Direct evidence of the incorporation of Cu species into ZrO_2 lattice over CuO/ZrO_2 for CO_2-to-methanol hydrogenation

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Abstract: We prepared CuO/ZrO_2 by a simple impregnation method and examined the incorporation of Cu species into ZrO_2. Based on PXRD results, Cu species was incorporated into ZrO_2 lattice, while the amount of the Cu species was limited. Methanol synthesis via CO_2 hydrogenation was carried out using the CuO/ZrO_2 catalysts. The methanol production rate increased as increasing the Cu loading from 6 to 12 wt%. Afterwards, the catalytic performance remained unchanged.

Keywords: Copper, Zirconia, Methanol synthesis.

1. Introduction

As Friedrich Asinger predicted, CO_2 can become a valuable feedstock when the fossil fuels diminish and become expensive [1]. Since the mid-1990s, methanol synthesis via CO_2 hydrogenation (Eq. 1) has been studied as a key process in the sustainable methanol-based economy, as an alternative to the current one based on fossil fuels [2]. Methanol is produced by hydrogenation of CO (Eq. 2), since Imperial Chemical Industries developed a $CuO/ZnO/Al_2O_3$ catalyst in the sixties. Because conventional catalysts for CO-to-methanol hydrogenation do not show enough activity for CO_2-to-methanol hydrogenation, it is vital to develop the specific catalyst for CO_2-to-methanol hydrogenation. Here, we focus on Cu/ZrO_2 catalysts for CO_2-to-methanol hydrogenation. It possesses the high activity in CO_2-to-methanol hydrogenation and minimizes the formation of CO via the competitive reverse water gas shift reaction (RWGS reaction, Eq. 3) [3, 4]. The main active sites are considered to be the interface between Cu and ZrO_2 [3]. We reported that CuO/a-ZrO_2 (a-ZrO_2: amorphous ZrO_2) was highly active and selective in CO_2-to-methanol hydrogenation. The reason of the high selectivity is that the produced methanol molecules could quickly detach from the surface of a-ZrO_2, resulting in the suppression of the undesirable methanol decomposition (the second reaction of the above CO_2 hydrogenation) [5]. In addition, when a-ZrO_2 was impregnated with Cu nitrate solution and then calcined, we obtained a green powder which can be attributed to the presence of green $Cu_aZr_{1-a}O_b$. It was expected that the formation of $Cu_aZr_{1-a}O_b$ mean the incorporation of Cu species into ZrO_2 lattice [5]. In this study, we evaluated the physicochemical properties of the green $Cu_aZr_{1-a}O_b$ and developed the new catalyst with high activity and selectivity in CO_2-to-methanol hydrogenation.

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad \Delta_r H_{(298K)} = -49\ \mathrm{kJ\ mol^{-1}} \qquad \text{(Eq. 1)}$$
$$CO + 2H_2 \rightleftarrows CH_3OH \qquad \Delta_r H_{(298K)} = -91\ \mathrm{kJ\ mol^{-1}} \qquad \text{(Eq. 2)}$$
$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad \Delta_r H_{(298K)} = 42\ \mathrm{kJ\ mol^{-1}} \qquad \text{(Eq. 3)}$$

2. Experimental

The Catalysis Society of Japan provided *a*-ZrO_2 (aZ, JRC-ZRO-5). CuO/ZrO_2 catalysts were prepared using an incipient wetness impregnation method. The above aZ 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 500 °C for 2 h. The obtained catalysts were named CZ-*x*, where *x* is the Cu loading (wt%). The crystalline phases of the catalysts were determined by powder X-ray diffraction (Rigaku, Ultima IV) with a Cu Kα radiation source at a voltage of 40 kV and a current of 40 mA.

3. Results and discussion

The as-prepared catalysts were tested for CO_2 hydrogenation to methanol using a high-pressure fixed bed flow reactor (10 bars, 230 °C) using a Micromeritics Microactivity Effi reactor. Figure 1a shows the production rates of methanol and CO for the catalysts. Both the production rates increased as the Cu loading increased from 6 wt% to 12 wt%, and then remained unchanged.

PXRD patterns of CZ-*x* are shown in Figure 1b. For the as-prepared catalysts, we observed the peaks of *t*-ZrO_2. Of note, the position of *t*-ZrO_2 (111) peak at ca. 30 ° was shifted to a higher angle as the Cu loading increased from 0 to 8 wt%, and then the position remained unchanged as shown in Figure 1b. We calculated the lattice space of *t*-ZrO_2 (111) from the above peak positions and summarized them as a function of the atomic ratio of Cu to Zr in Figure 1c. Interestingly, the lattice space decreased linearly from 2.95 to 2.93 Å with increasing the Cu loading from 0 to 0.15 at%, which was in accordance with Vegard's law (see a dotted line in Figure 1c). Afterwards, the lattice space was 2.93 Å and remained unchanged, indicating of the solubility limit of Cu species into ZrO_2.

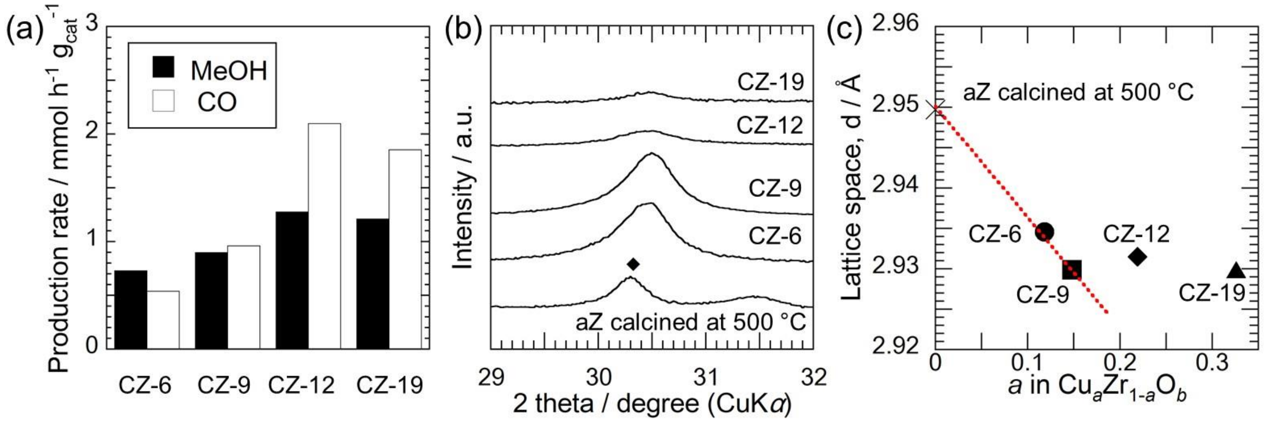

Figure 1. (a) Methanol and CO production rates for the prepared catalysts when W/F was 430 g_{cat} s $L(STP)^{-1}$. Reaction conditions: $CO_2/H_2/N_2$ = 1/3/1, catalyst loading = 500 mg, reaction temperature = 230 °C, pressure = 10 bar. Before the reaction test, all the catalysts were reduced at 300 °C by 16% H_2/N_2 (72 mL(STP) min^{-1}) for 2 h under ambient pressure. (b) PXRD patterns for CZ-*x*-500 in the range of 29-32 °. For comparison, the pattern for aZ calcined at 500 °C was also shown. The diamond symbol in (b) indicates the peak of *t*-ZrO_2 (111). (c) Lattice space of *t*-ZrO_2 (111) phase as a function of the atomic ratio of Cu to Zr for CZ-*x* and aZ calcined at 500 °C..

4. Conclusions

CuO/ZrO_2 showed the higher activity in CO_2-to-methanol hydrogenation with increasing the Cu loading from 6 to 12 wt%. Of note, the catalytic performance of CuO/ZrO_2 with 12 wt%_Cu was almost the same to that of CuO/ZrO_2 with 19 wt%_Cu. PXRD analyses revealed that Cu species can incorporate into ZrO_2 lattice and there is the solubility limit of Cu species into ZrO_2.

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