields declined slightly after 8 h of time on stream. No furfuryl alcohol or tetrahydrofurfuryl alcohol were detected during the experiment, while the 2MF yield slightly increased with increasing reaction time. The slow decrease of 2MTHF yields with time likely resulted from the catalyst deactivation as suggested by previous studies. It is demonstrated that carbonaceous deposits derived from reactants/products were formed on metal active sites during furfural hydrogenation, leading to a decrease in catalyst reactivity [44,45]. In this study, most carbon balance values of experiment tests were below 100 %, also suggesting the presence of coke deposition or polymerization during the reaction.

3.7. THFOL hydrodeoxygenation experiments

In theory, in addition to 2MF hydrogenation, 2MTHF could also be produced by furfural hydrogenation to form THFOL followed by THFOL

Table 5
One-pot conversion of furfural into 2MTHF with various catalysts at 1 MPa H_2 and 180 °C.[a] The catalyst loading amount is denoted in the parenthesis.

Catalyst	Conversion (%)	Selectivity (%)[b]						Carbon balance (%)
		2MTHF	2MF	PL	Furan	THFOL	Others[c]	
Co/Al_2O_3 (4.5 g)	100	3.7	93.8	1.2	1.3	–	–	93.7
Ni/Al_2O_3 (4.5 g)	100	25.9	7.0	0.8	2.2	56.4	7.6	94.1
Co/Al_2O_3 (2.1 g) + Ni/Al_2O_3 (1.5 g)[d]	100	78.0	12.6	3.3	–	4.5	1.7	94.2
Co/Al_2O_3 (2.5 g) + Ni/Al_2O_3 (2.0 g)	100	87.3	6.1	4.9	–	–	1.7	82.2
Co/Al_2O_3 (2.5 g) + Ni/SiO_2 (2.0 g)	100	83.6	–	9.5	–	–	6.9	83.5
Co/Al_2O_3 (2.5 g) + Co/CeO_2 (2.0 g)	100	4.6	72.7	2.6	5.5	–	13.9	93.5

[a] Reaction conditions: feed rate = 0.03 mL/min, H_2/furfural molar ratio = 8.4, WHSV = 0.46 h^{-1}.
[b] Abbreviations: 2MF, 2-methylfuran; PL, 2-pentanol; THFOL, tetrahydrofurfuryl alcohol; 2MTHF, 2-methytetrahydrofuran.
[c] Others include: furfuryl alcohol, tetrahydrofuran, 2-pentanone.
[d] WHSV = 0.58 h^{-1}.

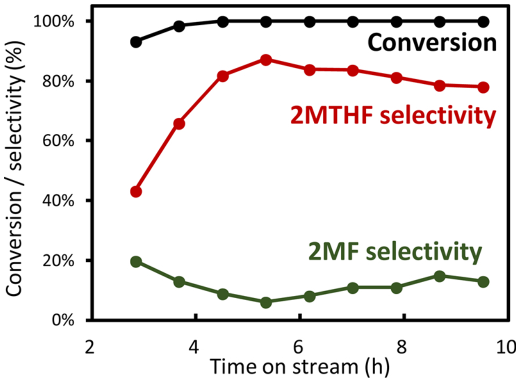


Fig. 7. Furfural conversion and product selectivity in the two-stage furfural hydrogenation as a function of time on stream. Reaction conditions: Co/Al_2O_3 (2.5 g) + Ni/Al_2O_3 (2.0 g), feed rate = 0.03 mL/min, H_2/furfural molar ratio = 8.4, WHSV = $0.46\ h^{-1}$.

Table 6
Hydrodeoxygenation of tetrahydrofurfuryl alcohol (THFOL) with various catalysts at 1 MPa H_2 and 180 °C.[a]

Catalyst	Conversion (%)	Selectivity (%)[b]					Carbon balance (%)
		2MF	THFA	2MTHF	BL	THP	
Co/Al_2O_3	3.7	78.9	–	–	–	21.1	101.0
Co/SiO_2	3.6	63.5	–	23.1	–	13.4	83.3
Co/CeO_2	1.9	49.4	–	26.6	23.9	–	89.1
Ni/Al_2O_3	3.2	–	32.6	10.0	–	57.4	83.1
Ni/SiO_2	1.8	–	89.1	10.9	–	–	90.0
Ni/CeO_2	5.2	–	10.1	–	68.5	21.4	87.0

[a] Reaction conditions: catalyst = 1.5 g, THFOL feed rate = 0.03 mL/min, H_2/THFOL molar ratio = 8.4, WHSV = $1.26\ h^{-1}$.

[b] Abbreviations: 2MF, 2-methylfuran; THFA, tetrahydrofuran; 2MTHF, 2-methytetrahydrofuran; BL, 1-butanol; THP, tetrahydropyran.

hydrodeoxygenation. Since experimental results in this study and in literature have demonstrated the feasibility of producing THFOL from furfural hydrogenation using Ni-based catalysts with high selectivity [46], the key step to convert furfural into 2MTHF via THFOL is the hydrodeoxygenation of THFOL. In order to explore this possibility, the hydrodeoxygenation of THFOL over 6 typical catalysts were tested and the results are shown in Table 6.

Interestingly, the hydrodeoxygenation of THFOL over synthesized catalysts turned out to be rather difficult. With similar WHSV, all catalysts exhibited low THFOL conversions (lower than 6 %), with 2MTHF yield lower than 1.5 %. This slow kinetics could be attributed to the weak adsorption of THFOL on metal active sites. Wan et al. [47] reported relatively weak adsorption of THFOL on Ir (111) and Co/Ir (111) surface, with binding energies being −0.29 and −0.32 eV, respectively. Due to this weak adsorption, the overlap between the molecular orbital of THFOL and the *d*-band of metal surface is small, resulting in a high activation barrier for further THFOL transformations into 2MTHF [48]. Moreover, it is proposed that the steric hinderance of the side hydroxymethyl group also hampered the bond scission of C—O bond in $-CH_2-OH$ to form 2MTHF [49]. Therefore, although furfural could be readily converted into THFOL, the hydrodeoxygenation of THFOL to form 2MTHF is kinetically difficult, leading to a low yield 2MTHF. This low reactivity of THFOL explicitly demonstrates the infeasibility of converting furfural into 2MTHF via THFOL.

4. Conclusion

In this work, the one-pot conversion of furfural into 2-methyltetrahydrofuran was achieved with non-precious metal catalysts using two-stage packing in a single reactor. A high 2MTHF yield (87 %) from furfural was achieved using non-precious metal catalysts. The two-stage reactor included the first stage for converting furfural into 2MF, and the second stage for converting 2MF into 2MTHF. It is discovered that Lewis acidity is crucial for the high reactivity of Co-based catalyst for converting furfural into 2MF, as demonstrated by a near-linear relationship between the 2MF production rate and Lewis acid site concentration. It is also discovered that 2MF could be formed from furfural without producing FOL as intermediate. Nickel-based catalysts showed a high selectivity toward 2MTHF in 2MF hydrogenation, while cobalt catalysts displayed potential in ring-scission. The hydrodeoxygenation of THFOL displayed low conversion with all catalysts tested, suggesting that converting THFOL into 2MTHF is kinetically difficult. This demonstrate the inability to produce 2MTHF via furfural hydrogenation to THFOL followed by THFOL hydrodeoxygenation.

CRediT authorship contribution statement

Ping Liu: Investigation, Writing - original draft, Formal analysis. **Luyang Sun:** Investigation. **Xinxin Jia:** Investigation. **Chen Zhang:** Conceptualization, Writing - review & editing, Funding acquisition. **Wei Zhang:** Methodology, Validation. **Yongji Song:** Supervision. **Hong Wang:** Supervision. **Cuiqing Li:** Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110951.

References

[1] M. Besson, P. Gallezot, C. Pinel, Conversion of biomass into chemicals over metal catalysts, Chem. Rev. 114 (2014) 1827–1870, https://doi.org/10.1021/Cr4002269.
[2] D.F. Aycock, Solvent applications of 2-methyltetrahydrofuran in organometallic and biphasic reactions, Org. Process Res. Dev. 11 (2007) 156–159, https://doi.org/10.1021/op060155c.
[3] V. Pace, P. Hoyos, L. Castoldi, P.D. de Maria, A.R. Alcantara, 2-methyltetrahydrofuran (2-MeTHF): a biomass-derived solvent with broad application in organic chemistry, Chemsuschem 5 (2012) 1369–1379, https://doi.org/10.1002/cssc.201100780.
[4] E. Christensen, J. Yanowitz, M. Ratcliff, R.L. McCormick, Renewable oxygenate blending effects on gasoline properties, Energy Fuels 25 (2011) 4723–4733, https://doi.org/10.1021/ef2010089.
[5] I. Obregón, I. Gandarias, A. Ocio, I. García-García, N. Alvarez de Eulate, P.L. Arias, Structure-activity relationships of Ni-Cu/Al2O3 catalysts for γ-valerolactone conversion to 2-methyltetrahydrofuran, Appl. Catal. B 210 (2017) 328–341, https://doi.org/10.1016/j.apcatb.2017.04.006.
[6] I. Obregon, I. Gandarias, N. Miletic, A. Ocio, P.L. Arias, One-pot 2-methyltetrahydrofuran production from levulinic acid in green solvents using Ni-Cu/Al2O3 catalysts, Chemsuschem 8 (2015) 3483–3488, https://doi.org/10.1002/cssc.201500671.
[7] T. Mizugaki, K. Togo, Z. Maeno, T. Mitsudome, K. Jitsukawa, K. Kaneda, One-pot transformation of levulinic acid to 2-methyltetrahydrofuran catalyzed by Pt–Mo/H-β in water, ACS Sustain. Chem. Eng. 4 (2016) 682–685, https://doi.org/10.1021/acssuschemeng.6b00181.
[8] X.-L. Du, Q.-Y. Bi, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, Tunable copper-catalyzed chemoselective hydrogenolysis of biomass-derived γ-valerolactone into 1,4-pentanediol or 2-methyltetrahydrofuran, Green Chem. 14 (2012) 935–939, https://doi.org/10.1039/C2GC16599F.

[9] M.G. Al-Shaal, A. Dzierbinski, R. Palkovits, Solvent-free γ-valerolactone hydrogenation to 2-methyltetrahydrofuran catalysed by Ru/C: a reaction network analysis, Green Chem. 16 (2014) 1358–1364, https://doi.org/10.1039/C3GC41803K.

[10] J.G. Stevens, R.A. Bourne, M.V. Twigg, M. Poliakoff, Real-time product switching using a twin catalyst system for the hydrogenation of furfural in supercritical CO2, Angew. Chem. Int. Ed. 49 (2010) 8856–8859, https://doi.org/10.1002/anie.201005092.

[11] F. Dong, Y.L. Zhu, G.Q. Ding, J.L. Cui, X.Q. Li, Y.W. Li, One-step conversion of furfural into 2-methyltetrahydrofuran under mild conditions, Chemsuschem 8 (2015) 1534–1537, https://doi.org/10.1002/cssc.201500178.

[12] S. Srivastava, G.C. Jadeja, J. Parikh, Copper-cobalt catalyzed liquid phase hydrogenation of furfural to 2-methylfuran: an optimization, kinetics and reaction mechanism study, Chem. Eng. Res. Des. 132 (2018) 313–324, https://doi.org/10.1016/j.cherd.2018.01.031.

[13] C.P. Jiménez-Gómez, J.A. Cecilia, R. Moreno-Tost, P. Maireles-Torres, Selective production of 2-methylfuran by gas-phase hydrogenation of furfural on copper incorporated by complexation in mesoporous silica catalysts, Chemsuschem 10 (2017) 1448–1459, https://doi.org/10.1002/cssc.201700086.

[14] P. Liu, W. Qiu, C. Zhang, Q. Tan, C. Zhang, W. Zhang, Y. Song, H. Wang, C. Li, Kinetics of furfural hydrogenation over bimetallic overlayer catalysts and the effect of oxygen vacancy concentration on product selectivity, Chemcatchem 11 (2019) 3296–3306, https://doi.org/10.1002/cctc.201900625.

[15] C. Nguyen-Huy, J. Lee, J.H. Seo, E. Yang, J. Lee, K. Choi, H. Lee, J.H. Kim, M.S. Lee, S.H. Joo, J.H. Kwak, J.H. Lee, K. An, Structure-dependent catalytic properties of mesoporous cobalt oxides in furfural hydrogenation, Appl. Catal. A 583 (2019) 117125, , https://doi.org/10.1016/j.apcata.2019.117125.

[16] E. Makela, R. Lahti, S. Jaatinen, H. Romar, T. Hu, R.L. Puurunen, U. Lassi, R. Karinen, Study of Ni, Pt, and Ru catalysts on wood-based activated carbon supports and their activity in furfural conversion to 2-methylfuran, Chemcatchem 10 (2018) 3269–3283, https://doi.org/10.1002/cctc.201800263.

[17] Y.F. Ma, G.Y. Xu, H. Wang, Y.X. Wang, Y. Zhang, Y. Fu, Cobalt nanocluster supported on ZrREnOx for the selective hydrogenation of biomass derived aromatic aldehydes and ketones in water, ACS Catal. 8 (2018) 1268–1277, https://doi.org/10.1021/acscatal.7b03470.

[18] S. Aghamohammadi, M. Haghighi, M. Maleki, N. Rahemi, Sequential impregnation vs. sol-gel synthesized Ni/Al2O3-CeO2 nanocatalyst for dry reforming of methane: effect of synthesis method and support promotion, Mol. Catal. 431 (2017) 39–48, https://doi.org/10.1016/j.mcat.2017.01.012.

[19] B. Wang, C. Wang, W. Yu, Z. Li, Y. Xu, X. Ma, Effects of preparation method and Mo2C loading on the Mo2C/ZrO2 catalyst for sulfur-resistant methanation, Mol. Catal. 482 (2020) 110668, , https://doi.org/10.1016/j.mcat.2019.110668.

[20] A.J. Reynoso, J.L. Ayastuy, U. Iriarte-Velasco, M.A. Gutiérrez-Ortiz, Cobalt aluminate spinel-derived catalysts for glycerol aqueous phase reforming, Appl. Catal. B 239 (2018) 86–101, https://doi.org/10.1016/j.apcatb.2018.08.001.

[21] W.D. Shafer, G. Jacobs, B.H. Davis, Fischer–Tropsch synthesis: investigation of the partitioning of dissociated H2 and D2 on activated cobalt catalysts, ACS Catal. 2 (2012) 1452–1456, https://doi.org/10.1021/cs300269m.

[22] J.H. Song, S. Yoo, J. Yoo, S. Park, M.Y. Gim, T.H. Kim, I.K. Song, Hydrogen production by steam reforming of ethanol over Ni/Al2O3-La2O3 xerogel catalysts, Mol. Catal. 434 (2017) 123–133, https://doi.org/10.1016/j.mcat.2017.03.009.

[23] S. Sitthisa, W. An, D.E. Resasco, Selective conversion of furfural to methylfuran over silica-supported Ni-Fe bimetallic catalysts, J. Catal. 284 (2011) 90–101, https://doi.org/10.1016/j.jcat.2011.09.005.

[24] P. Biswas, J.-H. Lin, J. Kang, V.V. Guliants, Vapor phase hydrogenation of 2-methylfuran over noble and base metal catalysts, Appl. Catal. A 475 (2014) 379–385, https://doi.org/10.1016/j.apcata.2014.01.054.

[25] D. Scholz, C. Aellig, I. Hermans, Catalytic transfer hydrogenation/hydrogenolysis for reductive upgrading of furfural and 5-(hydroxymethyl)furfural, Chemsuschem 7 (2014) 268–275, https://doi.org/10.1002/cssc.201300774.

[26] M.J. Gilkey, P. Panagiotopoulou, A.V. Mironenko, G.R. Jenness, D.G. Vlachos, B. Xu, Mechanistic insights into metal lewis acid-mediated catalytic transfer hydrogenation of furfural to 2-methylfuran, ACS Catal. (2015) 3988–3994, https://doi.org/10.1021/acscatal.5b00586.

[27] G.R. Jenness, D.G. Vlachos, DFT study of the conversion of furfuryl alcohol to 2-methylfuran on RuO2 (110), J. Phys. Chem. C (2015), https://doi.org/10.1021/jp5109015.

[28] X. Wang, F. Liang, C. Huang, Y. Li, B. Chen, Siliceous tin phosphates as effective bifunctional catalysts for selective conversion of dihydroxyacetone to lactic acid, Catal. Sci. Tech. 6 (2016) 6551–6560, https://doi.org/10.1039/C6CY00553E.

[29] X. Wang, J.C. Yu, P. Liu, X. Wang, W. Su, X. Fu, Probing of photocatalytic surface sites on SO42 − /TiO2 solid acids by in situ FT-IR spectroscopy and pyridine adsorption, J. Photochem. Photobiol. A 179 (2006) 339–347, https://doi.org/10.1016/j.jphotochem.2005.09.007.

[30] Y.F. Zhang, G.L. Fan, L. Yang, F. Li, Efficient conversion of furfural into cyclopentanone over high performing and stable Cu/ZrO2 catalysts, Appl. Catal. A 561 (2018) 117–126, https://doi.org/10.1016/j.apcata.2018.05.030.

[31] F. Dong, Y.L. Zhu, H.Y. Zheng, Y.F. Zhu, X.Q. Li, Y.W. Li, Cr-free Cu-catalysts for the selective hydrogenation of biomass-derived furfural to 2-methylfuran: the synergistic effect of metal and acid sites, J. Mol. Catal. A Chem. 398 (2015) 140–148, https://doi.org/10.1016/j.molcata.2014.12.001.

[32] J. Zhao, H. Chen, J. Xu, J. Shen, Effect of surface acidic and basic properties of the supported nickel catalysts on the hydrogenation of pyridine to piperidine, J. Phys. Chem. C 117 (2013) 10573–10580, https://doi.org/10.1021/jp402238q.

[33] C. Zhang, Q. Lai, J.H. Holles, Bimetallic overlayer catalysts with high selectivity and reactivity for furfural hydrogenation, Catal. Commun. 89 (2017) 77–80, https://doi.org/10.1016/j.catcom.2016.10.023.

[34] W.B. Gong, C. Chen, H.M. Zhang, G.Z. Wang, H.J. Zhao, In situ synthesis of highly dispersed Cu-Co bimetallic nanoparticles for tandem hydrogenation/rearrangement of bioderived furfural in aqueous-phase, ACS Sustain. Chem. Eng. 6 (2018) 14919–14925, https://doi.org/10.1021/acssuschemeng.8b03418.

[35] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sadaba, M. Lopez Granados, Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels, Energy Environ. Sci. 9 (2016) 1144–1189, https://doi.org/10.1039/C5EE02666K.

[36] M.M. Antunes, S. Lima, A. Fernandes, M.F. Ribeiro, D. Chadwick, K. Hellgardt, M. Pillinger, A.A. Valente, One-pot hydrogen production and cascade reaction of furfural to bioproducts over bimetallic Pd-Ni TUD-1 type mesoporous catalysts, Appl. Catal. B 237 (2018) 521–537, https://doi.org/10.1016/j.apcatb.2018.06.004.

[37] B. Seemala, C.M. Cai, C.E. Wyman, P. Christopher, Support induced control of surface composition in Cu-Ni/TiO2 catalysts enables high yield co-conversion of HMF and furfural to methylated furans, ACS Catal. 7 (2017) 4070–4082, https://doi.org/10.1021/acscatal.7b01095.

[38] Z.F. Jiang, W.M. Wan, Z.X. Lin, J.M. Xie, J.G.G. Chen, Understanding the role of M/Pt(111) (M = Fe, Co, Ni, Cu) bimetallic surfaces for selective hydrodeoxygenation of furfural, ACS Catal. 7 (2017) 5758–5765, https://doi.org/10.1021/acscatal.7b01682.

[39] V. Vorotnikov, G. Mpourmpakis, D.G. Vlachos, DFT study of furfural conversion to furan, furfuryl alcohol, and 2-methylfuran on Pd(111), ACS Catal. 2 (2012) 2496–2504, https://doi.org/10.1021/cs300395a.

[40] S.H. Pang, J.W. Medlin, Adsorption and reaction of furfural and furfuryl alcohol on Pd(111): unique reaction pathways for multifunctional reagents, ACS Catal. 1 (2011) 1272–1283, https://doi.org/10.1021/Cs200226h.

[41] Y. Nakagawa, H. Nakazawa, H. Watanabe, K. Tomishige, Total hydrogenation of furfural over a silica-supported nickel catalyst prepared by the reduction of a nickel nitrate precursor, Chemcatchem 4 (2012) 1791–1797, https://doi.org/10.1002/cctc.201200218.

[42] S.G. Wang, V. Vorotnikov, D.G. Vlachos, A DFT study of furan hydrogenation and ring opening on Pd(111), Green Chem. 16 (2014) 736–747, https://doi.org/10.1039/c3gc41183d.

[43] H.-Y. Zheng, Y.-L. Zhu, B.-T. Teng, Z.-Q. Bai, C.-H. Zhang, H.-W. Xiang, Y.-W. Li, Towards understanding the reaction pathway in vapour phase hydrogenation of furfural to 2-methylfuran, J. Mol. Catal. A Chem. 246 (2006) 18–23, https://doi.org/10.1016/j.molcata.2005.10.003.

[44] D. Liu, D. Zemlyanov, T. Wu, R.J. Lobo-Lapidus, J.A. Dumesic, J.T. Miller, C.L. Marshall, Deactivation mechanistic studies of copper chromite catalyst for selective hydrogenation of 2-furfuraldehyde, J. Catal. 299 (2013) 336–345, https://doi.org/10.1016/j.jcat.2012.10.026.

[45] C.P. Jiménez-Gómez, J.A. Cecilia, D. Durán-Martín, R. Moreno-Tost, J. Santamaría-González, J. Mérida-Robles, R. Mariscal, P. Maireles-Torres, Gas-phase hydrogenation of furfural to furfuryl alcohol over Cu/ZnO catalysts, J. Catal. 336 (2016) 107–115, https://doi.org/10.1016/j.jcat.2016.01.012.

[46] W. Gong, C. Chen, H. Zhang, Y. Zhang, Y. Zhang, G. Wang, H. Zhao, Highly selective liquid-phase hydrogenation of furfural over N-doped carbon supported metallic nickel catalyst under mild conditions, Mol. Catal. 429 (2017) 51–59, https://doi.org/10.1016/j.molcata.2016.12.004.

[47] W. Wan, G.R. Jenness, K. Xiong, D.G. Vlachos, J.G. Chen, Ring-opening reaction of furfural and tetrahydrofurfuryl alcohol on hydrogen-predosed iridium(1 1 1) and cobalt/iridium(1 1 1) surfaces, Chemcatchem 9 (2017) 1701–1707, https://doi.org/10.1002/cctc.201601646.

[48] G.R. Jenness, W.M. Wan, J.G.G. Chen, D.G. Vlachos, Reaction pathways and intermediates in selective ring opening of biomass-derived heterocyclic compounds by iridium, ACS Catal. 6 (2016) 7002–7009, https://doi.org/10.1021/acscatal.6b01310.

[49] J. Guan, J. Li, Y. Yu, X. Mu, A. Chen, DFT studies of the selective C–O hydrogenolysis and ring-opening of biomass-derived tetrahydrofurfuryl alcohol over Rh (111) surfaces, J. Phys. Chem. C 120 (2016) 19124–19134, https://doi.org/10.1021/acs.jpcc.6b05026.