

## Preparation and characterization of nonmetal promoter modified CuZnAl catalysts for higher alcohol from synthesis gas through complete liquid phase method

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**Abstract:** A complete liquid phase technology and a function regulator were applied to prepare CuZnAl catalysts for higher alcohol synthesis. Characterizations showed that the introduction of the function regulator can change the reduction ability of copper oxides and the surface basicity of catalysts. Activity tests indicated that the selectivity of higher alcohol is high when considerable medium-strong basicity and the synergistic effects of copper ion and metal copper exist on the catalytic surface. The optimized modified CuZnAl catalyst without any metal additives provides a CO conversion of 28.9%, C<sub>2+</sub>OH selectivity of up to 42.8%, and hydrocarbon selectivity of 2.5%, with a total alcohol selectivity of 67.4% under the reaction conditions of 5.0 MPa, 250 °C, H<sub>2</sub>/CO = 1, and a gas hourly space velocity of 360 mL/g<sub>cat</sub> h.

**Key words:** Complete liquid phase method, CuZnAl catalyst, higher alcohols, nonmetal promoter, syngas

### 1. Introduction

Higher alcohols can be used as pure unleaded fuels or as fuel additives in unleaded fuels and as sources of chemical products,<sup>1,2</sup> and have attracted interest in C1 chemistry. Heterogeneous catalysts have been employed for the synthesis of higher alcohols. Alkali-promoted Cu-ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts have been extensively studied for this purpose, since Cu-ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts have proved very efficient and cheap for methanol synthesis.<sup>3,4</sup> Alkali promoters neutralize the surface acidity, suppressing various side reactions such as hydrocarbon and dimethyl ether formation, dehydration, and coke deposition.<sup>5-8</sup> In addition, they have been found to increase the rate of carbon chain growth and to enhance the yield and selectivity of higher alcohol with increasing basicity. However, excess alkali loading might block the active sites on the catalyst surface and reduce the Brunauer–Emmett–Teller surface area, thereby leading to activity loss.<sup>4</sup> Alkali-promoted Cu-ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts produce a mixture of linear and branched alcohols that includes a large proportion of methanol and a large amount of hydrocarbons together with a small amount of other oxygenates. As a result, alkali-promoted Cu-ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts suffer from low selectivity for C<sub>2</sub>–C<sub>6</sub> alcohols, though substantial efforts have been devoted in this respect.<sup>3</sup> We found that the coexistence of copper ions and copper metal is in favor of carbon chain growth in previous experimental work.<sup>9</sup> Thereby, organic bases such as triethanolamine instead of alkali metal promoters were introduced during the preparation process of catalysts. Chelating agents such as N-methyl pyrrolidone were also introduced in

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order to improve resistance to the reducibility of copper oxides in our work. Catalysis is controlled not only by the chemical composition and size of the catalysts used, but also by the character of surface sites available on the catalyst surface.<sup>10–12</sup> These characteristics are associated with the catalyst preparation methods. Currently, heterogeneous catalysts are generally prepared by traditional methods, such as coprecipitation, impregnation, and sol-gel techniques.<sup>13–18</sup> A novel method invented by us, named the complete liquid-phase method, has been applied to prepare slurry catalysts. The main innovation is the preparation of slurry catalysts from the raw material solution in a liquid-phase environment.<sup>19–21</sup>

Here, we report the preparation, characterization, and performances of nonmetal promoter modified CuZnAl catalysts prepared by complete liquid-phase technology for higher alcohol from syngas in a slurry reactor.

## 2. Experimental

### 2.1. Catalyst synthesis

#### 2.1.1. Materials

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $(\text{C}_3\text{H}_7\text{O})_3\text{Al}$  were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Polyvinyl-pyrrolidone (PVP) was purchased from Tianjin Damao Chemical Reagent Factory. Triethanolamine (TEA) was obtained from Tianjin Hongyan Reagent Factory and 1-methyl-2-pyrrolidone (NMP) was purchased from Tianjin Hengxing Chemical Preparation Co., Ltd. All chemicals were of analytical reagent grade and were used without further purification. Deionized double-distilled water was used to make the solutions.

#### 2.1.2. Catalyst preparation method

First, 0.1 mol aluminum isopropylate ( $(\text{C}_3\text{H}_7\text{O})_3\text{Al}$ ) was dissolved in a mixture of ethanol, surfactant PVP, and deionized water, and kept at 80 °C for 1.5 h in a water bath. After that, a certain amount of nitric acid was added to the solution with vigorous stirring for 1 h at 95 °C; then another solution was added, which was prepared by dissolving 0.24 mol  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 0.12 mol  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in an appropriate amount of ethanol. Certain amounts of TEA and NMP were also added to the above solution. The mixture obtained was stirred under reflux at 95 °C for 10 h and then kept in a beaker at 30 °C for 10 days to obtain a gel. The gel was then heated in liquid paraffin from room temperature to 280 °C at a heating rate of 10 °C/min and held for 8 h at this temperature. A flow of 60 mL/min  $\text{N}_2$  was maintained throughout, and the CuZnAl slurry catalyst resulted from this process. The catalysts prepared with different TEA/NMP ratios are denoted as xTyN, where x and y refer to the added volumes (in mL) of TEA and NMP during the preparation, respectively.

### 2.2. Catalyst characterization

#### 2.2.1. X-ray diffraction

Powder X-ray diffraction (XRD) analysis was performed with a Rigaku D/max-2500 powder diffractometer (using  $\text{CuK}\alpha$  radiation with a tube voltage of 40 kV, a tube current of 100 mA, and scan rate of 4°/min). The phase identification was carried out by using the Joint Committee on Powder Diffraction Standards (JCPDS) files.

### 2.2.2. Temperature-program desorption

NH<sub>3</sub>-temperature-program-desorption (NH<sub>3</sub>-TPD) and CO<sub>2</sub>-temperature-program-desorption (CO<sub>2</sub>-TPD) were performed on a TP-5000 instrument. Samples (100 mg) were first reduced by 5% H<sub>2</sub> at 280 °C for 60 min in a quartz reactor and purged by He at 280 °C for 30 min. The catalyst was cooled down to 50 °C and adsorbed NH<sub>3</sub> (or CO<sub>2</sub>) at 50 °C until saturation and was purged with high-purity He for 30 min to remove the physisorbed NH<sub>3</sub> (or CO<sub>2</sub>). The TPD data were collected in a flow of He from 50 to 800 °C at a heating rate of 10 °C/min. The desorbed molecules were detected with a mass spectrometer (MS) by monitoring the signal at  $m/z = 17$  (NH<sub>3</sub>) or 44 (CO<sub>2</sub>).

### 2.2.3. Temperature programmed reduction

The reducibility of the catalysts was studied using temperature programmed reduction (TPR). H<sub>2</sub>-TPR was carried out in a laboratory-made microreactor. Prior to each TPR run, the 50.0 mg catalysts were heated to 150 °C for 60 min under a He flow of 30 mL/min. After the sample cooled down to 50 °C, the TPR analysis was then carried out by ramping the temperature to 500 °C under 5.0% H<sub>2</sub>/N<sub>2</sub> (30 mL/min), using a thermal conductivity detector to record the reduction peaks.

## 2.3. Catalyst activity measurements

### 2.3.1. Reaction conditions

The higher alcohol synthesis reaction was carried out in a 500-mL slurry-phase continuously stirred tank reactor equipped with a mechanical magnetic agitator. The reactant gas mixture of H<sub>2</sub> and CO (1:1) was introduced into the reactor at a pressure of 5.0 MPa, a gas hourly space velocity of 360 mL/g<sub>cat</sub> h, and a temperature of 250 °C. Each run was maintained over 120 h, and the liquid sample was sampled every 12 h. It was judged to have attained a steady state of reaction when the quantity of the sample of liquid product every 12 h was the same in 2 consecutive readings and the material balance calculation showed that the syngas consumption was equivalent to the yield of the product.

### 2.3.2. Product analysis

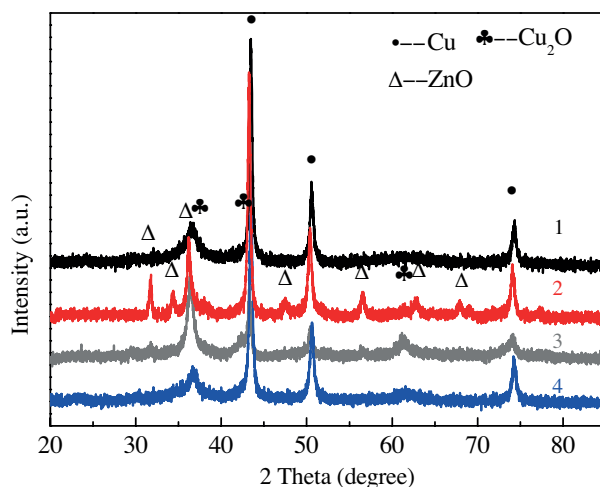
The products were analyzed using a gas chromatograph equipped with flame ionization and thermal conductivity detectors, using GDX-502 and TDX-01 columns, respectively. The gaseous products were analyzed by online gas chromatography, while the liquid products were collected in the trap and analyzed offline by gas chromatography.

## 3. Results and discussion

### 3.1. Catalyst characterization

#### 3.1.1. XRD analysis

The powder XRD patterns are shown in Figure 1. For all the fresh catalysts, the diffraction peaks located at  $2\theta = 36.5^\circ$  and  $61.5^\circ$  were assignable to Cu<sub>2</sub>O (JCPDS: 65-3288), and those at  $2\theta = 43.3^\circ$ ,  $50.4^\circ$ , and  $74.1^\circ$  were assignable to metallic Cu (JCPDS: 04-0836). In addition, the diffraction peaks at  $2\theta = 31.7^\circ$ ,  $34.4^\circ$ ,  $36.3^\circ$ ,  $56.6^\circ$ ,  $62.8^\circ$ ,  $67.9^\circ$ , and  $69^\circ$  corresponding to ZnO (JCPDS: 65-3411) were observed with the 5N10T catalysts. Note that the peaks of Cu metal on the 5N10T shift to the left compared with the others, which may indicate the formation of Cu–Zn alloy.

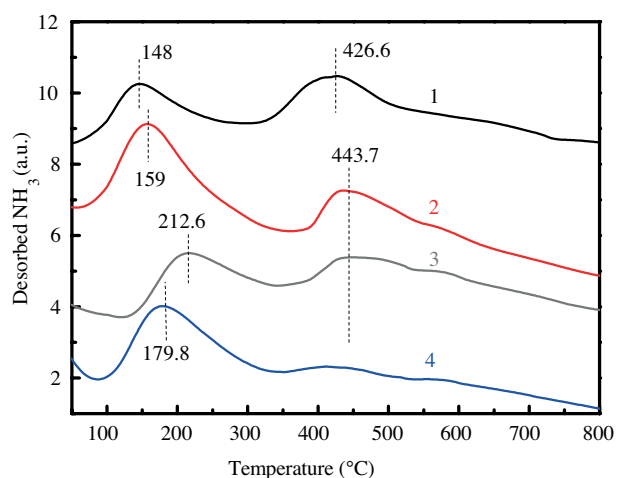


**Figure 1.** X-ray diffraction patterns for fresh 1. 0N0T; 2. 5N10T; 3. 5N15T; 4. 10N20T catalysts.

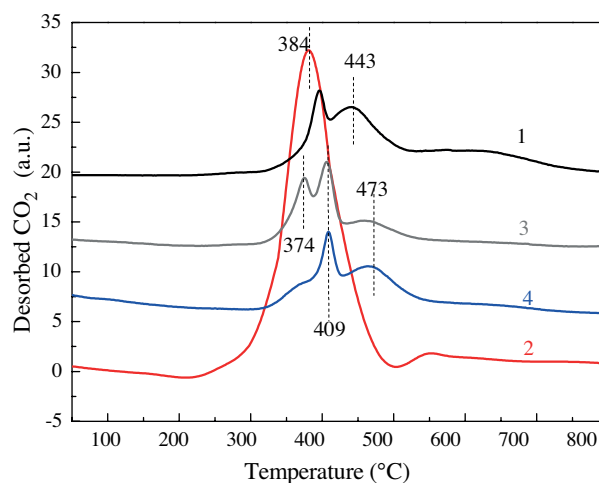
For the fresh catalysts, the presence of Cu metal and  $\text{Cu}_2\text{O}$  can be due to the decomposition of the paraffin by heat to produce a reductive compound to cause CuO reduction, which has been proved by our previous work.<sup>19,20</sup> The XRD patterns show that the intensity of the diffraction peak corresponding to Cu metal varies with different catalysts. The peak for 5N15T is lower in intensity than that for the others, while those of 10N20T are the strongest. This may be due to the effect of several factors, such as the size of the active metals, the concentration of organic bases, dispersion of Cu metal, and complexing agent dosage. In general, XRD profiles of fresh catalysts by traditional preparation method have commonly CuO, ZnO, and  $\text{Al}_2\text{O}_3$  diffraction peaks,<sup>3,4</sup> but  $\text{Al}_2\text{O}_3$  is amorphous in the catalysts prepared by complete liquid-phase technology. This is because the former is heated and decomposed statically in gas phase at 320–400 °C, while the latter is in liquid phase with continuously stirring at 280 °C.

### 3.1.2. Temperature-program desorption measurements

Both  $\text{NH}_3$ -TPD and  $\text{CO}_2$ -TPD were carried out on all catalyst samples.  $\text{NH}_3$  and  $\text{CO}_2$  thermodesorption were monitored by MS detectors (Figures 2 and 3, respectively).



**Figure 2.**  $\text{NH}_3$ -TPD spectra for fresh 1. 0N0T; 2. 5N10T; 3. 5N15T; 4. 10N20T catalysts.



**Figure 3.**  $\text{CO}_2$ -TPD spectra for fresh 1. 0N0T; 2. 5N10T; 3. 5N15T; 4. 10N20T catalysts.

NH<sub>3</sub>-TPD results are shown in Figure 2. For all the catalysts, the MS spectra of  $m/z = 17$  exhibited 2 NH<sub>3</sub> desorption peaks, corresponding to weak adsorption and medium-strong adsorption of NH<sub>3</sub> on the catalyst surface, respectively, but the relative amounts of weak acid and medium-strong acid are different. For 0N0T, the sites of medium-strong acid are more than those of weak acid. The opposite is true for 5N10T, 5N15T, and 10N20T. There are studies in the literature<sup>19,20</sup> reporting that the weak acid favors the formation of dimethyl ether (DME), and this is in agreement with the activity evaluation results. The wider desorption peaks are indicative of a wide distribution of strength of acid sites, varying from weak to strong. These acid sites are related to the contribution of different metal oxides, although the contribution of Al<sub>2</sub>O<sub>3</sub> is probably predominant.<sup>22</sup> Generally, the weak adsorption peak in the low temperature region is due to weak acid sites or hydrogen bonding to the hydroxyl groups of the surface, while the strong adsorption peak in the higher temperature region is due to the acid site resulting from the interaction between Cu, Zn, and Al compounds.<sup>23</sup>

As depicted in the NH<sub>3</sub>-TPD spectra, the peak areas provide information on the concentrations of acid sites on the catalysts. For the catalysts, the amounts of weak acid sites show little difference; however, the medium-strong acid sites decreased with the increase in TEA dosage, which is because TEA is a strong base and neutralizes part of the surface acid. This indicates that TEA dosage can change the medium acidity on the catalyst surface.

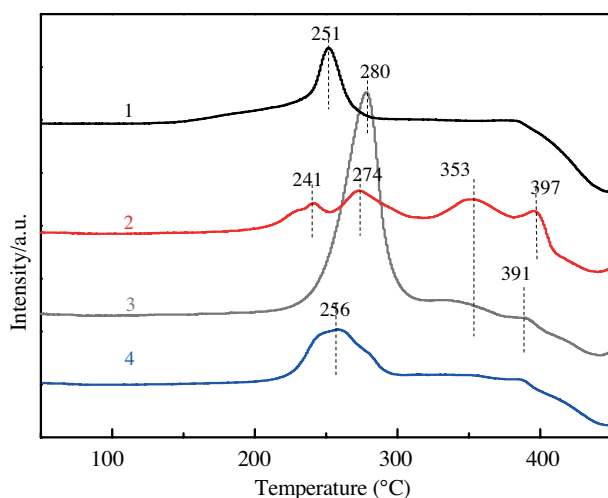
CO<sub>2</sub>-TPD results are reported in Figure 3. There are 2 CO<sub>2</sub>-TPD desorption peaks for all catalysts from 300 to 500 °C, corresponding to medium-strong basic sites on the catalyst surface, which is indicative of a wide strength distribution of basic sites, varying from medium to medium-high strength. Obviously, the amount of medium-strong basic sites on the 5N10T is much more than that of the others. Meanwhile, the amount of medium-strong basic sites is more than their own medium-strong acid sites in 5N10T by quantitative analysis.

### 3.1.3. Temperature programmed reduction of the catalysts

TPR was used to determine the reducibility of the CuZnAl catalysts. The TPR profiles of the catalysts are represented in Figure 4. The H<sub>2</sub>-TPR profiles of 0N0T and 10N20T display a broad reduction peak at 251 and 256 °C, respectively. Moreover, there is more than one peak on 5N10T and 5N15T. The 4 reduction peaks at 241, 274, 353, and 397 °C exist on 5N10T, with 3 peaks at 280, 353, and 391 °C on 5N15T. Although the peak at 241 °C is absent for 5N15T, the peak at 280 °C, which is asymmetric with a tail towards lower temperatures, reveals a complex overlapping arising from reduction processes of different copper oxide species. The higher temperature reduction peaks at around 353 and 391–397 °C can be attributed to the reduction of smaller copper oxide particles in zinc oxide or the partial reduction of zinc oxide. The process of reduction of smaller copper oxide particles in zinc oxide into metallic Cu is more difficult and requires higher temperatures.<sup>24</sup> and, in addition, the gas solid reaction suffers from particles' internal mass transfer resistance. Although ZnO is not generally reduced under our experimental conditions, partial reduction of surface ZnO cannot be ruled out<sup>25,26</sup> because the reduction of ZnO can occur via surface copper oxide by spilled hydrogen at a lower temperature.<sup>10</sup> The result indicates the rationality of the existence of Cu–Zn alloy on 5N10T.

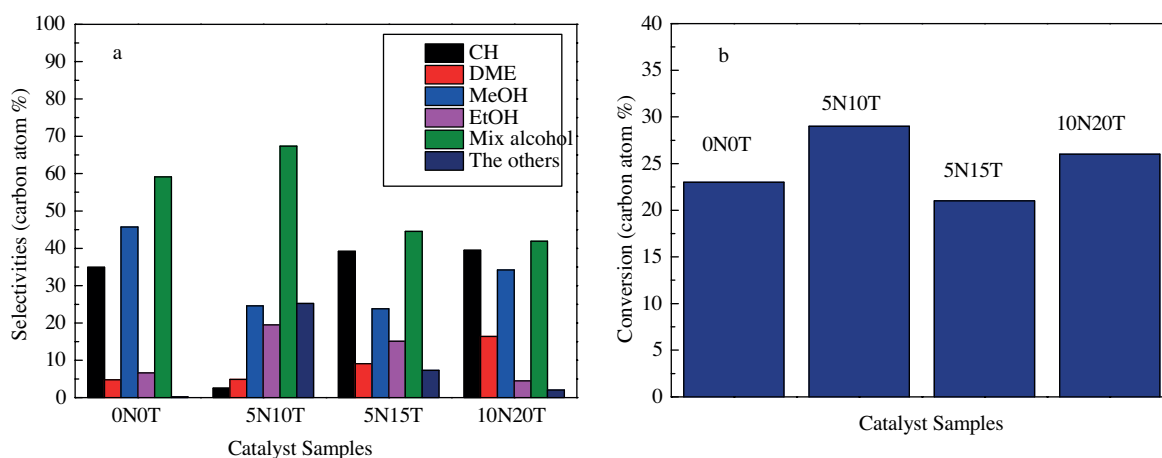
### 3.2. Catalytic activity measurements

The selectivities and conversions of CO hydrogenation over 0N0T, 5N10T, 5N15T, and 10N20T catalysts are shown in Figures 5a and b. CO conversion is 22.6%, 28.9%, 21.2%, and 25.8% for 0N0T, 5N10T, 5N15T, and 10N20T, respectively. As for 0N0T, the hydrocarbon and methanol were the major products, accounting for 34.9% and 45.7%, respectively, and the selectivity of C<sub>2+</sub> OH is 13.4%. As for 5N10T, C<sub>2+</sub> OH is the dominant



**Figure 4.** TPR profiles for fresh 1. 0N0T; 2. 5N10T; 3. 5N15T; 4. 10N20T catalysts.

product, whose selectivity is up to 42.8%, and the hydrocarbon selectivity is only 2.5%. As for 5N15T and 10N20T, the hydrocarbon is the main product, reaching 39.2% and 39.5%, and the selectivity of  $C_{2+}$  OH is 20.7% and 7.7%. From the characterization of the surface acid and base of the catalysts, we can find that the larger the ratio of base and acid is, the higher is the selectivity of  $C_{2+}$  OH. From the TPR profile of 5N10T, it can be concluded that the existence of copper oxide and the partial reduction of ZnO favor the formation of  $C_{2+}$  alcohols. It has been reported that copper oxides can stabilize the intermediate acyl species,<sup>27</sup> and 2 formaldehyde molecules can form ethanol via aldol condensation, thereby causing growth of the carbon chain. Furthermore, the basic environment can catalyze the reaction of aldol condensation, and suppress generation of hydrocarbon and DME.



**Figure 5.** a) Catalytic carbon-based selectivity towards hydrocarbon, DME,  $C_{2+}$  OH, methanol, the other oxygenates; b) CO conversion at GHSV = 360 mL/h  $g_{cat}$ ,  $H_2/CO = 1$ , 250 °C, and 5.0 MPa.

#### 4. Conclusion

CuZnAl catalysts were prepared using the complete liquid phase method invented by us with TEA and NMP as the function regulators. Characterizations clearly demonstrate that the ratio and amounts of TEA and NMP

have a great influence on the adjustment of the acidity and basicity of the catalyst surface and can alter the reducibility of copper and zinc oxides. Catalytic testing results show that the existence of a large amount of medium-strong basicity of catalytic surface favors the formation of C<sub>2+</sub> alcohols and suppress the generation of hydrocarbon and DME. The C<sub>2+</sub> alcohol selectivity of 42.8%, which in ethanol is 45.6%, can be achieved over CuZnAl catalyst without any alkali metal promoter. The present work exhibits a prospect for ethanol production from CO hydrogenation over CuZnAl catalysts without alkali metals.

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