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Catalytic Selective Hydrogenation and Rearrangement of 5-Hydroxymethylfurfural to 3-Hydroxymethyl-cyclopentone over Bimetallic Nickel-Copper Catalyst in Water

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The selective hydrogenation and rearrangement of 5-hydroxymethylfurfural (5-HMF) to 3-hydroxymethyl-cyclopentone (HCPN) was studied over MOFs-derived bimetallic nickel-copper catalyst in water. The combination of nickel and copper dramatically improved the efficiency both in the selective hydrogenation of carbonyl group of 5-HMF and hydrogenative ring-rearrangement of C5 ring, affording 70.3% yield for HCPN and 99.8% yield for rearrangement products. Moreover, it is indicated that water acts as solvent, reactant, and proton donor by dissociation at elevated temperature, which supplied slightly acidic conditions and promotes the rearrangement reaction.

Introduction

Production of chemicals and fuels from renewable biomass resources is an important topic in aspects of chemistry and chemical engineering.^[1,2] Due to the oxygen-rich nature and excellent water-solubility for lots of biomass-derived feedstocks, water is recognized as undoubtedly preferred clean solvent, and thus their corresponding water-phase transformation has become current research focus.[3-5] As a representative biomass-derived platform obtained from C6 sugars,^[6-8] 5-hydroxymethylfurfural (5-HMF) has been extensively investigated and upgraded to variety of downstream chemicals via catalytic dehydration, oxidation, esterification, hydrogenation, and rearrangement, etc.^[9-16] The initial research on the hydrogenation of 5-HMF mainly focused (FDA)^[17] achieving 2,5-furandimethanol and 2,5tetrahydrofuran dimethanol (THFDA)^[18] via the reduce of C=C and/or C=O groups. Recently, hydrogenative rearrangement of 5-HMF in water has attracted increasing attention. Water is recognized to play a crucial role in the rearrangement besides serving as solvent, although the mechanism is not yet clear and needs to be clarified. Up to now, precious metal catalysts (Ru, Pt, Au, and Pd, et al.), have achieved valuable cyclopentanone derivatives and aliphatic alcohols in water.[19-^{21]} In these studies, Lewis acidic supports or additives (Nb_2O_5 , Al₂O₃, ZrO₂, TiO₂, and Ta₂O₅)^[22,23] are generally required for purpose of promoting rearrangement, via improving the removal of the hydroxyl group, ring-open, and ringrearrangement.^[24] Despite Lewis acid possessed the remarkable promotion effect in hydrogenative rearrangement of 5-HMF, it simultaneously cause instability of 5-HMF and leaded to over-dehydration and polymerization by-products in water. In fact, nonacidic catalysts under acidic additives-free conditions may be more beneficial, but there have been few related reports so far.

Particularly, 3-hydroxymethyl-cyclopentone (HCPN), a high value-added chemical used as an intermediate chemical for production of fragrances, pesticides, and polymers,^[25] is rather difficult to achieve high selectivity in hydrogenation and rearrangement of 5-HMF, which still faces great challenge. To promote the yield of HCPN, two key problems should resolve as illustrated in Scheme 1. (1) The unsaturated furan ring of 5-HMF is readily reduced immediately after the initial hydrogenation of carbonyl group, leading to undesirable by-product THFDA, which is unable to undergo rearrangement.^[26] Thus, the hydrogenation activity requires to be suppressed in order to merely reduce the C=O group while retain the furan



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ring. (2) The hydrogenative rearrangement of FDA to HCPN involved ring-rearrangement and dehydration steps, which are seriously affected by protons (pH values) and Lewis acids; the acidic centres need to be accurately regulated to avoid generating the ring-opening alcohols as well as excessive dehydration products such as 2-methyl-furural (MF) and 2,5-dimethylfuran (DMF).^[27] Therefore, it is necessary to design new catalysts with multi-active sites to fulfil these coupled multiple reactions.

Our group has been dedicated to developing highperformance Ni-base catalysts for the catalytic hydrogenation of biomass and its derivatives. Ni/AC that has outstanding performances in the fragmentation-hydrogenolysis of lignin, was demonstrated incapable to catalyze rearrangement.^[29,30] In addition, Ni-Cu/SBA-15 catalyst that used to efficiently catalyze another biomass-derived platform furfural to cyclopentanone via hydrogenation and rearrangement was of poor selectivity for HCPN.^[31] We noticed that the dissociation of water could be promoted if increasing the reaction temperature. Theoretical concentration of proton reached 7.37×10⁻⁷ mol/L at 100 °C (pH=6.1) for water (pH=7.0 at 25 °C), suggesting water can act as proton donor and create a slightly acidic condition. However, little research has been made on the proton donor role of water. Herein, nickel was selected as the active component for hydrogenation, with activity suppressed through introduction of a secondary metal (copper). Water was selected as solvent, and its role was studied at adopted temperature by employing carbon as the carrier to exclude the influence of Lewis acidic sites. According to the above design, the hydrogenation-rearrangement of 5-HMF to HCPN could be realized by bimetallic Ni-Cu/C catalyst in water without any Lewis supports or additives.

Experimental section

Materials and reagents

Ni(NO₃)₂, Cu(NO₃)₂, Co(NO₃)₂, Fe(NO₃)₃, ethanol, buffer agents, N,N-dimethyl formamide (DMF), NaOH. dodecane. isopropanol, and tetrahydrofuran were obtained from Tianjin Kermel Chemical Reagent. 2,5-Dihydroxyterephthalic acid, 1,4dioxane, and tetrahydrofurfuryl alcohol were obtained from Aladdin Industrial Inc. ¹⁸O-enriched water (97% ¹⁸O abundance) was obtained from Shanghai Research Institute of Chemical Industry. D_2O (99.9% D abundance) was obtained from Energy Chemical Co., Ltd. FDA and 5-HMF were purchased from Innochem Co., Ltd. HCPN and HHD were synthesized in our laboratory. Distilled water was purified in laboratory.

Synthesis of catalysts

Ni-Cu-MOF-74 was prepared by the solvent-thermal method based on a previous literature.^[32] In a typical synthesis, 0.35 g (1.76 mmol) 2,5-dihydroxyterephthalic acid was first dissolved in 70 mL of N,N-dimethyl formamide (DMF), followed by addition of 0.79 g (3.29 mmol) Cu(NO₃)₂, 0.24 g (0.82 mmol) Ni(NO₃)₂, 4.7 mL of deionized water, and 4.7 mL of ethanol. The mixture was stirred and sonicated for 10 min, and then

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transferred into a Teflon-lined stainless steel autoclave te After solvent-thermal treatment at 120 °C for 20° h, 306 664 med sample was centrifuged, thoroughly washed with DMF and ethanol, and finally dried in oven overnight. Ni-MOF-74, Co-MOF-74, Cu-MOF-74, Fe-MOF-74, Ni-Fe-MOF-74, and Ni-Co-MOF-74 were prepared using the same method.

Ni-Cu/C material was prepared by pyrolysis of Ni-Cu-MOF-74 under N₂. The typical procedure was described as follows: Ni-Cu-MOF-74 was put in quartz tube and heated at a heating rate of 10 °C·min⁻¹ under continuous N₂ flow. After the target temperature (600 °C) reached, the material was held for 2 h and then cooled to room temperature. Ni/C, Co/C, Cu/C, Fe/C, Ni-Fe/C, and Ni-Co/C were prepared using the same method.

Characterization

X-ray powder diffraction (XRD) patterns were obtained using an Empyrean-100 powder diffraction system with Cu Ka radiation (λ =0.15406 nm) between 5° and 80° (40 kV, 40 mA). ¹H NMR and ¹³C NMR spectra were recorded on an AVANCE III 400 MHz spectrometer at room temperature. The acidity of the samples were measured using temperature programmed desorption of NH_3 (NH_3 -TPD) by a micromeritics autochem II apparatus with mass spectrometer (TPDE-MS) on a micromeritics AutoChem 2910 apparatus. The pH values of solvents were detected by Sartorius-PB-10 with combination silver electrode and BNC electrode. The TGA measurements were carried out under nitrogen on a Mettler Toleso TGA/SDTA 851 instrument at a heating rate of 10 °C ⋅ min⁻¹. The microstructure of the powder was characterized using scanning electron microscopy (JSM-7800F). The morphology of the materials was examined by transmission electron microscopy (TEM) on a HITACHI H7700 electron microscope. High-angle annular dark field scanning transmission electron microscope (HAADF-STEM) analysis and the corresponding energy-dispersive X-ray spectroscopy (EDX) was taken on a JEM-200F with Mo supporting film for the suspension of catalysts.

Reaction procedures and products analysis

The typical catalytic procedure is as follows: 0.126 g (1 mmol) 5-HMF, 5 mL of solvent and specified amount of catalyst were added into a 50 mL Parr autoclave, and then the autoclave was sealed. After charging H_2 , the reaction mixture was stirred and heated to the specified temperature. The reaction was stopped after desired hours, and then analyzed by gas chromatograph (Aligent GC-7890) with internal standard method. The mass spectrometry was measured by using an Agilent 6890N GC/5973 MS instrument.

Results and discussion

Characterizations of materials

Ni-Cu/C has been characterized in detail with SEM, TEM, XRD, and NH₃-TPD (Figure 1). SEM and TEM images confirmed that Ni-Cu/C retained the rod-like morphology of Ni-Cu-MOF-74. The XRD pattern showed peaks at 43.3° , 50.4° , and 74.2° assigned to Cu(111), (200), (220) diffraction planes, while

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 44.3° , 51.6° , and 76.1° was attributed to Ni (111), (200), and (220)



Fig. 1 SEM (a-c), TEM (d), XRD (e), and NH₃-TPD (f) of Ni-Cu/C.

face. And diffraction peak at 36.4° was assigned to Cu₂O (111). These indicated pyrolysis of Ni-Cu-MOF-74 at 600 °C in N2 atmosphere leaded to the decomposition of Ni-Cu-MOF-74, with metal cations reduced to metallic Ni, Cu, and Cu₂O dispersed on carbon. Furthermore, the XRD pattern of Cu/C displayed Cu⁰ and Cu₂O, and Ni/C possessed Ni⁰ and NiO. Afterwards, the chemical compositions within the surface near region were compared by XPS analysis, and the results were listed in Tables S2 and S3. It was clear that, for Ni-Cu/C, the content of Ni⁰ and Ni₂O₃ was much lower than that of Ni/C, while the content of NiO consequently increased. On the other hand, Cu₂O changed to be the major surface metal species for Ni-Cu/C catalyst, with an obvious decrease in Cu⁰ and CuO contents in comparison with Cu/C. Moreover, the absence of NH₃ desorption peaks (Figure 1f) gave evidence that the effect stems from acidic sites of Ni-Cu/C catalyst could be excluded. The elemental compositions of the Ni-Cu/C measured by EDX mapping (Figures 2b-d) and line-scan (Figures 2e,f) confirmed the smaller particles with average size of 11 nm distributed on carbon surface and inside were bimetallic Ni-Cu nanoparticles,



Fig. 2 HAADF-STEM image of Ni-Cu/C (a), the corresponding energy-dispersive X-ray spectroscopy (EDX) mappings C (b), Cu

(c), and Ni (d), and line-scan (recorded along the line marked) of smaller NPs (e) and bigger NPs (f) of Ni+Co/C3(RedCimer) Cut, green line: Ni, and grey line: C in e and f).

while larger ones (around 50-80 nm) were Cu nanoparticles, due to its facial aggregation during pyrolysis at the high temperature. Cu nanoparticles are well-dispersed on carbon.

Preliminary comparison of nickel-based catalysts

In the initial study, the as-synthesized MOFs-derived monometallic catalysts (Ni/C, Cu/C, Fe/C, and Co/C) and bimetallic catalysts (Ni-Cu/C, Ni-Fe/C, and Ni-Co/C) were tested in the hydrogenation and rearrangement of 5-HMF. The exploratory experiments were performed at 140 °C under 2.0 MPa H₂ in water, and the catalytic results were listed in Table 1. As expected, Ni/C achieved >99% conversion with 79.1% yield to THFDA, suggesting completely hydrogenation of C=O groups and unsaturated C=C groups in furan ring. As discussed above, if the intermediate FDA was further hydrogenated to THFDA, the following hydrogenation rearrangement reaction could be seriously suppressed. It is noted that Cu/C showed decreased activity (45.5% conversion) but a certain activity for rearrangement as detected by 22.7% yield to HHD. In contrast, Co/C reached nearly completely conversion and showed some activity for generating rearrangement products, affording yield of 19.0% to HCPN, 22.8% to HCPEN, and 14.4% to HHD. Fe/C showed poor activity and achieved only 18.6% conversion without any hydrogenation and rearrangement products detected under the same conditions. Considering introduction of a secondary metal may alter the catalytic performance, transition metals such as Cu, Co, and Fe were respectively added to Ni/C. Among them, Ni-Cu/C was screened out as the best bimetallic catalyst, with 93.8% conversion and 87.2% yield to rearrangement products. It afforded 50.4% yield to HCPN. Further decreasing the molar ratio of 5-HMF and metal contributed to hydrogenative rearrangement (70.3% yield of HCPN and 99.8% yield for rearrangement products). These results indicated Cu displayed a remarkable promotion towards production of unsaturated HCPN, and Ni could endow the bimetallic catalyst the capacity for hydrogenation of C=O and groups, simultaneously Cu may contribute to rearrangement and suppress the activity in C=C hydrogenation. Then, Cu was replaced with Co or Fe, the consequent Ni-Co/C and Ni-Fe/C catalysts showed unsatisfied results, with plenty of humins (brown polymer) generated, which is consistent with the previous literatures.[33] These comparative results strongly indicated that the combination of Cu and Ni guaranteed an excellent activity in the hydrogenation and rearrangement of 5-HMF to HCPN.

The effect of solvent

Generally, the solvents play an important role in the catalytic conversion of 5-HMF in term of products distribution. The effect of solvents was investigated by examining the catalytic performance of Ni-Cu/C in isopropanol (IPA), tetrahydrofuran (THF), tetrahydrofurfural alcohol (THFA), ethanol, and 1,4-Dioxane (Diox). As shown in Figure 3, the solvents remarkably

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influenced the distribution of hydrogenation products (FDA HHCPEN). As mentioned above, 5-HMF mainly converted into and THFDA) and rearrangement products (HCPN, HHD, and

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Table 1 Hydrogenation and rearrangement of 5-HMF over various transition metal cataly	ysts
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	Catalysts	Conv. (mol%)	Yield _{hydro.} (mol%)		Yield _{rear.} (mol%)			
Entry			OH OH FDA	OH OH THFDA	HO HCPN	о — — — — — — — — — — — — — — — — — — —	HO HO HHCPEN	total rear.
1	Ni/C	>99	-	79.1	-	-	-	-
2	Co/C	>99	-	-	19.0	14.4	22.8	56.2
3	Cu/C	45.5	-	-	-	22.7	-	22.7
4	Fe/C	18.6	-	-	-	-	-	-
5	Ni-Cu/C	93.8	-	-	50.4	36.8	-	87.2
6	Ni-Fe/C	>99	51.6	-	25.2	-	-	25.2
7	Ni-Co/C	>99	-	-	29.8	-	16.4	46.2
8 a	Ni-Cu/C	>99			65.5	24.0		89.5
9 ^b	Ni-Cu/C	>99	-	-	70.3	29.5	-	99.8

Reaction condition: 2 mmol 5-HMF, 50 mg catalyst, 5 mL of water, 140 °C, 5 h, 2.0 MPa H₂. ^a 1 mmol 5-HMF, 25 mg catalyst. ^b 0.5 mmol 5-HMF, 25 mg catalyst.

HCPN via hydrogenation and rearrangement when using water as solvent. In contrast, only hydrogenation of furan ring and carbonyl groups occurred in these five organic solvents. In ethanol, Diox, and THFA, Ni-Cu/C was in favour of selective transformation of 5-HMF to FDA, suggesting mainly carbonyl groups were reduced. isopropanol, a fine transfer hydrogenation reagent,^[34] resulted in yield of 48.9% to THFDA, probably due to transfer hydrogenation from isopropanol to furan ring and carbonyl. It is noted that only in water could Ni-Cu/C show activity in hydrogenation and rearrangement reaction. As illustrated by previous literatures, dehydration is a key step in the hydrogenative rearrangement of 5-HMF, and is



Fig. 3 The effect of solvents on the hydrogenation and rearrangement of 5-HMF. Reaction condition: 1 mmol 5-HMF, 25 mg Ni-Cu/C catalyst, 5 mL of solvent, 140 °C, 5 h, 2.0 MPa H₂.

easier proceed in organic solvent than water.[35] Ni-Cu/C elucidated to be ineffective for dehydration even by variation of solvents, as evidenced in all these cases neither HCPN nor HHD could be detected. It has been recognized HCPN and HHD represented the occurrence of dehydration, which is generally in the presence of acidic sites. But in our case, Ni-Cu/C was demonstrated to have no acidic sites by NH₃-TPD results (see Figure 1f). That is to say, the effect stemmed from acidic sites in catalyst could be excluded, and we speculate water may play a crucial role in the rearrangement reaction besides as solvent.

The effect of temperature

To demonstrate our speculation, a set of experiments were conducted at reaction temperature ranged from 80 °C to 160 °C. At relative lower temperature of 80 °C, FDA is the main product with 80.8% yield, without detecting any ring-opening product. Further increasing temperature to 140 °C, leaded to the yield of FDA decreased from 80.8% to zero, and HCPN was consequently generated, indicating that HCPN came from the transformation of FDA. As the temperature was increased to 160 °C, the yield to HCPN decreased to 56.6% and the ringopening product HHD increased from 24.0% to 39.5%. Therefore, lower temperature (80 °C) was in favour of hydrogenation, while elevated temperature (≥120 °C) was beneficial for generating rearrangement products (HHD and

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HCPN). At 150 and 160 °C, the ring-opening product (HHD) was facilitated to generate. The distinct product distribution may be due to higher active energy was required for rearrangement and ring-open. In our previous work, we also observed that the hydrogenation and rearrangement of furfural to cyclopentanone only occur if at the temperature of 100 °C or higher.^[31] Similar effect of temperature were also



Fig. 4 The influence of temperature on hydrogenation and rearrangement of 5-HMF. Reaction condition: 1 mmol 5-HMF, 25 mg Ni-Cu/C catalyst, 5 mL of water, 5 h, 2.0 MPa H_2 .

observed by Marthew's group.^[28] They found that increasing temperature over 140 °C leaded to HCPN. Huo et al.^[36] also proposed that water acted as proton donor at high temperature (250 °C). The dissociation of water is an endothermic process in thermodynamics. Elevating the temperature would greatly facilitate the dissociation, and the calculated concentration of H⁺ increased from 8.3×10^{-8} mol/L (20 °C) to 7.37×10^{-7} mol/L (100 °C). The pK_a value at 100 °C is 6.13, indicating water may donate H⁺ to create a slightly acidic conditions. Obviously, the products distribution changed with temperatures, suggesting it might have a close connection with the dissociation of water. Thus, we supposed another role



Fig. 5 The relevance of main product with the ratio of ethanol/water. Reaction condition: 1 mmol 5-HMF, 25 mg Ni-Cu/C catalyst, 5 mL of solvent (ethanol/water), 5 h, 140 °C, 2.0 MPa H_2 .

of water was to supply $\mathsf{H}^{\scriptscriptstyle +}$ at elevated temperature besides as solvent.

As is well known that ethanol is miscible with water and hardly provides H⁺ at elevated temperature. Thus, we carefully controlled the concentration of H⁺ by using a mixture solvent of ethanol and water at different proportion. As expected, the catalytic activity of Ni-Cu/C at 140 °C decreased as the ethanol/water ratio rose. As illustrated in Scheme 2, for hydrogenation and rearrangement of FDA, H⁺ from water is the key factor for the evolved dehydration and is crucial for the following ring-open simultaneously. In the presence of water, FDA can gradually convert to HCPN and HHD. For example, at ethanol/water ratio of 80%, it achieved yields of 1.9% and 11.3% for HCPN and HHD, respectively. When the ethanol/water ratio reached 20%, yield to rearrangement products were increased (yield of HCPN: 36.8%; yield of HHD: 33.0%). In the absence of ethanol, the selectivity of HPCN was the highest in water. When using ethanol alone, 5-HMF only converted into the hydrogenation product FDA, without ringopening product detected. These phenomena directly proved that water is necessary in reaction, by releasing H⁺ at elevated temperature.

To further investigate the role of water, the hydrogenation and rearrangement of 5-HMF was conducted in water with different pH values. As seen in Figure 6, only neutral or slightly acidic solution can lead to a better activity and selectivity for hydrogenation and rearrangement, and the reaction cannot reach a satisfied yield to HCPN in acidic or basic solutions. When pH was 2.01, only small amount of 5-HMF could convert to HHD, and by-products such as humins generated, consisting with the colour change of the solution from colourless to dark yellow (Figure S3). It agrees well with literatures that adjusting pH to 2-3 could result in HHD as main product in 5-HMF conversion over Pd/C catalyst.^[37] When pH was adjusted from

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4.00 to 6.18, the yield of rearrangement products (HHD + HCPN) increased to maximum (89.5%). Further increasing pH value to 9.18 leaded to a distinct products distribution, and the absence of HCPN indicated the ring-open and rearrangement cannot successfully proceed in basic solution, but only occurred hydrogenation of carbonyl with FDA as the dominant product. These results indicated that the protons arisen from dissociation of water can promote the dehydration of FDA at natural or slightly acidic water, but inhibited hydrogenation-rearrangement of 5-HMF to HCPN at the acidic or basic solutions.

Reaction mechanism and time course

The hydrogenation and rearrangement of 5-HMF over Ni-Cu/C was detailed investigated under the conditions specified above. ¹⁸O–enriched water was employed as solvent to study how water participates in the reaction and to better understand the pathways. From Figure 7, mass spectrum of HCPN showed that 98% of the oxygen at cyclopentyl is O¹⁸, which was undoubtablely from ¹⁸O–enriched water. This strongly proved that water serve as a reagent of rearrangement, behaving as



Fig. 6 The influence of different initial pH value on the hydrogenation and rearrangement of 5-HMF. Reaction condition: 1 mmol 5-HMF, 25 mg Ni-Cu/C catalyst, 5 mL of water, 5 h, 140 $^{\circ}$ C, 2.0 MPa H₂.

nucleophile. The time course was shown in Figure S2. For the whole reaction, the first step was the selective hydrogenation of 5-HMF to generate intermediate FDA, which rapidly formed with 25.0% yield at 36.5% conversion of 5-HMF, and TOF reached 38.35 h⁻¹ at initial 2 min. Similar to the consumption trend of 5-HMF, the yield of FDA decreased and down to zero at 3 h. At the same time, the rearrangement products (HHD, HHCPEN, and HCPN) gradually formed with the reaction preceded. These indicated the Ni-Cu/C firstly catalyzed the hydrogenation of C=O to afford FDA, as well as the following ring-rearrangement reactions in water. Afterwards, FDA undergoes hydration and dehydration steps, and the latter was promoted by water, which may act as nucleophile reagent attacks C2 and lead to furan ring-open as demonstrated above. Subsequently, carbenium ion intermediate may form by furan ring-open, then transformed into HHCPEN via ring-closing,



Fig. 7 Mass spectra of HCPN for hydrogenation and rearrangement of 5-HMF in water and ¹⁸O-enriched water, respectively.

followed by dehydration-hydrogenation to HCPEN, which further hydrogenated to the main product HCPN. On the other hand, carbenium ion may convert into chain product HHD. As illustrated in the time curse, HHCPEN showed a trend of first increasing and then decreasing, confirming its consumption to HCPN. After 1 h, the yield of HHD remained at 24.1%-28.2%, because HHD is unable to continuously transform into HCPN by intramolecular aldol condensation over Ni-Cu/C catalyst. To elucidate this, hydrogenative rearrangement further experiment over Ni-Cu/C catalyst using HHD as the starting substrate were performed. As detected by GC-MS, HHD mainly converted to 5-methyl-2-hydroxymethyl-tetrafuran, which obtained through dehydration of 1,2,5-hexanetriol (generated from the hydrogenation of HHD). Here we did not detect this short-lived intermediate HCPEN in the reactions because it rapidly hydrogenated to HCPN. To demonstrate its presence, enlarged experiment was conducted and verified its existence by GC-MS and NMR.

As illustrated in Scheme 2, the assumed mechanism of hydrogenation and rearrangement of HMF. Multi-active sites are required respectively for selective hydrogenation, dehydration, and rearrangement. It is suggested that Ni metal ensured a high activity for hydrogenation via dissociation of H₂. The combination of Cu with Ni could suppress the hydrogenation activity of the bimetallic metal catalyst, which is in favour of selective hydrogenation of the carbonyl group, not for C=C groups. Afterwards, FDA further may undergo Piancatelli rearrangement reaction to generate HHCPEN via a carbenium ion (C⁺) and then hydrogenate to HCPEN and HCPN.^[38] H₂O was conjectured to stabilize carbenium ion (C⁺), which is consensus. At elevated temperature, slightly acidic conditions have been created by water dissociation, which is the key of high selectivity to rearrangement product in the absence of acidic sites or additives. Due to HMF and FDA are unstable under higher temperature and acidic conditions,





Scheme 2 Proposed reaction pathway for hydrogenation and rearrangement of 5-HMF in $H_2^{18}O$.

humin-based polymers as well as excessive dehydration products may generated. So it is one important reason of the low carbon balancing.^[39] Rearrangement of carbenium ion (C⁺) gave rise to HHCPEN, which can dehydrate to form HHCPN at elevated temperature water. Besides, strong Lewis acid or Brønsted acid caused by catalysts or additives at high temperature can devoted to chain product HHD or low conversion of 5-HMF. Furthermore, hydrogenation and rearrangement of 5-HMF over Ni-Cu/C by using additives of ZrO₂ and Nb₂O₅ were leaded to 83.9% conversion with 37.8% to HCPN, 14.5% to HHD, and 10.4% to HCPEN, which means that the ratio of chain product HHD raised as Lewis acid oxides was combined with Ni-Cu/C. But if the catalytic hydrogenation activity is too high, HCPN will further convert to by-product 3hydroxymethylcyclopentan-1-ol (HCPL), in other words, carbonyl group can be hydrogenated.

Conclusion

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In conclusion, we prepared Ni-Cu-MOF-74 derived Ni-Cu bimetallic catalyst using pyrolysis method. Ni-Cu/C catalyst exhibited high efficiency for the selective hydrogenation and rearrangement of 5-HMF to HCPN in water, without any acidic sites or additives. It afforded 70.3% yield for HCPN and 99.8% vield for rearrangement products. The remarkable promotion effect on rearrangement products could be attributed to the combination of Cu with Ni, as well as the crucial role of water. As the completely hydrogenation of 5-HMF was well inhibited, the selective hydrogenation of C=O groups in 5-HMF could be fulfilled, together with the rearrangement of C5 rings. The isotopic experiments in H₂¹⁸O and MS technique demonstrated a crucial role of water, which not only acts as solvent and reactant, but proton donor to create slightly acidic conditions, and thus promoted the ring-rearrangement reaction at elevated temperature (140 °C). This work provides a new

efficient catalyst for hydrogenation and rearrangement nin water, which is a green, recyclable, atomic economy progress for water-phase utilization of biomass-derived platform 5-HMF.

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Conflict of interest

The authors declare no conflict of interest.

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