

# Catalytic Activity of Nanosized CuO–ZnO Supported on Titanium Chips in Hydrogenation of Carbon Dioxide to Methyl Alcohol

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In this study, titanium chips (TC) generated from industrial facilities was utilized as TiO<sub>2</sub> support for hydrogenation of carbon dioxide (CO<sub>2</sub>) to methyl alcohol (CH<sub>3</sub>OH) over Cu-based catalysts. Nano-sized CuO and ZnO catalysts were deposited on TiO<sub>2</sub> support using a co-precipitation (CP) method (CuO–ZnO/TiO<sub>2</sub>), where the thermal treatment of TC and the particle size of TiO<sub>2</sub> are optimized on CO<sub>2</sub> conversion under different reaction temperature and contact time. Direct hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH over CuO–ZnO/TiO<sub>2</sub> catalysts was achieved and the maximum selectivity (22%) and yield (18.2%) of CH<sub>3</sub>OH were obtained in the range of reaction temperature 210~240 °C under the 30 bar. The selectivity was readily increased by increasing the flow rate, which does not affect much to the CO<sub>2</sub> conversion and CH<sub>3</sub>OH yield.

**Keywords:** Titanium Chip, CuO, ZnO, Carbon Dioxide, Hydrogenation, Methyl Alcohol.

## 1. INTRODUCTION

The increased concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere causes a green house effect, which has recently become an important global issue.<sup>1</sup> In order to control the concentration of CO<sub>2</sub> in the air, various kinds of technologies that transform CO<sub>2</sub> into useful products via chemical reactions have been studied intensively. Catalytic hydrogenation of carbon dioxide (CO<sub>2</sub>) has been used to diminish the CO<sub>2</sub> because large amounts of CO<sub>2</sub> can be converted to reusable chemical resources such as methanol (CH<sub>3</sub>OH) and other oxygenates compounds.<sup>2,3</sup> Among various catalysts, the most extensive work were performed on CuO–ZnO-based catalysts because they showed a highly active and selective for CH<sub>3</sub>OH synthesis from CO<sub>2</sub> and H<sub>2</sub>.<sup>4–7</sup>

Until now oxide-based supports such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO utilized for the catalyst support. However, un-desired products are formed during the hydrogenation of CO<sub>2</sub>,

such as CO, hydrocarbons, and higher alcohols. Therefore, a highly selective catalyst is in need for CH<sub>3</sub>OH synthesis. High activity for CH<sub>3</sub>OH synthesis from CO<sub>2</sub> and H<sub>2</sub> was obtained on CuO–ZnO catalyst supported on TiO<sub>2</sub>, regarding as a promoter.<sup>8,9</sup>

In a previous study, simple thermal treatment of titanium chip (TC) has proven to be an efficient means of forming TC into useful TiO<sub>2</sub> support for the supported CuO–ZnO/TiO<sub>2</sub> catalyst.<sup>10</sup> The effects of preparation method and reaction pressure on the catalytic activity were tested. It was shown that the activity at 250 °C under 30 bar of CuO–ZnO/TiO<sub>2</sub> catalyst prepared by co-precipitation (CP) method was higher than that of catalyst prepared by impregnation method. However, the effects of other parameters (such as particle size of catalyst, reaction temperature, and flow rate) were also needed to gain information on the relationships between physicochemical properties and the catalytic activity of CO<sub>2</sub> hydrogenation on CuO–ZnO/TiO<sub>2</sub> catalysts. In this work, CuO–ZnO/TiO<sub>2</sub> catalysts with different particle size were prepared by CP method

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and the reaction properties for catalytic hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH were investigated.

## 2. EXPERIMENTAL DETAILS

### 2.1. Catalysts Preparation

Thermal treatment of TC to form TiO<sub>2</sub> was performed at 900, 1000, 1100 °C under air atmosphere. CP method was used to prepare CuO–ZnO/TiO<sub>2</sub> catalyst containing weight ratio copper, zinc and TC (40.6:50.3:9.1 wt%). Aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, and TiO<sub>2</sub> powder were mixed, and the mixture was added to the deionized water with vigorous stirring as well as the aqueous solution of Na<sub>2</sub>CO<sub>3</sub> as a precipitant and pH of the suspension liquid was kept constant at the value of 8.0. After filtration and washing, the catalyst was dried at 100 °C for 24 hrs, calcined at 200 °C for 1 hr and then at 300 °C for 3 hrs.

The prepared CuO–ZnO/TiO<sub>2</sub> catalysts were characterized by using N<sub>2</sub> gas adsorption analyzer (ASAP-2010, Micromeritics), scanning electron microscopy (SEM, S-3500N, Hitachi) and transmission electron microscopy (TEM, JEM-2100F, Jeol). The chemical composition of representative surface particles was analyzed by energy dispersive spectroscopy (EDS).

### 2.2. Catalytic Activity

Catalytic activities were tested for CH<sub>3</sub>OH synthesis using a fixed-bed down stream flow reactor. Catalyst was loaded in the reactor and the reduced in a stream of a gas H<sub>2</sub> at 300 °C for 3 hrs. The temperature of pre-heater and reactor were controlled by PID controller, and total reaction pressure was regulated with a back pressure regulator. After cooling the catalyst bed to the reaction temperature 250 °C, the reaction gas, which consisted of CO<sub>2</sub> (27 mol%) and H<sub>2</sub> (73 mol%), was fed at 40 mL min<sup>−1</sup> using a mass flow controller. The exit line from the reactor to the gas sampler was heated to prevent condensation of any volatile products. Reactant and product gas mixtures were analyzed by using the gas chromatograph (GC-2014, Shimadzu) with a thermal conductivity detector, in which two parallel connected columns, Porapak-Q and MS-5A, were used to separate reaction products. Gas chromatograph was equipped with a two 6-way valves for on-line sampling.

## 3. RESULTS AND DISCUSSION

Table I shows the BET specific surface area of all samples tested in this study. Untreated TC used as a raw material exhibited very low surface area with near zero and it was increased when it was treated by thermal oxidation (data not shown), which would expect to improved adhesive ability of metal oxide active species to treated TC surface. BET surface area of CuO–ZnO/TiO<sub>2</sub> catalyst is increased with increasing the treated temperature up to 1000 °C and

**Table I.** Preparation conditions and physical parameters of CuO–ZnO/TiO<sub>2</sub> catalysts prepared by CP method.

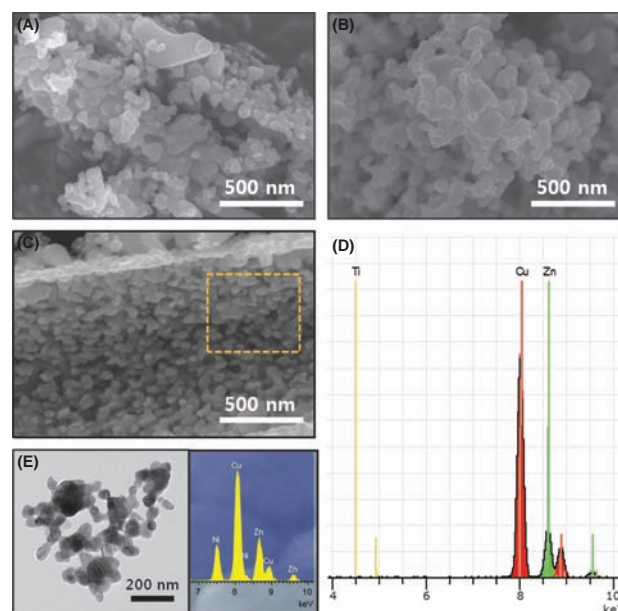
Catalyst	<sup>a</sup> T <sub>Cal.</sub> (°C)	<sup>b</sup> D <sub>TC</sub> (mesh)	<sup>c</sup> S <sub>BET</sub> (m <sup>2</sup> g <sup>−1</sup> )
CuO–ZnO/TiO <sub>2</sub> (900-4)	900	40–60	7.8
CuO–ZnO/TiO <sub>2</sub> (900-2)	1000	20–30	23.6
CuO–ZnO/TiO <sub>2</sub> (900-4)	1000	40–60	16.8
CuO–ZnO/TiO <sub>2</sub> (900-6)	1000	60–80	14.3
CuO–ZnO/TiO <sub>2</sub> (1100-4)	1100	40–60	12.4

Notes: <sup>a</sup>Temperature of thermal treatment. <sup>b</sup>Particle size of catalysts. <sup>c</sup>BET specific surface area.

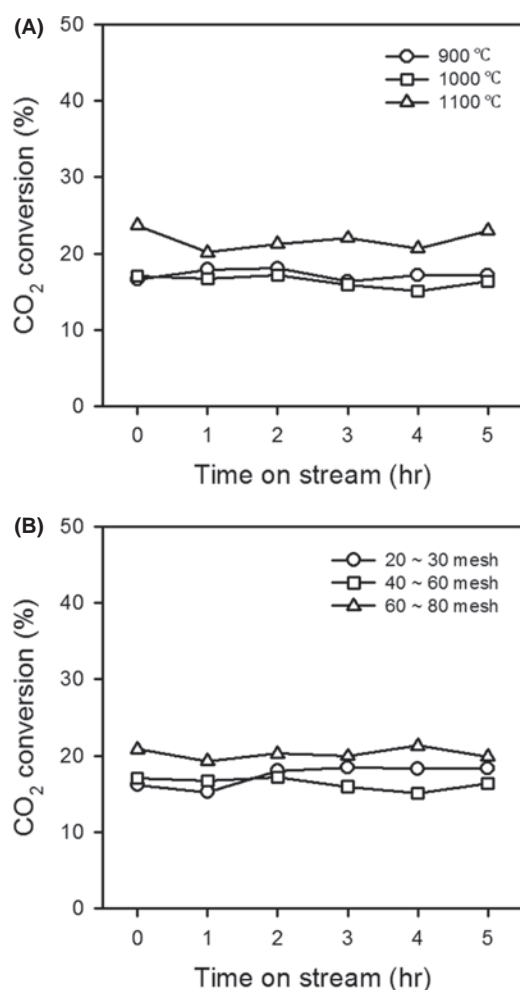
is readily decreased above 1100 °C. The sieved different particles had similar values in the range of 14–23 m<sup>2</sup> g<sup>−1</sup>.

SEM images of as-prepared CuO–ZnO on different size of treated TC are shown in Figures 1(A)–(C). It can be seen that well dispersed nanosized CuO and ZnO particles are formed on treated TC surface and the particles contained Cu, Zn, and Ti species (Fig. 1(D)). TEM image (Fig. 1(E)) shows that the well-dispersed small particles are CuO–ZnO species, indicating that strong adhesion of CuO–ZnO nanoparticles on thermally treated TC could be obtained by improving superficial roughness, which could enhance the both catalytic activity and selectivity toward CH<sub>3</sub>OH synthesis.

Activity results for CH<sub>3</sub>OH synthesis from CO<sub>2</sub> hydrogenation over the CuO–ZnO/TiO<sub>2</sub> catalysts prepared from treated TC at different temperature are shown in Figure 2(A). Maximum treatment temperature of TC was performed at 1100 °C because TC became to be so brittle when it was treated at above 1100 °C. The CuO–ZnO/TiO<sub>2</sub> (1100-4) catalyst shows over 20% CO<sub>2</sub>



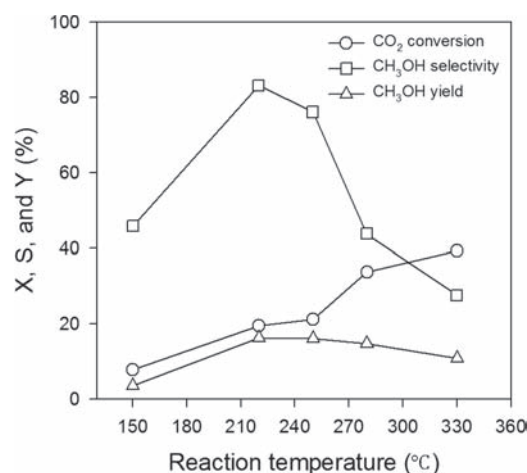
**Figure 1.** SEM images of CuO–ZnO/TiO<sub>2</sub> catalysts using TC treated at (A) 900 °C, (B) 1000 °C, and (C) 1100 °C. (D) EDS spectrum of dotted square in (C). (E) TEM image of CuO–ZnO nanoparticles prepared by CP method (Insert of EDS spectrum).



**Figure 2.** (A) Effect of treatment temperature of TC with the size of 40~60 mesh and (B) effect of size of treated TC at 1100 °C on CO<sub>2</sub> conversion over CuO–ZnO/TiO<sub>2</sub> catalysts. (Reaction temperature = 250 °C, pressure = 30 bar, W/F = 4.67 g<sub>cat</sub>.hr mol<sup>-1</sup>).

conversion. Figure 2(B) shows effect of size of treated TC at 1100 °C on CO<sub>2</sub> conversion. Highest conversion was obtained over the CuO–ZnO/TiO<sub>2</sub> (900-6) catalyst having smaller particle size. Therefore, TC treated at 1100 °C with smaller particle size (CuO–ZnO/TiO<sub>2</sub> (900-6)) was considered to further investigations.

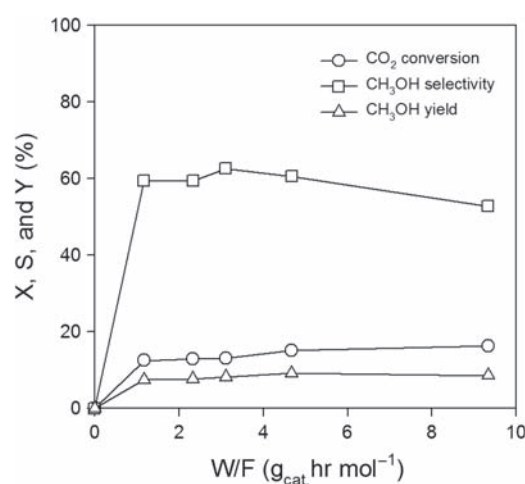
Figure 3 shows the effect of reaction temperature on CO<sub>2</sub> conversion, CH<sub>3</sub>OH selectivity, and CH<sub>3</sub>OH yield over CuO–ZnO/TiO<sub>2</sub> (900-6) catalyst. X, S and Y on x-axis in Figures 3 and 4 denote CO<sub>2</sub> conversion, CH<sub>3</sub>OH selectivity, and CH<sub>3</sub>OH yield, respectively. With increasing reaction temperature, the CO<sub>2</sub> conversion was increased, while CH<sub>3</sub>OH selectivity and yield were decreased, which is due to increased CO formation instead of CH<sub>3</sub>OH according to reverse water gas shift reaction ( $\text{CO}_2 + \text{H}_2 \rightarrow 2\text{CO} + \text{H}_2\text{O}$ ,  $\Delta H_{298\text{K}} = 41.2 \text{ kJ mol}^{-1}$ ). From the thermodynamic point of view ( $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ ,  $\Delta H_{298\text{K}} = -49.5 \text{ kJ mol}^{-1}$ ), a decrease in reaction temperature or an increase in reaction pressure could favor



**Figure 3.** Effect of reaction temperature on catalytic activity over CuO–ZnO/TiO<sub>2</sub> (900-6) catalyst. (Pressure = 30 bar, W/F = 4.67 g<sub>cat</sub>.hr mol<sup>-1</sup>).

the synthesis of CH<sub>3</sub>OH.<sup>11</sup> The formation of CH<sub>3</sub>OH and CO is almost independent of the partial pressure of CO<sub>2</sub>. Therefore, further optimization should lead to increases in selectivity and yield of CH<sub>3</sub>OH. The maximum selectivity to CH<sub>3</sub>OH from CO<sub>2</sub> hydrogenation over CuO–ZnO/TiO<sub>2</sub> (900-6) catalyst was obtained in the range of reaction temperature 210~240 °C.

The effect of contact time on catalytic activity in CO<sub>2</sub> hydrogenation over CuO–ZnO/TiO<sub>2</sub> catalyst is shown in Figure 4. Flow rates of reactant were varied from 20 mL min<sup>-1</sup> (9.33 g<sub>cat</sub>.hr mol<sup>-1</sup>) to 100 mL min<sup>-1</sup> (1.17 g<sub>cat</sub>.hr mol<sup>-1</sup>). Conversion of CO<sub>2</sub> and yield of CH<sub>3</sub>OH show similar values in varied flow rates, while the selectivity was readily increased with increasing the flow rate. It is well known that the rate-determining step is CO



**Figure 4.** Effect of contact time (W/F) on catalytic activity over CuO–ZnO/TiO<sub>2</sub> (900-6) catalyst. W/F is defined as weigh of used catalyst per flow rate of reactant in the reaction. (Reaction temperature = 250 °C, pressure = 30 bar).

hydrogenation to produce formate (HCO) intermediates, which is then react with chemisorbed H<sub>2</sub>, subsequently CH<sub>3</sub>OH for the overall reaction. However, no formation of the CO was observed in all tested reactions over the CuO–ZnO/TiO<sub>2</sub> catalyst. More systematic study is needed to understand the mechanism on this system.

#### 4. CONCLUSION

We have investigated the hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH synthesis over CuO–ZnO/TiO<sub>2</sub> catalysts, where the effect of thermal treatment and the particle size of TC are optimized on CO<sub>2</sub> conversion under different reaction temperature and contact time. Nanosized CuO and ZnO particles were well supported on thermally treated TC using the CP method. High CO<sub>2</sub> conversion was obtained at a higher reaction temperature, while selectivity and yield of CH<sub>3</sub>OH were decreased. Maximum selectivity (22%) and yield (18.2%) of CH<sub>3</sub>OH were obtained in the range of reaction temperature 210~240 °C under the 30 bar. The selectivity was readily increased by increasing the flow rate; however, it does not much affect to the CO<sub>2</sub> conversion and the CH<sub>3</sub>OH yield.

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