

# Development of highly stable catalyst for methanol synthesis from carbon dioxide



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## ABSTRACT

Zr-doped Cu-Zn-Zr-Al (CZZA) catalyst showed excellent performances for the methanol synthesis from carbon dioxide and hydrogen such as activity, selectivity and especially stability under mild conditions (such as 230 °C and 3.0 MPa). The catalyst showed excellent tolerance against water vapor. It was found that added alumina promoted the dispersion of Cu whereas it suppressed the reduction of copper oxide. On the other hand, added Zr promoted the catalytic activity of methanol synthesis from CO<sub>2</sub> and suppressed the inhibitive effect of water for the reaction as well as the catalyst deactivation. It was concluded that the methanol formation from CO<sub>2</sub> proceeds through two routes: one is the direct hydrogenation of CO<sub>2</sub> to methanol and another is the one which pass through the CO formation. The Zr-promoted catalyst gave methanol and CO at the selectivity ratio of 0.4 to 0.6, whereas the un-promoted catalyst gave only CO at the initial stage of the reaction. It was claimed that the doped Zr promote the in-situ reduction of oxidized Cu (which should be caused by the reaction with the co-product H<sub>2</sub>O) by H<sub>2</sub> to increase the content of reduced Cu (active site) and thus the catalyst activity. The promoted reductivity of the Zr-containing catalyst prevents the crystal growth of CuO<sub>x</sub> which cause the irreversible deactivation of catalyst.

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## 1. Introduction

Utilization of carbon dioxide has become an important global issue due to the significant and continuous rise in CO<sub>2</sub> concentrations, accelerated growth in the consumption of petrified carbon-based energy in the worldwide, depletion of carbon-based energy resources [1]. Catalytic hydrogenation of carbon dioxide to produce various kinds of chemicals or fuels such as methanol or hydrocarbons has been recently considered as one of the most promising processes for the utilization of CO<sub>2</sub> as well as the acceptor of hydrogen [2–7]. Generally, methanol has been produced industrially from CO and H<sub>2</sub> containing small amount of CO<sub>2</sub>. During the reaction, part of the CO<sub>2</sub> is converted to CO and H<sub>2</sub>O. Thus, the industrially made methanol contains H<sub>2</sub>O. However, it is not clear whether CO<sub>2</sub> is converted to methanol or to CO. It has been pointed out that for CO hydrogenation zero valent copper (Cu<sup>0</sup>) is the active component [8]. Al<sub>2</sub>O<sub>3</sub> has been pointed out to work as physical promoter to disperse Cu. Recently, many works concerned with the methanol synthesis from CO<sub>2</sub>/H<sub>2</sub> mixture have been presented. It has been shown that Cu/Zn-based catalysts are the most useful systems for the catalytic hydrogenation of CO<sub>2</sub> to methanol. They are used under rather high temperature (above 250 °C) and high pressure (more than 5 MPa) and show short life time [5,9,10].

Al<sub>2</sub>O<sub>3</sub> has been used often as the promoter in order to increase the stability and the activity. One of the present authors has shown that a conventional Cu/Zn/Al (CZA) catalyst showed high activity and stability for CO<sub>2</sub> hydrogenation when it was mixed with Pd/SiO<sub>2</sub>, and showed that the Pd/SiO<sub>2</sub> acts to keep the content of Cu<sup>0</sup> at high level [11]. Gao et al. claims that the doped Zr promote the basicity of CZA and the adsorption of CO<sub>2</sub> [12]. Development of active and stable catalyst under mild reaction conditions will attract high attention from the point of the CO<sub>2</sub> utilizing technology. For the direct CO<sub>2</sub> hydrogenation, the formation of water vapor is inevitable (CO<sub>2</sub> + 3H<sub>2</sub> → CH<sub>3</sub>OH + H<sub>2</sub>O), which inhibit the reaction strongly and leads to serious catalyst deactivation. However, little attention has been paid to elucidate the influence or to suppress its negative effects. In the present study, we will report our new findings on the effects of promoters (Al and Zr) on the methanol synthesis from CO<sub>2</sub> hydrogenation. Also, the promotive effects of Zr on the catalysis are analyzed from the relationship between the structure and the reaction performances. The Zr oxide doped Cu-Zn based catalyst was prepared by a simple co-precipitation method.

## 2. Experimental

### 2.1. Catalyst preparation

The investigated catalysts were prepared by a conventional co-precipitation method. It was precipitated from

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an aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (all Wako, total cation concentration 1M) by dropwise addition of a 1M aqueous solution of  $\text{Na}_2\text{CO}_3$  at 65 °C to final pH of 7. The precipitate was then filtered, dried, and then calcined in air at 400 °C for 5h. The resulting catalyst has the composition of CZA ( $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3 = 4/3/3$ ), CZZA ( $\text{Cu}/\text{ZnO}/\text{ZrO}_2/\text{Al}_2\text{O}_3 = 4/3/1.5/1.5$ ), CZZ ( $\text{Cu}/\text{ZnO}/\text{ZrO}_2 = 4/3/3$ ) by weight. Finally, the resultant powder was shaped into granules and to 20–40 meshes for the reaction.

## 2.2. Catalyst characterization

XRD patterns of catalyst samples were measured under ambient atmosphere with a RIGAKU X-ray diffract meter equipped with a Cu  $K\alpha$  radiation. The specific surface area of the catalysts was determined by BET method using a Micromeritics ASAP 2010. X-ray photoelectron spectra (XPS) of the calcined catalysts were recorded on an ESCALAB 250 spectrometer using Al  $K\alpha$  radiation (1486.6 eV). The binding energies were calculated with respect to C 1s peak at 284.6 eV.

TPR carried out with a BELCAT-B instrument. The sample (50 mg) was previously treated in He flow up to 350 °C and kept for 2h followed by cooling to 50 °C. The 10%  $\text{H}_2/\text{He}$  mixture was passed over samples at a flow rate of 30 ml/min with a heating rate of 10 °C/min up to 400 °C. The effluent gas was passed over a molecular sieve trap to remove the generated water and then analyzed by GC equipped with TCD.

The surface of Cu metal number was measured by  $\text{N}_2\text{O}$  titration method by using the same BELCAT-B instrument. Prior to titration, the sample with about 50 mg was reduced at 250 °C for 2h with 10%  $\text{H}_2/\text{He}$  flow, followed by purging and cooling with He flow to 50 °C. The consumption of  $\text{N}_2\text{O}$  as well as the evolution of  $\text{N}_2$  on the metallic Cu sites ( $2\text{Cu} + \text{N}_2\text{O} \rightarrow \text{Cu}_2\text{O} + \text{N}_2$ ) was measured at 50 °C by a thermal conductivity detector (TCD). The surface area of metallic Cu was calculated by assuming  $1.46 \times 10^{19}$  Cu atoms/ $\text{m}^2$  and  $\text{N}_2\text{O}/\text{Cu}$  molar stoichiometry of 0.5 and the particle size of Cu was calculated with the equation of  $6000/(8.92 \times \text{Cu metal surface area}/\text{Cu fraction in gram catalyst})$  [13,14].

## 2.3. Procedures for catalytic reaction and product analysis

A pressurized flow type reaction apparatus with a fixed-bed reactor was used for this study. The apparatus was equipped with an electronic temperature controller for a furnace, a tubular reactor with an inner diameter of 8 mm, thermal mass flow controllers for gas flows and a back-pressure regulator. A thermocouple was set at the axial center of the tubular reactor. One gram of catalyst was placed in the reactor with inert quartz sands above and under the catalyst. All catalysts were reduced in the flow of 5%  $\text{H}_2$  in nitrogen at 250 °C for 4h before reaction. All the products from the reactor were analyzed by on line gas chromatograph (GC).

## 3. Results and discussion

### 3.1. Catalyst structure and their character

#### 3.1.1. Structure

The XRD patterns of (1) calcined, (2) reduced and (3) used catalysts are shown in Fig. 1. Results obtained suggest the presence of a CuO phase ( $2\theta = 35.5^\circ$ ,  $38.5^\circ$ ) for calcined samples. In addition to these peaks, there also appeared peaks that were assigned to ZnO at  $31.8^\circ$ ,  $48^\circ$ ,  $56.6^\circ$ ,  $62.8^\circ$ ,  $68^\circ$  for CZZ sample, which is agreed well with that obtained by Wang [15]. After reduction,

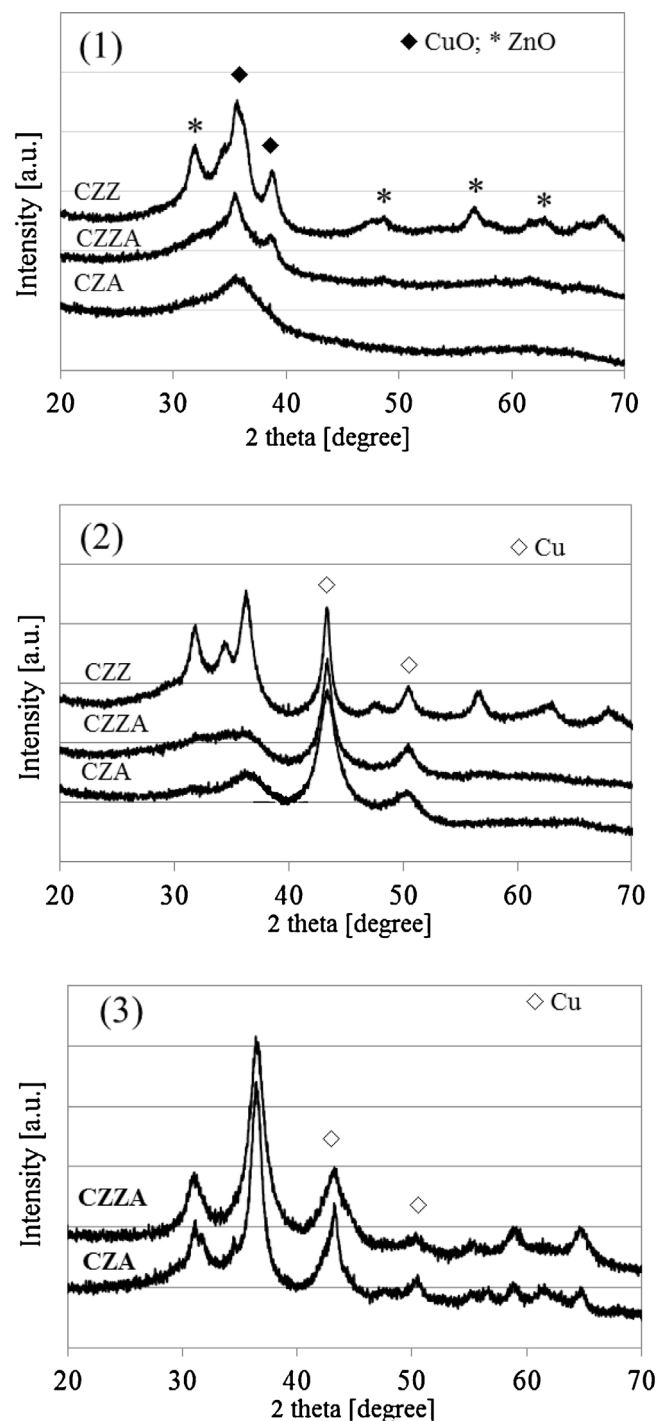


Fig. 1. XRD patterns of catalysts: (1) calcined; (2) reduced and (3) after 100 h reaction.

the peaks at  $43^\circ$  and  $50^\circ$  were attributed to metallic Cu, which performed as a role as active component for methanol synthesis [16,17]. Using Debye–Scherrer Formula, the crystallite sizes of Cu are calculated as 8.8 nm in CZA, 9.4 nm in CZZA and 12.5 nm in CZZ, respectively.

The crystallite size growth of Cu occurred as well as CuO during stability test, which could be estimated to be 11.4 nm for CZZA and 13.8 nm for CZA, respectively, implying the significant negative effect of crystal growth in the  $\text{CO}_2$  hydrogenation.

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