# Influences of preparation methods of $ZrO_2$ support and treatment conditions of $Cu/ZrO_2$ catalysts on synthesis of methanol via CO hydrogenation

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## ARTICLE INFO

## ABSTRACT

$ZrO_2$ supports were prepared by different methods (conventional precipitation method, shortened as "CP", and alcogel/thermal treated with nitrogen method, shortened as "AN"), and $Cu/ZrO_2$ catalysts were prepared by impregnation method. The supports and catalysts were characterized by BET, XRD, TEM and TPR. The effects of the preparation methods of $ZrO_2$ supports and the treatment conditions (calcination and reduction temperatures) of the catalyst precursors on the texture structures of the supports and catalysts as well as on the catalytic performances of $Cu/ZrO_2$ in CO hydrogenation were investigated. The results showed that the support $ZrO_2$-AN had larger BET specific surface area, cumulative pore volume and average pore size than the support $ZrO_2$-CP. $Cu/ZrO_2$-AN catalysts showed higher CO hydrogenation activity and selectivity of oxygenates ($C_1$–$C_4$ alcohols and dimethyl ether) than $Cu/ZrO_2$-CP catalysts. Calcination and reduction temperatures of supports and catalyst precursors affected the catalytic performance of $Cu/ZrO_2$. The conversion of CO and the STY of oxygenates were 12.7% and 229 g/kg h, respectively, over $Cu/ZrO_2$-AN-550 at the conditions of 300 °C, 6 MPa.

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## 1. Introduction

The catalytic conversion of syngas to methanol, DME (dimethyl ether) and higher alcohols ($C_2$–$C_4$ alcohols) is generally recognized as an important way to provide chemical stocks and clean fuel or fuel additives. Methanol is an important raw material in chemical industries, which can be used as the starting feedstock for $C_1$ chemistry. DME is considered to be an important chemical material and potential clean fuel substituting for LPG [1]. The most promising application of higher alcohols, especially iso-butanol, is as an additive of blending stock for automotive fuel to meet the octane requirement for replacing MTBE (methyl t-butyl ether) [2]. Therefore, from the aspect of utilizing coal resources rationally, it is of significant importance to carry out researches on the synthesis of methanol, DME and higher alcohols.

$ZrO_2$, which is known to be an active isosynthesis (CO hydrogenation to iso-$C_4$ hydrocarbons) catalyst [3–6], has shown selectivity to isobutene in CO hydrogenation. Recently, it has been discovered that $ZrO_2$ also exhibits selectivity to isobutanol, however, at the same time, it suffers from low reactivity and harsh reaction conditions such as high temperature and high pressure. Cai et al. [7] have employed $ZrO_2$ modified by 2.0% $K_2O$ as

catalysts and obtained the results that under the reaction conditions of 420 °C, 10 MPa and 5000 $h^{-1}$, the space time yield (STP) of isobutanol was 3.99 mL/(L h), which accounted for 15.13 wt% of the products. Therefore, it is necessary to improve the activity of $ZrO_2$ and decrease the reaction temperatures. As a catalyst for methanol synthesis, $Cu/ZrO_2$ has been investigated to a great extent, including its preparation method [8,9], redox properties [10,11] and the disperse state of CuO [12,13]. However, as a catalyst for higher alcohol synthesis, $Cu/ZrO_2$ has not been reported in detail [14]. Considering the isosynthesis properties of $ZrO_2$ [15–17], in the present work, the effects of the preparation methods of $ZrO_2$ supports and the treatment conditions (calcination and reduction temperatures) of $Cu/ZrO_2$ catalysts on the catalytic performances of the catalysts in CO hydrogenation were investigated.

## 2. Experimental

### 2.1. Preparation of catalysts

All the chemicals used in present study are of analytical grade. $ZrO_2$ supports were prepared by two different methods, conventional precipitation method (denoted as CP method) and the method of drying and calcinating of $ZrO(OH)_2$ alcogel in $N_2$ (denoted as AN method) [18]. Firstly, $ZrO(NO_3)_2$ aqueous solution (0.17 M) was added dropwise into diluted $NH_3$ solution (2.5 wt%)

with vigorous stirring, which were continued for another 30 min after titration. Then the white precipitate of $ZrO(OH)_2$ was aged at room temperature for 10 h. Subsequently, the precipitate was filtered and washed thoroughly with deionized water till pH 7. $ZrO(OH)_2$ hydrogel was divided into two equal parts. One part of $ZrO(OH)_2$ hydrogel was dried at 110 °C for 10 h in air and then calcined at 550 °C for 5 h, yielding $ZrO_2$, which was denoted as $ZrO_2$-CP-550, where 550 represented the temperature of calcination (this preparation method was named as CP method). The other part was thoroughly washed with pure ethanol twice and the formed alcogel was dried at 110 °C for 10 h in a flowing $N_2$ and then further calcined at 550 °C for 5 h in a flowing $N_2$. The calcined sample was denoted as $ZrO_2$-AN-550. The samples prepared with the same procedure as $ZrO_2$-AN-550 but calcined at 400 °C and 700 °C were denoted as $ZrO_2$-AN-400 and $ZrO_2$-AN-700, respectively. $Cu/ZrO_2$ catalysts were obtained by impregnating $ZrO_2$-CP and $ZrO_2$-AN with $Cu(NO_3)_2$ aqueous solution for 24 h, and then dried at 110 °C for 10 h in air and calcined at 350 °C for 3 h. The prepared $CuO/ZrO_2$ precursors were denoted as $CuO/ZrO_2$-AN-T1-T2 and $CuO/ZrO_2$-CP-T1-T2, in which T1 represented the calcination temperatures of $ZrO_2$-AN or $ZrO_2$-CP and T2 represented the calcination temperatures of $CuO/ZrO_2$.

## 2.2. Characterization of catalysts

$N_2$ adsorption isotherms were measured at 77 K using an ASAP-2010C gas adsorption analyzer (Micromeritics Corp). X-ray diffraction (XRD) measurements were performed on a Bruker D8 advance X-ray diffractometer, using Ni filtered Cu radiation at room temperature and instrumental settings of 40 kV and 40 mA. The average size of crystal could be measured by X-ray line broadening analysis (XLBA) using the well-known Debye–Scherrer equation [19]. Transmission electron microscope (TEM) measurements were carried out on JEOL-2010 to investigate the morphology and microstructure of samples.

$H_2$-temperature programmed reduction ($H_2$-TPR) was carried out on a homemade analysis system. The sample (100 mg) was first pretreated in a flow of Ar at 250 °C for 2 h and then cooled down to room temperature. Subsequently, under a flowing of 5% $H_2$/Ar mixture (30 ml/min), the sample was again heated from 20 °C to 700 °C at a heating rate of 10 °C/min.

## 2.3. Catalyst testing

The purities of $H_2$ and CO used in the study are 99.999% and 99.9%, respectively. CO hydrogenation was carried out in a specially designed high-pressure flow fixed-bed reactor. It was a quartz-lined stainless-steel tubular reactor in which the quartz line (10 I.D.) was tightly fixed in a stainless-steel tube. The catalyst (0.5 ml, 20–40 mesh) was packed in the reactor. Before the reaction was conducted, the catalyst was reduced at a certain temperature for 2 h in 20% $H_2$/$N_2$. Then the temperature was adjusted to reaction temperature and syngas ($H_2$/CO = 1:1) was introduced into the reactor. Both gaseous and liquid products were analyzed by gas chromatographs. $H_2$, CO, $CO_2$ and $C_1$–$C_5$ hydrocarbons were determined on-line by thermal conductivity detector (TCD) with a TDX-01 column, and oxygenates were analyzed off-line by flame ionization detector (FID) with an OV-17 capillary column.

## 3. Results and discussion

### 3.1. Influence of preparation methods of $ZrO_2$ supports on textural properties and catalytic performance

The adsorption and desorption isotherms of $ZrO_2$-AN, $ZrO_2$-CP, $CuO/ZrO_2$-AN and $CuO/ZrO_2$-AN are given in Fig. 1 and the BJH pore
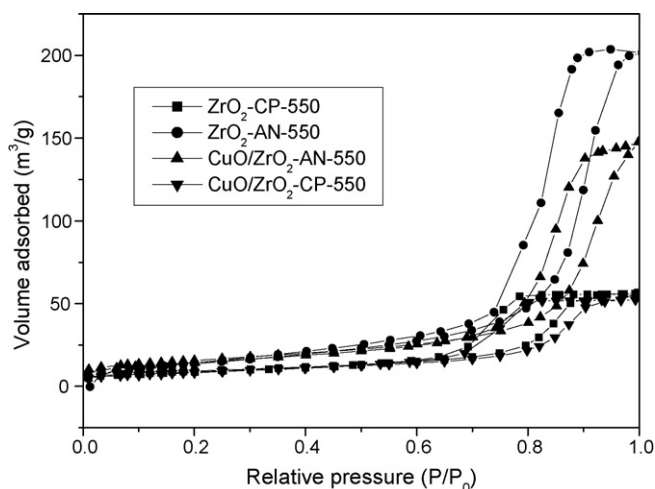


**Fig. 1.** $N_2$ adsorption–desorption isotherms of samples.
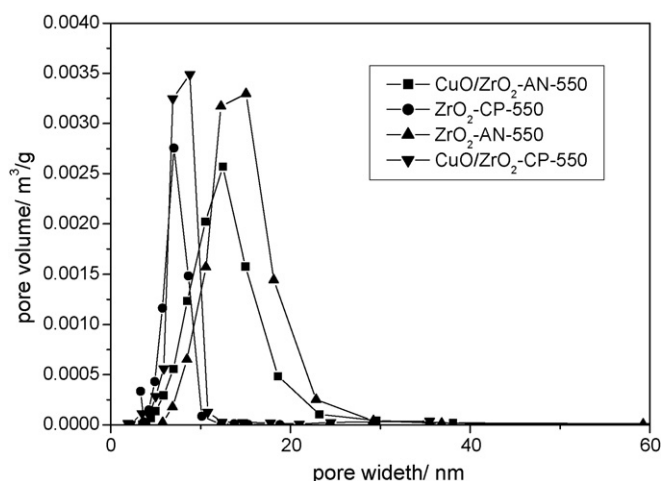


**Fig. 2.** BJH pore size distributions of samples.

size distributions of these samples are given in Fig. 2. Obviously, these samples showed the same type of adsorption isotherms (type IV) and hysteresis loops [20]. However, compared with $ZrO_2$-CP-550, $ZrO_2$-AN-550 had higher adsorption capacity and larger cumulative pore volume. In addition, the pore size distributions of $ZrO_2$-AN-550 were in the range of 7–35 nm, while those of $ZrO_2$-CP-550 were in the range of 4–11 nm. After the loading of CuO over $ZrO_2$-AN-550, the adsorption capacity and the cumulative pore volume decreased, and the pore size distributions shifted to a lower range.

The information about the textural structures of $ZrO_2$-AN, $ZrO_2$-CP, $Cu/ZrO_2$-AN and $Cu/ZrO_2$-CP is presented in Table 1. The specific surface area of $ZrO_2$-AN-550 was 61 m²/g, which was almost twice that of $ZrO_2$-CP-550. Moreover, the cumulative pore volume and the average pore size of $ZrO_2$-AN-550 were three and

**Table 1**
Effects of preparation methods of $ZrO_2$ on texture structure of $ZrO_2$.

| Sample | $S_{BET}$ (m² g⁻¹) | Cumulative pore volume (cm³ g⁻¹) | Average pore size (nm) | Crystal size of $ZrO_2$ (nm)[a] |
|---|---|---|---|---|
| $ZrO_2$-AN-550 | 61 | 0.28 | 14 | 15 |
| $ZrO_2$-CP-550 | 33 | 0.09 | 7 | 18 |
| $CuO/ZrO_2$-AN-550 | 56 | 0.21 | 13 | 14 |
| $CuO/ZrO_2$-CP-550 | 31 | 0.16 | 7 | – |

[a] Calculated from the X-ray line broadening analysis.