CO2 hydrogenation to methanol using Cu-Zn catalyst supported on reduced graphene oxide nanosheets

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A B S T R A C T

Supported Cu-Zn/reduced graphene oxide (rGO) catalysts were synthesized via an incipient wetness impregnation and evaluated for a CO_2 hydrogenation to methanol. The structure, surface reactivity, and adsorption properties were investigated extensively by FE-SEM, TEM, XRD, Raman, FT-IR, N_2 sorption, TGA, TPR, and XPS techniques. The effects of Cu-Zn metal loading content and the reaction temperature were investigated toward the methanol production from the CO_2 hydrogenation. It was found that supported rGO nanosheets could greatly enhance the catalytic performance and help the dispersion of bimetallic compounds Cu-Zn particles. The 10 wt%CuZn/rGO catalyst yielded the highest space time yield (STY) of $424\,\mathrm{mg_{MeOH}\,g_{cat}^{-1}\,h^{-1}}$ at a reaction temperature and pressure of 250 °C and 15 bar, respectively.

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1. Introduction

Recently, global warming has become a serious problem affecting humanity due to a rapid increase of CO_2 emission which has consequently led to an increase in the average global temperature [1]. Therefore, various techniques have been proposed to reduce the atmospheric CO_2 accumulation, for example: carbon capture and storage (CCS) [2–4] that aims to capture and store large quantities of CO_2, and carbon capture and utilization (CCU) [5–7] that aims to convert CO_2 to fuels such as dimethyl ether (DME) dimethyl carbonate (DMC), and methanol (MeOH) [8–13]. Especially for the production in the latter case, DME, DMC, and MeOH are key feedstock for industrial chemicals, which can be converted into high molecular weight hydrocarbons and alternative fuels, where the CO_2 hydrogenation process is one of the most efficient and economical routes for CO_2 emission utilization [14–20]. However, the hydrogenation reaction is highly exothermic and it is difficult to activate CO_2 owing to its high stability [21,22]. Therefore, catalysts are employed to reduce the activation energy of the hydrogenation step and break the CO_2 bonds [23,24].

Cu-Zn oxide-based catalysts have been widely reported for the CO_2 hydrogenation to methanol process [25–30]. The role of Zn oxide is to improve the dispersion of metallic copper particles. Additionally, it has been found that Zn oxide exhibits an active site for hydrogen spillover. Moreover, the interaction between Cu and Zn oxide causes an electron transfer from Zn oxide to Cu metal that occurs as Cu^0 and Cu^+ species, which are crucial for CO_2 hydrogenation to methanol [31–36]. It has been confirmed by other studies that copper metal alone cannot be the sole active site for higher activities in methanol synthesis [37,38]. While Cu-Zn oxide-based catalysts have been well-researched for methanol synthesis, these catalysts are not prevalent because the metals have low active surface area and are prone to sintering.

Hence, catalyst supports are used as a metal receptor to increase surface area and improve metal dispersion [39–43]. Carbon materials such as carbon nanotubes (CNTs) and activated carbon (AC) have been commonly used as the catalyst supports due to their attractive physical and thermal properties such as high surface area (i.e., 180–200 $m^2\,g^{-1}$ [44–47]), uniform and straight pores, inert graphitic surface, and high thermal stability, while also exhibiting good performance for adsorption of hydrogen [48–51]. However, CNTs and AC still have lower specific surface areas when compared with graphene [50].

The unique physical, chemical, and mechanical properties of graphene make it an ideal support material for the catalysts such as high theoretical surface area of 2630 m^2 g^{-1}, which provides an attractive platform for surface interactions and surface chemistry, tensile strength of 130 GPa, thermal conductivity of 4840–5300 W m K^{-1}, and electron mobility of 15,000 cm^2 V^{-1} [52–57]. Beside, graphene has been used worldwide as a catalytic support material for various chemical reactions and used in photoelectric catalysis, lithium ion battery, and fuel cell.

In this work, supported Cu-Zn on reduced graphene oxide (rGO) catalysts were synthesized via incipient wetness impregnation and evaluated for CO$_2$ hydrogenation to methanol. The supporting materials were synthesized via an oxidation of graphite to graphene oxide, followed by a chemical reduction method. The reaction temperature and percent loading of the bimetallic Cu-Zn compounds on the graphene support were finely tuned to achieve the high performance of CO$_2$ hydrogenation to methanol.

2. Experimental

2.1. Chemicals and materials

The chemicals used in this study were graphite powder (20–40 μm, Sigma Aldrich), sodium nitrate (99.5% NaNO$_3$, Qrec), potassium permanganate (99% KMnO$_4$, Ajax Finechem), sulfuric acid (98% H$_2$SO$_4$, Qrec), hydrogen peroxide (30% H$_2$O$_2$, Merck), hydrazine hydrate (80% N$_2$H$_4$, Merck), copper nitrate trihydrate (99.5% Cu(NO$_3$)$_2$·3H$_2$O, Qrec), zinc nitrate hexahydrate (98% Zn (NO$_3$)$_2$·6H$_2$O, Lobachemie), and water, which was purified via a Milli-Q system (>18 MΩ cm, Millipore).

2.2. Preparation of rGO

Graphene oxide (GO) was synthesized according to the modified Hummers method [58], with additional modifications following Sawangphruk et al. [59]. First, graphite powder (5.0 g) and NaNO$_3$ (7.5 g) were mixed in H$_2$SO$_4$ (500 ml). Then, KMnO$_4$ (40.0 g) was slowly added under stirring at 200 rpm in an ice bath for 24 h. Water (500 ml) and H$_2$O$_2$ (150 ml) were added into mixture solution in an ice bath under stirring at 200 rpm for 24 h. The product was collected by centrifuge and washed with water several times until the pH was neutral. The as-synthesized product was dried at 50 °C for 24 h. Next, rGO was prepared via a chemical reduction of GO. First, the as-prepared GO (1.0 g) was dispersed in 300 ml of water under sonication for 1 h. Then, hydrazine (30 ml) was added into the suspension while stirring at 200 rpm at 98 °C for 24 h to eliminate oxygen functional groups. Finally, the as-synthesized product was collected via vacuum filtration and
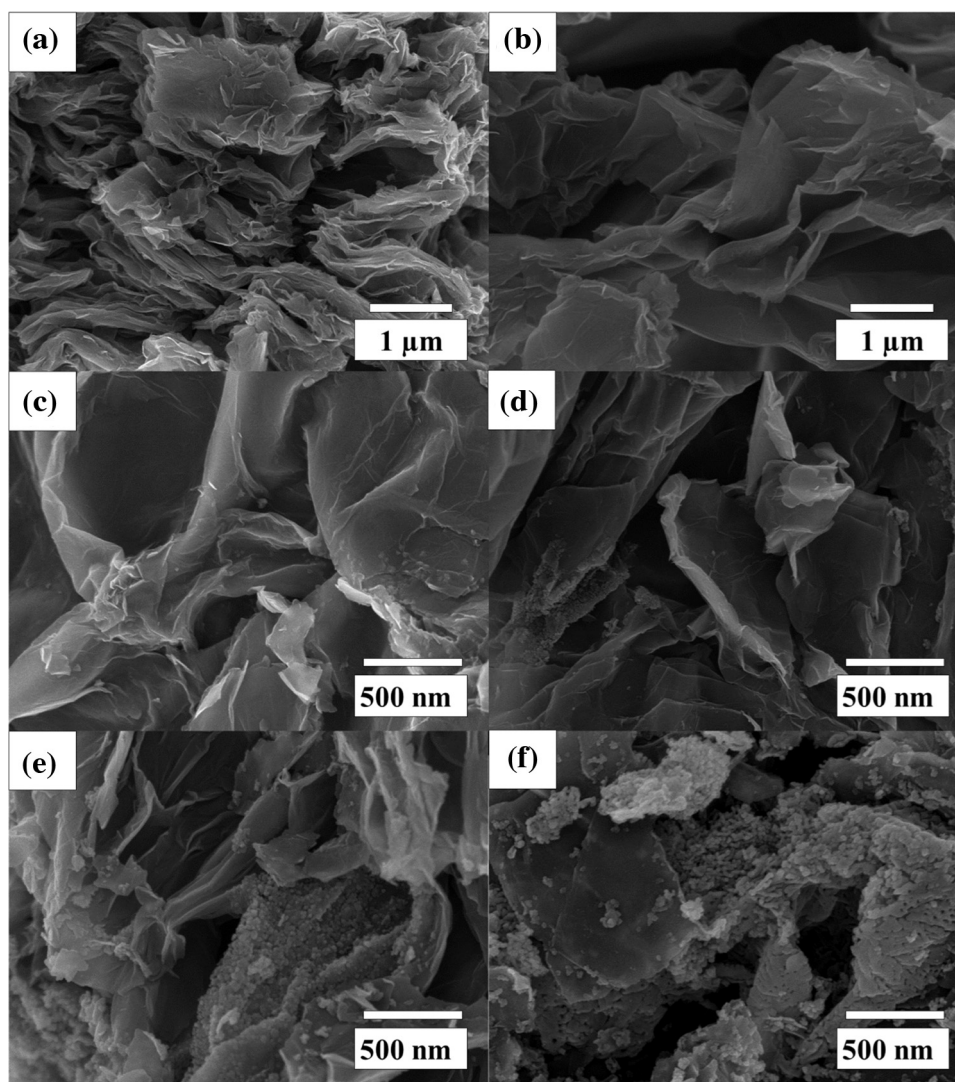

Fig. 1. SEM images of (a) rGO, (b) calcined rGO, (c) 5%CuZn/rGO, (d) 10%CuZn/rGO, (e) 20%CuZn/rGO, and (f) 30%CuZn/rGO.