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Journal of
Nanoscience and Nanotechnology
Vol. 15, 570–574, 2015
www.aspbs.com/jnn

Nanosized CuO and ZnO Catalyst Supported on Honeycomb-Typed Monolith for Hydrogenation of Carbon Dioxide to Methyl Alcohol

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The greenhouse effect of carbon dioxide (CO_2) has been recognized as one of the most serious problems in the world. Conversion of CO_2 to methyl alcohol (CH_3OH) was studied using catalytic chemical methods. Honeycomb-typed monolith used as catalyst support was 400 cell/inch^2. Pretreatment of the monolith surface was carried out by thermal treatment and acid treatment. Monolith-supported nanosized CuO–ZnO catalysts were prepared by wash-coat method. The prepared catalysts were characterized by using SEM, TEM, and XRD. The catalytic activity for CO_2 hydrogenation to CH_3OH was investigated using a flow-type reactor with varying reaction temperature, reaction pressure and contact time. Conversion of CO_2 was increased with increasing reaction temperature, but selectivity to CH_3OH was decreased. Optimum reaction temperature was about 250 °C under 20 atm. Because of the reverse water gas shift reaction.

Keywords: Honeycomb-Typed Monolith, CuO, ZnO, Carbon Dioxide, Hydrogenation, Methyl Alcohol.

1. INTRODUCTION

The greenhouse effect of carbon dioxide (CO_2) has been recognized as one of the most serious problems in the world.[1] Synthesis of valuable chemicals by CO_2 hydrogenation has received much attention as one of the technologies to solve the CO_2 problem in recent year. Among them, CH_3OH synthesis is one of most attractive applications.

CH_3OH is one of the basic intermediates in the chemical industry and is also being used as a fuel additive and as a clean burning fuel.[2] It is the starting point for formaldehyde, methyl tert-butyl ether and several solvents.[3] CH_3OH can be also converted to olefins by recently developed processes.[4]

Catalytic monoliths consist of catalytic particles supported on a structured support made up of parallel channels of either a metal or a ceramic.[5] Ceramic or metallic foams also represent (more randomly) structured supports with similar properties and applications, and are sometimes also referred to as monoliths. Ceramic (channeled) monoliths are usually produced by extrusion, while metallic monoliths are conventionally made from rolled layers of corrugated and flat sheets.[5] Catalytic layer is often prepared by wash coating the monoliths with a high surface

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1533-4880/2015/15/570/005 doi:10.1166/jnn.2015.8337

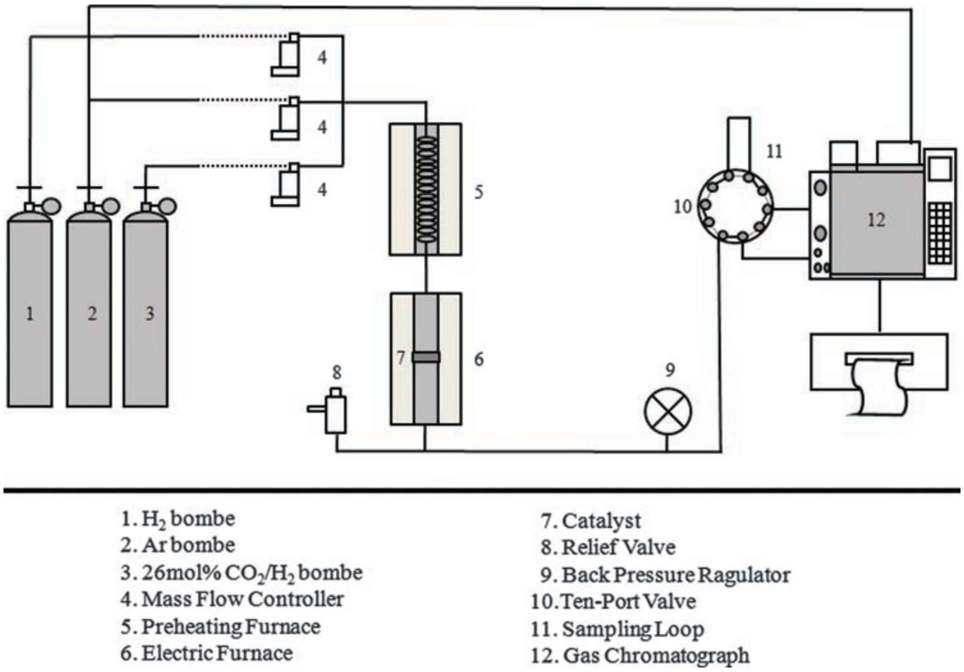

Figure 1. Schematic diagram of experimental apparatus for conversion of CO_2 to CH_3OH.

area support and subsequent impregnation with the active metals.

In this study, monolith (M) supported CuO and ZnO catalysts were prepared by wash-coat method. After charactering the catalysts by means of some instrumental techniques, the hydrogenation activity for CO_2 to CH_3OH was investigated.

2. EXPERIMENTAL DETAILS

2.1. Catalysts Preparation

The CuO–ZnO/M catalysts (CuO; 44.7 wt%, ZnO; 55.3 wt%) were prepared by wash-coat method. Honeycomb monolith (400 cell/inch^2, Ordeg) was cutted to be diameter 1.5 cm (2.4 g). Precursor solution of $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were added to distilled water. Precursor concentrations in the solution were varied. After dipping the monolith in the solution for 30 min, it was slowly drawn up at a rate 6 cm h^{-1}. CuO–ZnO/M catalyst was obtained by repeated calcinations in air at 400 °C for 3 h.

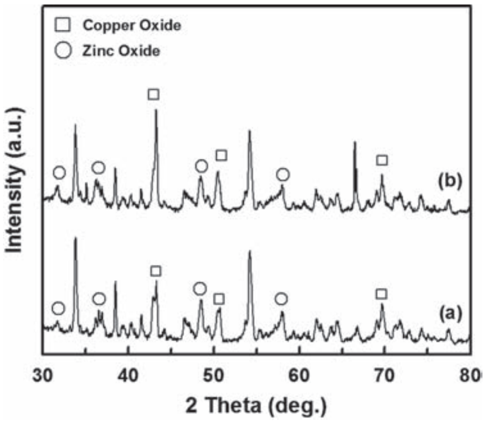

Figure 2. XRD patterns of CuO–ZnO/M catalyst prepared using the solution with different precursor concentrations. (a) 13.6 w/v%, (b) 25.7 w/v%.

The prepared catalysts were characterized by using SEM (S-3500N, Hitachi), BET specific surface area (ASAP-2010, Micromeritics), TEM (JEM-2100F, Jeol), and X-ray diffraction (XRD, D/Max 2200, Rigaku). The chemical composition of representative surface particles was analyzed by energy dispersive spectroscopy (EDS).

2.2. Catalytic Activity

The prepared CuO–ZnO/M catalyst was tested for CH_3OH synthesis using a fixed-bed down flow reactor. Figure 1 shows experimental apparatus for hydrogenation of CO_2 to CH_3OH. The catalyst was loaded in the reactor and was reduced in a gas stream of H_2 (40 mL min^{-1}) at 300 °C for 3 h. The temperature of preheater and reactor was controlled by PID controller, and total reaction pressure was regulated with a back-pressure-regulator. After cooling the catalyst bed to the reaction temperature, reaction gas (26 mol%-CO_2, 73 mol%-H_2) were fed at 60 mL min^{-1} using a mass flow controller. The exit line from the reactor to the gas sampler was heated to prevent condensation of any volatile products. Feed and product gas mixtures were analyzed by using the gas chromatograph (GC-14B, Shimadzu) with a thermal conductivity detector.

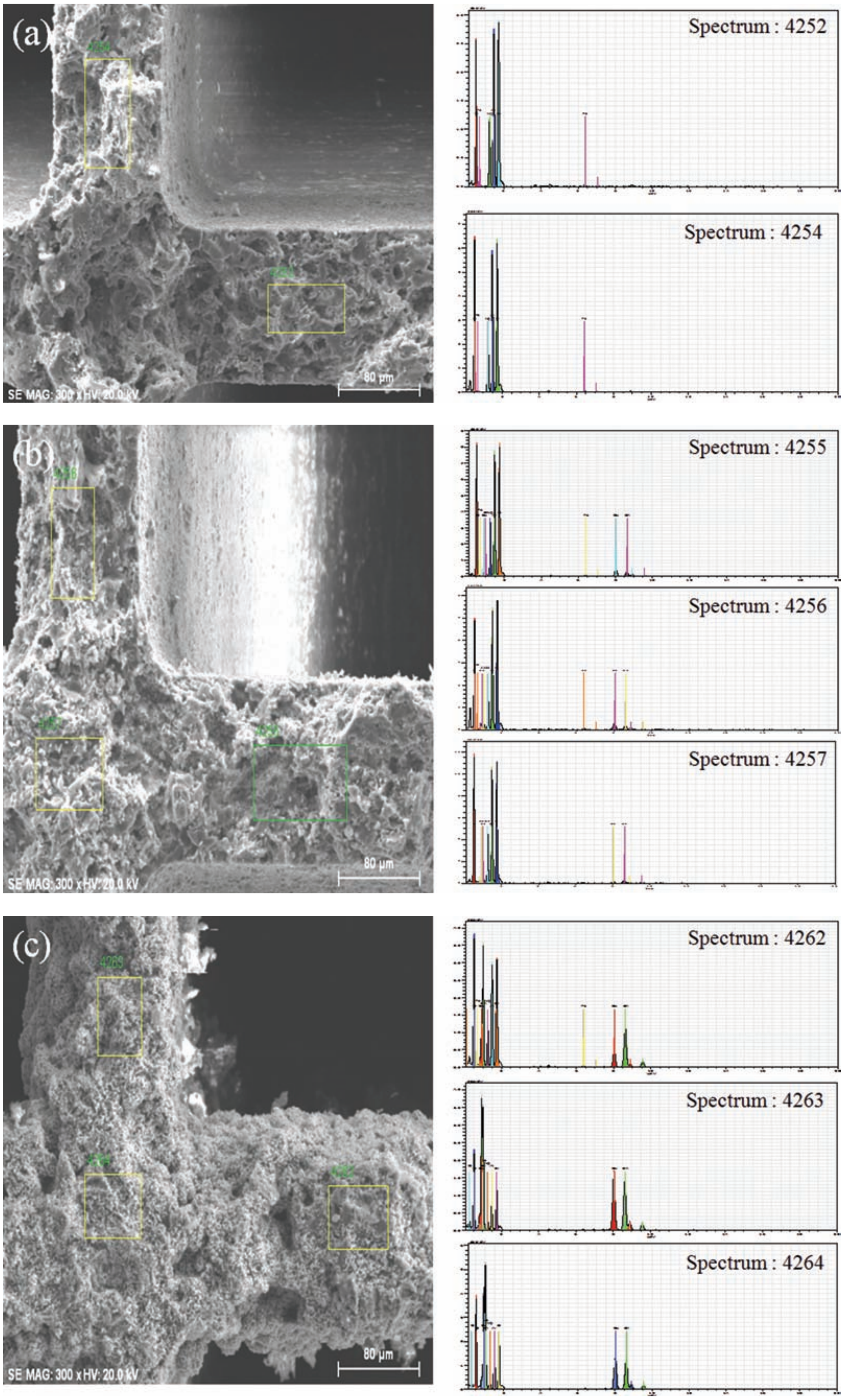

Figure 3. SEM images and EDS spectra of CuO–ZnO/M catalysts with various impregnation numbers. (a) No coated, (b) once, and (c) twice.

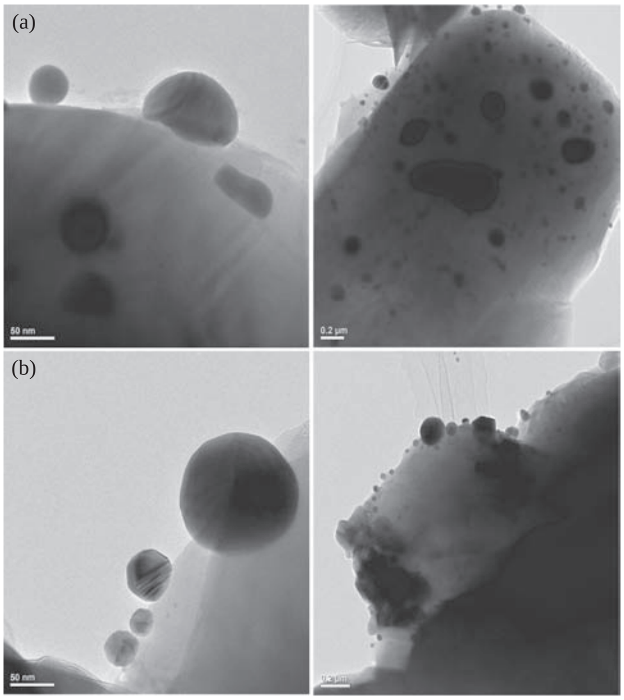

Figure 4. TEM images of CuO–ZnO/M catalyst with various precursor concentrations (right images show magnified TEM images). (a) 25.7 w/v% and (b) 73.6 w/v%.

Two serial columns (Porapak-Q and MS-13X) were connected to a 10-way valve for on-line sampling.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of CuO–ZnO/M catalyst prepared using the solution with different precursor concentrations. Characteristic peaks of CuO are $2\theta = 43.3°$, $50.7°$, $72.9°$, and those of ZnO are $2\theta = 36.9°$, $42.8°$, $62.5°$, $74.3°$, $77.43°$. It was confirmed that the CuO and ZnO on both catalysts prepared by wash-coat method were well formed on ceramic monolith.

Figure 3 shows SEM images and EDS spectra of CuO–ZnO/M catalyst with various impregnation numbers. The particles of CuO and ZnO were coated on the monolith, and it was confirmed that the particles were composed of CuO and ZnO from EDS spectra.

Figure 4 shows TEM images of CuO–ZnO/M catalyst with various precursor concentrations. The particles of CuO and ZnO were well dispersed to be nanosized. It was confirmed that the particles in both cases were composed of CuO and ZnO confirmed.

Figure 5 shows effect of time on stream on CO_2 conversion, selectivity and yield of CH_3OH over CuO–ZnO/M catalyst with various impregnation numbers. The monolith was pretreated at 600 °C. Cell of monolith can be clogged up with catalyst materials if impregnation number is increased. Conversions for CO_2 hydrogenation were all more or less similar. Selectivity of CH_3OH was increased with decreasing the impregnation number. The reaction temperature and reaction pressure were 250 °C and 20 atm, respectively.

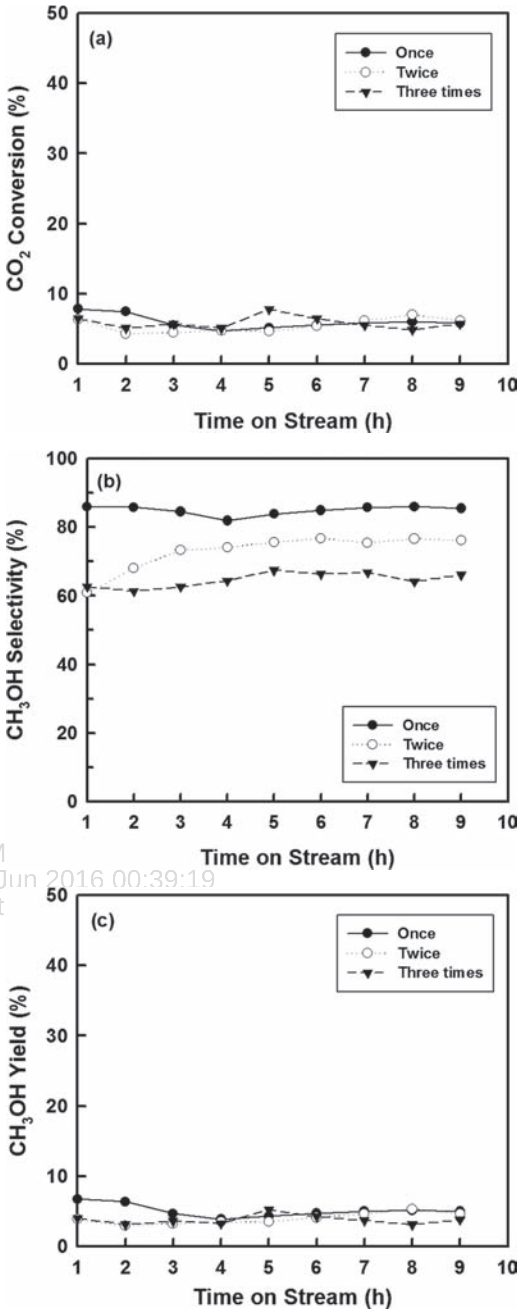

Figure 5. Effect of time on stream on CO_2 conversion (a), CH_3OH selectivity (b) and CH_3OH yield (c) over CuO–ZnO/M catalyst with various impregnation numbers.

Figure 6 shows effect of reaction temperature on CO_2 conversion, selectivity and yield of CH_3OH over CuO–ZnO/M catalyst. CuO and ZnO was once coated with precursor solution of 25.7 w/v%. With increasing reaction temperature, CO_2 conversion was increased, but selectivity and yield of CH_3OH was decreased. Optimum reaction temperature was about 250 °C under 20 atm because of the reverse water gas shift reaction.

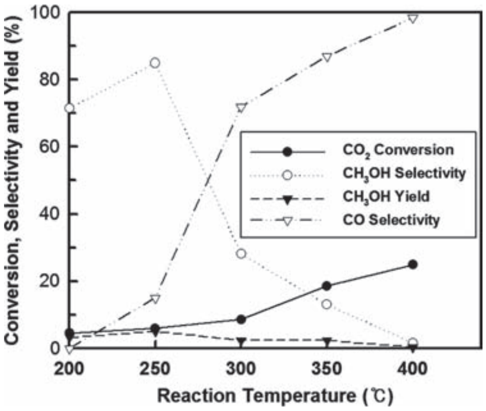

Figure 6. Effect of reaction temperature on CO_2 conversion, selectivity and yield of CH_3OH over CuO–ZnO/M catalyst.

4. CONCLUSION

The catalytic activity for CO_2 hydrogenation to CH_3OH over CuO–ZnO/M catalysts was investigated using a flow-type reactor. The particles of CuO and ZnO were well coated on monolith. Conversion of CO_2 was increased with increasing reaction temperature, but CH_3OH selectivity was decreased. Optimum reaction temperature was about 250 °C under 20 atm because of the reverse water gas shift reaction. Maximum CH_3OH yield over CuO–ZnO/M at 250 °C were ca. 5.1% at 20 atm.

Acknowledgment: This research was financially supported by the Ministry of Education, Science Technology (MEST) and National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation.

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Received: 22 March 2013. Accepted: 22 April 2013.