



Carbon nanofiber-based copper/zirconia catalyst for hydrogenation of CO₂ to methanol



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ABSTRACT

This article describes the synthesis of methanol by the direct hydrogenation of CO₂ over Cu/ZrO₂ catalyst at different ZrO₂ concentrations (5, 10, 15, 20 and 25 wt.%) in a three-phase phase reactor. The techniques of N₂ adsorption/desorption, x-ray diffraction, x-ray photoelectron spectroscopy, transmission electron microscopy, temperature-programmed desorption by CO₂, N₂O chemisorption and inductively coupled plasma optical emission spectrometry were employed for catalyst characterization. At a reaction temperature of 180 °C, pressure of 3.0 MP and 0.020 g/mL of the catalyst, the conversion of CO₂ and the yield of methanol were 10% and 25 g/kg.h, respectively. Surface area of the metallic copper was increased from 8.1 to 9.5 m²/g with the presence of ZrO₂ from 5 to 15 wt.%. The methanol turnover frequency exhibited a linear relationship with ZrO₂ concentration. Methanol synthesis rate was progressively increased with increasing fraction of dispersed copper. A comparative study with the literature revealed better activity of this novel catalyst at relatively low reaction conditions.

1. Introduction

Carbon dioxide is considered as one of the main greenhouse gases that contributes to global climate change [1,2]. Concentrations of carbon dioxide has consistently been increasing in the environment due to combustion of fossil fuels and massive industrialization. Stabilizing greenhouse-CO₂ gas emissions to avoid catastrophic climate change is possible by converting the promising carbon source to a range of industrially relevant products. Therefore, the utilization of CO₂ as a raw material in the synthesis of valuable chemicals has attracted extensive research activities [3–5]. Among all proposed strategies, catalytic CO₂ hydrogenation to methanol has been declared as an economical way by Oah et al. [6,7].

Currently, methanol production is carried out over Cu-ZnO/Al₂O₃ catalysts by feeding syngas (CO + H₂) containing CO₂ at industrial scale. Nevertheless, unsatisfactory performance of this catalyst was recorded when applied to pure CO₂ hydrogenation [8]. Alumina is hydrophilic in nature, hence its activity is adversely affected due to water formation during course of reaction. The poor performance of methanol synthesis catalyst (Cu-ZnO/Al₂O₃) for pure CO₂ hydrogenation is the main driving force to discover an alternative catalytic

system.

Carbon nanofibers (CNFs) due to its hydrophobic character is a good alternative for methanol synthesis catalysts support. Furthermore, CNFs is chemically inert and shows greater resistance in acidic as well as basic medium as compared to conventional oxide supports like silica and alumina. CNFs being a combination of both active carbon and mechanically strong graphite, surpasses other oxides catalyst supports like silica and alumina [9]. CNFs due to higher thermal conductivity, evacuates heat generated during reaction [10]. Furthermore, CNFs being good thermal conductor has an extra advantage as catalyst support in exothermic reactions [11]. Another extra feature associated with CNFs as catalyst support is the easy recovery of precious metallic phase by burning the carbon. Furthermore, being a carbonaceous material CNFs is provided with well-developed pore structure which is helpful in preventing sintering as well as to achieve good metal dispersions [12]. Additionally, CNFs is considered to be an excellent catalyst support due to its chemically active outer and inner end planes [13]. CNFs is preferred over conventional catalyst support for its higher surface area, greater thermal stability, more resistance to corrosion in both basic and acidic medium and the advantage in recovery precious metal particles [14]. Rodriguez et al. [15] in 1994 conducted comparative study on

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CNFs, activated carbon and alumina as catalyst support for ethene hydrogenation. Magnitude of higher activity was displayed by CNFs based catalyst as compared to alumina and active carbon-based catalysts.

Catalyst composition is one of the fundamental parameters affecting the performance of catalysts towards methanol synthesis. The Cu/ZrO₂ catalyst system has been widely used for methanol synthesis by CO₂ hydrogenation. Zirconia is a very promising catalyst component due to its basic character. Furthermore, incorporation of zirconia has been reported to increase copper dispersion and surface basicity [16]. Consequently, the catalytic activity and CO₂ adsorption has been improved by introduction of zirconia. Moreover, Guo et al. [17] reported enhancement of methanol selectivity as a consequent of zirconia doping by facilitating the distribution of basic sites. Therefore, the variation of zirconia concentration is a pivotal study to determine the optimum amount of zirconia in Cu/ZrO₂ catalyst system.

In the above context, the specific objectives of this work are to study the effect of ZrO₂ promoter on the physicochemical properties and activity of carbon nanofiber supported copper catalyst for the direct hydrogenation of carbon dioxide to methanol in a slurry reactor.

2. Experimental

2.1. Functionalization of carbon nanofibers

CNFs (GNF-100), a herringbone type was purchased from Carbon Nano-material Technology Co. Ltd., Korea. Prior to use as a catalyst support, CNFs were treated with 35 vol.% HNO₃ solution. The refluxing was conducted at elevated temperature (90 °C) for 16 h. During this process, CNFs transformed to oxidized CNFs (CNFs-O). CNFs-O was filtered via vacuum filtration, washed and dried in oven for overnight at 100 °C.

2.2. Synthesis of catalysts

Deposition precipitation method was employed to synthesize Cu-ZrO₂/CNFs-O catalysts with different ZrO₂ loadings. A required amount of copper nitrate trihydrate was completely dissolved in deionized water. Subsequently, given quantity of zirconyl nitrate hydrate was added to copper nitrate solution. When both nitrate salts were dissolved, required amount of CNFs-O was added to stirring solution and temperature was raised to 90 °C. Urea solution (1 g/10 ml distilled water) was poured as precipitating agent to the slurry solution. The slurry was continuously stirred for 20 h, cooled to room temperature and filtered via vacuum filtration. Precipitates were dried at 110 °C in oven for overnight. The prepared catalyst Cu-ZrO₂/CNFs (with 15 wt.% of CuO) was loaded with five different ZrO₂ concentrations namely 5, 10, 15, 20 and 25 wt.% and labeled as xCZC, where “x” is the wt.% of ZrO₂ in the CNFs-O based Cu/ZrO₂ catalysts. The dried catalysts were calcined in N₂ flow at temperatures of 450 °C for 3 h.

2.3. Characterization of catalysts

PerkinElmer's Optima 8300 inductively coupled plasma optical emission spectroscopy (ICP-OES) was utilized to quantify the concentrations of bulk phase Cu and ZrO₂. Catalyst were dissolved in aqua regia and high-performance microwave digestion system (Milestone) was applied to completely dissolve the sample matrix.

Phase determination of catalyst components was conducted by using model PANalytical Empyrean X-ray diffractometer. The XRD analyses were performed from 20 to 80° at 2θ Bragg angle at room temperature.

Nitrogen adsorption-desorption isotherms technique was employed to measure the surface area, pore volume and pore diameter of catalysts. Micrometrics ASAP 2020 was used for this purpose. Pore size distribution was assessed by BJH method and BET method was used to

evaluate adsorption isotherms.

Nitrous oxide (N₂O) chemisorption technique was utilized to measure metallic copper surface area (S_{Cu}), copper dispersion (D_{Cu}) and average copper particle size (d_{Cu}) [18]. Firstly, catalysts were subjected to reduction with H₂ flow at 500 °C. The reduced catalysts were cooled in He flow to 60 °C and subsequently purged for about 30 min. The samples were then treated with N₂O gas for 1 h at 60 °C. The residual N₂O gas was flushed out by He flow. Finally, catalysts were again reduced in H₂ flow at 500 °C. Spherical shape of Cu particles was assumed to calculate magnitudes of S_{Cu} and d_{Cu} . A chemisorption stoichiometry ratio of Cu:N₂O = 2:1 was used with density of Cu atoms at 1.46×10^{19} Cu atom/m². Similarly, D_{Cu} was calculated by number of surface Cu atoms/tot no. of Cu atoms and S_{Cu} was calculated according to mathematical expression in Eq. (1).

$$S_{Cu}(m^2/g) = (nC_{Cu} \times N)/(1.4 \times 10^{19} \times W) \quad (1)$$

Where, S_{Cu} is the exposed Cu surface area per gram catalyst, nC_{Cu} is the number of moles of copper, N is Avogadro's constant (6.02×10^{23} atoms mol⁻¹), and 1.4×10^{19} is the number of atomic copper atoms per square meter and W represents weight of the catalyst in grams.

In addition, d_{Cu} was calculated as follows [19,20]:

$$d_{Cu}(nm) = \frac{104}{D_{Cu}(\%)} \quad (2)$$

Similarly, distribution of copper content (R_{Cu}) was measured by Eq. (3) [21].

$$R_{Cu} = \frac{S_{Cu}}{Cu \text{ content} \times BET \text{ surface area}} \quad (3)$$

Morphology as well as particle size measurements of catalysts components were investigated by transmission electron microscopy (TEM). The Zeiss LIBRA 200TEM with 200 kV accelerating voltage was employed for this study. Catalysts dispersed in isopropanol were sonicated for 60 min. The sample suspensions were placed on the Cu grid for analysis.

Temperature Programmed Reduction (TPR) was employed to examine the reduction behavior as well as metal support interaction of catalysts components by using TPDR01100 MS supplied with thermal conductivity detector (TCD). The reduction study was performed in 35–800 °C temperature range with 10 °C min⁻¹ heating rate. TPR investigations were conducted in 5 vol.% H₂/N₂ flow with 20 cm³ min⁻¹ flow rate.

Chemical nature as well as surface composition of catalyst components were studied by X-ray photoelectron spectroscopy (XPS). ThermoFisher K-Alpha equipped with monochromitised AlK source with ultimate energy resolution of ≤ 0.5 eV was utilized in this study. Chemical state identification and peak fitting were performed by using Avantage software.

The basic profiles of catalysts were examined by CO₂ temperature programmed desorption (CO₂-TPD). Initially, the catalysts were degassed under helium flow at 200 °C with a heating rate of 10 °C min⁻¹. The samples were saturated with pure CO₂ at 150 °C for 2 h. The samples were cooled down to room temperature in the He flow. In the final step, adsorbed CO₂ was desorbed in temperature range of 40–800 °C with 10 °C min⁻¹ heating rate. Desorption of gas was quantified using a calibrated TCD.

2.4. Activity studies

Activity of catalysts for CO₂ hydrogenation to methanol was assessed in slurry reactor (Parr 4593). Catalysts were reduced in H₂ with 2000 cm³/h flow rate for duration of 6 h at 380 °C. A 0.5 g of reduced catalyst was suspended in 25 ml ethanol placed in the reaction vessel. Reactor was purged and pressurized to 3.0 MPa with mixture of 3:1 molar ratio of H₂/CO₂ reactant gases. Reaction studies were carried out at 180 °C. Reaction mixture was continuously stirred at 1300 rpm to

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