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Graphene supported Cu nanoparticles as catalysts for the synthesis of dimethyl carbonate: Effect of carbon black intercalation

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ABSTRACT

Reduced graphene oxide (rGO) intercalated with a carbon black (CB) supported copper catalyst (Cu/rGO-CB) was employed in the synthesis of dimethyl carbonate (DMC) via liquid-phase oxidative carbonylation of methanol. The conversion of methanol and the space-time yield of DMC (STY_{DMC}) over Cu/rGO-CB reached 5.6% and 2757 mg/(g h), higher than over a Cu/rGO catalyst, 4.7% and 2334 mg/(g h), respectively. The characterization indicates that CB particles, acting as spacers, ensured the high utilization of graphene layers and enhanced the interaction between Cu and the support, and the oxygen containing groups on the surface of CB play an important role in stabilizing Cu clusters. In comparison with Cu/rGO, the loss of copper concentration in Cu/rGO-CB is significantly decreased, from 15.37% to 1.96%. Catalyst reusability tests show that Cu/rGO-CB could be reused five times without almost any catalytic activity loss, implying distinct enhanced catalytic stability compared to the Cu/rGO catalyst.

1. Introduction

The research and development of dimethyl carbonate (DMC) have recently received significant attention because of its low toxicity and high biodegradability, which make it a promising environmentally benign compound and a safer alternative to poisonous dimethyl sulfate and phosgene [1,2]. The direct oxidative carbonylation of methanol using CuCl as a catalyst in the liquid phase is one of the most promising commercial processes for the production of DMC. Nevertheless, severe catalyst deactivation is frequently observed. The short lifespan of conventional catalysts inhibits their applications because of the loss of active species under elevated reaction conditions. In fact, in addition to the DMC synthesis, many liquid phase reactions are also faced with this problem [3–5], such as biorefineries [6], ammoxidation [7], the hydrolysis of cellulose [8] and dehydration of carbohydrates [9]. In summary, the loss of active species is a common and urgent problem in liquid phase reactions.

In order to solve this problem, a variety of catalysts have been explored for the synthesis of DMC. Li et al. [10] found that the addition of 1, 10-phenanthroline, used as a ligand, could dramatically enhance the catalytic performance of CuCl and effectively inhibit the corrosion of the reaction system. However, the recovery and reuse of the efficient homogeneous catalyst, CuCl/Phen, are not so easy. Liu [11] and coworkers first demonstrated that ionic liquid-mediated Cu salts are an efficient catalyst system for oxidative carbonylation of methanol to produce DMC. Furthermore, the catalytic system can be reused for at least five recycles with only a slight decrease in activity. Meanwhile, different materials have been employed to stabilize the active Cu species, such as SBA-15 [12], SiO_2-TiO_2 [13], zeolite [14], activated carbon (AC) [15,16] and carbon hollow spheres [17].

In our previous study [17], Cu@carbon york-shell nanocomposite exhibited promising catalytic property and stability towards DMC synthesis, which could be attributed to a spatially confined effect on the enhanced immobilization of Cu nanoparticles (NPs). Furthermore, Li et al. [15] investigated the catalytic properties of Cu/AC catalysts in DMC synthesis. It was indicated that the increased surface oxygenated groups have a significant influence on both the dispersion and valence distributions of Cu species, as well as the catalytic performance of the resulting Cu-based catalysts. In conclusion, the modification of the spatial structure or surface chemistry can be an effective method to improve the catalytic performance of carbon-supported Cu catalysts.

Recently, a variety of carbon materials representing a unique family of supports that possess unique structures and properties, including highly porous frameworks and enhanced stability in both acidic and basic media, have been synthesized successfully, such as AC, carbon nanotubes, graphite, diamond, fullerenes, carbon black (CB) and graphene [18–20]. Among all carbon allotropes, graphene,

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a two-dimensional (2D) single-layer sheet of graphite comprising a planar hexagonal lattice of carbon atoms [21], exhibiting considerable potential as excellent supporting material for various heterogeneous catalysts since it affords high theoretical specific surface area of about 2600 $m^2 g^{-1}$, has attracted increasing attention [22–24]. Generally, graphene samples with two or more layers have being investigated with equal interest [25]. Notably, the high surface area of graphene materials does not depend on the distribution of pores in solid state, but comes from the interconnected open channels between graphene layers distributed in a 2D architecture [26]. In addition, due to the inevitable carbon vacancy defects and functional groups presented in chemically derived graphene, metal ions can be adsorbed and intercalated into graphene sheets to form thermally stable composite materials. More importantly, usage of the support can increase the stability of the catalyst, optimize the dispersion of the active components of the catalyst and provide important chemical, mechanical, thermal and morphological properties. Fu et al. [27] reported that interfaces between graphitic overlayers and metal surfaces act as 2D confined nanoreactors, in which catalytic reactions are promoted. This finding contrasts with the conventional knowledge that graphitic carbon poisons a catalyst surface but opens up an avenue to enhance catalytic performance through the coating of metal catalysts with controlled graphitic covers.

Tremendous progress has so far been achieved in composite materials. CB, which has a large specific surface area, cheap price and can form an open space network channel, is recognized as a promising candidate as a carbon support material. Flexible reduced graphene oxide (rGO)-CB hybrid films with different CB contents have been prepared by a simple vacuum filtration method. The CB particles between the graphene layers act as spacers that prevent the restacking of graphene layers and inhibit the agglomeration of graphene sheets [28]. Fan et al. [26] prepared rGO-CB pulverous composites by ultrasonication and in-situ reduction methods. The as-fabricated rGO-CB powder-composite electrode shows enhanced capacitance and rate capability. Currently, the reported rGOCB material has only been used in electrochemistry. It is desirable to develop a new-type of supported-catalysts for the synthesis of DMC to take full advantage of rGO-CB. Therefore, extensive efforts have been exerted to develop such catalysts in our work.

It is well known that metal oxide (or metal hydroxide) NPs can also act as spacers in the interlayers of graphene sheets to prevent aggregation, thereby increasing the interplanar spacing and contact area with the reactant [29,30]. Various strategies have been developed for the synthesis of metal or metal oxide-embedded graphene composites, including chemical methods [31], photo-synthesis [32] and microwave-assisted synthesis [33,34]. Several studies have addressed the applications of graphene for various catalytic reactions. Most of the reported graphene-based catalysts exhibit high activity and stability [35]. Some studies [36] have demonstrated that the catalytic activity can be influenced by the metal active site supported on graphene. Meanwhile, the oxygen functional groups on the surface of the support also have an effect on the catalyst structure and catalytic activity [37].

In our work, an innovative and economical approach has been employed for synthesizing a Cu/rGO-CB catalyst by a simple ultrasonication and vacuum filtration process. The synthetic effects of rGO sheets and CB lead to a large accessible surface area for the Cu NPs. As spacers, CB particles can not only increase the distance between the graphene sheets, but also provide rapid diffusion paths for reactants in double-layer films. Furthermore, CB can also provide adsorption sites for Cu NPs. As a result, the CB spacers ensure high specific surface utilization of graphene layers, as well as the open nanochannels provided by the three-dimensional rGO-CB hybrid material. Using catalyst characterization, the interaction between Cu NPs and graphene, as well as CB, has been investigated, which is also useful for understanding the interaction between Cu NPs and the support. The properties of the Cu/rGO-CB catalyst were evaluated by liquid-phase oxidative carbonylation of methanol, with excellent cycling stability exhibited.

2. Experimental

2.1. Materials

GO was obtained from Jinneng Co., Ltd. of Institute of the Coal Chemistry, Chinese Academy of Sciences (Taiyuan, China). CB was obtained as a commercial product from the Xinhua chemical plant (Taiyuan, China). Copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) was purchased from Sinopharm Chemical Reagent Co., Ltd. Methanol, ethanol, hydrazine and *N*,*N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). Hexadecyltrimethyl-ammonium Bromide (CTAB) was obtained from Shanghai Nuotai Chemical Co., Ltd. All chemicals were of analytical grade and were used without any further purification.

2.2. Cu/rGO-CB and Cu/rGO nanocomposite synthesis

For the preparation of the Cu/rGO-CB catalyst, GO (200 mg) was first mixed with 200 mL of absolute ethanol under ultrasonic sonication at room temperature for 2 h. Meanwhile, 50 mg of CB (>200 mesh) was dispersed into 200 mL of absolute DMF under ultrasonic sonication for 1 h. Subsequently, the as-prepared CB dispersions with a volume of 5 mL were diluted with 50 mL of DMF. Then, the two suspensions were mixed and kept under ultrasonic sonication for another 2 h. Next, the mixture was magnetically stirred to form a homogeneous mixture using a water bath at room temperature. In the subsequent step, 80 mg of $Cu(NO_3)_2{\cdot}3H_2O$ and a small quantity of CTAB, acting as a dispersing agent, were added to the mixture, while maintaining a vigorous agitation for 3 h at 90 °C. Ultimately, 0.5 mL of hydrazine (50 wt.% in water) was added to the mixture dropwise. The solution turned from deep orange to black within minutes, followed by the appearance of a black precipitate to yield Cu/rGO-CB composites. Finally, the solid was filtered and washed several times with distilled water and alcohol, then dried at 100 °C for 12 h in a vacuum oven. Hitherto, the resulting sample labeled as Cu/rGO-CB was prepared. Similarly, as a comparison, Cu/rGO was synthesized without CB. Scheme 1 shows the fabrication scheme for the Cu/rGO-CB nanocomposite.

2.3. Catalyst characterization techniques

The analysis of the crystal structure and phase composition of the catalyst was completed using X-ray diffraction (XRD) on a Rigaku D/Max 2500 system with a Cu Kα radiation ($\lambda = 1.54056$ Å) and a graphite monochromator. The voltage and current of the measurements were operated at 40 kV and 100 mA, and the scanning speed was 8°/min at a scanning region of 5–85°. The crystallite size of Cu metal for the catalysts was calculated using the Scherrer equation.

The Cu K-edge X-ray absorption fine structure (XAFS) analysis of the catalysts was performed by the Soft X-ray Microcharacterization Beamline (SXRMB) of the Canadian Light Source. SXRMB is a medium energy beamline with a range of 1.7–10 keV. The monochromator of the beamline consists of two pairs of crystals, InSbC (111) and Si (111).

A Fourier transform infrared (FT-IR) spectroscopy analysis was conducted to explore the change of oxygen-containing functional groups on GO after reduction by hydrazine using a FT-IR spectrometer (Nicolet Nexus 470, Thermo Nicolet, Madison, WL USA) in the range of 500–4000 cm^{-1}.