



Effects of ZrO₂ on the Performance of CuO-ZnO-TiO₂-ZrO₂ Catalysts Used in Methanol Synthesis from CO₂ Hydrogenation

YUNPENG ZHAO^{1,2,*}, LIHUA JIA², TAO JING^{1,2}, DEZHI SUN^{1,3} and JONG SHIK CHUNG^{1,4}

¹School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, P.R. China

²College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, P.R. China

³College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, P.R. China

⁴Department of Chemical Engineering, School of Environmental Engineering, POSTECH, Pohang 790-784, South Korea

*Corresponding author: E-mail: zhypp@163.com

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CuO-ZnO-TiO₂-ZrO₂ catalysts were prepared by a parallel-slurry-mixing-precipitation method combined with addition of surfactant. Characterization and performance of the catalysts were investigated by BET, XRD, SEM, H₂-TPR and methanol synthesis from CO₂ hydrogenation. Carbon dioxide conversion and methanol selectivity were found to increase with increasing ZrO₂ content on catalysts. The results show that CuO-ZnO-TiO₂-ZrO₂ (2:1:2:1 molar ratio) catalyst exhibited an optimum catalytic performance.

Key Words: CuO-ZnO-TiO₂-ZrO₂ catalyst, Parallel-slurry-mixing-precipitation, Surfactant, CO₂ hydrogenation, Methanol synthesis, Zirconia.

INTRODUCTION

Carbon dioxide is a cheap and abundant carbon resource in nature and its emission is a serious threat to the living environment of mankind. Thus, the disposal and fixation of CO₂, a primary greenhouse gas, are of great significance and urgent issues at present¹. To solve the CO₂ problem, carbon dioxide hydrogenation to methanol has received much attention in recent years²⁻⁸. Methanol is considered a fundamental chemical and an alternative to fossil fuels, used mainly as a feedstock such as in the manufacture of formaldehyde, acetic acid, methyl tertiary-butyl ether, methyl methacrylate and as a solvent^{9,10}. It has been well documented that Cu-Zn-based catalysts containing ZrO₂ are active in the synthesis of methanol from CO₂ hydrogenation^{3-7,11-13}. Besides ZrO₂, including Al₂O₃¹³⁻¹⁶, SiO₂^{17,18}, Cr₂O₃¹³ and Ga₂O₃^{13,17-19} have been investigated for methanol synthesis from CO₂ hydrogenation. The conventional methods such as impregnation and co-precipitation were used to prepare the copper-based catalysts. Some novel techniques like ultrasound irradiation co-precipitation^{5,12} and urea-nitrate combustion method¹ have been reported recently. In this paper, CuO-ZnO-TiO₂-ZrO₂ catalysts for methanol synthesis from CO₂ hydrogenation were prepared by a novel parallel-slurry-mixing-precipitation method combined with addition of surfactant. The catalyst structure, physical properties and catalytic activity were investigated and the effects of ZrO₂

content on catalytic performance were discussed. The addition of ZrO₂ can markedly improve the structure and catalytic performance of CuO-ZnO-TiO₂ catalysts.

EXPERIMENTAL

Catalyst preparation: CuO-ZnO-TiO₂-ZrO₂ catalysts were prepared using a parallel-slurry-mixing-precipitation method combined with addition of cetyltrimethyl ammonium bromide surfactant. TiO₂-water (2 g TiO₂ and 80 mL H₂O) slurry combined with addition of cetyltrimethyl ammonium bromide (0.4 g) surfactant and ethanol (20 mL) was first obtained in a beaker. An aqueous solution (1.0 mol/L) containing copper, zinc and zirconium nitrate [Cu/Zn/Zr molar ratio = 2:1: (0.1, 0.5 or 1)] and an aqueous solution of sodium carbonate (1.0 mol/L) were simultaneously added dropwise with constant stirring to the precipitating vessel containing TiO₂-water slurry in parallel-flow manner. The precipitation temperature and pH value were maintained at 323 K and 8.0, respectively. The final precipitate was kept at room temperature for 12 h. After filtration and washing, the catalysts were dried at 383 K for 12 h and further calcined in air at 623 K for 5 h to give the CuO-ZnO-TiO₂-ZrO₂ (CuO:ZnO:TiO₂ molar ratio = 2:1:2) catalysts. For convenience, the catalysts were designated by the abbreviation CZTZ(χ), where χ denoted the content of ZrO₂ (molar ratio) in the CuO-ZnO-TiO₂-ZrO₂ catalysts.

Catalyst characterization: BET surface area, pore volume and pore diameter were measured by the nitrogen adsorption/desorption isotherms at 77 K, using a fully automated Micromeritics NOVA2000e gas adsorption apparatus. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus diffractometer with $\text{CuK}\alpha$ radiation at 40 kV, 40 mA and a scanning of $4.5^\circ/\text{min}$ in the 2θ range $10\text{--}80^\circ$. The catalyst morphology was observed by a Hitachi S-4300 scanning electron microscope (SEM).

H_2 temperature-programmed reduction (H_2 -TPR) measurements at 323–973 K were carried out in a Chem-BET3000 continuous-flow apparatus. The catalyst samples (10 mg) were reduced in a U-tube quartz microreactor. The flow rate of a 10 % H_2/Ar reducing gas was kept at 80 mL/min and the temperature was increased from 323–973 K at rate of 10 K/min. The amount of H_2 consumption was monitored by a thermal conductivity detector.

Catalytic activity test: The catalytic activity tests were carried out in a tubular, high-pressure, continuous-flow, fixed-bed reactor. The catalyst sample (2.5 mL) was packed into a 5 mm i.d. stainless-steel tubular reactor. The pressure in the reactor was maintained by means of a back pressure regulator. The flow rates of feed gases were controlled by mass flow controllers. Prior to the activity measurement, the catalysts were reduced with a H_2 gas stream of 50 mL/min at 583 K for 3 h under atmospheric pressure. The reactant gases of H_2 and CO_2 were introduced after the temperature was decreased to reaction temperature. The reaction of methanol synthesis from CO_2 hydrogenation was determined under the following conditions: temperature ranged from 483–543 K, pressure 2.0 MPa, reactant gases $\text{H}_2/\text{CO}_2 = 3:1$ (molar ratio) and space velocity 2100 h^{-1} . The gaseous product stream was analyzed by an on-line GC1490 gas chromatograph instrument using a carboxieve column and a thermal conductivity detector. Methanol and H_2O were determined by a GC9800 gas chromatograph instrument equipped with a GDX102 column and a thermal conductivity detector.

RESULTS AND DISCUSSION

Catalyst characterization: BET surface areas, pore volume and pore diameter of the calcined catalysts are listed in Table-1. It is evident that the addition of ZrO_2 is favourable to increase the surface areas and pore volume of the catalysts. The CZT catalyst shows very low surface area of $26.103\text{ m}^2/\text{g}$, which is the smaller than those of the containing ZrO_2 , hence the smallest among all catalysts in the experiment. With the increase of ZrO_2 content, the $\text{CuO-ZnO-TiO}_2\text{-ZrO}_2$ catalysts show larger surface areas and pore volume. The CZTZ(1) catalyst is the largest surface areas and pore volume of $73.506\text{ m}^2/\text{g}$ and $0.108\text{ cm}^3/\text{g}$, respectively.

TABLE-1

PHYSICAL PROPERTIES OF THE CALCINED CATALYSTS

Catalysts	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
CZT	26.103	0.078	3.7436
CZTZ(0.1)	29.515	0.075	3.8988
CZTZ(0.5)	49.870	0.100	3.9046
CZTZ(1)	73.506	0.108	3.7540

The XRD patterns of $\text{CuO-ZnO-TiO}_2\text{-ZrO}_2$ catalysts are shown in Fig. 1. The peaks at 2θ of 35.6 , 38.8 and 48.9° were attributed to CuO phase, while those at 2θ of 31.8° and 34.5° were assigned to ZnO phase. The diffraction peaks of CuO , ZnO and TiO_2 are observed in all catalysts. Along with the addition of ZrO_2 and the increase of ZrO_2 content, the intensity of the diffraction peaks of CuO and ZnO weakened gradually, while the width of the diffraction peaks broadened slightly. It indicates that ZrO_2 promoted the dispersion of CuO and ZnO species. Furthermore, no ZrO_2 diffraction peaks were detected by XRD on $\text{CuO-ZnO-TiO}_2\text{-ZrO}_2$ catalysts. This result indicates that ZrO_2 was highly dispersed on $\text{CuO-ZnO-TiO}_2\text{-ZrO}_2$ catalysts. As a conclusion, there are strong interactions between the CuO (and ZnO) species and the ZrO_2 species to a large extent.

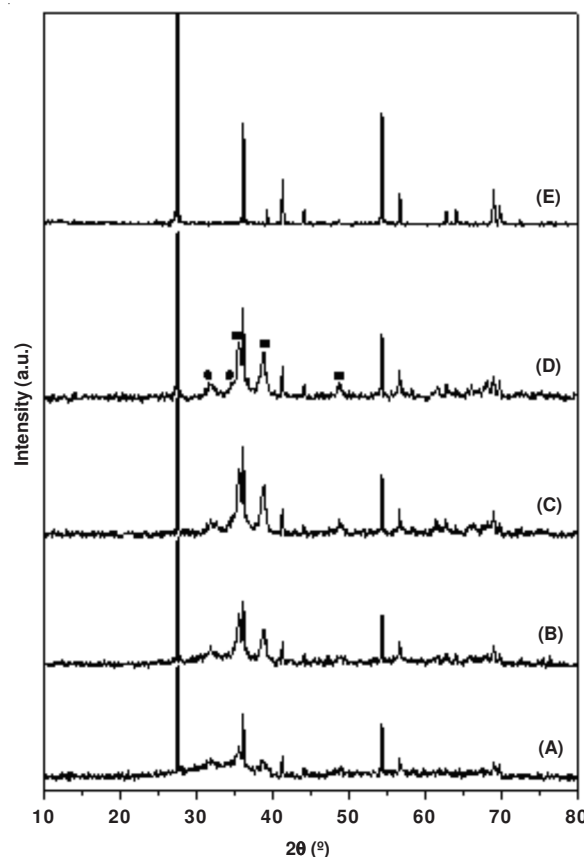


Fig. 1. XRD patterns of the $\text{CuO-ZnO-TiO}_2\text{-ZrO}_2$ catalysts: (A) CZTZ(1); (B) CZTZ(0.5); (C) CZTZ(0.1); (D) CZT; (E) pure TiO_2 (rutile). (■) CuO and (●) ZnO

Fig. 2 presents the SEM photographs of the catalysts. The results clearly show that the degree of the clustered particles decreases as the ZrO_2 content of catalysts increases. The particle sizes become smaller with increasing the ZrO_2 content of catalysts. It indicates that the addition of ZrO_2 has an important influence on the structure and dispersion of the catalysts. This is in good agreement with the XRD results.

H_2 -TPR: The H_2 -TPR profiles of $\text{CuO-ZnO-TiO}_2\text{-ZrO}_2$ catalysts are shown in Fig. 3. The H_2 -TPR profiles of the catalysts exhibited two reduction peaks of CuO . The occurrence of two reduction peaks indicates the reduction of the highly dispersed CuO species and the bulk-like CuO phases^{7,20}, which

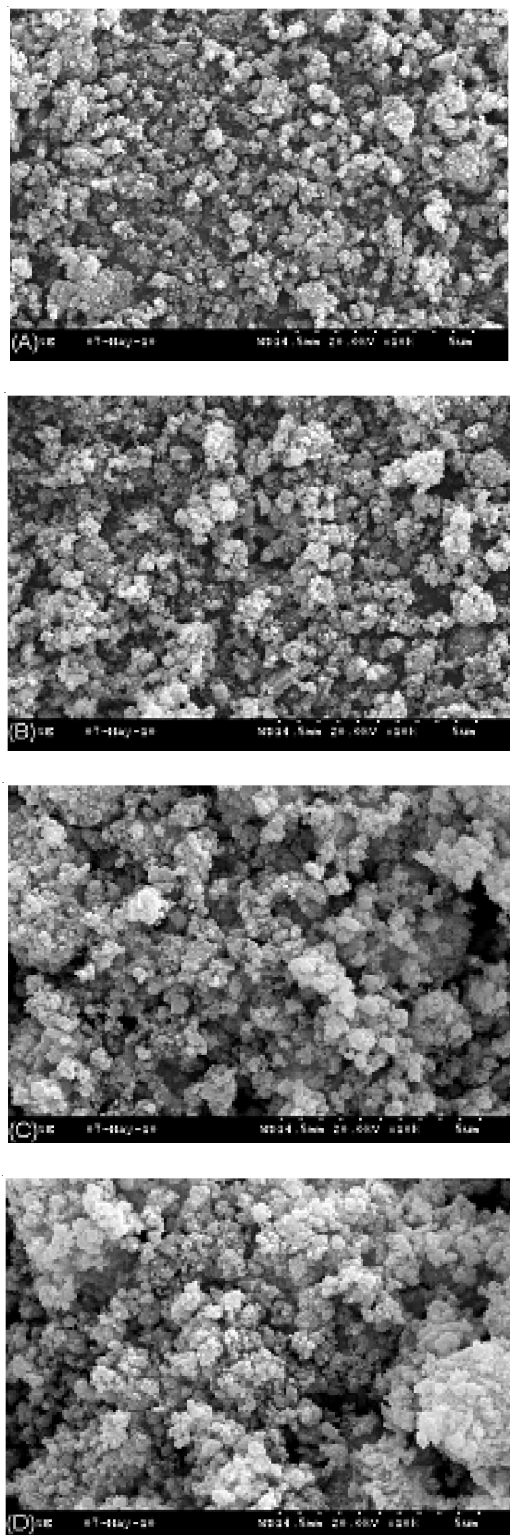


Fig. 2. SEM images of the catalysts: (A) CZTZ(1); (B) CZTZ(0.5); (C) CZTZ(0.1); (D) CZT

are attributed to the low-temperature and high-temperature peak, respectively. The reduction peaks changed with the variation of ZrO₂ content. It can be seen that the reduction temperature of the high-temperature peak decreased with the increase of ZrO₂ content. This indicates that the particle size became smaller with increasing the ZrO₂ content of catalysts because the reduction of CuO particles became easier. The inference is in accordance with the results of XRD.

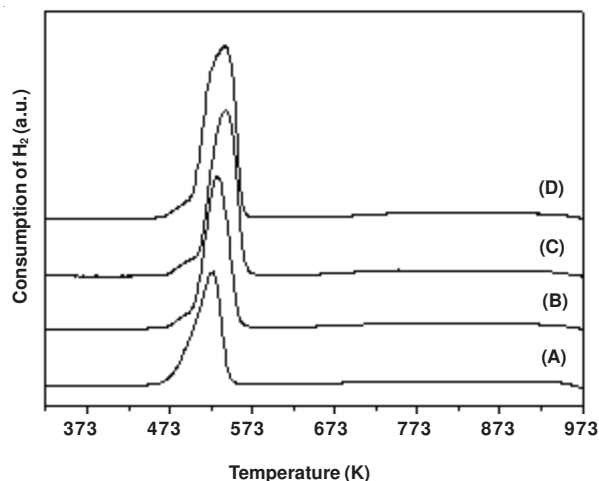


Fig. 3. H₂-TPR profiles of the CuO-ZnO-TiO₂-ZrO₂ catalysts: (A) CZTZ(1); (B) CZTZ(0.5); (C) CZTZ(0.1); (D) CZT

Catalytic activity: Methanol synthesis from CO₂ hydrogenation was determined by the following two reactions (**Scheme-I**): reaction eqn. 1 is the methanol formation and reaction eqn. 2 is the reverse water gas shift (RWGS) reaction⁹.



$$\Delta H_{298\text{ K}}^{\circ} = -49.58 \text{ kJ}\cdot\text{mol}^{-1}$$



$$\Delta H_{298\text{ K}}^{\circ} = 41.19 \text{ kJ}\cdot\text{mol}^{-1}$$

Scheme-I: Methanol synthesis from CO₂ hydrogenation

The effects of ZrO₂ content on the performance of catalysts for methanol synthesis from CO₂ hydrogenation are listed in Table-2. The CO₂ conversion, CH₃OH selectivity and CH₃OH yield of all catalysts increased with the increase of ZrO₂ content. It indicates that the addition of ZrO₂ can improve the catalytic performance of CuO-ZnO-TiO₂ catalysts. The largest CH₃OH yield is obtained on the CZTZ(1) catalyst under the reaction conditions.

TABLE-2 EFFECTS OF ZrO ₂ CONTENT ON THE PERFORMANCE OF CATALYSTS FOR METHANOL SYNTHESIS FROM CO ₂ HYDROGENATION			
Catalysts	CO ₂ conversion (%)	CH ₃ OH selectivity (%)	CH ₃ OH yield (%)
CZT	11.50	19.68	2.26
CZTZ(0.1)	12.83	20.00	2.57
CZTZ(0.5)	15.69	24.31	3.81
CZTZ(1)	16.41	27.42	4.50

Reaction conditions: T = 503 K, P = 2.0 MPa, H₂/CO₂ = 3:1 (molar ratio), GHSV = 2100 h⁻¹.

The effect of temperature on the catalytic performance of the CZTZ(1) catalyst is shown in Fig. 4. The CO₂ conversion, CH₃OH selectivity and CH₃OH yield for catalyst were studied at P = 2.0 MPa, H₂/CO₂ = 3:1 (molar ratio), GHSV = 2100 h⁻¹ and for different temperature. It can be seen that the CO₂ conversion increased with the increase of reaction temperature

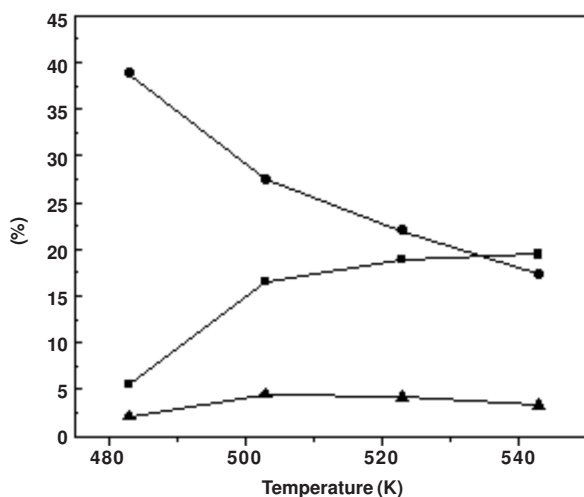


Fig. 4. Effect of temperature on the catalytic performance of CZTZ(1) catalyst: (■) CO₂ conversion, (●) methanol selectivity and (▲) methanol yield

and the CH₃OH selectivity decreased with the increase of reaction temperature at 483-543 K. The maximum of CH₃OH yield is 4.50 % at 503 K. From the thermodynamics, methanol synthesis from CO₂ hydrogenation is an exothermal reaction, so it is disadvantageous to methanol synthesis with the increase of reaction temperature. Meanwhile, the increase of CO selectivity with the increase of reaction temperature was due to an endothermic reaction of the reverse water gas shift.

Conclusion

CuO-ZnO-TiO₂-ZrO₂ catalysts of the variable ZrO₂ content were prepared by parallel-slurry-mixing-precipitation method combined with addition of cetyltrimethyl ammonium bromide surfactant and tested for methanol synthesis from CO₂ hydrogenation. With the increase of ZrO₂ content, it could be promoted the dispersion and reduction of CuO species on CuO-ZnO-TiO₂-ZrO₂ catalysts. ZrO₂ acted as a structural promoter and improved the catalytic performance of the catalysts. The optimal CZTZ(1) catalyst exhibited a favourable catalytic performance for methanol synthesis from CO₂ hydrogenation.

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