



Ag addition to CuO-ZrO₂ catalysts promotes methanol synthesis via CO₂ hydrogenation



Shohei Tada^{a,*}, Fumihito Watanabe^a, Keiko Kiyota^a, Naohiro Shimoda^a, Reina Hayashi^a, Makoto Takahashi^b, Akane Nariyuki^b, Akira Igarashi^a, Shigeo Satokawa^{a,*}

^a Department of Materials and Life Science, Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan

^b Nikki-Universal Co., Ltd., 7-14-1 Hiratsuka-shi, Kanagawa 254-0014, Japan

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ABSTRACT

The effect of adding Ag to CuO-ZrO₂ catalysts for the hydrogenation of CO₂ to methanol was investigated using CuO-ZrO₂, Ag/CuO-ZrO₂, and Ag/ZrO₂. The addition of Ag to CuO-ZrO₂ catalysts decreased the specific surface area and also broke its mesostructure. Thus, Ag played a significant role as a sintering aid in the preparation of Ag/CuO-ZrO₂ catalysts. We note that the as-prepared Ag/CuO-ZrO₂ catalysts contained Ag⁺ and Zr^{q+} ($q < 4$) sites and that the Zr^{q+} content increased with increasing Ag⁺ content. Furthermore, the presence of CuO in the Ag/CuO-ZrO₂ catalyst appeared to stabilize Ag⁺ and Zr^{q+} species under air. Based on H₂ chemisorption and powder X-ray diffraction patterns, formation of a Ag-Cu alloy was observed on completely reduced and spent Ag/CuO-ZrO₂ catalysts. Completely reduced Ag/CuO-ZrO₂ catalysts exhibited a higher methanol production rate (7.5 mL h⁻¹ g_{cat}⁻¹) compared to completely reduced CuO-ZrO₂ (6.9 mL h⁻¹ g_{cat}⁻¹) and Ag/ZrO₂ catalysts (2.2 mL h⁻¹ g_{cat}⁻¹) under the following reaction conditions: CO₂/H₂/N₂ = 1/3/1, catalyst loading = 500 mg, W/F_{total} = 1000 mg_{cat} s mL⁻¹, reaction temperature = 230 °C, pressure = 10 bar.

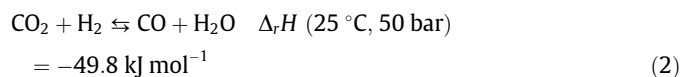
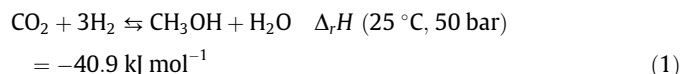
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1. Introduction

Methanol synthesis from syngas is a key reaction in the petrochemical industry. In the 1960s, Imperial Chemical Industries developed the process using a CuO/ZnO/Al₂O₃ catalyst at relatively low pressures and temperatures (50–100 bar, 200–300 °C). With the emerging interest in mitigating the increasing concentration of CO₂ by storing energy as liquid fuels, the direct hydrogenation of CO₂ instead of CO into methanol has become a very active field of research [1]. Here, we aim for a reaction with “CO₂ as a carbon source” and “H₂ produced by water electrolysis using renewable sources.” For instance, the Research Institute of Innovative Technology for the Earth (RITE) performed a national R&D project in Japan for CO₂-to-methanol hydrogenation from 1990 to 1999 [2]. For the industrialization of plants that perform the title reaction, new catalysts specific to CO₂-to-methanol hydrogenation should be developed. Because of the reactivity difference between CO and CO₂, conventional catalysts for CO-to-methanol hydrogenation do not show enough activity for the title reaction. According to the

RITE's investigation, Mitsui Chemicals succeeded in the operation of a pilot plant for hydrogenation of CO₂ to methanol in 2008–2010 [3].

CO₂ hydrogenation to methanol is exothermic, and the total moles of product is lower than that of the reactants (Eq. (1)). The endothermic reverse water gas shift reaction (RWGS reaction, Eq. (2)), which converts CO₂ into CO, can also compete, particularly at high temperatures.



Cu-based catalysts have been used to hydrogenate CO₂ into methanol. Catalyst improvements have explored many supports and promoters, such as ZnO [4–6], ZrO₂ [4,7–11], CeO₂ [12], and MgO [13]. Among the many supports, ZrO₂ has been particularly promising because it leads to a highly active, selective, and stable catalyst. According to a recent study [14], a plausible mechanism for CO₂-to-methanol hydrogenation by Cu/ZrO₂ catalysts involves the adsorption of CO₂ on ZrO₂, leading to the formation of formate

* Corresponding authors.

E-mail addresses: s-tada@ejs.seikei.ac.jp (S. Tada), satokawa@st.seikei.ac.jp (S. Satokawa).

species on ZrO₂. Concomitantly, H₂ dissociatively adsorbs to the Cu surface [15] and then transfers to the ZrO₂ surface, enabling the conversion of a formate species to a methoxy species. Finally, the methoxy species is hydrogenated to methanol [14].

Here, we examined the metal additives with CuO-ZrO₂ and considered the creation of new active sites. Numerous metal oxide additives have been reported, including oxides of Zn, Zr, Ce, Al, Si, V, Ti, Ga, B, and Cr [16]. However, few reports exist on the influence of metal additives on CO₂-to-methanol hydrogenation catalysis; these studies examined PtCu/SiO₂ [17] and Cu-Ag/ZrO₂ catalysts [18]. Little attention has been given to the location of the active sites on these catalysts. In this study, we investigated the effect of adding Ag to CuO-ZrO₂ catalysts on CO₂-to-methanol hydrogenation, and we also examined the potential active sites on our Ag/CuO-ZrO₂ catalysts. Despite the knowledge that the Ag/ZrO₂ catalyst is capable of hydrogenating CO₂ to methanol [18–20], we report that the presence of Ag species in the Ag/CuO-ZrO₂ catalyst changes the surface condition of metallic Cu via the formation of a Ag-Cu alloy, which imparts high activity and selectivity on CO₂-to-methanol hydrogenation.

2. Experimental

2.1. Catalyst preparation

CuO-ZrO₂ was prepared by a co-precipitation method. Cu(NO₃)₂·3H₂O (Wako Pure Chemical Industries) and ZrO(NO₃)₂·3H₂O (Wako Pure Chemical Industries) were dissolved in 200 mL of deionized water. An NH₃ solution (10%, Wako Pure Chemical Industries) was added dropwise to the obtained solution under vigorous stirring. The pH of the solution was controlled as follows: pH = 8.0 (**CuZr-1**), pH = 8.7 (**CuZr-2**), and pH = 9.7 (**CuZr-3**). The product was aged at 70 °C for 1 h under stirring and then was filtered and washed with the deionized water. Finally, the crude material was dried at 80 °C for 12 h and then calcined at 500 °C for 5 h. ZrO₂ (**mZr**) was also prepared by a precipitation method that was nearly identical to the co-precipitation method described above. Next, 10 wt%Ag/CuZr-1 (**Ag(10)/CuZr-1**), 5 wt%Ag/CuZr-1 (**Ag(5)/CuZr-1**) and 10 wt%Ag/mZr (**Ag(10)/mZr**) were prepared by an incipient wetness impregnation method. The prepared **CuZr-1** or **mZr** catalyst was impregnated with an aqueous solution of AgNO₃ (Wako Pure Chemical Industries). The crude materials were dried at 80 °C for 12 h and then calcined at 500 °C for 5 h. Commercial CuO/ZnO/Al₂O₃, MDC-7 (Clariant Catalysts (Japan) K. K.), with a Cu loading is 34wt%, was used for comparison to the prepared catalysts. The Cu and Ag loadings are summarized in Table S1.

2.2. Characterization

2.2.1. Powder X-ray diffraction (PXRD)

The crystalline phases of the catalysts were determined by powder X-ray diffraction (Rigaku, Ultima IV) with a Cu K α radiation source at a voltage of 40 kV and a current of 40 mA. The crystallite size (*D*) was estimated from the diffraction peak using Scherrer's equation,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

where *K* is the shape factor (0.89), λ is the X-ray wavelength (0.154 nm), β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle.

2.2.2. N₂ adsorption

The specific surface area and pore width for each catalyst were estimated by N₂ adsorption using a MicrotracBEL BELSORP-mini II. After the sample (*ca.* 100 mg) was loaded into a sample cell, it was dried under vacuum at 150 °C overnight.

2.2.3. Inductively coupled plasma atomic emission spectrometry (ICP-AES)

The Cu loading was measured by ICP-AES (Shimadzu, ICPS-7500). 30 mg of the sample was dissolved in a mixture of 0.5 mL of HNO₃ (69–70%, Wako Pure Chemical Industries) and 1 mL of HF (46–48%, Morita Chemical Industries) prior to the measurements.

2.2.4. N₂O titration

An N₂O titration was carried out according to the previous report [15]. Approximately 500–900 mg of catalyst was placed in a quartz tube connected to a flow system (MicrotracBEL, BELCAT-A) and treated at 300 °C for 30 min with 4%H₂/Ar. He gas was used as a carrier gas at 30 mL min⁻¹, and successive doses of 10 wt% N₂O/He gas were subsequently introduced into the He stream using a calibrated injection valve (27 mL_{N₂O}(STP) pulse⁻¹) at 90 °C. A thermal conductive detector analyzed the amount of outlet N₂O and N₂. The number of accessible Cu surface atoms (Cu_s) was estimated according to Eq. (4).



Using N₂O consumption, the average particle size of Cu, *d*_{Cu} (m), was calculated by Eqs. (5) and (6), which assume that the Cu particles on the supports are spherical and have uniform volume and density.

$$S_{\text{Cu}} = \frac{Y_{\text{N}_2\text{O}} N_{\text{av}}}{W_{\text{Cu}} n_{\text{N}_2\text{O}} A} \quad (5)$$

$$d_{\text{Cu}} = \frac{6}{S_{\text{Cu}} \rho_{\text{Cu}}} \quad (6)$$

In these equations, *S*_{Cu} is the surface area of Cu (m² g_{Cu}⁻¹), *Y*_{N₂O} is the amount of N₂O uptake (mol_{N₂O} g_{cat}⁻¹), *W*_{Cu} is the Cu loading (g_{Cu} g_{cat}⁻¹), *N*_{av} is Avogadro's constant (6.02 × 10²³ atom mol⁻¹), *n*_{N₂O} is the stoichiometry of N₂O to Cu (0.5 mol_{N₂O} mol_{Cu}⁻¹), *A* is the number of Cu surface atoms per unit area (1.46 × 10¹⁹ atom_{Cu} m⁻²), and ρ_{Cu} is the density of Cu (8.94 g_{Cu} cm⁻³).

2.2.5. Temperature programmed reduction by H₂ (H₂-TPR)

The reducibility of the Cu and Ag species in the prepared catalysts was investigated by H₂-TPR in a flow system (MicrotracBEL, BELCAT-A). 50 mg of the samples were placed in a quartz tube and heated at 300 °C for 1 h in an Ar flow. Next, the samples were cooled to 50 °C in an Ar flow, after which the cell was purged with 4%H₂/Ar. The temperature was then raised from 50 °C to 500 °C at a heating rate of 10 °C min⁻¹ under a 4%H₂/Ar flow (30 mL min⁻¹).

2.2.6. H₂ chemisorption

H₂ chemisorption by the prepared samples was investigated using a BELSORP-mini II (MicrotracBEL). *Ca.* 100 mg of the samples were reduced at 300 °C for 1 h in a 5%H₂/Ar atmosphere and then loaded into sample cells without exposure to air. As a pretreatment, the samples were heated at 150 °C overnight under vacuum. The experimental points were fitted with a dissociative Langmuir adsorption equation (Eq. (7)) and a non-dissociative Langmuir adsorption equation (Eq. (8)), and the amount of H₂ uptake at saturation (*Q*_{max}, μmol_{H₂} g_{cat}⁻¹) was calculated.

$$Q_{\text{ads}} = \frac{\sqrt{K_0 \frac{P}{P_0}}}{1 + \sqrt{K_0 \frac{P}{P_0}}} Q_{\text{max}} \quad (7)$$

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