Copper nanoparticles on amorphous zirconia for methanol synthesis via carbon dioxide hydrogenation

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Abstract: We prepared Cu/*a*-ZrO_2 (*a*-ZrO_2: amorphous ZrO_2) and Cu/*m*-ZrO_2 (*m*-ZrO_2: monoclinic ZrO_2), by a simple impregnation method and examined the effect of ZrO_2 phase on CO_2-to-methanol hydrogenation. We found the Cu/*a*-ZrO_2 catalyst was highly active and selective in CO_2-to-methanol hydrogenation. Methanol vapor sorption revealed that methanol adsorbed more weakly on *a*-ZrO_2 than on *m*-ZrO_2. Therefore, the weak adsorption of methanol on Cu/*a*-ZrO_2 led to high selectivity in CO_2-to-methanol hydrogenation.

Keywords: Copper, Zirconia, Methanol synthesis.

1. Introduction

Today, $CuO/ZnO/Al_2O_3$ catalysts have been used for conventional methanol synthesis from syngas (CO-to-methanol hydrogenation, Eq. 1). Since the middle of the 1990s, methanol synthesis via CO_2 hydrogenation (Eq. 2) has been studied as a key process for the methanol-based economy [1]. Because of the reactivity difference between CO and CO_2, new catalysts specific to CO_2-to-methanol hydrogenation should be developed. At a high temperature, the endothermic reverse water gas shift reaction (RWGS reaction, Eq. 3) becomes dominant, resulting in the conversion of CO_2 to CO. Thus, high activity and selectivity in CO_2-to-methanol hydrogenation (Eq. 2) are required for the new catalysts.

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad \Delta_r H_{(298K)} = -91\ \mathrm{kJ\ mol^{-1}} \qquad \text{(Eq. 1)}$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad \Delta_r H_{(298K)} = -49\ \mathrm{kJ\ mol^{-1}} \qquad \text{(Eq. 2)}$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad \Delta_r H_{(298K)} = 42\ \mathrm{kJ\ mol^{-1}} \qquad \text{(Eq. 3)}$$

Combination of Cu species with metal oxides (such as ZnO, ZrO_2, CeO_2, and MgO)[2] is known to produce the effective active sites. Among the supports, ZrO_2 is particularly promising because ZrO_2-containing catalysts led to highly active, selective and stable catalysts. According to several studies[3], a plausible mechanism for CO_2-to-methanol hydrogenation over Cu/ZrO_2 catalysts involves the CO_2 adsorption on ZrO_2, leading to the formation of formate species on ZrO_2. Simultaneously, H_2 dissociatively adsorbs to the Cu surface and then transfers to the ZrO_2 surface, allowing the conversion of the formate species to methoxy species at the Cu-ZrO_2 interface. In the end, the methoxy species is hydrogenated to methanol. In the present study, we investigated the effect of ZrO_2 phase on both Cu species formation of Cu/ZrO_2 catalysts and CO_2-to-methanol hydrogenation. We focused on *a*-ZrO_2, and found the high activity and selectivity in CO_2-to-methanol hydrogenation over Cu/*a*-ZrO_2.

2. Experimental

The Catalysis Society of Japan provided *a*-ZrO_2 (aZ, JRC-ZRO-5) and *m*-ZrO_2 (mZ, JRC-ZRO-3). Supported Cu catalysts were prepared using an incipient wetness impregnation method. The above aZ or mZ was impregnated with an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (Wako Pure Chemical Industries, Ltd.), dried at 110 °C overnight, and calcined at 350 °C for 2 h. The catalysts containing aZ and mZ were named C/aZ, and C/mZ, respectively. The loadings of Cu for the prepared catalysts were 9 wt%.

3. Results and discussion

The CO_2 hydrogenation was conducted in a fixed-bed tubular reactor at 10 bars and 230 °C. Figure 1a shows CO_2 conversion, methanol selectivity and CO selectivity against the contact time over the prepared catalysts. For the catalysts, CO_2 conversion rose as the contact time increased. When W/F_{total} was 430 g_{cat} s $L(STP)^{-1}$, the methanol production rate for C/aZ (0.70 mmol h^{-1} g_{cat}^{-1}) was higher than that for C/mZ (0.64 mmol h^{-1} g_{cat}^{-1}). We note that CO selectivity rose with an increase in contact time, while methanol selectivity decreased. Based on the shape of the selectivity curve, this reaction is considered to be a step-wise reaction of CO_2-to-methanol hydrogenation (Eq. 2) and methanol decomposition to CO (the reverse reaction of CO-to-methanol hydrogenation, Eq. 1). In addition, C/aZ exhibited higher selectivity in methanol production than C/mZ, as shown in Figure 1a. Taking into consideration the above step-wise reaction, we assumed that C/aZ suppressed the latter reaction.

Next, we adsorbed methanol on aZ and mZ and measured IR spectra. The powder samples (ca. 20 mg cm^{-2}) were pressed into a thin self-supporting disk and set in the cell, heated at 280 °C for 2 h under vacuum, and cooled down to 205 °C under vacuum. Then background spectra were collected at 205 °C. The samples were exposed to methanol vapor (3 kPa) for 20 min at 205 °C. Afterwards, the methanol vapor was removed by vacuum treatment at 205 °C. As shown in Figure 1c, after evacuation of the gaseous methanol at 205 °C, no peak observed for aZ, while two sharp peaks at 2930 and 2817 cm^{-1} were observed due to the methoxy species on ZrO_2. Through these studies, we elucidated that at 205 °C methanol molecules did not adsorb on the aZ surface and strongly adsorbed on the mZ surface. Therefore, we hypothesized that the produced methanol molecules could easily detach from the surface of *a*-ZrO_2, resulting in the suppression of methanol decomposition.

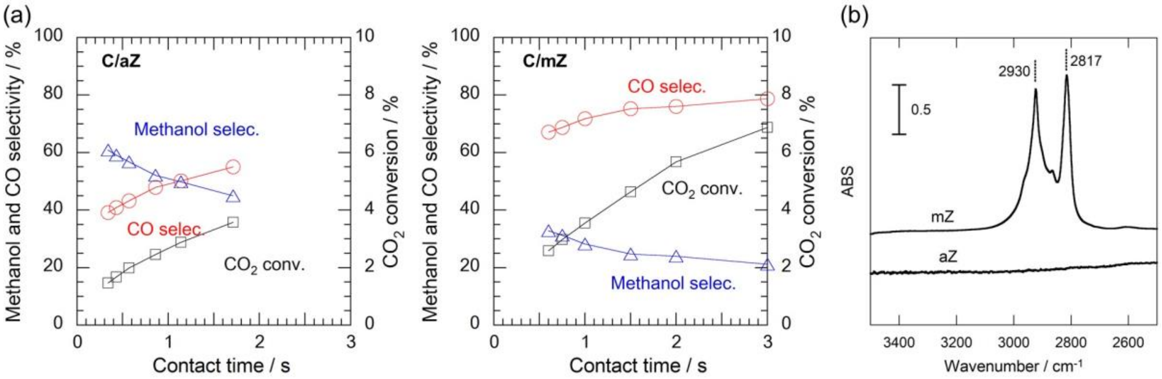

Figure 1. (a) CO_2 conversion, methanol selectivity and CO selectivity against contact time over C/aZ and C/mZ. Reaction conditions: $CO_2/H_2/N_2$ = 1/3/1, catalyst loading = 500 mg, reaction temperature = 230 °C, pressure = 10 bar. Before the reaction test, all the catalysts were reduced at 300 °C by 16% H_2/N_2 (72 mL(STP) min^{-1}) for 2 h under ambient pressure. (b) FTIR spectra of aZ and mZ at 205 °C after admission of methanol (3 kPa) for 20 min at 205 °C and then evacuation of methanol for 10 min at 205 °C.

4. Conclusions

We found the high activity and selectivity in CO_2-to-methanol hydrogenation over Cu/*a*-ZrO_2, due to the weak adsorption of methanol on *a*-ZrO_2 [4].

Acknowledgements

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