



## Short communication

## CO hydrogenation to higher alcohols over Cu/Zn/Al catalysts without alkalis or Fischer–Tropsch elements: The effect of triethanolamine content



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## ABSTRACT

Cu/Zn/Al catalysts were prepared by a complete liquid-phase method with various triethanolamine (TEA) contents. Results showed that the mass fractions of higher alcohols in the total alcohols reached approximately 36.0% over Cu/Zn/Al catalyst without promoters and a suitable amount of TEA promoted the formation of higher alcohols. Characterization results showed that TEA mainly decreased the amount of weak acidic and increased the Cu content on the catalyst surface. It was speculated that a suitable amount of weak acid was beneficial to C–O hydrogenolysis and a relatively higher Cu content was beneficial for hydrogenation in the higher alcohols synthesis.

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## 1. Introduction

Higher alcohols have attracted researchers' interest due to their potential usage as fuels and intermediates for value-added chemicals [1–3]. At present, catalysts for higher alcohols synthesis (HAS) from syngas over Cu-based catalysts are mainly modified Fischer–Tropsch (F–T) synthesis catalysts [4–6] and alkalis modified methanol synthesis catalysts [7]. Cu-modified F–T catalysts require the synergism between the Cu and F–T elements. For these catalysts, Cu–X (X = Fe, Co, or Ni) is thought to be the active center for the synthesis of higher alcohols, in which Cu act as CO non-dissociative adsorption and insertion and X act as CO dissociation and chain growth [8,9]. The loss of this synergism destroys the active centers and leads to lower higher alcohols selectivity. Alkalis are believed to play a key role in the higher alcohols formation over alkali modified methanol synthesis catalysts [9,10].

It is well known that Cu/Zn/Al catalysts are usually used to synthesize methanol from CO or CO<sub>2</sub> hydrogenation [11–13]. However, in our previous studies, it is found that syngas could be directly catalyzed to ethanol over Cu/Zn/Al catalysts without alkalis or F–T elements [14]. Unfortunately, it is difficult to reproduce the former results. In addition, our group finds that the acidity–basicity of the solution has a significant effect on the hydrolysis of aluminum isopropylate (AIP). In addition, triethanolamine (TEA) is a kind of alkaline complexing agent and is considered to be stable in slurry catalysts due to its high boiling point of 633 K. Thus, we added TEA to adjust the pH in order to change

the surface properties of the catalysts and improve the mass fractions of higher alcohols in the total alcohols. Therefore, in this paper, the catalysts were prepared with different TEA content which was equal to the molar quantity of metallic M (M = Al, Cu and Cu + Zn). And the influence of TEA content on the higher alcohols formation was also investigated and the catalytic performance was clarified.

## 2. Experiment

## 2.1. Catalyst preparation

Cu/Zn/Al catalysts with various TEA content were prepared by a complete liquid-phase method. The Cu/Zn/Al atomic ratio in the initial solution was kept at 2:1:0.8, while the TEA content was equal to the molar quantity of metallic M (M = Al, Cu and Cu + Zn). Typically, 6.4 g of citric acid was dissolved in 90 mL distilled water, followed by the addition of 19.8 g of [(C<sub>3</sub>H<sub>7</sub>O)<sub>3</sub>Al] and maintained the temperature at 323 K for 3 h, the temperature was then raised to 368 K and the solution was stirred for 1 h. Next, the TEA solution was slowly added to the Al solution. After 30 min, 58.6 g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and 36.15 g of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in glycol and the resulting solution was slowly added to the above solution. The resulting Cu/Zn/Al solution was stirred at 368 K until a homogeneous sol was obtained. The sol was aged at room temperature for 10 d, dispersed in liquid paraffin and heated under N<sub>2</sub> atmosphere from 333 to 573 K with a heating rate of 5 K/min and then maintained for 8 h at 573 K. As a result, a slurry catalyst was subsequently obtained. For convenience, the catalysts were

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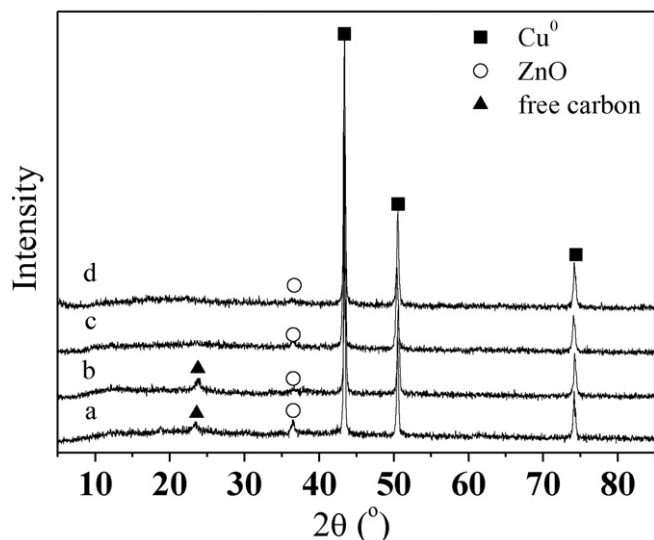


Fig. 1. XRD patterns of catalysts with different TEA contents. (a) SC/0, (b) SC/0.8, (c) SC/2 and (d) SC/3.

abbreviated as SC/X ( $X = 0.8, 2, 3$ ). The Cu/Zn/Al catalyst without the addition of TEA was named as SC/0.

## 2.2. Catalyst characterization

Before catalyst characterization, the slurry catalysts were centrifuged, extracted with petroleum ether for 2 d and dried at room temperature to obtain the solid samples.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500 diffractometer in a  $2\theta$  range of  $5\text{--}85^\circ$  with Cu K $\alpha$  radiation (40 kV and 100 mA).

H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) tests were carried out in a fixed-bed reactor. For each TPR test, the sample (50 mg) was purged with He (30 mL/min) at 423 K to remove physically adsorbed water and other impurities, it was then reduced in a flow of 5 vol.% H<sub>2</sub> + N<sub>2</sub> (30 mL/min) at a heating rate of 10 K/min up to 773 K. A thermal conductivity detector (TCD) was used to record the reduction peaks.

The acidity of the samples was measured by temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD-MS). The samples were first reduced at 553 K in a flow of 5 vol.% H<sub>2</sub> + N<sub>2</sub> (30 mL/min)

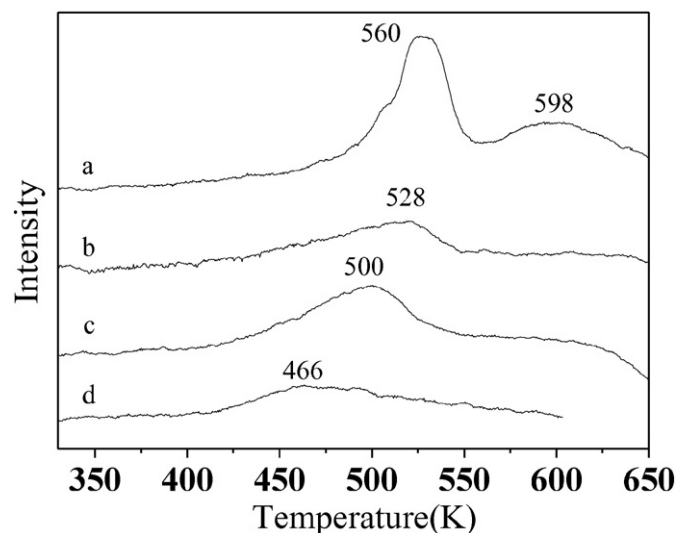


Fig. 2. H<sub>2</sub>-TPR profiles of catalysts with different TEA contents. (a) SC/0, (b) SC/0.8, (c) SC/2 and (d) SC/3.

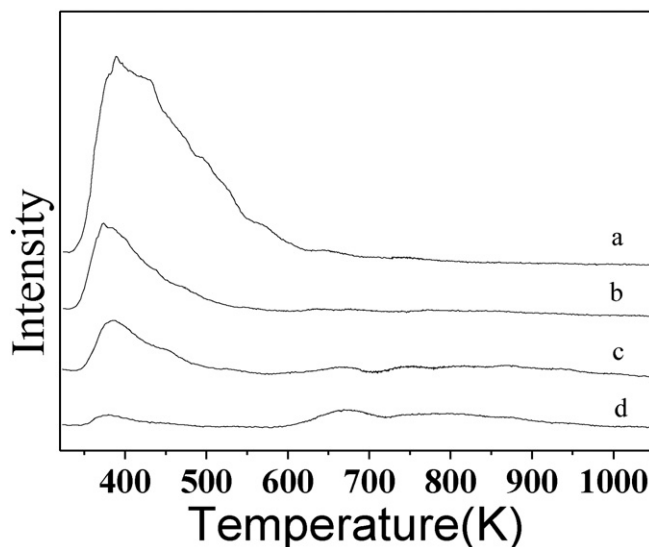


Fig. 3. NH<sub>3</sub>-TPD-MS profiles of catalysts with different TEA contents. (a) SC/0, (b) SC/0.8, (c) SC/2 and (d) SC/3.

for 30 min. After cooling to 323 K, the samples were saturated with pure NH<sub>3</sub> for 30 min and then flushed with He flow to remove all physically adsorbed molecules. After that, the TPD experiments were started with a heating rate of 10 K/min under He flow (30 mL/min), and the desorbed NH<sub>3</sub> molecules were detected by an AMETEK mass spectrometer.

X-ray photoelectron spectroscopy (XPS) experiments were conducted on an ESCALAB 250 spectrometer (VG Scientific Ltd., UK) equipped with Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV) under ultrahigh vacuum ( $10^{-7}$  Pa), and the pass energy was 30 eV. The binding energies were calibrated internally by an adventitious carbon deposit C (1 s).

## 2.3. Catalytic activity test

First, 15 g of catalyst was dispersed in 300 mL liquid paraffin, and the slurry catalyst was placed in a continuous-flow, 500 mL slurry reactor with continuous mechanical agitation for higher alcohols synthesis. The syngas (H<sub>2</sub>/CO = 2) was introduced into the reactor with a feed flow rate of 150 mL/min under 523–563 K and 4.5 MPa. The steady-state activity measurement was taken after at least 24 h on the stream. The gaseous products were analyzed online with a gas chromatograph equipped with a flame ionization detector (FID) to detect gaseous hydrocarbons and a thermal conductivity detector (TCD) to detect gaseous inorganic, respectively. The liquid products were collected daily and analyzed offline using the gas chromatograph.

## 3. Results and discussion

### 3.1. XRD characterization

The XRD patterns of the catalysts with different TEA content were presented in Fig. 1. As seen in Fig. 1, all the catalysts shared similar structural characteristics, with Cu<sup>0</sup> and ZnO being the dominant phases

Table 1  
XPS parameters of the Cu/Zn/Al catalysts with different TEA contents.

Catalysts	Binding energy (eV)			Atomic ratio Cu/Zn
	Cu <sub>2</sub> p <sub>3/2</sub>	Zn <sub>2</sub> p <sub>3/2</sub>	Al <sub>2</sub> p	
SC/0	932.0	1021.7	74.5	0.27
SC/0.8	931.9	1021.8	73.9	0.40
SC/2	932.3	1021.6	73.9	0.32
SC/3	932.4	1021.3	73.6	0.38

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