A graphene-supported copper-based catalyst for the hydrogenation of carbon dioxide to form methanol

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ABSTRACT

The use of reduced graphene oxide (rGO) as a novel support for the CuO-ZnO-ZrO$_2$-Al$_2$O$_3$/rGO (CZZA/rGO) catalyst in forming methanol by carbon dioxide hydrogenation has been studied herein. Furthermore, the CuO-ZnO-ZrO$_2$-Al$_2$O$_3$ (CZZA) catalyst was also prepared to compare catalytic performance. The catalysts were characterized using BET specific surface area, X-ray diffraction (XRD), H$_2$-temperature-programmed reduction (H$_2$-TPR), scanning electron microscopy (SEM), H$_2$-temperature-programmed desorption (H$_2$-TPD) and CO$_2$-temperature-programmed desorption (CO$_2$-TPD) techniques and were evaluated by a fixed-bed reactor for methanol synthesis from the hydrogenation of carbon dioxide. The characterization results show that the surface area of the CZZA/rGO catalyst was 125.6 m^2/g and the adsorption capacity of H$_2$ and CO$_2$ increased remarkably due to the support of rGO. Moreover, the CO$_2$ conversion over the CZZA/rGO catalyst was 14.7% under optimum reaction conditions (a temperature of 513 K, a pressure of 20 bar, and a space velocity of 6075 h^{-1}). The methanol yield was 11.6%, while that of CZZA catalyst without rGO support was only 9.8%. The superior activity of the CZZA/rGO catalyst could be attributed to its large surface area and high H$_2$ and CO$_2$ adsorption capacity, which prevent the catalyst sintering and led to a higher CO$_2$ conversion and methanol selectivity.

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1. Introduction

Carbon dioxide, a greenhouse gas, is the main pollutant currently damaging the environment at an alarming rate [1]. Global greenhouse gas emissions have reached 30.6 billion tons in 2010 [2]. Therefore, reducing carbon dioxide emission is a crucial issue that needs to be addressed immediately. The current methods to control carbon dioxide emission include carbon capture and storage (CCS) and chemical reaction conversion. In addition, methanol (CH$_3$OH) is not only an important industrial chemical, but it can also be used directly as a fuel in a fuel cell [3]. The Nobel Prize winner George Andrew Olah once put forward that using hydrogen, which comes from renewable sources, to react with carbon dioxide to form methanol to provide energy, and this becomes one of the most promising research areas in the CO$_2$ utilization in recent years. Researchers have noted that catalyst research is a key part in the hydrogenation of carbon dioxide to form methanol, the commonly used catalysts for the hydrogenation of carbon dioxide to form methanol include copper-based catalysts and noble metal catalysts [4]. Copper-based catalysts are

becoming popular because they can be used at relatively high temperature and pressures [5–9]; however, as reported earlier, the methanol yield using copper-based catalysts is only 9.6% under a temperature of 513 K and a pressure of 30 bar [10].

Previous research has demonstrated that copper-based catalysts have the following problems due to copper sintering: a low selectivity, a low activity, and a short life time [11–13]. The active centers of copper-based catalysts (Cu^0 or Cu$^{\delta+}$ species) can be oxidized easily to CuO using water vapor [14–16], which is formed by the hydrogenation of carbon dioxide. Arena et al. [17] reported that the increase in the partial pressure of water vapor across the catalyst bed caused the sintering of copper at higher contact time, which lowered the reaction rate. Another important factor responsible for copper sintering is Cu dispersion. Karelovic et al. [18] showed that catalysts with higher copper loading and low Cu dispersion exhibited strong sintering. To conclude, low Cu dispersion and copper oxidation by water vapor are the two main contributing factors for copper sintering, which results in deactivation of the catalysts.

To solve the problem of Cu sintering, various attempts have been made such as adding metal oxides to improve Cu dispersion. According to these studies, Cu dispersion can be increased by the addition of Mn, La, Ce, Zr, and Y to the Cu-Zn-Al catalyst [19].

Moreover, many modified supports have been used to develop the copper-based catalysts with Cu^0 or $Cu^{\xi+}$ sites. Natesakhawat et al. [16] found that the incorporation of Ga_2O_3 and Y_2O_3 into the Cu-Zn-Zr catalyst enhanced its reducibility. Arena et al. [20] reported that oxide carriers controlled the catalyst texture and metal surface exposure, thereby affecting the adsorption properties as observed in the case of the CeO_2 support. Although Cu dispersion and reducibility of copper-based catalysts have been improved over the years, their catalytic activity is still low.

To this end, for the first time, rGO is used as the novel support for copper-based catalysts to increase the dispersion of copper and to promote the reduction of CuO in this study. Due to its large surface area [21], rGO improves the dispersion of active copper species. The objective of this work is to study and compare the structure and adsorption properties of CZZA and CZZA/rGO catalysts. The catalytic activity has also been investigated using a fixed bed reactor.

2. Experimental

2.1. Preparation of catalysts

First graphite oxide is prepared by the oxidation of graphite using strongly acidic under oxidizing conditions. Followed graphene oxide was prepared by ultrasonic exfoliation of graphite oxide. Graphene or called reduced graphene oxide was prepared through the chemical reduction of graphene oxide.

2.1.1. Preparation of graphene oxide (GO)
Graphene oxide was synthesized from graphite powder using the Hummers method [22]. The graphite powder (2 g) and H_2SO_4 were cooled to 273 K. Approximately 1 g of sodium nitrate ($NaNO_3$) and 6 g of potassium permanganate ($KMnO_4$) were added to the suspension under vigorous agitation. Next, 92 ml of de-ionized water was added slowly to the mixture over a period of 30 min at 308 K, which caused violent effervescence and increased the temperature to 371 K. The suspension was then diluted with warm water and oxidized with hydrogen peroxide (H_2O_2, 30 wt.%). After washing, filtering and ultrasonication, the as-synthesized graphene oxide was characterized.

2.1.2. Synthesis of the CZZA/rGO catalyst
The CZZA/rGO catalyst was synthesized using CZZA (20 wt.%) and GO (80 wt.%) by a conventional co-precipitation method. First, 0.8 g of GO was added to a flask with 100 ml of N-methyl-pyrrolidone, and the GO solution was prepared. The mixture was maintained at a pH of approximately 9 throughout the synthesis by the addition of a 1 M NaOH solution. A 0.2 g sample of prepared CZZA was added dropwise into the mixture and 6 g of vitamin C were added to reduce the GO to rGO, which was stirred vigorously in an oil bath at 363 K for 2 h. After the precipitation was complete, the precipitate was washed and dried overnight at 323 K. Dried samples were ground to a powder with a 40–60 mesh particle size.

2.1.3. Synthesis of CZZA catalyst
The catalyst was prepared by a conventional co-precipitation method described in detail elsewhere [5]. Initially, aqueous solutions of Cu $(NO_3)_2\cdot3H_2O$, Zn $(NO_3)_2\cdot6H_2O$, Zr $(NO_3)_4\cdot5H_2O$, Al $(NO_3)_3\cdot9H_2O$ (total cation concentration of 1 M) were prepared and mixed in a flask. Then, a 1 M aqueous solution of Na_2CO_3 was added dropwise into the resulting mixture at 338 K until the solution reached pH 7. After filtering, washing, and drying, the sample was calcined at 673 K for 5 h in air. CZZA ($CuO/ZnO/ZrO_2/Al_2O_3$) catalyst was prepared with a mass ratio of 4/3/1.5/1.5, and the catalyst sample (40–60 mesh) was used for the evaluation.

2.2. Characterization of the catalysts

The surface area and pore volume of the catalysts used in this study were calculated by BET and BJH methods from nitrogen adsorption-desorption isotherms at 77 K determined with a Micromeritics Belsorp-mini II (BEL Japan, Inc.).

X-ray diffraction (XRD) measurements were performed using a D/MAX-RA X-ray diffractometer (Rigaku, Japan) with a copper anode at 40 kV and 40 mA.

The scanning electron microscopy (SEM) images of the catalysts were obtained using a SU-8010 SEM (Hitachi, Tokyo, Japan).

The temperature-programmed reduction (TPR) was carried out with a Micromeritics AutoChem II 2920 to test the interaction between CuO and the catalyst support. The column tubes were filled with 50 mg of catalyst and placed under a feed gas of 5% H_2 in N_2.

The temperature-programmed desorption (TPD) study was conducted using the same apparatus as TPR, Micromeritics AutoChem II 2920. For CO_2-TPD and H_2-TPD experiments, the catalysts (100 mg) were reduced in situ with 10% H_2/Ar. Adsorption was subsequently investigated by exposing the reduced samples to CO_2 or 10% H_2/Ar followed by Ar purging for 120 min to remove any weakly adsorbed species.

2.3. Evaluation of the catalysts

A single column reactor with a stainless steel tube 320 mm in length and 10 mm in inner diameter was set up as shown in Fig. 1. A programmable heat controller was installed to maintain a stable reaction temperature. A back-pressure regulator was used to control the reaction pressure and a condenser was used to condense the CH_3OH and water vapors. A gas chromatograph
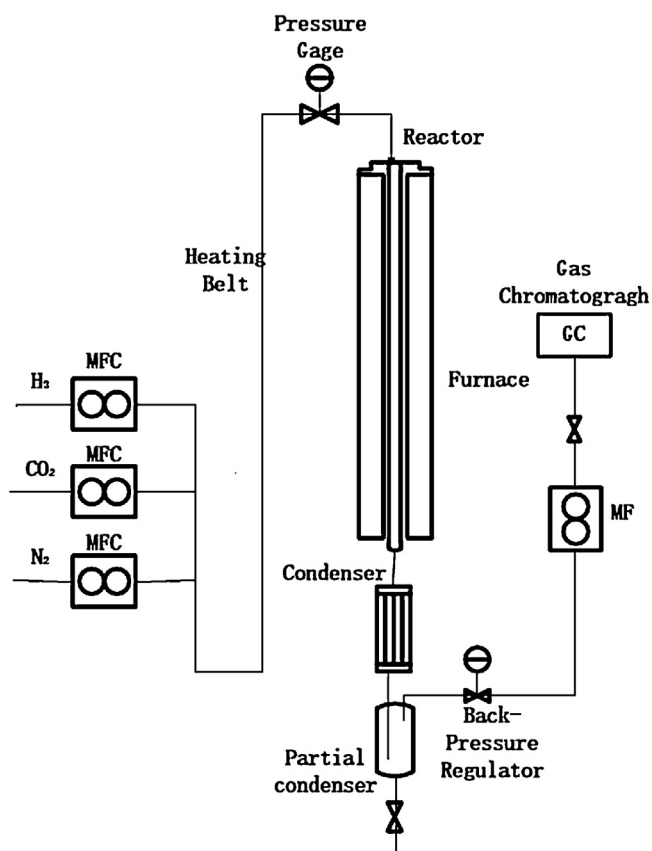
Fig. 1. Schematic diagram of the experimental setup used for CH_3OH production.