Enhancing the Dispersion of Cu-Ni Metals on the Graphene Aerogel Support for Use as a Catalyst in the Direct Synthesis of Dimethyl Carbonate from Carbon Dioxide and Methanol

Varisara Deerattrakul, Apichaya Panitprasert, Pralachoak Puengampholsrisook, and Paisan Kongkachuichay

ABSTRACT: Graphene has attracted attention because of its interesting properties in catalyst applications including as a catalyst support; however, it is known that the graphene can be restacked, forming a graphite-like structure that leads to poor specific surface area. Hence, the high-porosity graphene aerogel was used as a Cu–Ni catalyst support to produce dimethyl carbonate (DMC) from carbon dioxide and methanol. In this work, we have introduced a new synthesis route, which can improve the dispersion of metal particles on the graphene aerogel support. Cu–Ni/graphene aerogel catalysts were synthesized by a two-step procedure: forming Cu–Ni/graphene aerogel catalysts via hydrothermal reduction and then Cu–Ni loading by incipient wetness impregnation. It is found that the catalyst prepared by the two-step procedure exhibits higher DMC yield (25%) and MeOH conversion (18.5%) than those of Cu–Ni loading only by an incipient wetness impregnation method. The results prove that this new synthesis route can improve the performance of Cu–Ni/graphene aerogel catalysts for DMC production.

1. INTRODUCTION

Carbon dioxide (CO₂) is well recognized as a major greenhouse gas causing global warming, leading to tendentious climate change and rises in the sea level; however, it is also considered as the most abundant C1 resource. Therefore, the conversion of CO₂ to environmentally friendly alternative chemicals and fuels has become an increasingly attractive interest in the chemical industry. Dimethyl carbonate (DMC) is one of the most valuable target products for the conversion of CO₂ because it has low toxicity and can be widely used as a nontoxic substitute for highly poisonous phosgene and dimethyl sulfate, an electrolyte in lithium batteries, oxygen enhancer to gasoline for decreasing exhaust emission, and as a raw material in biodiesel production. There are many approaches that have been applied to synthesize DMC, for example, carbon monoxide–methyl nitrite process, transesterification process, oxidative carbonylation of MeOH process, methanalysis of phosgene, and direct synthesis of DMC from CO₂ and MeOH. Among these approaches, the direct synthesis of DMC from CO₂ and MeOH is a promising way from the viewpoint of green chemistry and sustainable development because of it being an environmentally benign green chemical process. However, there remain the limitations of thermodynamic equilibrium and activation of MeOH and CO₂; thus, the development of effective catalysts plays a significant role in the overcoming of these limitations.

A variety of catalysts has been applied for DMC production such as solid acidic/basic catalysts, H₃PW₁₂O₄₀⁻Ce₄⁺O₂, and H₃PW₁₂O₄₀⁻Ce₄⁺Zr⁺O₂ (called “heteropoly acids”) and metal oxide catalysts. Al-Darwish et al. studied the role of ceria nanostructures (i.e., nanooctahedra, nanocubes, and nanorods) and metal doping (i.e., Ca, Ni, Cu, and Co) for direct synthesis of DMC. They found that the ceria nanorod catalyst produced the highest DMC yield while ceria octahedral sites improved the stability of catalyst. Moreover, the order of catalytic activities displayed as CeO₂ > CoO/CeO₂ > NiO/CeO₂ > CaO/CeO₂ > CuO/CeO₂. In another study, Dhana Lakshmi et al. reported that the active catalysts for urea methanolysis to produce DMC were ZnO–SrO mixed oxide catalysts. Moreover, a series of metal–organic frameworks, MOF-808-X (6-connected), were applied for the direct synthesis of DMC because of their high surface area, highly developed porosity, and a large number of active sites in the metal nodes. However, the metal oxide catalysts are more widely used for DMC production because of their easier
preparation and lower cost, and they can be easily loaded on supports with high dispersion of active metals.27 There are many works that have used metal oxides with supports as the catalysts in the direct synthesis of DMC; for example, the Cu–Ni/SBA-15 catalyst provided a CH₃OH conversion of 26.7% and a DMC yield of 4.3% at 110 °C and 1.2 MPa.28 Zhou et al.29 prepared the Cu–Fe/SiO₂ catalyst for the direct synthesis of DMC at 120 °C and 1.2 MPa, at which conditions they obtained the highest CH₃OH conversion (5.37%) and DMC selectivity (85.9%). Zheng et al.30 found that in their experiments, Cu species are highly dispersed on the SiO₂–ZrO₂ support, giving good activity for CH₃OH conversion (10%) and DMC selectivity (79.4%). Multivalled carbon nanotube-supported Cu–Ni catalysts have also been reported to achieve the high CH₃OH conversion (4.3%) and DMC selectivity (85.0%) at 120 °C and 1.2 MPa.31 Chiang et al.32 in addition, reported that the activated carbon-supported Cu–Ni catalyst gave a CH₃OH conversion of 6.1% and a DMC selectivity of 88.2% at 170 °C and 5 MPa.

Recently, graphene has been recognized as a promising host material24,33 because of its high theoretical surface area (2630 m² g⁻¹),34 being simply functionalized by heteroatoms,35 having a high thermal stability (up to 600 °C in air),36 and possessing good electron transfer, which can promote the dispersion of metal nanoparticles, thus leading to enhancement of catalytic activity.37 These extraordinary properties have led to using graphene as a novel material in many fields such as sensors,38 energy storage,39 and electrocatalysis.40 However, there are very few works using graphene as a carbonaceous catalyst support, particularly, CO₂ utilization. In our previous work, we first demonstrated the potential use of graphene as a support for the Cu–Zn catalyst in CO₂ hydrogenation to methanol, with results exhibiting the highest space time yield of 424 mgMeOH g⁻¹cat⁻¹ h⁻¹.38 Unfortunately, these two-dimensional graphene sheets can be easily restacked into a graphite-like form because of the van der Waals interactions between adjacent graphene layers, resulting in poor surface area;41 thus, a graphene aerogel having a three-dimensional network of interconnected pores was prepared to avoid this issue. In this work, the Cu–Ni-based catalyst is used for the first time to provide the active metal on a graphene aerogel support in the direct synthesis of DMC from CO₂ and MeOH.

Herein, we have introduced a new synthesis route, so-called “two-step” loading, to enhance the dispersion of bimetallic Cu–Ni metals on graphene aerogel by first loading Cu–Ni simultaneously with hydrothermal reaction of graphene oxide and subsequently adding the required metal content by an incipient wetness impregnation. The performance of the obtained catalyst was tested and compared to that of Cu–Ni/graphene aerogel prepared by incipient wetness impregnation only (so-called “one-step” loading).

2. RESULTS AND DISCUSSION

Morphologies of Cu–Ni catalyst supported on graphene aerogel obtained via two different synthetic routes were observed by field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), and the images are shown in Figure 1. Overall, both Cu–Ni/graphene aerogel catalysts from route A (Figure 1a) and route B (Figure 1b) show an interconnected structure and a porous 3D framework, which is characteristic of graphene aerogel morphology36 (see Figure S1 for characterization of pristine graphene aerogel). It can be clearly seen that the size of Cu–Ni particles from route B is much larger than that of Cu–Ni particles from route A, which may result from the easier agglomeration of metals obtained by one-step loading. In hydrothermal process from route A, it is notable that a significant part of nanoparticles is covered by the graphene layers, indicating that effective conglomeration between the metal oxide nanoparticles and the graphene sheets leads to increase in their interface contact and decrease in the aggregates of metals, attributed as high dispersion of active phase, thus enhancing the catalytic performance.42 Moreover, the TEM image of Cu–Ni/graphene aerogel catalyst from route A (Figure 1c) shows metal nanoparticles and many wrinkled structures on the support, confirming the existence of a porous 3D framework. In contrast, the TEM image of Cu–Ni/graphene aerogel catalyst from route B (Figure 1d) shows aggregation of metals, which is in line with the FE-SEM result.

To further describe the physical properties of the prepared catalysts, structural changes of Cu–Ni/graphene aerogel catalysts from both routes were observed by X-ray diffraction (XRD), as shown in Figure 2 (cf. Figure S2 for the support itself). All catalysts exhibit a peak at around 2θ = 25°, which is assigned to diffraction from the (002) plane of graphene aerogel43 and also display the peaks of bimetallic Cu–Ni, corresponding to the crystal phases of CuO, NiO, Cu, Ni, and Cu–Ni alloy.44,45 The XRD results confirm the successful loading of Cu–Ni onto graphene in each of the two synthesis routes. In order to confirm the crystallite sizes (D) of CuO and NiO, the Scherrer equation was applied as follows46

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where β is the full width at half-maximum of the main diffraction peak relating to 2θ and the Scherrer constant (K) is 0.94. It is found that the crystallite sizes of CuO are 6.7 and 8.0 nm, and the crystallite sizes of NiO are 5.2 and 8.7 nm for 15% Cu–Ni/graphene aerogel from route A and route B, respectively, which are in good agreement with FE-SEM and TEM results. This suggests that two-step metal loading (route A) is an efficient way to avoid the aggregation of metals, which can thus enhance the metal dispersion on graphene aerogel. To investigate the structural properties of the catalysts, N₂ sorption isotherms were obtained; in Figure 2c,d, there can
be seen the type-IV behavior with a H3 hysteresis loop, demonstrating a mesoporous structure. This implies that the effect of metal loading from route A and route B does not affect the graphene aerogel structure. Additionally, the Brunauer–Emmett–Teller (BET) surface areas, pore volumes, and average pore diameters of the as-synthesized catalysts are shown in Table 1. It can be concluded that to prevent agglomeration of metals while still having a high surface area and metal content, the optimum content of loaded Cu–Ni is 15% for these Cu–Ni/graphene aerogel catalysts obtained from both routes. However, the pristine graphene aerogel provides a surface area of about 421 m$^2$ g$^{-1}$, which is higher than those of the prepared catalysts. This is because the loaded metal particles seal the pores of graphene aerogel. Moreover, the pore size distributions of the as-synthesized catalysts (see inset Figure 2c,d) show a major peak at around 3.8 nm, which corresponds to the mesopores inside the graphene aerogel structure.

In order to explain the surface chemical composition of the prepared catalysts, the wide X-ray photoelectron spectroscopy (XPS) spectra of both samples (i.e., 15% Cu–Ni/graphene aerogel from both route A and route B) are presented in Figure 3. There are no impurities found in the survey XPS spectra of 15% Cu–Ni/graphene aerogel catalysts. Only the presence of C, O, Cu, and Ni can be seen on the sample surface (see Figure 3a,d). For both routes, the Cu 2p spectra of 15% Cu–Ni/graphene aerogel catalysts (Figure 3b,e) display two peaks at about 933 and 953 eV, corresponding to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ transitions, respectively, and indicating the presence of metallic copper (Cu$^0$) and CuO (Cu$^{2+}$) species. The Ni 2p XPS spectra in Figure 3c,f illustrate characteristic peaks for Ni species (i.e., Ni$^0$ and NiO), with multiple occurring peaks for the Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ transitions at 854 and 872 eV, respectively. Therefore, the presence of metallic copper and nickel confirms the formation of Cu–Ni alloy in the as-prepared catalysts, which is in line with XRD results. This alloy formation can enhance the electronic activity at the catalytic active sites.

| Table 1. BET Surface Area and Pore Volume of Cu–Ni-Based Catalysts from Route A and Route B |
|---------------------------------|---------------------------------|
| catalysts                        | route A                          | route B                          |
|                                 | BET surface area (m$^2$ g$^{-1}$) | pore volume (cm$^3$ g$^{-1}$)   | BET surface area (m$^2$ g$^{-1}$) | pore volume (cm$^3$ g$^{-1}$) |
| 10% Cu–Ni/graphene aerogel       | 99                               | 0.2653                           | 86                               | 0.1441                           |
| 15% Cu–Ni/graphene aerogel       | 108                              | 0.2567                           | 162                              | 0.1862                           |
| 20% Cu–Ni/graphene aerogel       | 74                               | 0.2382                           | 82                               | 0.1360                           |
| 25% Cu–Ni/graphene aerogel       | 82                               | 0.3306                           | 86                               | 0.1481                           |

The direct synthesis of DMC from CO$_2$ and MeOH was investigated over the prepared Cu–Ni/graphene aerogel catalysts having different bimetallic contents, as shown in Figure 4. As expected, the 15% Cu–Ni/graphene aerogel catalysts from route A and route B provide the best performance in terms of MeOH conversion and DMC yield compared with other loadings. MeOH conversion and DMC yield are found to increase when the Cu–Ni content was increased from 10 to 15% because of the higher amounts of active Cu–Ni metals. However, beyond 15% loading, MeOH conversion and DMC yield decreased because of the lower amounts of active sites, resulting from the agglomeration of Cu–Ni metals. It was found that the 15% Cu–Ni/graphene
aerogel catalyst from route A exhibits a higher MeOH conversion (12.8%, Figure 4a) and DMC yield (ca. 0.5 mgDMC gcat⁻¹, Figure 4b) than that of the best catalyst from route B. This is because the doping of Cu−Ni metals in the first step during hydrothermal process facilitated the dispersion of active phases onto the graphene aerogel framework, leading to enhancement of the catalytic performance. On the other hand, the MeOH conversion and DMC yield of the 15% Cu−Ni/graphene aerogel catalyst from route B are about 10.8% and 0.4 mgDMC gcat⁻¹, respectively. Although the surface area of 15% Cu−Ni/graphene aerogel catalyst from route A is lower than that of 15% Cu−Ni/graphene aerogel catalyst from route B, the former still provides higher catalytic activity. Therefore, it can be concluded that the two-step Cu−Ni loading plays an important role in enhancing catalytic performance.

3. CONCLUSIONS

In summary, we have demonstrated an alternative catalyst preparation route so-called two-step loading of Cu−Ni metals on the graphene aerogel support for use in the production of DMC from CO₂ and methanol. The amounts of Cu−Ni loaded onto graphene aerogel were finely tuned to be 5, 10, 15, and 20% (equimolar Cu/Ni). The 15% Cu−Ni/graphene aerogel catalyst exhibits the highest catalytic performance when compared with other loading amounts. Indeed, the two-step loading of Cu−Ni metals improved the MeOH conversion by 18.5% and DMC yield by 25% compared to that of the Cu−Ni/graphene aerogel catalyst from one-step loading because loading Cu−Ni metals during hydrothermal process can prevent the agglomeration of Cu−Ni metals. This work provides key evidence that two-step loading of Cu−Ni metals on graphene aerogel can be used and may be further developed for other related catalyst families.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Graphite Oxide. Graphite oxide (GO) was prepared using a modification of Hummer’s method. Briefly, 5.0 g of graphite powder (20–40 μm, Sigma Aldrich) and 7.5 g of sodium nitrate (99.5% NaNO₃, QREC) were mixed with 500 mL of sulfuric acid solution (98% H₂SO₄, QREC) and kept under stirring using a magnetic stirrer. Afterward, 40.0 g of potassium permanganate (99% KMnO₄, Ajax Finechem) was gently added to this mixture, and the resulting solution was continuously stirred for 24 h. Deionized
water (500 mL) was diluted into the mixture, and 150 mL of hydrogen peroxide (30% H₂O₂, Merck) was then added dropwise to the diluted mixture while maintaining a vigorous agitation for 24 h. Note that, as these last two steps constitute an exothermic reaction, an ice bath is required to maintain the reaction temperature. Then, the as-synthesized product was washed with deionized water several times in order to remove residual acid and other organic impurities. The prepared GO was collected by centrifugation at 9000 rpm and eventually dried at 50 °C for 24 h.

4.2. Synthesis of Cu−Ni/Graphene Aerogel Catalysts by “Two-Step” Loading. The Cu−Ni/graphene aerogel catalysts were synthesized by two-step loading, as shown in Scheme 1. In the first step, equimolar Cu−Ni precursor was introduced onto GO suspension during the hydrothermal process. In the second step, the mixed Cu−Ni precursor was loaded by incipient wetness impregnation onto the graphene aerogel, which had been obtained via a freeze-drying process (referred as “route A”). Briefly, 0.170 g of GO and 0.060 g of copper nitrate trihydrate [99.5% Cu(NO₃)₂·3H₂O, QREC] were dispersed in 85 mL of deionized water by ultrasonic vibration for 1 h. Then, 0.073 g of nickel nitrate hexahydrate [98% Ni(NO₃)₂·6H₂O, QREC] was added into this mixture, and the mixture was then sonicated for 1 h. The mixture was transferred to a Teflon-lined autoclave and heated at 140 °C for 24 h. Subsequently, the as-synthesized material was frozen at 0 °C for 24 h and freeze-dried at −50 °C for 72 h. Note that, the Cu−Ni metal contents of the as-synthesized material were characterized by inductively coupled plasma optical emission spectroscopy (ICP–OES) analysis, which are given in Table S1. Next, copper nitrate trihydrate (0.204 g) and nickel nitrate hexahydrate (0.379 g) were added onto 1.0 g of the as-synthesized material to obtain the 15% Cu−Ni/graphene aerogel catalyst and then dried at 100 °C for 12 h. Finally, the 15% Cu−Ni/graphene aerogel catalyst was reduced by sodium borohydride solution (98% NaBH₄, HIMEDIA) with a 1:2 molar ratio of metals/NaBH₄. The product was collected by centrifugation and washed with deionized water several times. The as-synthesized catalyst was dried at 100 °C for 12 h. Note that, 10, 20, and 25% of Cu−Ni/graphene aerogel catalysts were also prepared by the same synthesis route as that used for the 15% Cu−Ni/graphene aerogel catalyst.

4.3. Synthesis of Cu−Ni/Graphene Aerogel Catalysts from “One-Step” Loading. The same series of Cu−Ni/graphene aerogel catalysts, as described in Section 4.2, were synthesized by one-step loading—Cu−Ni was loading onto the freeze-dried graphene aerogel by incipient wetness impregnation (so-called “route B”), as shown in Scheme 1. Briefly, Cu(NO₃)₂·3H₂O and Ni(NO₃)₂·6H₂O were loaded onto the graphene aerogel, and the resulting catalyst was dried at 100 °C for 12 h. The Cu−Ni/graphene aerogel catalyst was obtained after reduction by NaBH₄ solution with a 1:2 molar ratio (Cu−Ni:NaBH₄) and dried at 100 °C for 12 h.

4.4. Characterization of Catalysts. XRD patterns were obtained by an X-ray diffractometer (XRD: Bruker D8 ADVANCE) with Cu Kα radiation (λ = 1.54 Å) at 40 kV and 30 mA in the 2θ range from 5° to 90°. Nitrogen physisorption measurements were obtained at −196 °C using a Quantachrome Autosorb-IC analyzer to determine the specific surface area. The pore size distribution was evaluated by BET and Barrett–Joyner–Halenda methods. The amounts of loaded Cu−Ni metals were measured by ICP–OES, (Agilent 700-ES series). XPS analysis was conducted with monochromatic Al Kα radiation (hv = 1486.6 eV) on AXIS Ultra DLD (Kratos Analytical Ltd.), in order to analyze the surface chemical compositions. The surface morphology of the samples was assessed by a field-emission scanning electron microscope (FE-SEM; JEOL, JSM-7600F), operating at 5 kV with Pt-coating of the sample (thickness of ca. 2 nm). The nanostructure of the samples was observed by a transmission electron microscope (TEM; JEOL JEM-3100F) operating at 300 kV. Note that, the samples were prepared by dispersion in ethanol solution through sonication and then coated on copper grids having 200 mesh.

4.5. Catalytic Reaction Test. The catalytic activity of the as-synthesized catalysts for direct synthesis of DMC from CO₂ and MeOH was evaluated via a liquid-phase reaction between MeOH and pressurized CO₂ using a stainless steel reactor (3 cm diameter and 12 cm height) equipped with a temperature controller and a magnetic stirrer. First, 0.1 g of catalyst and 5 mL of MeOH were added into a stainless steel reactor, and CO₂ was then pressurized into the reactor, until the desired pressure (3 MPa) was attained. Subsequently, the reactor was heated to 110 °C under continuous stirring and kept isothermal for 4 h; after this, it was cooled to below 5 °C. Finally, the obtained product was analyzed by a gas chromatograph (Hewlett Packard 5890-series II) equipped with a flame ionization detector and capillary column HP-1.
Characterization of the graphene aerogel support, including FE-SEM images, TEM images, and N₂ sorption isotherms, and the characterization of the GO, graphene aerogel, and 15% Cu–Ni/graphene aerogel catalysts including XRD patterns, XPS spectra, and Raman spectra.

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Notes

The authors declare no competing financial interest.

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