

# Promotional Influence of Hydroxyl Complexing Agent on Ethanol Synthesis from Syngas Over CuZnAl Catalysts Without Other Metal Promoters

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# Abstract

Ternary CuZnAl catalysts promoted with three kinds of hydroxyl complexing agents were prepared by a complete liquidphase method and tested for ethanol synthesis from syngas in a slurry bed reactor. The catalysts were characterized by XRD,  $H_2$ -TPR, NH<sub>3</sub>-TPD, N<sub>2</sub> adsorption, XPS and TEM techniques. Activity results showed that ethanol selectivity enhanced significantly after the addition of hydroxyl complexing agents. Overall, the catalyst promoted by ethanolamine exhibited the best catalytic performance, with the concentration of ethanol and higher alcohols in the total alcohols reached up to 56.5% and 75.1%, respectively. The addition of hydroxyl complexing agents caused the reduction temperature of Cu<sup>+</sup> shifted to be higher and the amount of weak acid sites to be decreased. It also favored the formation of AlOOH and Cu particles with larger particle size. These factors together contributed to the remarkable selectivity of ethanol and higher alcohols.

# **Graphical Abstract**



Keywords Ethanol · Syngas · Complete liquid-phase method · CuZnAl · Hydroxyl complexing agents

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# **1** Introduction

Gasification of coal to syngas and its subsequent conversion to hydrocarbons and alcohols via the Fischer–Tropsch reaction has been identified as a promising process for the production of "green" [1]. Ethanol obtained from this process has attracted researcher's close attention due to its potential application as a promising route for the production of fuel blends and value-added chemicals in fine chemical synthesis [2, 3]. Typically, catalysts investigated for CO hydrogenation to ethanol mainly includes noble metal Rhbased catalysts [4], Mo-based catalysts [5], alkalis modified Cu-based methanol synthesis catalysts [6], and Cu-modified Fischer–Tropsch (F–T) synthesis catalysts [7]. Among them, Cu-based catalysts with low cost have become the optimal option.

Ternary CuZnAl catalysts have been widely employed in the industrial low-temperature methanol synthesis since the early 1960s [8]. The catalytic conversion of syngas to obtain relatively higher selectivity of ethanol over CuZnAl catalysts without alkalis or F-T elements (Fe, Co and Ni) is rarely reported except our group. And some researchers also surprised that the syngas could be directly catalyzed to ethanol and  $C_{2+}OH$  with relatively higher selectivity over ternary CuZnAl catalysts without promoters according to our previous results [9, 10]. However, the carbon number distributions of alcohols and hydrocarbons always meet the Anderson-Schulz-Flory (ASF) distribution, causing the concentration of ethanol in the total alcohols is not high, which is similar with CuFe or CuCo catalysts [11-13]. Thus, research and development of catalysts with higher selectivity and efficiency for the short-chain alcohols (such as ethanol) is highly desirable.

In order to narrow the distribution of alcohols and then improve the ethanol selectivity, a suitable promoter is necessary. Feng et al. [14] found that the addition of pyrogallol in preparing the Cu–Co catalyst favored the distribution of Cu, Co species as well as their interaction, as a result, the selectivity of ethanol increased from 33.1 to 43.5%. Yu et al. [15] reported that a certain amount of complexing agents enhanced the basicity on catalyst surface and the ethanol selectivity reached up to 24.5% in CO hydrogenation reaction. Gao et al. [16] prepared ZnCr catalysts at different pH value by ammonia solution, results showed that the catalysts prepared at pH=2 had more hydroxyl groups and a relative small size particle of ZnO and ZnCr<sub>2</sub>O<sub>4</sub>, exhibiting the optimal catalytic performance both on CO conversion (20.9%) and isobutanol selectivity (24.2 wt%).

In our previous study, several kinds of metal promoters (include La, Zr etc) also were added and investigated, unfortunately, these catalysts still produced a wide distribution of  $C_1-C_5$  linear alcohols and methanol remained the major product among the alcohols formed [17]. In addition, it was found that Cu<sup>+</sup> might have positive effect on the CO hydrogenation to ethanol, while ethanolamine, glucose and glycerol was a kind of reducing agent and complexing agent. Meanwhile, compared with glucose and glycerol, ethanolamine itself was an alkaline substance which could adjust the acidity on the catalyst surface. Thus, in this manuscript, three kinds of hydroxyl complexing agents including ethanolamine, glucose and glycerol are added during the process of the catalysts preparation. The influence of these promoters on the catalytic performance is investigated and the catalysts are characterized by X-ray diffraction (XRD),  $H_2$  temperature-programmed reduction ( $H_2$ -TPR), temperature-programmed desorption of ammonia ( $NH_3$ -TPD-MS),  $N_2$  adsorption, X-ray photoelectron spectrometry (XPS) and transmission electron microscopy (TEM).

# 2 Experiment

#### 2.1 Catalyst Preparation

The CuZnAl catalysts with various hydroxyl complexing agents were prepared by a complete liquid-phase method which was invented by our group [9]. The atomic ratio of Cu/Zn/Al in the starting solution was kept at 2/1/0.8, and the amount of hydroxyl complexing agent was equal to that of 1/4 copper molar content. Typically, 6.4 g of citric acid was dissolved in 90 mL of distilled water, then 19.8 g of aluminum isopropane[ $(C_3H_7O)_3Al$ ] was added to the above solution and the mixture was hydrolyzed at 50 °C for 3 h. After a solution of Cu(II) and Zn(II) nitrates was mixed with the hydroxyl complexing agent in 100 mL ethylene glycol solution, the mixture was slowly added dropwise to the above Al solution and stirred constantly until a sol was formed. After aging for 10 days to obtain the sel, then it was dispersed in 300 mL liquid paraffin and heated under N<sub>2</sub> atmosphere from 60 to 300 °C with a heating rate of 5 °C min<sup>-1</sup> and maintained for 8 h at 300 °C. After that, a slurry catalyst was consequently obtained. For convenience, the catalysts promoted with glucose, ethanolamine and glycerol were denoted as CAT-GB, CAT-MEA and CAT-GL, respectively, and the catalyst without the addition of hydroxyl complexing agent was named as CAT-Al.

#### 2.2 Catalyst Characterization

Prior to characterization, all liquid-phase slurry catalysts were centrifuged, extracted with petroleum ether for 48 h and then dried at room temperature for 24 h to obtain powder samples.

Powder X-ray diffraction (XRD) patterns were collected using Rigaku D/MAX-2500 Diffractometer with Cu K $\alpha$  radiation. The instrument was operated at 40 kV accelerating voltage and 40 mA current in a scanning angle (2 $\theta$ ) range of 5°–85° at a speed of 2° min<sup>-1</sup>.

 $H_2$  temperature-programmed reduction ( $H_2$ -TPR) tests were carried out in a quartz reactor at atmospheric pressure to investigate the reducibility of the samples using a chemisorption instrument (TP-5080). For each TPR test, the sample (100 mg) was pre-treated at 150 °C under a flow of He (40 mL min<sup>-1</sup>) for 30 min to remove physically adsorbed water and other impurities. It was then reduced in a flow of 5 vol%  $H_2/N_2$  gaseous mixture at a heating rate of 10 °C min<sup>-1</sup>. A thermal conductivity detector (TCD) was used to record the consumption of  $H_2$ .

Temperature programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) experiments were conducted on the TP5080 instrument equipped with a mass spectrum detector. Prior to tests, the samples were first pre-treated in He flow at 150 °C to remove the adsorbed species for 1 h. After coolling down to 50 °C, the samples were saturated with pure NH<sub>3</sub> for 30 min and then purged with He to remove the physisorbed molecules at 50 °C for 30 min. Subsequently, The TPD data were collected from 100 to 800 °C by an AMETEK mass spectrometer.

 $N_2$  adsorption-desorption measurement was performed by a Micromeritics Quantachrome instrument at – 196 °C. Prior to analysis, the samples were degassed at 200 °C in high vacuum for 5 h. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface areas, the pore size analysis were evaluated by Barret-Joyner-Halenda (BJH) method using the desorption branch.

X-ray photoelectron spectroscopy (XPS) experiments were performed on an ESCALAB 250 spectrometer equipped with monochromatic Al K $\alpha$  to obtain the information of oxidation state. The binding energies were calibrated internally by adventitious carbon deposit C(1*s*) with  $E_b = 284.60$  eV.

Transmission electron microscopy (TEM) experiments were carried on G2F-20 FEITECNAI apparatus with an accelerating voltage of 300 kV. Prior to each measurement, the samples were dispersed in ethanol, ultrasonicated, and deposited on carbon-film-covered copper grids for measurement.

#### 2.3 Catalytic Activity Measurements

The CO hydrogenation to ethanol reaction was carried out in a 0.5 L slurry bed reactor with a mechanical agitator. The syngas (CO/H<sub>2</sub>=1/2) was introduced into the reactor under the reaction conditions of 280 °C and 4.5 MPa with a feed flow rate of 150 mL min<sup>-1</sup> without reduction process. After passing through a cold trap (0–5 °C), the tail gas was analyzed online by GC which equipped with a thermal conductivity detectors (TDX-01 column) to analyze H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub>, and a flame ionization detector (PLOT/Q) to analyze C<sub>1</sub>–C<sub>5</sub> hydrocarbons, respectively. The alcohols products were collected from the cold trap daily and analyzed off-line using the flame ionization detector. CO conversion and selectivity of products were calculated according to the following equations:

Conversion for CO (%) =  $(CO_{in} - CO_{out})/CO_{in} \times 100\%$ 

Selectivity for M (%) = Quantity of M/

total quantity of products  $\times 100\%$ .

# **3** Results and Discussion

#### 3.1 XRD Characterization

The XRD patterns of all catalysts with different hydroxyl complexing agents before reaction were presented in Fig. 1. As seen in Fig. 1, the diffraction peaks at  $2\theta$  angles of  $43.3^{\circ}$ .  $50.4^{\circ}$  and  $74.1^{\circ}$  were corresponded to the (111), (200) and (220) reflections of Cu<sup>0</sup> crystalline phase. One could not see the diffraction lines of Cu<sup>+</sup> and Cu<sup>2+</sup> which might below the detection limit of XRD since the following TPR characterization showed two reduction peaks. This was due to the partly decomposition of liquid paraffin which resultantly generated the free carbon and then caused the reduction of most oxidized copper to Cu<sup>0</sup> [18]. In addition, no obvious diffraction peaks of Zn and Al species were observed in the range of diffraction angle. Therefore, it was hypothesized that the two species were homogeneously dispersed in the catalysts. Nonetheless, in our previous studies, it had been convinced that Zn existed in the form of ZnO, and Al was in the form of AlOOH when the catalyst preparing by the complete liquid phase method [19, 20].

## 3.2 H<sub>2</sub>-TPR Characterization

To provide an insight into the reduction behavior of catalysts, H<sub>2</sub>-TPR measurement was performed and the results were displayed in Fig. 2. As seen in Fig. 2, all of them showed two reduction peaks in the temperature range of 150–350 °C, which indicated that two different types of Cu species existed in the catalysts. Zhu et al. [21] reported that the peak at about 250 °C was ascribed to the reduction of Cu<sup>2+</sup> species, and the reduction peak at relatively higher



Fig. 1 XRD patterns of fresh catalysts with different hydroxyl complexing agents



Fig. 2  $H_2$ -TPR profiles of fresh catalysts with different hydroxyl complexing agents

temperature was attributed to the reduction of Cu<sup>+</sup>. Gao et al. [22] found that an excess of Zr would cause strong interaction of some Cu<sup>+</sup> species and t-ZrO<sub>2</sub>/mZrO<sub>2</sub>, which led to higher reduction temperature. In light of this, for this manuscript, it was speculated that the peak at the lowertemperature side was ascribed to the reduction of  $Cu^{2+}$ , and the higher-temperature profiles could be assigned to the reduction of Cu<sup>+</sup>. Meanwhile, it could be found clearly that the second reduction profiles of CAT-GB, CAT-MEA and CAT-Gl shifted to higher temperature compared with CAT-Al, which indicated that Cu<sup>+</sup> could be reduced more difficultly to Cu<sup>0</sup> after the addition of these promoters. It was generally thought that the synergistic effect between Cu<sup>0</sup> and Cu<sup>+</sup> species are responsible for the activity of the catalyst with high yield of ethanol [23, 24]. Such as latest work by Heracleous et al. [25] reported that the incorporation of Mn into Cu-based catalysts increased the percentage of Cu<sup>+</sup> species which adsorbed CO more strongly, and thus favored the formation of  $C_{2+}$ OH. In our previous work, it was also revealed that the strong interactions between Cu<sup>+</sup> and zinc or aluminum oxide would increase the ethanol selectivity [26], which was also proved by molecular-level theoretical study [27]. The following activity results also confirmed it, which further suggested that Cu<sup>+</sup> was indispensable for CO hydrogenation to ethanol over Cu-based catalysts.

#### 3.3 NH<sub>3</sub>-TPD-MS Characterization

Figure 3 presented the NH<sub>3</sub>-TPD-MS profiles of the fresh catalysts and the acidity of all catalysts (expressed as mmol of desorbed NH<sub>3</sub>/g) was compared in Table 1. It could be found from Fig. 3 that all catalysts only had a desorption peak at around 150 °C, suggesting that all catalysts only



Fig. 3  $NH_3$ -TPD-MS profiles of fresh catalysts with different hydroxyl complexing agents

lable I	The desorbed amount	
of NH <sub>3</sub>	over different catalysts	

Catalyst	Acidity (mmol g <sup>-1</sup> )
CAT-GB	7.76
CAT-MEA	6.37
CAT-Gl	7.73
CAT-Al	8.36

possessed weak acid sites which was assigned to the desorption of NH<sub>3</sub> that occurred between the OH groups of the oxides and  $NH_3$  [28], indicating that the addition of hydroxyl complexing agents had little effect on the strength of the surface acid sites. However, it could be found that the density of peak decreased after hydroxyl complexing agent added, corresponding to the decrease of weak acid (see Table 1). Interestingly, combined with the following catalytic activity results, it was noticed that there was inverse correlation between the amount of surface weak acid and the ethanol/C<sub>2+</sub>OH concentration in total alcohols. This inverse correlation between selectivity and acidity was in accordance with the general notion that ethanol formation required basic sites for the aldol-type condensation from lower alcohols to higher alcohols, which was also consistent with E. Heracleous et al. results [6, 29]. The addition of hydroxyl complexing agents in CuZnAl catalyst reduced acidity and thus promoted the production of ethanol. Therefore, it was concluded that a certain number of weak acid was beneficial to the synthesis of ethanol over our novel catalytic system.

## 3.4 N<sub>2</sub> Adsorption Characterization

The  $N_2$  adsorption isotherms of the four catalysts prepared with different hydroxyl complexing agent before and after



Fig. 4 Nitrogen adsorption-desorption isotherms and pore size distributions of different catalysts

reaction were presented in Fig. 4. As seen in Fig. 4, the N<sub>2</sub> adsorption isotherms of all catalysts were belonged to type IV isotherms with H3 hysteresis loops in the IUPAC classification. This type of hysteresis loop indicated significant presence of mesoporous material with a relatively uniform size. After reaction, the hysteresis loop of the four catalysts was assigned to type H4, which suggested also the presence of micropores [30]. The Barrett–Joyner–Halenda (BJH) model was presented to calculate the pore size distributions of the catalysts. As observed, these catalysts showed less uniform mesopores with size larger than 5 nm before reaction, indicating that no regular and well-defined channel structures were exist. Interesting, these catalysts had a similar pore size distribution with a pronounced peak at around 3.5 nm after reaction. Table 2 displayed the detailed textural properties of the four catalysts before and after reaction. One could see that no obvious changes for the textural properties were observed before reaction after these promoters added, which suggested that these hydroxyl complexing agents had little effect on the textural properties. However, it was clearly seen that the specific surface areas of all catalysts significantly increased after reaction, which illustrated that the reaction process was the main reason for the increase of BET surface area. It was speculated due to the slurry bed reactor with continuous mechanical agitator during the reaction, which resulted in the change of bigger pores into smaller pores, and even some micropores. However, any correlation between the BET surface area and the catalytic performance was not shown.

## 3.5 XPS Characterization

The chemical states of CuZnAl catalysts with different hydroxyl complexing agents were analyzed by XPS, and the binding energies (B.E) of Cu2 $p_{3/2}$ , Al2p, Zn LMM and the X-ray excited Auger electron spectroscopy (XAES) spectra were presented in Fig. 5. For all fresh catalysts, XPS peaks of Cu2 $p_{3/2}$  were found at around 931.5–932.5 eV (BE) and no shake-up satellite peaks were observed in the range of 940–945 eV (Fig. 5a), indicating that copper species had

been reduced to  $Cu^{\delta+}$  ( $\delta$  < 2) with lower valences (e.g.,  $Cu^{0}$ and Cu<sup>+</sup>), which was consistent with XRD results. However, it was difficult to differentiate the Cu<sup>+</sup> species from Cu<sup>0</sup> species since the peaks of all catalysts were widely dispersed from the XAES spectra, thus, the concentration of copper species on the catalyst surface was too low to detect (Fig. 5b). This was also ascribed to the special catalyst preparation method, which would cause a certain amount of carbon membrane on catalysts surface and thus the signal of Cu was very weak [31]. Nonetheless, it could be found that Cu  $2p_{3/2}$  peaks slightly shifted toward higher binding energy values for CAT-MEA catalyst, suggesting that the proportion of  $Cu^+/Cu^0$  increased over the catalyst surfaces after the addition of ethanolamine. The Zn Auger peak (Zn LMM) was used to obtain the state of Zn species. As seen in Fig. 5c, the auger peak of Zn species was located at around 987 eV, which could be assigned to ZnO according to the standard data [32]. Similarly, the Al 2p peak was located at about 73.5 eV for CAT-Al catalyst, and a slightly shift toward higher binding energy value was observed after these hydroxyl complexing agents added. Ebina et al. [33] reported that the binding energy values of tetrahedral and octahedral Al sites were about 73.7 and 74.5 eV, respectively. Meanwhile, several groups reported that these tetrahedral and octahedral Al sites were associated with Al<sub>2</sub>O<sub>3</sub> and AlOOH, respectively [34, 35]. Therefore, it was speculated that the catalysts contained more octahedral AlO<sub>6</sub> sites of AlOOH after the addition of hydroxyl complexing agents, especially for CAT-MEA. The octahedral AlO<sub>6</sub> site of AlOOH was believed to play an important role in ethanol and higher alcohols synthesis according to our previous study of density functional theory [36].

# 3.6 TEM Characterization

TEM analysis was conducted to confirm the copper dispersion and the particle size in CuZnAl samples, the obtained figures were shown in Fig. 6. As shown, the component of dark-field for all catalysts was copper nanoparticles, while the white domain contained both elemental Zn and Al. The Cu particle of CAT-Al catalyst were

Table 2 The textural property   of catalysts with different hydroxyl complexing agents	Catalyst	Before reaction	on		After reaction		
		Surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore diam- eter (nm)	Surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore diameter (nm)
	CAT-GB	68.2	0.6	12.4	216.6	0.4	17.6
	CAT-MEA	41.3	0.5	17.5	185.6	0.4	3.1
	CAT-Gl	46.7	0.5	6.5	234.7	0.4	3.1
	CAT-Al	48.7	0.5	17.5	187.9	0.3	3.1



Fig. 5 Cu 2p (a), Cu XAES (b), Zn LMM (c) and Al 2p (d) spectra of fresh catalysts





Table 3 CO hydrogenation   parformance on different	Catalyst	CO conversion	Selectivit	y (C-mol%)			C <sub>2+</sub> OH/	
catalysts		(%)		ROH	CnHm	CO <sub>2</sub>	ROH (wt%)	
	CAT-GB	4.6	13.1	36.4	9.8	40.7	59.8	
	CAT-MEA	4.5	0.3	28.3	28.8	42.6	75.1	
	CAT-Gl	5.1	21.1	13.9	11.6	53.4	62.4	
	CAT-Al	14.0	31.9	38.5	2.8	26.9	39.6	

grouped together separate from the support and their size was about 20–40 nm. After the addition of hydroxyl complexing agent, the black region became larger, which indicated that the Cu species aggregated to larger particles and intimately bound up with Zn and Al oxide, especially for CAT-GB and CAT-MEA catalysts. It was speculated that these enhanced metal-support interactions, together with the formation of Cu particles with larger size favored the ethanol synthesis according to Zhu et al. results [37].

#### 3.7 Catalytic Performance

The catalytic performance of the CAT-Al catalyst towards CO hydrogenation to ethanol was tested and compared with that of CAT-Gl, CAT-MEA and CAT-GB under the reaction conditions: 4.5 MPa, 553 K, flow rate of 150 mL min<sup>-1</sup>,  $n(H_2)/n(CO) = 2.0$ . The data were presented in Tables 3 and 4. It could be seen that the CAT-Al catalyst exhibited a relatively higher CO conversion (14.0%) and lower concentration of ethanol (14.5%) and  $C_{2+}OH$  (39.6%) in the total alcohols. After the addition of these hydroxyl complexing agents, the CO conversion decreased, while the concentration of ethanol and  $C_{2+}OH$ in the total alcohols increased significantly. Among these catalysts, the highest concentration of ethanol (reaching 56.5%) and  $C_{2+}OH$  (reaching 75.1%) with a narrow range distribution was obtained for CAT-MEA catalyst. These results indicated that alcohols did not obtain the ASF distribution and ethanol showed a positive deviation from the ASF behavior. In addition, compared with CAT-Al catalyst, the CO<sub>2</sub> selectivity also increased for these promoted catalysts overall, this might probably be due to the synthesis of ethanol often accompanied by the production of water, which would promote the water gas shift reaction  $(CO + H_2O \rightarrow CO_2 + H_2)$ . Interestingly, formation of the undesirable by-product dimethyl ether (DME) appeared to be suppressed over the CAT-MEA catalyst, on which the DME selectivity was the lowest, which suggested that the synthesis of ethanol and DME might be controlled by the opposite active center. Moreover, for all promoted catalysts, the ethanol concentration nearly increased to 40% and the C<sub>2+</sub>OH concentration nearly increased to ~60%, which were considerably higher than that of our previously results [9, 10].

# **4** Conclusions

To summarize, we have demonstrated that ternary CuZnAl catalysts prepared by the complete liquid-phase method could directly catalyze syngas to a rather higher selectivity of ethanol (56.5%) and  $C_{2+}OH$  (75.1%) with a narrow range distribution during CO hydrogenation in a slurry bed reactor. It was concluded from the characterizations that the addition of hydroxyl complexing agents caused the reduction temperature of Cu<sup>+</sup> shifted to be higher and the amount of weak acid sites to be decreased. It also favored the formation of AlOOH and enhanced metal-support interactions as well as the formation of Cu particles with larger size. These factors together contributed to the remarkable selectivity of ethanol and higher alcohols.

Table 4	Product distributions of
catalysts	s with different hydroxyl
complex	king agents

Catalyst	ROH distribution (wt%)				HC distribution (wt%)					
	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5
CAT-GB	40.2	37.9	8.9	12.5	0.5	10.8	38.7	24.6	15.5	10.3
CAT-MEA	24.9	56.5	9.4	9.0	0.2	18.8	25.1	29.6	13.9	12.6
CAT-Gl	37.6	40.0	8.7	13.1	0.6	10.2	36.8	22.4	17.9	12.7
CAT-Al	60.4	14.5	7.8	16.8	0.5	12.7	33.3	21.6	22.7	9.6

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#### **Compliance with Ethical Standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

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