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# CuZnCoO<sub>x</sub> multifunctional catalyst for *in situ* hydrogenation of 5-hydroxymethylfurfural with ethanol as hydrogen carrier



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#### ABSTRACT

Catalytic *in situ* hydrogenation of 5-hydroxymethylfurfural (5-HMF) to 2,5-dimethylfuran (DMF) has received a great interest in recent years. However, the issue of the consumption of expensive hydrogen donors, such as secondary alcohols, limits its applications. In this work, a ternary CuZnCoO<sub>x</sub> catalyst, exhibiting a 99% yield of DMF from *in situ* hydrogenation of 5-HMF with ethanol as economical hydrogen donor, is developed. High resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS-mapping), X-ray diffraction (XRD) and temperature programmed reduction (TPR) reveal the synergy effect of each components. Reaction mechanism studies unravel the CoO<sub>x</sub> results in promoting *in situ* H<sub>2</sub> production from ethanol, the zinc oxide accelerates the aldehyde group (–CHO) hydrogenation to hydroxymethyl group (–CH<sub>2</sub>OH) and the formation of Cu-Co alloy significantly facilitate the hydrogenation of 5-HMF. Additionally, this ternary CuZnCoO<sub>x</sub> catalyst exhibits superior recyclability without losing any activity during 6 cycles experiment.

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# 1. Introduction

The increasingly severe energy crisis and serious environmental problems spur the utilization of alternative renewable and green resources. Biomass, especially lignocelluloses, is an important renewable solar primary energy that can be converted into varieties of value-added chemicals and fuels [1-4]. 5hydroxymethylfurfural (5-HMF), a carbohydrate-derived product through acid-hydrolysis of sugars [5,6], has been considered as one of the most valuable feedstocks [7]. Among all the important derivatives of 5-HMF, 2,5-dimethylfuran (DMF) with high boiling point, high energy content and high research octane number has been identified as a highly interesting biomass-derived liquid fuel [8]. As a result, the selective catalytic hydrogenation of 5-HMF to produce DMF has become more and more important [9–11].

Since the pioneer works of Dumesic and co-workers [12], the noble metal based monometallic and bimetallic catalysts have been extensively investigated in the selective hydrogenation of

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5-HMF to DMF [13–16]. In order to reduce the cost of catalyst, recent studies have turned to the inexpensive non-noble metal based catalysts [17–20]. Among these catalysts, the bimetallic Cu-Co/C catalyst showed a highly catalytic performance in which 99.4% DMF yield was achieved at 180 °C after 8 h under 5.0 MPa H<sub>2</sub> [20]. Despite of the great progress in the development of direct selective hydrogenation of 5-HMF, the employment of high pressure molecular H<sub>2</sub> inevitably leads to the problems of large scale H<sub>2</sub> storage and transportation. Moreover, the complicated operation using gaseous H<sub>2</sub> is not suitable for the distributed lignocellulose treatment system [21–24]. In the early studies, the formic acid which releases H<sub>2</sub> at a relatively low temperature was used as hydrogen donor [25]. However, the strongly corrosive property of formic acid limits its range of application.

In the pursuit of a greener hydrogen donor, Vlachos and coworkers [23] introduced 2-propanol into this system, 81% DMF yield was obtained by using Ru/C as catalyst at 190 °C for 6 h. While Scholz et al. developed Pd/Fe<sub>2</sub>O<sub>3</sub> catalyst, giving 72% DMF yield with 2-propanol as hydrogen source [26]. Although secondary alcohols have been demonstrated their effectiveness, the exorbitant price as well as the relatively low gravimetric hydrogen density make its too luxury to be used in large scale [27–28].

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Therefore, an alternative in situ hydrogenation method using hydrogen donor from biomass derived primary alcohols (methanol, ethanol), other than H<sub>2</sub> or secondary alcohols has become a more economical strategy [9,29–31]. However, the hydrogen evolution from primary alcohols is usually more difficult kinetically and requires crucial reaction condition. The well integration of H<sub>2</sub> production and hydrogenation centre is the crucial factor to enhance the efficiency of in situ hydrogenation catalysts. In a recent attempt, Riisager et al. employed a non-noble Cu-doped porous metal oxide catalyst with methanol as solvent and hydrogen donor. 48% DMF yield were achieved at 260 °C for 3 h, which was far below other secondary alcohol systems [32]. Exploring suitable catalytic systems with high efficiency in the selective hydrogen evolution from ethanol, a greener biomass product, for the hydrogenation of 5-HMF without excessively hydrogenating and opening the furan ring is still a challenging problem in this area.

Herein, we report the development of a ternary CuZnCoO<sub>v</sub> catalyst for highly efficient and selective hydrogenation of 5-HMF to produce DMF with ethanol as the hydrogen source (Scheme 1). The reaction behaviors of intermediates 5-HMF, 5-methyl furfural (5-MF). 5-methylfurfuryl alcohol (MFA) and 2.5-bis (hydroxymethyl)furan (BHMF) over ternary CuZnCoO<sub>x</sub> and their corresponding binary catalysts were investigated. HRTEM, EDSmapping, XRD and H<sub>2</sub>-TPR were utilized to reveal the synergistic effect of each component. Under optimized condition, the CuZnCoO<sub>x</sub> catalyst achieved over 99% DMF yield in 5 h and exhibited excellent recyclability.

# 2. Experimental section

#### 2.1. Materials

5-HMF (99%), 5-MF (98%), BHMF (99%),  $Co(NO_3)_2 \cdot 6H_2O$  and Cu  $(NO_3)_2 \cdot 3H_2O$  were purchased from Aladdin Reagent Limited Company. Zn(NO\_3)\_2 \cdot 6H\_2O was purchased from Sigma Aldrich. MFA (97%) was purchased from Thermo Fisher Acros Organics. DMF (99%) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Ethanol, Na<sub>2</sub>CO<sub>3</sub> and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification.

# 2.2. Catalyst synthesis

The CuZnCoO<sub>x</sub> precursor was prepared by a co-precipitation method. Typically, 16 mmol Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with different Cu/Zn molar ratios were dissolved in 200 mL deionized water with a mass composition of (Cu-ZnO)/  $Co_3O_4 = 20/80$ . An alkali liquor composed of  $Na_2CO_3$  and NaOHaccording to the molar amount of alkali required for the metal precipitation was used as precipitant, and the molar ratio of  $OH^{-}/CO_{3}^{2-}$ was determined as 2. The alkali was introduced into a 1 L round bottom flask after being dissolved in 150 mL deionized water. The resulting metal salt solution was added dropwise into alkali liquor at 25 °C under vigorous stirring. After precipitation, the mixture was heated to 90 °C for 3 h and aged for another 3 h in the mother liquor, then washed and dried at 100 °C for 12 h. The asprepared precursor was calcined at 350 °C for 3 h to get the corresponding CuO/ZnO/Co<sub>3</sub>O<sub>4</sub>. The obtained material was reduced in a tube furnace under H<sub>2</sub> atmosphere at 350 °C for 1 h with a ramp of  $5 \,^{\circ}$ C/min. After the reduction, the catalysts are pretreated in N<sub>2</sub> overnight, and then immediately transferred into a 3 mL bottle which was purged by N<sub>2</sub> three times for next use of reaction and characterization. The resulting samples were marked as CuZnCo-x, in which x indicates the molar ratio of Cu/Zn in ternary CuZnCoO<sub>x</sub>. Additionally, CoO<sub>x</sub>, Cu, ZnO, CuZn (Cu/Zn mole ratio is

3), CuCo and ZnCo were synthesized using the same method, in which CuCo, CuZn and ZnCo refer to the reduced 20 wt% Cu/CoO<sub>x</sub>, 20 wt% Cu/ZnO and 20 wt% ZnO/CoO<sub>x</sub> respectively.

# 2.3. Experimental procedures

Catalytic activity tests: a certain amount of 5-HMF, ethanol and catalyst were added into a 1.67 mL stainless steel autoclave purchased from Swagelok, as shown in Fig. S1. The sealed reactor was put in a fluidized sand bath (Techne SBL-2) which was preheated to the desired temperature. After the reaction, the reactor was cooled down to room temperature by immediately loading water and then removing the solid catalyst by filtration. Recycling experiments: the solid catalyst was separated by centrifugation, after removal of the reaction liquid, washed with ethanol for several times, dried at 40 °C in a vacuum oven to prevent oxidation, and then reused for the next reaction run.

Ethanol dehydrogenation experiment: 3.5 mL ethanol and 15 mg catalyst were added into 8 mL stainless steel autoclave, then the sealed reactor was pressurized with N<sub>2</sub> three times to remove air and charged with the N<sub>2</sub> at atmospheric pressure. After reaction, the reactor was cooled down to room temperature, and then recording the final pressure in reactor and collecting the gaseous products for GC analysis.

# 2.4. Analysis method

The products were diluted to 10 mL with ethanol and then quantified by using an Agilent 7890A gas chromatography equipped with a 30 m  $\times$  0.32 mm  $\times$  0.25  $\mu m$  HP-5 column. The carrier gas was nitrogen with a flow of 25 mL/min, the liquid volume was 1  $\mu$ L with a split ratio of 5:1 and the temperature of the injector and detector were 300 °C and 320 °C respectively. The temperature program for analysis was: 30 °C kept for 4 min, 10 °C/min to 140 °C and 20 °C/min to 300 °C kept for 2 min. In addition, an Agilent 1260 high performance liquid chromatographs (HPLC) equipped with a Synergi Hydro-RP 80A column and a UV detector was used to separate and quantify the intermediates 5-MF and MFA. A 40 vol% methanol aqueous solution was employed as mobile phase at 35 °C column temperature and 240 nm wavelength with a flow rate of 0.6 mL/min. A Shimadzu GC-2018 gas chromatography with Agilent PLOT 5A molecular sieve filled column was used to analyse the gaseous products. The oven temperature was 60 °C, the volume was 1 mL with a split ratio of 1 and the temperature of TCD detector and FCD detector were 100 °C and 180 °C respectively.

The conversion and selectivity of liquid product were based on the external standard method. The molar conversion of reactant was shown as the number of moles consumed divided by the initial moles of the reactant, the selectivity of product was shown as the number of moles of carbon in specific product divided by the number of moles of carbon in consumed reactant, the yield was shown as the conversion multiply by selectivity. H<sub>2</sub> content was also calculated based on external standard method. Specifically, the actual pressure (P<sub>1</sub>) after reaction was recorded at room temperature, and volume of gases (V<sub>1</sub>) was also been estimated based on the volume of the autoclave. Then, the actual volume of gases (V<sub>2</sub>) at 101.3 kPa (P<sub>2</sub>) was determined by Clausius-Clapeyron equation (P<sub>1</sub>V<sub>1</sub> = P<sub>2</sub>V<sub>2</sub>). Finally, H<sub>2</sub> molar content was obtained combined with V<sub>2</sub> and percentage of H<sub>2</sub> in gaseous products from GC. Each result was confirmed by repeated experiments for three times.

# 2.5. Catalyst characterization

The ex-situ synchrotron X-ray diffraction (XRD) data of the reduced CuZnCo-x samples in capillary were collected at 17BM



Scheme 1. Reaction pathway for the in situ hydrogenation of 5-HMF.

 $(\lambda = 0.45226 \text{ Å})$  of the Advanced Photon Source (APS). Prior to analysis, the as-synthesized CuZnCo-x samples were reduced by H<sub>2</sub> in a capillary and sealed by AB glue. A Perkin-Elmer flat Si detector was used to collect two-dimensional XRD images, which were subsequently processed with GSAS-II to obtain diagrams of Intensity versus 20 [33]. The XRD data of CuCo and ZnCo samples were obtained using the same method with the  $\lambda$  as 0.24141 Å.

Transmission electron microscopy (TEM) images, electron diffraction patterns (EDPs) and high-angle annular dark field (HAADF) images with an energy dispersive X-ray spectroscopy (EDS) elemental mapping of reduced CuZnCo-3 were carried out by a JEOL-ARM 200CF microscope which equipped with a cold-field emission gun and operated at 200 kV. The microscope is

equipped with the JEOL and Gatan HAADF detectors for incoherent HAADF imaging.

The N<sub>2</sub> adsorption-desorption isotherms (BET) were performed via a Micromeritics 3Flex adsorption instrument. Prior to the measurements, the sample was degassed under N<sub>2</sub> for 12 h at 300 °C. The Brunauer-Emmett-Teller equation was used for the calculation of the specific surface areas. The total amount of N<sub>2</sub> adsorbed at  $p/p_0 = 0.99$  was used to calculate the total pore volume.

The metal contents of catalysts were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on Agilent 730 device. Prior to the analysis, catalysts were dissolved in mixture of HCl and HNO<sub>3</sub>. H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were carried out in FineSorb-3010 equipped



**Fig. 1.** Electron microscopy characterization for CuZnCo-3 catalyst. (a, b, c) TEM images of CuZnCo-3 with low and high magnification respectively; (d, e, f) HRTEM images of CuZnCo-3; (g-i) STEM image and EDS mapping profiles of CuZnCo-3 for (g) copper, (h) cobalt, and (i) zinc. As the colour becomes brighter, the metal content means higher.



Fig. 2. X-ray diffraction patterns for ternary CuZnCo-x with different Cu/Zn ratios.



Fig. 3. H<sub>2</sub>-TPR profiles of calcined Co<sub>3</sub>O<sub>4</sub>, CuCo, CuZnCo-3, CuZn and ZnCo.

with a TCD detector, the gas mixture was 10 vol% hydrogen in argon at a flow rate of  $15 \text{ cm}^3/\text{min}$ , the temperature rises from 60 °C to 300 °C with a heating rate of 10 °C/min and changed to 5 °C/min to reach 500 °C, and then heating up to 800 °C with a ramp of 10 °C/min.

# 3. Results and discussion

#### 3.1. Characterizations

Representative transmission electron microscope (TEM) images of CuCo, CuZnCo-3, CuZnCo-2 and ZnCo catalysts after reduction at 350 °C are shown in Fig. S2 (The CuZnCo-x, in which x indicates the molar ratio of Cu/Zn in CuZnCo mixed oxide catalysts; CuCo, CuZn and ZnCo refer to reduced Cu/CoO<sub>x</sub>, Cu/ZnO and ZnO-CoO<sub>x</sub> respectively). The results in Fig. S2 show blurred particles shape was discovered in CuCo, and the catalyst tends to be more granular with the addition of zinc. The TEM images of CuZnCo-3 with different magnification are shown in Fig. 1a-c. It is hard to distinguish the distribution of CuZnCo-3, due to the similar Z-contrast of the three elements. Therefore, the distribution of ZnO, CoO and Co/Cu is further confirmed with high resolution transmission electron microscopy (HRTEM) images of Fig. 1d-f, which are based on the determination of local electron diffraction patterns and fringes. Furthermore, the ternary CuZnCo-3 catalyst is imaged by energydispersive X-ray spectroscopy (EDS) mapping (Fig. 1g-j), which shows that Cu signals is not found where there is no Co signals. These results indicate the possible exsitence of Cu-Co alloy in CuZnCo-3 catalyst. The distribution of Zn is much more dispersed and there seems no clear strong correlation with Cu or Co.

X-ray diffraction (XRD) patterns of a series of ternary CuZnCo-x (x ranges from 0.5 to 4) catalysts after reduction at 350 °C are collected using synchrotron based XRD instrument to understand the crystal structure of the ternary catalysts (Fig. 2). For all five samples, a strong diffraction of the metallic cobalt phase is observed at  $2\theta = 12.7^{\circ}$  (1 1 1), 14.7° (2 0 0), 20.8° (2 2 0) and 24.4° (3 1 1) (ICSD 76632). And the diffraction peaks at  $2\theta = 12.2^{\circ} (200)$  can be attributed to CoO (ICSD 9815) [34]. With the decrease of Cu/ Zn mole ratio (Table S1, ICP-OES results), from CuZnCo-4 to CuZnCo-0.5, the intensity of diffraction peaks corresponding to ZnO at  $2\theta = 9.2^{\circ}$  (100),  $9.9^{\circ}$  (002),  $10.5^{\circ}$  (101),  $13.6^{\circ}$  (102) and 16.0° (110) (ICSD 52362) gradually increase. As no obvious diffraction peaks ascribed to Cu are observed, suggesting Cu may be incorporated with the major species Co to form Cu-Co alloy particles. The obvious diffraction peaks ascribed to Cu (JCPDS 04-0836) and ZnO (ICPDS 36-1451) is found in XRD pattern of CuZn in Fig. S3, confirm the existence of Cu-Co allov in CuZnCo-3, Additionally, the diffraction peaks ascribed to Co in partial reduced CuZnCo-3 shifts to lower 20 value compared with partial reduced ZnCo in Fig. S4, further indicate the existence of Cu-Co alloy in reduced CuZnCo-3. These XRD results are in good agreement with HRTEM and EDS-mapping results. XRD patterns of CuCo and ZnCo in Fig. S5 reveal that the main diffraction peaks corresponding to Co and CoO was discovered in both CuCo and ZnCo, and the diffraction peak about ZnO was also seen in ZnCo.

Temperature programmed reduction (TPR) results of calcined Co<sub>3</sub>O<sub>4</sub>, CuCo, CuZnCo-3, CuZn and ZnCo are shown in Fig. 3. The profile of Co<sub>3</sub>O<sub>4</sub> sample shows two H<sub>2</sub> consumption peaks, which are ascribed to the reduction of Co<sub>3</sub>O<sub>4</sub> to CoO and CoO to the metallic Co according to the literature [35]. For calcined CuZn sample, the only reduction peak at around 250 °C is attributed to the reduction of CuO to Cu. For CuCo and CuZnCo-3 samples, the reduction peak at lower temperature of 160 °C should be attributed to the reduction of CuCoO<sub>x</sub> to Cu-Co alloy, since alloy oxides sometimes can be reduced more easily [22]. The second peak between 200 and 400 °C should be the overlapping peaks corresponding to the reduction of Co<sub>2</sub>O<sub>4</sub> to CoO and the reduction of CoO to Co. For calcined ZnCo sample, it shows that the first H<sub>2</sub> consumption peak is in good agreement with the  $Co_3O_4$  sample, indicating the reduction of Co<sub>3</sub>O<sub>4</sub> to CoO. However, it is clearly seen that the addition of Zn into Co makes the reduction peak of CoO to Co shifts to higher temperature, which is in good agreement with the previous studies [36–38]. As a result, more CoO species is discovered in ZnCo than that in CuCo, as revealed in Fig. S5.

The textural properties of reduced CuCo, CuZnCo-3 and ZnCo catalysts are summarized in Table S2. The total surface area of CuCo, CuZnCo-3 and ZnCo is 7.5, 15.7 and 20.4 m<sup>2</sup>/g respectively. The lower surface area of CuZnCo-3 compared to ZnCo catalyst was attributed to the addition of Cu. Replacing Cu with a certain amount of Zn will enhance the total surface area of catalyst when comparing CuCo and CuZnCo-3 catalysts. The pore volume increses with the increase in the surface area, and the highest pore volume is  $0.09 \text{ cm}^3/\text{g}$  in ZnCo catalyst. Compared to CuCo catalyst, the higher surface area and pore volume in CuZnCo-3 catalyst will contribute to the higher dispersion of Cu-Co alloy, and then benefites the reaction rate.

# 3.2. Catalytic activity of different catalysts

Prior to the optimization of  $CuZnCoO_x$  catalysts, other ternary catalysts with random combination between Cu, Ni, Fe, Zn, Co, and Al was also tested as a comparison. The results in Table S3 revealed  $CuZnCoO_x$  and  $NiZnCoO_x$  were the best two candidates, and  $CuZnCoO_x$  performed slightly better than  $NiZnCoO_x$  at the same reaction conditions. Thereafter,  $CuZnCoO_x$  catalysts were selected as the main research objectives. As depicted in Fig. 4a,



Fig. 4. (a) Reaction behaviours of 5-HMF over CuCo, ZnCo and CuZnCo-x catalysts at 200 °C for 5 h; (b) Reaction behaviours of 5-HMF over different catalysts at 210 °C for 5 h. Reaction condition: 5-HMF loading = 10 mg, catalyst loading = 3 mg, ethanol loading = 0.7 mL.

Table 1         Performance of ternary CuZnCo-3 catalyst for in situ hydrogenation of 5-HMF and the comparison with previous published works.							
Entry	Catalysts	Temp./°C	Time/h	Hydrogen donors	Conv./%	DMF yield/%	
1	CuZnCo-3	210	5	ethanol	100	99	
2	Ru/C	190	6	2-propanol	100	81 [23]	
3	Pd/Fe <sub>2</sub> O <sub>3</sub>	180	24	2-propanol	100	72 [26]	
4	Cu-PMO	270	2	methanol	100	46 [32]	
5	Cu/Al <sub>2</sub> O <sub>3</sub>	240	6	methanol	100	74 [39]	
6	Ni-Co/C	210	24	formic acid	99	90 [40]	
7	NC/Cu/MgAlO	220	0.5	cyclohexanol	100	96 [41]	

5

2-propanol



Ru/Hydrotalcite

220

**Fig. 5.**  $H_2$  content obtained from the conversion of ethanol over per gram catalysts at 210 °C for 5 h. Reaction condition: catalyst loading = 15 mg, ethanol loading = 3.5 mL.

CuCo, ZnCo and a series of CuZnCo-x are tested for the *in situ* hydrogenation of 5-HMF at 200 °C for 5 h with ethanol as hydrogen carrier. In the binary catalysts, 57.7% conversion of 5-HMF with 26.8% DMF yield is achieved over CuCo, while only 1.6% DMF yield is observed over ZnCo. Interestingly, the ternary CuZnCo-x catalysts show significant improvement and remarkable performance in the *in situ* hydrogenation of 5-HMF compared with their binary counterparts. For example, the CuZnCo-4 achieves 94.4% 5-HMF conversion and 61.8% DMF yield. With the changing of the composition, the highest DMF yield (77.8%) is achieved over CuZnCo-3. The further increment of ZnO in the catalysts tends to decrease the yield of DMF, indicating the suitable Cu/Zn ratio is much important for the *in situ* hydrogenation of 5-HMF. Compared with



14 [42]

**Fig. 6.** DMF yield with  $H_2$  as hydrogen donor. Reaction conditions: 5-HMF loading = 50 mg, catalyst loading = 15 mg, 2.0 MPa  $H_2$ , T = 210 °C, time = 5 h.

single-component and/or double-component catalysts, the yield in CuZnCo-3 is almost two and five times higher than the second and third highest candidates (CuCo 26.8% and CuZn 1.6%). When increasing the temperature to 210 °C, CuZnCo-3 manages to increase yield of DMF to over 99.0% and its performance is much better than all other catalysts in Fig. 4b.

In comparison, DMF yield over CuCo is 72.6% and 75.3% respectively by further enhancing the reaction temperature up to 220 °C and 230 °C for 5 h. The relative lower selectivity to DMF over CuCo catalyst may be ascribed to the production of byproducts derived from the polymerization and condensation reactions [32]. Because, the volatile side-products detected by GC-MS are negligible, as seen in the Fig. S6. The relative lower DMF yield are very similar

8



**Fig. 7.** Reaction behaviours of 5-MF, MFA over CoCo and CuZnCo-3 at 200  $^{\circ}$ C for 5 h. Reaction condition: reactant loading = 10 mg, catalyst loading = 3 mg, ethanol loading = 0.7 mL.



**Fig. 8.** Reaction behaviours of MFA over CuCo and CuZnCo-3 at different reaction time at 180 °C. Reaction condition: MFA loading = 10 mg, catalyst loading = 3 mg, ethanol loading = 0.7 mL.

#### Table 2

The intrinsic rates (conversion) over CuCo and CuZnCo-3 catalysts from the in situ hydrogenation of 5-HMF, 5-MF and MFA at 180  $^\circ$ C for 0.5 h.

	CuCo/h <sup>-1</sup>	CuZnCo-3/h <sup>-1</sup>
5-HMF	1.33 (8.8%)	2.15 (11.1%)
5-MF	0.74 (4.3%)	2.68 (12.1%)
MFA	0.99 (5.8%)	1.19 (5.5%)

with the previous reports, in which DMF yield do not exceed 80% with alcohols as the hydrogen donors due to the production of heavy byproducts [11,23,26,32,39]. The remarkable catalytic performance of the *in situ* hydrogenation of 5-HMF with ethanol as hydrogen source requires both excellent performance of hydrogen extraction from ethanol and effective active site for the hydrogenolysis of aldehyde (--CHO) and hydroxymethyl (--CH<sub>2</sub>OH) groups. The performance of CuZnCo-3 catalyst for the *in situ* hydrogenation of 5-HMF and the comparison with relative works is shown in Table 1, which suggests the superiority of our catalytic system.

# 3.3. The role of each component of catalysts

To understand the role of each component plays in the reaction, the evaluations on both steps are carried out respectively. As shown in Fig. 5, all the Co containing catalysts show high  $H_2$  pro-

duction rate. Among these, H<sub>2</sub> production rate is calculated by the obtained H<sub>2</sub> content over per gram of different catalysts at a certain reaction time of 5 h. While the Cu, ZnO and CuZn catalysts shows relative poor hydrogen evolution ability, which is probably the reason for the low reactivity of these catalysts in the conversion of 5-HMF. On the other hand, even though both of the ZnCo (120 mmol/g) and  $CoO_X$  (123 mmol/g) exhibit the strong H<sub>2</sub> production ability, these catalysts are unable to catalyze the in situ hydrogenation of 5-HMF to DMF (nearly 0 yield in Fig. 4b), indicating Cu species are probably the essential active site for the reduction of 5-HMF. When using gaseous H<sub>2</sub> as the hydrogen source (Fig. 6), a similar trend of target product yield with the ethanol as hydrogen source is observed. Compared with CuCo catalyst, the superior performance of ternary CuZnCo catalysts is mainly related with its high selective hydrogenation ability rather the H<sub>2</sub> production from ethanol. Basically, no gaseous products are detected other than H<sub>2</sub>. Additionally, acetal, which can be produced from ethanol and acetaldehyde, is detected in the liquid products in Fig. S6. These results reveal that ethanol is transformed to acetaldehyde after providing H<sub>2</sub>.

Also, CuZnCo-3 exhibits extremely higher catalytic activity than CuZn towards to the conversion of 5-HMF using H<sub>2</sub> as hydrogen donor in Fig. 6, revealing the importance of Cu-Co alloy in hydrogenation process. The in situ hydrogenation of 5-HMF with acetone and molecular H<sub>2</sub> as solvent and hydrogen donor is also investigated. The results in Fig. S7 exhibits a similar trend, and CuZnCo-3 performs best among all catalysts. Based on the obtained  $H_2$  content from the conversion of ethanol in Fig. 5, the  $H_2$  pressure over CuZnCo-3 catalyst is approximately ~1 MPa, exactly 0.93 MPa. Therefore, we have added the experiment about 5-HMF hydrogenation with 1 MPa H<sub>2</sub> over CuZnCo-3 catalyst in different solvent systems. The obtained DMF yield in four solvent systems (non-solvent, acetone, dodecane and tetrahydrofuran) are all less than that with ethanol as hydrogen donor at the same reaction conditions, as shown in Fig. S8. Taking acetone as an example, a higher H<sub>2</sub> pressure of 4 MPa is found for obtaining higher DMF yield, as seen in Fig. S7. However, it is noteworthy that ring-opening and overhydrogenated products are observed as the main byproducts in Fig. S9. The above results indicate that hydrogenation of 5-HMF with ethanol as hydrogen donor seems to be more effective than that using molecular  $H_2$ , which is in good agreement with the previous study [23]. We speculated that the possible reason is a part of free H achieved from ethanol dehydrogenation might be directly used for 5-HMF hydrogenation before H<sub>2</sub> formation.

For further understanding the relationship of the components on the *in situ* hydrogenation of 5-HMF, especially the promotion effect of ZnO species in CuZnCo catalysts. The catalytic transformation of the important intermediates is investigated respectively. 5-MF and MFA hydrogenation reaction to DMF can be used to distinguish the catalytic behavior of the catalyst in the reduction of -CHO and -CH<sub>2</sub>OH to methyl (-CH<sub>3</sub>). CuZnCo and CuCo catalysts with the highest activities are chosen to understand the role of ZnO species. As shown in Fig. 7, the DMF yields from 5-MF hydrogenation are 51% and 98.5% over CuCo and CuZnCo-3 respectively, suggesting the existence of ZnO remarkably promoted the reduction of the ---CHO in furan ring (Scheme 1). However, CuZnCo-3 and CuCo catalysts exhibit similar in situ hydrogenation activity of --CH2OH in MFA, which is highly probably that the C–O bond cleavage were catalyzed by CuCo species and ZnO mainly promote the hydrogenation of C=O to corresponding alcohol. For further confirm of this role of ZnO, time dependent experiments (1-3 h) are carried out at lower temperature (180 °C) to better observe the reaction behaviors of the transformation of MFA over CuCo and CuZnCo-3. As depicted in Fig. 8, in terms of both MFA conversion and DMF yield, the results over CuCo are in good accordance with that over CuZnCo-3. In the first 1 h, 11.6% and 11.0% MFA conversion is



Fig. 9. Products distribution from the conversion of 5-HMF (a) of 5-MF (b). Reaction conditions: reactant loading = 10 mg, catalyst loading = 3 mg, ethanol loading = 0.7 mL, T = 200 °C.



**Fig. 10.** The reuse performance of CuZnCo-3 catalyst at  $210 \degree$ C for 3 h. Reaction condition: 5-HMF loading = 10 mg, catalyst loading = 3 mg, ethanol loading = 0.7 mL.

consumed to produce 2.1% and 2.2% DMF yield over CuCo and CuZnCo-3 respectively, and the catalytic activity and selectivity keeps almost similar with variable time.

The conclusion obtained from the results within kineticallycontrolled region should be more convincing. Thereafter, the in situ hydrogenation of 5-MF, MFA and 5-HMF are carried out at 180 °C for 0.5 h. The corresponding conversion of 5-HMF. 5-MF and MFA is summarized in Table 2, and all conversion are no more than 15%. As revealed in the above discussion, Cu species are probably the essential active site for the reduction of 5-HMF since enough H<sub>2</sub> is provided for driving the 5-HMF upgrade under both CuCo and CuZnCo-3 catalysts. Therefore, we use the moles of Cu to assess an average efficiency of CuCo and CuZnCo-3 catalysts for catalyzing the in-situ hydrogenation of 5-HMF. The intrinsic rates derived from Cu species are estimated by dividing the moles of consumed 5-HMF by the reaction time (h) and moles of Cu atoms in the catalysts. For the conversion of MFA, the intrinsic rates over CuCo and CuZnCo-3 catalysts are almost similar in Table 2, further suggesting that the addition of Zn do not affect the reduction of --CH2OH. However, CuZnCo-3 affords higher intrinsic rates than CuCo for the conversion of 5-HMF and 5-MF, further indicating that the zinc oxide does catalyze the --CHO hydrogenation to --CH<sub>2</sub>OH.

## 3.4. Reaction pathway and catalyst stability

The catalytic performances of the physical mixing of Cu and ZnCo, as well as CuCo and ZnO (the content of each element is

same with that in CuZnCo-3) are measured and shown in Fig. S10. CuZnCo-3 and the mixing of CuCo and ZnO catalysts exhibited very similar catalytic activity, much higher than the mixing of Cu and ZnCo. These results also confirmed that the existence of Cu-Co alloy is crucial for the *in situ* hydrogenation activity of the ternary catalysts. The experiments about the conversion of 5-HMF and 5-MF with variable time over CuZnCo-3 exhibits that both 5-MF and MFA are the intermediates during the *in situ* hydrogenation of 5-HMF, and MFA can be achieved during the conversion of 5-MF in Fig. 9. It is noteworthy that only 77.8% yield of DMF is observed with complete conversion of intermediates 5-MF and MFA for the conversion of 5-HMF. The relative lower selectivity to DMF may be mainly attributed to the production of high molecular weight byproducts or ethers [32]. The conversion of BHMF over CuCo and CuZnCo-3 in Fig. S11 revealed these two catalysts exhibit almost similar catalytic reactivity, which further confirms that the addition of ZnO does not affect the C-O bond cleavage. Based on these understandings, the role of Cu, Co and Zn related species in the conversion of 5HMF to DMF are listed in Scheme 1.

The effect of catalyst loading and reaction temperature on the in situ hydrogenation of 5-HMF over CuZnCo-3 is investigated for obtaining the optimized results (Table S4). With the increase of catalyst loading from 10 wt% to 50 wt%, DMF yield increases continuously, and top at 89.9% with 40 wt% catalyst loading at 200 °C (Entries 1-5). Reaction temperature also shows a significant effect on the production of DMF (Entries 3, 6-8), only 52.7% conversion and 23.9% DMF yield is obtained at 180 °C. However, as the reaction temperature increasing, the yield of DMF increased, giving the highest 99.0% DMF yield at 210 °C, which shows ternary CuZnCo-3 is capable for the in situ hydrogenation of 5-HMF with ethanol as the hydrogen source. For the practical application, the stability of catalyst is of great importance. The stability of CuZnCo-3 is evaluated at 210 °C after 3 h for 6 cycles (Fig. 10). The conversion of 5-HMF maintains at 100% steadily, and 84.6% DMF yield can be achieved even after five times reuse. The stability test proves the superior recyclability of our CuZnCo-3 catalyst for the in situ hydrogenation of 5-HMF.

# 4. Conclusions

In summary, the ternary CuZnCo-3 catalyst exhibits remarkable efficiency for *in situ* hydrogenation of 5-HMF into DMF with ethanol as hydrogen carrier. Characterization results reveal that CuZnCo-3 is the mixture of Cu-Co alloy, ZnO and CoO<sub>x</sub>. The experiment results show that  $CoO_x$  is a crucial factor for the

*in situ* H<sub>2</sub> production from ethanol, and co-existence of Cu and Co species significantly enhance *in situ* hydrogenation activity of 5-HMF. The reaction behaviors of intermediates 5-MF, BHMF and MFA over CuCo and CuZnCo-3 show the addition of ZnO promotes the hydrogenation of —CHO to form —CH<sub>2</sub>OH. The remarkable catalytic cactivity of CuZnCo-3 for *in situ* hydrogenation of 5-HMF is attributed to the synergistic catalytic effect between Cu-Co alloy, ZnO and CoO<sub>x</sub>. The 99.0% DMF yield at 210 °C after 5 h is achieved under the optimized reaction conditions. More importantly, CuZnCo-3 shows remarkable stability in a 6-time catalyst recycle test.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.04.011.

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