



Synthesis, characterization and activity pattern of carbon nanofibers based copper/zirconia catalysts for carbon dioxide hydrogenation to methanol: Influence of calcination temperature



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HIGHLIGHTS

- A new CNFs based Cu/ZrO₂ catalyst for CO₂ hydrogenation to methanol was investigated.
- CNFs served well as a catalyst support in slurry reactor for the title reaction.
- Phase transformation of zirconia with calcination temperature was observed by XRD analysis.
- The efficiency of the catalyst was influenced by calcination temperature.
- N₂O chemisorptions and activity data revealed dependency of CO₂ conversion on Cu surface area.

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ABSTRACT

A series of novel carbon nanofibers (CNFs) supported bimetallic copper/zirconia catalysts are synthesized by deposition precipitation method and calcined at different temperatures. Calcined catalysts are characterized by various techniques like X-ray diffraction, N₂ adsorption–desorption, N₂O chemisorption, high resolution transmission electron microscopy, temperature programmed reduction, X-ray photoelectron spectroscopy and temperature programmed desorption (CO₂ & NH₃). The structure–activity correlation is discussed in details. The results demonstrate 450 °C as optimum calcination temperature for methanol synthesis rate with CO₂/H₂ feed volume ratio of 1:3. CO₂ conversion is found to be directly proportional to copper metallic surface area (S_{Cu}), while a linear relationship is observed between methanol synthesis rate and fraction of dispersed Cu.

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1. Introduction

Global warming has been a serious threat to the natural environment and carbon dioxide is the main contributor to the phenomenon [1]. Nature has maintained the balance of natural CO₂ in the atmosphere by its natural fixation, where it is converted to organic compounds. However, it is the human induced CO₂ that has created a state of imbalance of carbon dioxide. Several ways like reduction of carbon dioxide emissions, CO₂ capture and chemical transformation to valuable products were proposed to mitigate carbon dioxide. However, chemical transformation of this human induced CO₂ will not only mitigate this problem but will also produce valuable products. A

number of products like salicylic acid, urea, plastics and methanol have been synthesized from carbon dioxide [2,3].

Currently, methanol has been produced industrially in gas phase from mixture of syngas and CO₂ over Cu–ZnO/Al₂O₃ catalyst at 220–300 °C temperature and 5–10 MPa pressure. It is believed that methanol formation takes place mainly from CO₂ whereas CO acts as scavenger of surface oxygen [4–6]. Nevertheless, application of this current methanol synthesis catalyst CuO/ZnO/Al₂O₃ does not look promising for CO₂ hydrogenation. This is due to the production of CO as a sequence of parallel reverse water gas shift reaction (RWGS) observed with CO₂ hydrogenation to methanol. This triggered the investigations to find a new catalyst system that can effectively hydrogenate CO₂ to methanol.

CNFs have special physiochemical characteristics like higher surface area, higher mechanical strength and surface defects for

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holding catalyst particles. These properties make them a suitable choice as catalyst support. Moreover, CNFs are more advantageous in slurry phase reactors due to their mesoporous nature. Furthermore, due to lack of any 2D porosity in CNFs, accessibility of the reacting molecules to the active sites is enhanced, which in turn improves the activity profile of catalyst [7,8]. Consequently, CNFs based catalysts have shown better activity and selectivity as compared to traditional supports based catalysts [9]. Moreover, a special hexagonal thin morphology adopted by nickel particles based on CNFs resulted in higher metal support interaction. Subsequently, nickel deposited CNFs catalysts exhibited better performance for hydrogenation reactions as compared to classical supported catalysts like silica and alumina [10,11]. Similarly, higher metal support interaction produced in CNFs based platinum–ruthenium catalysts also resulted in better dispersion of Pd metal [12]. Furthermore, Ledoux et al. reported that greater thermal conductivity of CNFs enabled a rapid evacuation of heat generated during the course of reaction [13]. This additional ability of CNFs will further support their application as catalyst support in exothermic reactions.

Several factors like starting material and preparation method affect the catalytic properties of catalyst. Among such factors calcination temperature is a vital factor to alter the catalytic profile for certain reactions [14]. Irmawati et al. studied effect of calcination temperature on physiochemical properties of antimony vanadium mixed oxide catalysts [15]. In their work, escalation in calcination temperature not only led to increase agglomeration of catalyst particles but surface area was also adversely affected. Similar observation was also reported by Al-Zeghayer et al. where rise in calcination temperature declined activity of catalyst towards cyclohexyl benzene formation [16]. Moreover, intensification of calcination temperature also enhanced interaction between the active components of the catalyst. However, sintering of active sites was observed at elevated calcination temperature [17].

In this work, CNFs based Cu/ZrO₂ catalysts were synthesized by deposition precipitation method. In order to scrutinize effect of calcination temperature, catalysts were calcined at different temperatures. Physiochemical parameters as well as activity studies for liquid phase methanol synthesis were investigated in slurry reactor.

2. Experimental

2.1. Functionalization of carbon nanofibers (CNFs)

The CNFs with herringbone type morphology (GNF-100) were purchased from Carbon Nano-material Technology Co. Ltd., Korea. The diameter, length and specific surface area are 50–100 nm, 10–30 μm and 100–300 m² g⁻¹, respectively. CNFs were modified by treating with 35 volume % nitric acid solution. The refluxing was performed for 16 h at elevated temperature (90 °C). During this process carbon nanofibers (CNFs) were oxidized and converted to oxidized carbon nanofibers (CNFs-O). After cooling to room temperature, CNFs-O were filtered by vacuum filtration, washed several times with distilled water and then dried overnight in oven at 100 °C.

2.2. Synthesis of Cu-ZrO₂/CNFs-O (CZC) catalysts by deposition precipitation method

A series of Cu·ZrO₂/CNFs-O catalysts with constant loading of Cu (15 wt%), ZrO₂ (10 wt%) and CNFs-O (75 wt%) has been synthesized by deposition precipitation method [18,19]. Firstly, a required amount of Cu (NO₃)₂·3H₂O (R&M Chemicals, UK) was dissolved in 400 ml distilled water. Similarly a known quantity of zirconyl

nitrate hydrate (SIGMA-ALDRICH, USA) was added to the stirring solution. After complete dissolution of both nitrate salts, required quantity of CNFs-O was added to the solution. Temperature of the solution was increased to 90 °C. A 10 ml of urea solution having 1 g of urea was added to the slurry solution as a precipitating agent. The slurry was stirred for 20 h, cooled and filtered by vacuum filtration. The precipitates were dried in oven at 110 °C for overnight. The dried catalysts were calcined in N₂ flow at four different temperatures (350, 450, 500 and 550 °C) for 3 h and labeled as CZC350, CZC450, CZC500 and CZC550, respectively.

2.3. Characterization

PANalytical model Empyrean X-ray diffractometer was used for crystallographic analysis of catalyst components. Phase identification was performed by PANalytical HighScore Plus. The XRD data were measured at room temperature from 20° to 80° at 2θ Bragg angle.

Surface area and pore volume of CZC catalysts were analyzed by N₂ adsorption–desorption isotherms technique, using Micrometrics ASAP 2020 device. BET method was utilized for the evaluation of adsorption isotherms while BJH method was used to evaluate pore size distribution [20].

Metallic surface area of copper (S_{Cu}) was determined by N₂O chemisorption technique [21]. Catalysts were first reduced with a flow of H₂ at 500 °C. After reduction, samples were cooled to 60 °C in He flow and purged for 30 min. Then N₂O was introduced at 60 °C for 1 h. Residual N₂O was removed by He flow for 1 h. Finally Temperature Programmed Reduction (TPR) analysis was conducted for the second time at 500 °C. Surface area and dispersion of Cu were calculated by assuming surface atomic density of 1.46 × 10¹⁹ Cu_{at} m⁻² and stoichiometry of Cu:N₂O = 2, respectively.

Average particle size (d_{Cu}) was obtained by a conventional formula as follows

$$d_{\text{Cu}} (\text{nm}) = \frac{X}{2Y}$$

where X is the H₂-uptake for first reduction and Y is H₂-uptake for second reduction.

Likewise, distribution of Cu content was estimated by the following equation [22].

$$R_{\text{Cu}} = \frac{\text{Cu}^0 \text{ surface area}}{\text{Cu content} \times \text{BET surface area}}$$

Morphology and particle size measurement of the catalysts were conducted by using transmission electron microscopy (Zeiss LIBRA 200TEM), Accelerating Voltage: 200 kV. Samples were dispersed in isopropanol and sonicated in ultrasonic device for about 1 h and the suspensions were dropped onto a copper grid [23].

Reduction behavior and metal support interaction were investigated by Temperature Programmed Reduction (TPR) in temperature range of 30–800 °C with heating rate of 10 °C min⁻¹, using TPDRO1100 MS equipped with thermal conductivity detector (TCD). TPR analysis were performed in 5 vol.% H₂/N₂ flow with a flow rate of 20 cm³ min⁻¹.

X-ray photoelectron spectroscopy was utilized to investigate chemical nature and surface composition of copper. X-ray photoelectron spectroscope (XPS, Thermo-Fisher K-Alpha) equipped with monochromitised AlK source having ultimate energy resolution of ≤0.5 eV was employed for this purpose. Advantage software was used for peak fitting and chemical state identification.

Surface acidity and basicity were examined by NH₃ temperature programmed desorption (NH₃-TPD) and CO₂ temperature

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