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Conversion of furan derivatives for preparation of biofuels over Ni–Cu/C catalyst

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ABSTRACT

Conversions of furfural and 5-hydroxymethylfurfural as model components in bio-oil were investigated over Ni–Cu/C catalyst with formic acid as hydrogen donor in isopropanol solvent to produce biofuels. The effects of reaction temperature, feed ratio, and reaction time were studied. A high yield of 2-methylfuran up to 91 mol% was obtained from furfural in 8 h at 200°C, and under same conditions 80 mol% yield of 2,5-dimethylfuran could also be obtained from 5-hydroxymethylfurfural in 6 h. The results verified the catalyst performance and the availability of the reaction conditions for producing biofuels from furan derivatives.

KEYWORDS

Biofuel; 2,5-dimethylfuran; furfural; hydrogen donor; 5-hydroxymethylfurfural; 2-methylfuran

1. Introduction

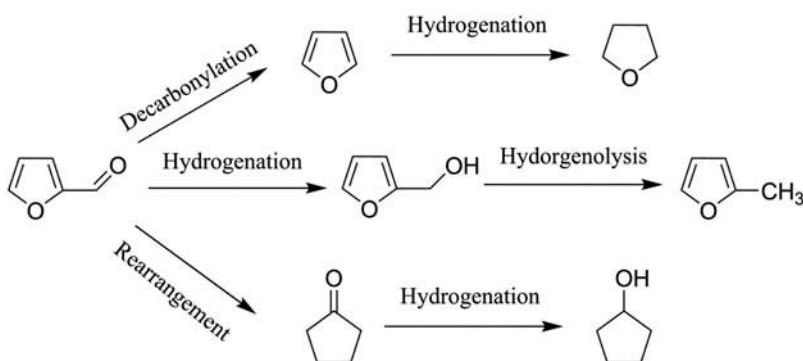
With the continuous diminishing of fossil resources, the development of biomass resource is quite urgent and promising (Huber et al., 2006). Furfural (FU) and 5-hydroxymethylfurfural (HMF) are two abundant furan derivatives in bio-oil (Demirbas, 2006; Huber et al., 2006; Hassan et al., 2009). Particularly, FU is regarded as one of the top 10 biorefinery building chemicals (Bozell and Petersen, 2010), since FU can be widely used to produce fuels and chemicals such as furan, furfural alcohol (FOL), 2-methylfuran (2-MF), tetrahydrofuran (THF), and cyclopentanone, as shown in Scheme 1 (Pushkarev et al., 2012; Bohre et al., 2015). Among the products, 2-MF can be used as a fuel additive with high research octane number (103 > 97 of gasoline) and adequate energy density (28.5 MJ/L > 21.0 MJ/L of ethanol) (Bohre et al., 2015). Due to the high activity of FU, a high yield of 2-MF is usually hard to be achieved under mild conditions. At present, the highest 2-MF yield is 95.5 mol% over Cu/SiO₂ catalyst with a high H₂ to vaporous furfural ratio of 17:1 (Dong et al., 2016). However, the application of gaseous H₂ causes severe challenges in securities of storage and operation.

Therefore, in-situ hydrodeoxygenation process is put forward (Xu et al., 2015), where the hydrogen source is offered from hydrogen donors such as formic acid, methanol, and isopropanol. Activated carbon-supported Ni–Cu catalyst, with the advantage of low price, has been proved effective in producing FOL from conversion of FU in isopropanol solvent (Reddy Kannapu et al., 2015). However, FOL is not a qualified biofuel due to its low heat value and relative high oxygen content. Therefore, the conversion of FU over Ni–Cu/C in isopropanol solvent is investigated to enhance the product selectivity to 2-MF, with a stronger hydrogen donor of formic acid. Furthermore, the availability of the optimized catalytic reaction conditions to the conversion of HMF to 2,5-dimethylfuran (DMF) is also tested, since DMF is also a good fuel additive with research octane number (101) and high energy density (29.3 MJ/L) (Bohre et al., 2015).

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Scheme 1. The potential reaction pathways of furfural.

2. Experimental section

The bimetallic catalyst 10%Ni–10%Cu/C was prepared by incipient wetness impregnation method: 0.55 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sinopharm, $\geq 99\%$) and 0.42 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sinopharm, $\geq 99\%$) were dissolved in 2.5 g deionized water; and then impregnated on 1 g activated carbon (Sinopharm, mean particle size: 55–65 μm , surface area: 715 m^2/g , average pore size: 2.51 nm, and measured by N_2 physisorption), aging for 10 h at room temperature; then, the sample was dried at 80°C for 10 h and calcined at 500°C for 5 h under N_2 atmosphere; finally, the sample was reduced at 550°C for 2 h in a reduction atmosphere (50 vol% H_2 and 50 vol% Ar, 300 mL/min).

The experiments on conversion of FU were conducted in a 100 mL autoclave (C276 Hastelloy, CJF-0.1 L). In each run, the catalyst of 10%Ni–10%Cu/C (0.05–0.2 g), FU (0.5–2 g), formic acid (0–4 g), and isopropanol (10 g) were loaded into the reactor. Before heating, the reactor was flushed by N_2 three times and then remained at 1 MPa. The reactor was then heated to 180–260°C and kept for 1–7 h. The liquid product was analyzed by GC-MS (Varian 320GC/300MS) and quantified through internal standard method using ethylene glycol as the standard substance.

3. Results and discussion

3.1. Effect of reaction temperature on furfural conversion and product yields

The conversions of FU under different temperatures are shown in Figure 1. It could be seen that the conversion of FU increased rapidly with increasing temperature in low temperatures and then became stable around 97 mol% above 200°C. The product distribution remarkably changed with varied temperatures. Furan from decarbonylation of FU was more generated at higher temperatures since it is an endothermic process (Pushkarev et al., 2012). THF and butanol, respectively, derived from deep hydrogenation and ring-opening conversion of furan, were more generated at high temperatures as well, making the product distribution complex. The yield of FOL decreased with increasing temperature, since FOL would further convert to 2-MF by hydrogenolysis at higher temperatures. However, the decarbonylation of FU became more prevalent at higher temperatures too, so a maximum 2-MF yield of 65.5 mol% appeared at middle 220°C. In general, from the perspective of high yield of 2-MF with low energy cost, 200°C was the optimal temperature in this reaction system.

3.2. Effect of feed ratios on furfural conversion and product yields

The conversion of FU and product yields varied with mass ratios of catalyst to FU to formic acid was investigated as shown in Table 1. It could be seen that the conversions of FU were generally all above

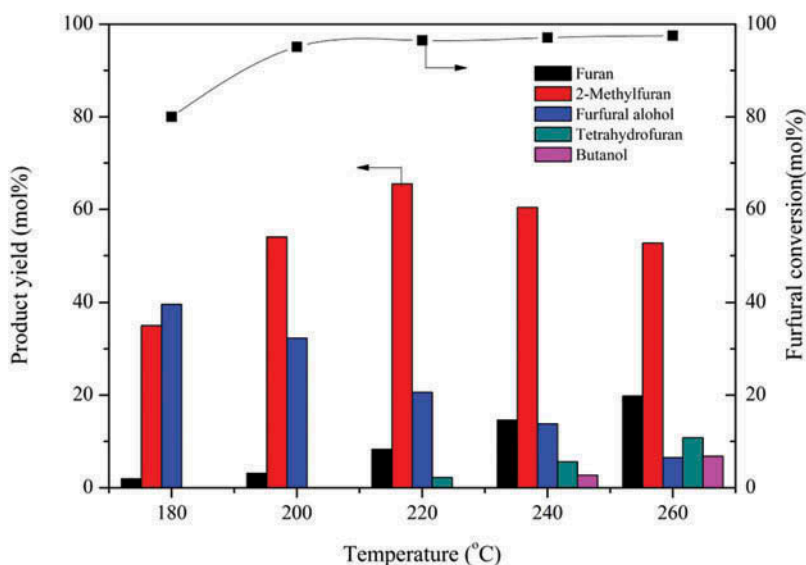


Figure 1. Furfural conversions and product yields under different reaction temperatures. Feedstock: 1 g furfural, 2 g formic acid, 10 g isopropanol, 0.1 g catalyst, and reaction time = 4 h.

Table 1. Furfural conversion and product yields varied with different feedstock ratios over Ni–Cu/C catalyst.

Entry	Mcat.:M _{FU} :M _{acid}	FU Conversion	Yield			
			Furan	2-MF	FOL	Butanol
1	0.1:1:0	82.7	2.8	3.4	75.1	0.0
2	0.1:1:1	93.4	3.0	35.6	53.1	0.0
3	0.1:1:2	95.1	3.1	57.6	32.3	0.0
4	0.1:1:4	97.5	4.6	66.2	22.1	2.5
5	0.05:1:2	83.3	2.3	36.1	44.4	0.0
6	0.2:1:2	100.0	4.1	59.4	31.2	2.4
7	0.1:2:2	79.7	3.6	31.4	42.1	0.0
10	0.1:0.5:2	98.1	4.4	70.4	20.4	2.7

Reaction time: 4 h, reaction temperature: 200°C, FU: furfural, 2-MF: 2-methylfuran, FOL: furfural alcohol.

80%, and a high catalyst proportion favored the increase of FU conversion. FOL and 2-MF were two major products, while the yields of furan and butanol were rather low for all cases. If no formic acid was added, a high FOL yield of 75.1 mol% was achieved. With increasing proportion of formic acid the selectivity to 2-MF increases remarkably, while the yield of FOL decreased reversely. It indicates hydrogenation of FU to FOL can happen even with no formic acid, which could be attributed to the hydrogen donating conversion of isopropanol with the formation of acetone (Gilkey et al., 2015). However, the hydrogen donation capacity of isopropanol is relatively weak for further hydrogenolysis of the hydroxyl group, and with the addition of more formic acid as a stronger hydrogen donor (Zeng et al., 2016), furfural alcohol was more converted to 2-methylfuran. Generally, Mcat.:M_{FAL}:M_{acid} = 0.1:1:2 was the optimal ratio for maximizing the yield of 2-methylfuran at 200°C.

3.3. Effect of reaction time on furfural conversion and product yields

The influence of reaction time was investigated as shown in Figure 2. It could be seen that FU was completely consumed in 8 h and the conversion proceeded faster in the early 4 h. The yield of furan just kept in low level. The yield of FOL increased with evolution of the reaction in early stage and

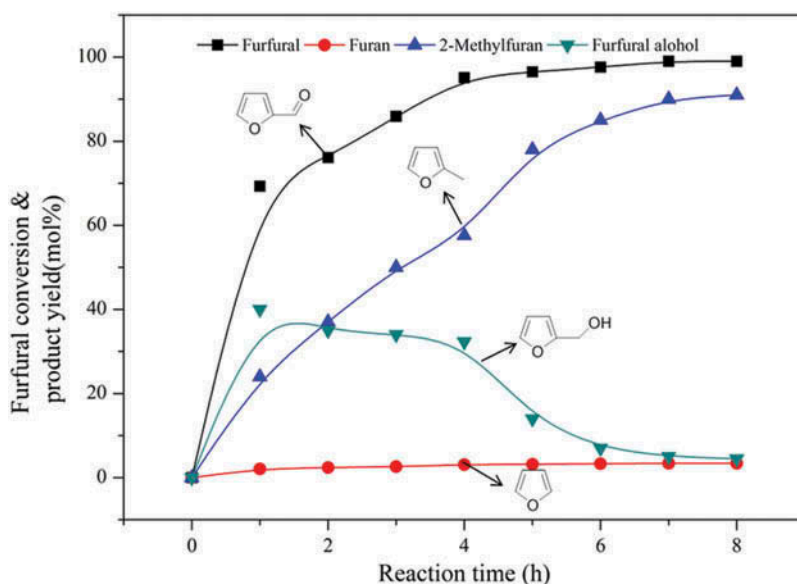


Figure 2. The furfural conversion and product yields with varied reaction time over 10%Ni–10%Cu/C at 200°C. Feedstock: 1 g furfural, 2 g formic acid, 10 g isopropanol, and 0.1 g catalyst.

then became nearly stable in middle stage and finally transformed to a declining trend. Correspondingly, the yield of 2-MF monotonously increased with prolonging of the reaction time in the first 6 h, with the highest 2-MF yield of 91 mol% at the end of reaction with the consecutive reaction mechanism for FOL as intermediate (Gilkey et al., 2015).

3.4. Effect of reaction time on 5-hydroxymethylfurfural conversion and product yields

Since HMF was another significant furan derivative in bio-oil with similar molecular structure and chemical properties to FU (Huber et al., 2006), the prior optimized reaction conditions were therefore tested for the conversion of HMF for preparation of DMF. The results are shown in Figure 3. Due to the more active functional groups in HMF, the product distribution was more complex. It showed the decreasing trend of HMF conversion, the monotonous increasing trend of DMF, and the arch-shape variation of the carbonyl reduction products of 2,5-bis-hydroxymethylfuran (BHMF) and 5-methyl furfural alcohol (MFA). The yield of others, consisting of 2-MF, FOL, and 5-methylfurfural, was augmented under longer reaction times, which could be an explanation for the slow increasing rate of DMF at longer times. The yield of DMF reached up to 80 mol% in 6 h, verified the availability of the catalyst with optimized reaction conditions for generation of DMF from conversion of HMF. There could be two reaction routes for the formation of DMF from HMF (Shi et al., 2016). The first one is that DMF was derived from hydrogenation of the carbonyl group, followed by consecutive hydrolysis of the obtained BHMF as intermediates. In the second route, DMF was generated from first hydrogenolysis of the hydroxyl group in HMF with 5-methylfurfural as the intermediate, followed by total reduction of the carbonyl group. Herein, the obtained product distribution indicated that DMF was predominantly derived from the first route rather than the second one under present catalytic reaction conditions, since only a little amount of 5-methylfurfural was detected in the liquid.

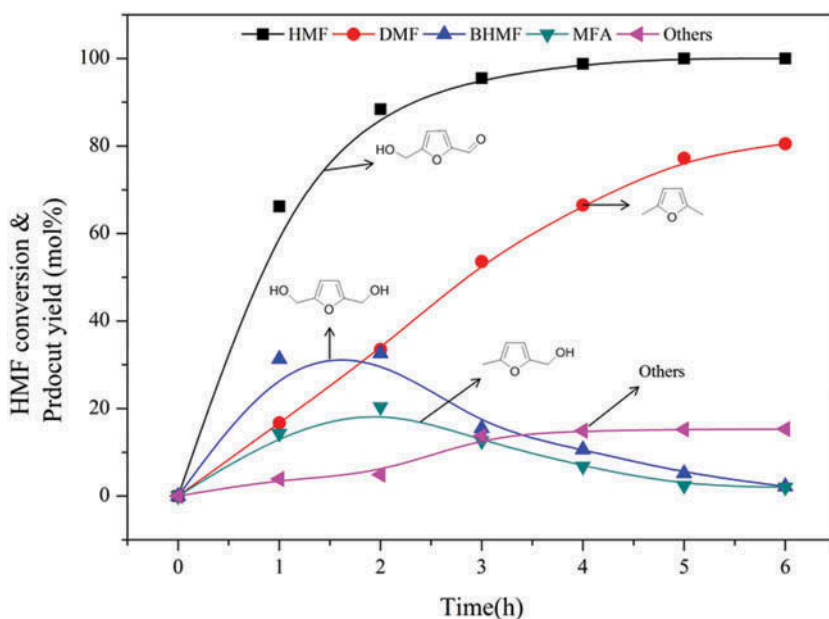


Figure 3. The conversion of HMF and the product yield with reaction time over 10%Ni–10%Cu/C at 200°C with formic acid as the hydrogen donor. HMF: 5-hydroxymethylfurfural; DMF: 2,5-dimethylfuran, BHMF: 2,5-bis-hydroxymethylfuran, MFA: 5-methyl furfural alcohol. Others include 2-methylfuran, furfural alcohol, 5-methylfurfural. Feedstock: 1 g HMF, 2 g formic acid, 10 g isopropanol, and 0.1 g catalyst.

4. Conclusions

Conversions of FU and HMF as model components in bio-oil were investigated over Ni–Cu/C catalyst with formic acid as hydrogen donor in isopropanol solvent. A higher temperature was found promotive to the conversion of FU but with complex product distribution. Isopropanol could promote the hydrogenation of carbonyl group with the formation of FOL. The existence of formic acid could further enhance the hydrogenolysis of FOL to 2-MF. The high yield of 2-MF up to 91 mol % was obtained in 8 h at 200°C, and under same conditions DMF could also be obtained from HMF with 80 mol% high yield in 6 h, which verified the high catalyst performance and the availability of the reaction conditions for conversion of furan derivatives to biofuels.

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