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Novel application of thermally expanded graphite as the support of catalysts for direct synthesis of DMC from CH_3OH and CO_2

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ABSTRACT

Novel Cu–Ni bimetallic catalysts supported on thermally expanded graphite (TEG) were prepared as an example to show the particular characteristics of TEG as a carbon support material. The structures of TEG and the synthesized Cu–Ni/TEG catalysts were characterized using BET, FTIR, TG, SEM, TEM, XRD and TPR techniques. The catalytic activities of the prepared catalysts were investigated by performing micro-reaction in the direct synthesis of dimethyl carbonate (DMC) from CH_3OH and CO_2. The experimental results indicated that the prepared Cu–Ni/TEG catalysts exhibited highly catalytic activity. Under the optimal catalytic conditions at 100 °C and under 1.2 MPa, the highest conversion of CH_3OH of 4.97% and high selectivity of DMC of 89.3% can be achieved. The highly catalytic activity of Cu–Ni/TEG in DMC synthesis can be attributed to the synergetic effects of metal Cu, Ni and Cu–Ni alloy in the activation of CH_3OH and CO_2 and the particular characteristics of TEG as a carbon support material.

1. Introduction

Dimethyl carbonate (DMC), an environmentally building block, can be used as fuel additives (replacement for methyl tert-butyl ether (MTBE)), carbonylating agents, alkylating agents and polar solvents. Moreover, DMC exhibits wide applications in the synthesis of polycarbonate and polyurethane [1]. Several commercial processes have been developed for the synthesis of DMC, including the methanolysis of phosgene [1], oxidative carbonylation of methanol [2] and transesterification route [3]. However, these processes have some shortcomings. In contrast, the direct synthesis of DMC from CH_3OH and CO_2 is a much more attractive method, because CO_2 is utilized as a carbon source and poisonous or corrosive reagents such as phosgene are avoided in this route [4,5]. Although this route is the most promising method to synthesis DMC, nevertheless, DMC yield in this route is relatively low due to the fact that CO_2 is highly thermodynamically stable and kinetically inert and due to the deactivation of catalysts by in-situ produced water. In order to solve these problems, many attempts have been tried. However, very limited progress has been made. Therefore, novel catalysts with high performance are required.

Up to date, some catalysts have been reported to be effective for one-step synthesis of DMC from CH_3OH and CO_2, including organometallic compounds [6,7], metal tetra-alkoxides [8], potassium carbonate [9], zirconia [10], $H_3PW_{12}O_4$–ZrO_2 [11], H_3PO_4–V_2O_5 [12], Cu–Ni/VSO [13] and Cu-(Ni,V,O)/SiO_2 [14]. However, the yield of DMC was reported to be low, even in the presence of dehydrates, additives such as $CaCl_2$ [15], 2.2-dimethoxy propane (DMP) [16], molecular sieves [17] and light illumination [14,18]. More recently, this reaction has been performed under supercritical conditions [19,20]. However, the rigorous method is difficult to control.

The supported transition metal particles exhibit high catalytic effects in DMC synthesis [12,14,18]. To develop efficient catalytic systems, more efforts have been devoted to the uses of various metals as catalysts. However, the support used in this catalytic system is much less explored. A catalyst support is not merely a carrier, but it may also contribute significantly to the activity of catalyst, since the surface of the support may determine its interaction with the precursor of the active catalytic species. Therefore, the choice of a suitable supporting material is an important factor to be considered, and it may affect the performance of supported catalysts [21,22]. To date, the supports of loaded catalysts used in the direct synthesis of DMC were mainly inorganic oxides or compound oxides, including SiO_2 [14,23], ZrO_2 [11], MgO–SiO_2 (MgSiO) [24], V_2O_5–SiO_2 (VSO) [13], ZrO_2–SiO_2 (ZrSiO) [25] and ZrO_2–CeO_2 [16]. However, the rather high cost of commercial supports, the low activity and short longevity of catalysts limited the scale of their application in the industrial catalysis. The development of novel supports with the required properties from inexpensive raw materials is highly desired.

Carbonaceous materials have long been used in heterogeneous catalysis as they satisfy most of the characteristics required for a

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suitable support [26]. A number of carbon materials have been used to prepare carbon-supported catalysts (activated carbon, activated carbon fiber, graphite, carbon black, graphite intercalation compounds and carbon nanotubes) [26–30]. Among them, graphite has many unique properties and is attracting increasing attention as a novel candidate of supporting material in heterogeneous catalysis. Graphite is the most stable allotrope of carbon in STP conditions, and there is a vast amount of natural graphite mined worldwide. Graphite provides good electrical conductivity (10^6 S/m at ambient temperature) and layered structure with a *c*-axis lattice constant. However, very little graphite is currently used as a catalyst support due to its low surface area and low surface activity. Thermally expanded graphite (TEG), however, is a kind of wormlike material came from the vaporization of the graphite intercalation compounds (GICs) and hence, a significant expansion of the material along the crystallographic *c*-axis occurs. As a result, the volume of TEG increased tens and hundred times compared to GICs [31], and meso-porous structure, big surface area and high surface activity were created in the structure of TEG. The special "sandwich" structure and long distance between the carbon layers made it easy to insert atoms or molecules into the carbon sub-layers. Furthermore, the multi-pores, functional acids and the OH groups will facilitate physical and chemical adsorption between the graphite and the transition metal solution [32–34]. These functional groups on the graphite surfaces that anchor the metal cations and benefit the dispersion provided crucial necessities to prepare the supported catalysts using TEG as substrates. The morphology and pore structure of TEG can be modified by altering preparation conditions, and there are several reports on the preparation procedures, pore structures and applications of TEG [35–37].

TEG has been widely used in gasketing, adsorption, electromagnetic interference shielding, vibration damping, electrochemical applications, stress sensing, thermal insulator and supporting material. However, the information about the use of TEG as a catalyst support in DMC synthesis is sparse. In our previous work [38], TEG supported Cu–Ni bimetallic catalysts have been prepared and applied successfully to the direct synthesis of DMC from CH_3OH and CO_2. In this report, Cu–Ni/TEG bimetallic catalysts were prepared using a conventional wetness impregnation method, and applied to one-step direct synthesis of DMC with an attempt to illustrate the superior properties of TEG and discuss its performance as a novel catalyst support. This is the first demonstration that TEG can be used as an efficient catalyst support for the direct synthesis of DMC.

2. Materials and methods

2.1. Materials and preparation

TEG was prepared from natural flake graphite (NFG). Graphite intercalation compounds yielding TEG upon a thermal shock were obtained using chemical oxidation intercalation. The schematic illustrating the preparation of TEG was shown in Fig. 1. The NFG (supplied by Hua Dong Shi Mo Co., Ltd., China) was dried at 110 °C in a vacuum oven for 24 h before use. NFG, concentrated H_2SO_4 (A.R. 98%) and $KMnO_4$ (A.R.) were mixed in a flask at a weight ratio of 5:30:1, with constant stirring at 50 °C for 24 h to yield GICs. $KMnO_4$ served as an oxidizer and H_2SO_4 was an intercalant. The mixture was carefully washed and filtrated with distilled water until the pH level of the solution reached 6. After being dried at 100 °C for 24 h, the GICs were rapidly expanded at 900 °C for 15 s in a laboratorial muffle furnace to form TEG. The produced wormlike TEG had a low density (0.01–0.005 g/cm^3). The prepared TEG was washed with NaOH (0.1 mol/L) aqueous solution and distilled water to remove the remaining acid on TEG and the filtrated specimen was dried at 100 °C for 12 h.

The Cu–Ni/TEG bimetallic catalysts were prepared via the impregnation of the TEG with a water–alcohol solution containing $Cu(NO_3)_2{\cdot}3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$. The simple mechanism of preparation was shown in Fig. 1. The mixture solution was stirred at ambient temperature for 24 h, ultrasonacated for 2 h, aged for 24 h, followed by rotavaporating to eliminate the solvent. After being dried at 90 °C overnight, the resulted product was calcined at 500 °C for 3 h in N_2 flow to give the catalyst precursors (CuO–NiO/TEG), and further reduced in H_2 at 600 °C for 3 h. The total metal content in the catalyst varied from 0 to 30 wt.%, and Cu/Ni molar ratio ranged from 1/5 to 5/1. According to the experimental results, when no metal was loaded on TEG, the reaction did not take place at all. With an increase in metal content, catalytic activity was found to generally increase. When metal content reached 20 wt.% and Cu/Ni ratio was 2/1, the catalyst showed the best catalytic activity in the direct synthesis of DMC. Therefore, a total loading of metal CuO + NiO = 20 wt.% and the metal molar ratio of Cu/Ni = 2/1 were used in the optimized catalytic system.

2.2. Characterizations

2.2.1. BET measurement

The BET surface area and pore size distribution of sample were measured by N_2 physisorption in liquid N_2 (77 K) using a Micromeritics ASAP 2010 instrument. Prior to analysis, the samples were degassed at 300 °C for 3 h in a stream of helium to obtain a residual pressure of less than 10^{-3} torr. The range of relative pressures (P/P_0) varied from 0.0009 to 0.95 and the equilibration time was 10 s. The adsorption data on a nonporous carbon [39] were used to evaluate the adsorbed film thickness (t) values at various relative pressures (P/P_0). The t-plots were constructed by plotting the adsorbed amount V vs. t at various relative pressures. The modified MP method was then used to calculate the pore size distribution. More details can be found elsewhere [40].

2.2.2. Infra-red spectroscopy measurement (FTIR)

The FTIR spectra of samples were recorded on an Analect RFX-65A type FTIR spectrophotometer in a KBr matrix in region 4000–400 cm^{-1}.

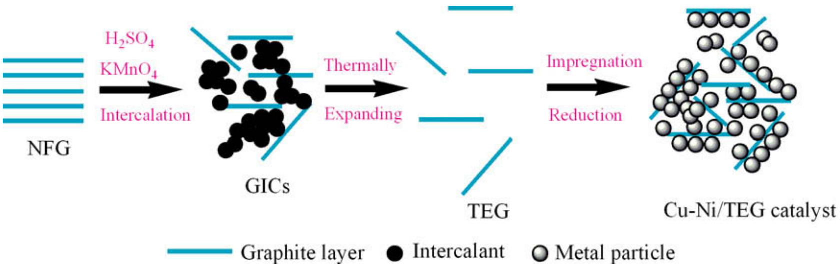

Fig. 1. A schematic illustration the formation of TEG and the synthesis of Cu–Ni/TEG bimetallic catalyst.