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. 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. Methanol is produced by hydrogenation of CO (Eq. 2), since Imperial Chemical Industries developed a CuO/ZnO/Al$_2$O$_3$ catalyst in the sixties. Because conventional catalysts for CO$_2$-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). The main active sites are considered to be the interface between Cu and ZrO$_2$. 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). 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$_2$Zr$_{1-x}$O$_6$. It was expected that the formation of Cu$_2$Zr$_{1-x}$O$_6$ mean the incorporation of Cu species into ZrO$_2$ lattice. In this study, we evaluated the physicochemical properties of the green Cu$_2$Zr$_{1-x}$O$_6$ and developed the new catalyst with high activity and selectivity in CO$_2$-to-methanol hydrogenation.

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\begin{align*}
\text{CO}_2 + 3\text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} & \Delta H \text{ (298 K)} = -49 \text{ kJ mol}^{-1} & (\text{Eq. 1}) \\
\text{CO} + 2\text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} & \Delta H \text{ (298 K)} = -91 \text{ kJ mol}^{-1} & (\text{Eq. 2}) \\
\text{CO}_2 + \text{H}_2 & \rightleftharpoons \text{CO} + \text{H}_2\text{O} & \Delta H \text{ (298 K)} = 42 \text{ kJ mol}^{-1} & (\text{Eq. 3})
\end{align*}
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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$_3$)$_2$·3H$_2$O (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](image-url) (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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References