Ordered mesoporous silica-carbon-supported copper catalyst as an efficient and stable catalyst for catalytic oxidative carbonylation

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HIGHLIGHTS

- Cu/MSC behaves high activity and stability than that without silica doping.
- The hybrid structure of Cu/MSC shows enhanced metal support interaction.
- The presence of silica promotes the dispersion of Cu species in MSC support.
- Cu/MSC shows more resistance to aggregate and difficult to be oxidized than Cu/MC.

GRAPHICAL ABSTRACT
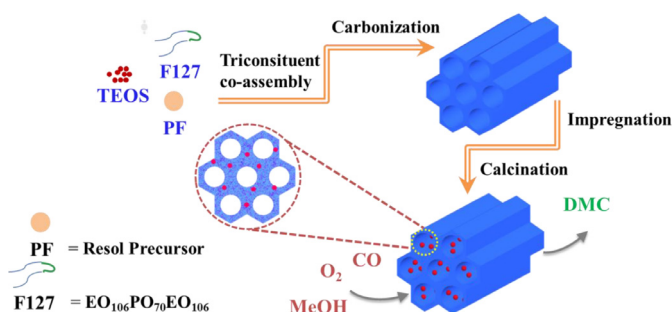
ABSTRACT

Ordered mesoporous silica-carbon (MSC) nanocomposites with homogeneously distributed networks were synthesized by the triconstituent co-assembly method and used as supports of Cu catalysts for dimethyl carbonate (DMC) synthesis. The introduced silica contributes to the considerably increased pore size (~5.8 nm), the enhanced metal-support interaction and high dispersion of Cu nanoparticles (~3.8 nm) confined in the mesopores. An improved catalytic performance of Cu/MSC is achieved, reaching a DMC selectivity up to 90% at a methanol conversion of 1.5%, and a stable performance during five recycling runs. On the other hand, the benchmark Cu/MC catalyst undergoes a dramatic decrease of methanol conversion, from 1.3 to 1.0%, accompanied by a 27% reduction of DMC space-time yield (STY_{DMC}). The mechanism through which the hybrid carrier affects the catalytic performance is analyzed using DFT calculations. The results show that the binding energy of Cu on MSC is greatly increased while the energy barrier to CO insertion for DMC formation is reduced evidently, thus enhancing the metal-support interaction and, in turn, the catalytic performance.

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1. Introduction

With raising awareness of environmental problems, the design of green chemicals as well as clean and eco-friendly synthesis processes, which avoid or minimize the utilization of poisonous or harmful substances, is attracting increasing attention. Dimethyl carbonate (DMC) has attracted immense interest because of its biodegradability, low toxicity and low bioaccumulation, as well as excellent solubility [1,2]. In the synthetic chemistry and alternative energy industries, DMC is utilized widely as a versatile synthetic reaction intermediate, a nonpoisonous solvent and a safe substitute for phosgene and fuel additives [3–5]. In addition, among several methods for DMC synthesis, oxidative carbonylation using CO, O_2 and methanol as raw materials is in line with the principles of green chemistry and represents one of the proposed favorable processes [6–9].

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The catalysts used in this reaction can be divided into two categories: chlorine-containing and chlorine-free catalysts. Since chloride-containing systems usually suffer from many problems, such as the degradation of DMC quality, equipment corrosion, and catalyst deactivation, chloride-free catalyst are being investigated extensively [10–12]. Recently, copper and copper oxide supported on activated carbon (AC), have been widely studied due to their good catalytic performance [13–15]. The main drawback of these catalysts is that the activated carbon-based materials traditionally used are characterized by a broad pore size distribution, ranging from micropores to macropores [16] and the dominating microporous structure has restricted the dispersion of the active component on the support, hindering the catalytic activity [17,18]. Highly competitive carbon materials for catalysis should therefore combine a controlled porosity and surface chemistry. In comparison with conventional AC carriers, periodic mesoporous carbon (MC) materials have higher specific surface areas, larger pore volumes, and a more uniform and tunable pore sizes, all of which facilitate the diffusion of reactants and products [19–21]. Nevertheless, contrarily to traditional refractory oxide supports such as silica, alumina or titania, the carbon surface is less reactive and hydrophobic; thus, a weak interaction between the guest and the support generally favors an agglomeration of the guest molecules, limiting their dispersion [22,23]. Hence, there is still a desire to modify the surface chemistry of carbon materials to increase their hydrophilicity and favor dispersion.

Hybrid mesoporous materials, such as organic-inorganic nanocomposites, have received considerable attention because they can be designed to generate remarkable and complementary properties, which cannot be obtained in a single component [24–27]. Similarly, mesoporous silica-carbon (MSC) nanocomposites carry the advantages of both their organic carbon constituent, such as flexibility and versatility for further functionalization, and of the inorganic silica component, such as hydrophilicity, good thermal and mechanical properties and an acceptable stability [28,29]. These superior textural characteristics make MSC promising candidates for their use as catalyst supports. For instance, Wan and co-workers have reported that the ordered MSC nanocomposite supported palladium catalysts show superior catalytic activity in water-mediated coupling reactions of chlorobenzene, and the catalyst can be reused more than 20 times with negligible metal leaching [16]. Based on these results, it is reasonable to envisage that MSC-supported Cu catalyst will display an enhanced catalytic activity and excellent stability when applied to DMC synthesis. To the best of our knowledge, little research has been carried out in this direction.

Herein, MSC was selected as supporting material for the preparation of Cu catalyst (Cu/MSC) and its catalytic performance for DMC synthesis was studied. Am MC-supported Cu catalyst (Cu/MC) was also studied to allow a comparative evaluation of the catalytic performance of the Cu/MSC catalyst. Through comprehensive characterizations and density functional theory (DFT) calculations, the influence of silica doping in MC supports on the physicochemical properties and the catalytic activity of Cu/MSC catalyst in DMC synthesis has been investigated in detail.

2. Experimental section

2.1. Materials

Pluronic F127, a block copolymer of ethylene oxide (EO) and propylene oxide (PO) (M_{av} = 12,600, $EO_{106}PO_{70}EO_{106}$), was purchased from Sigma-Aldrich (St. Louis, MO, USA). Phenol, formaldehyde (37 wt%), tetraethyl orthosilicate (TEOS), sodium hydroxide (NaOH), hydrochloric acid (HCl), methanol (CH_3OH), ethanol (C_2H_5OH) and copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were of analytical grade and used without further purification. Deionized water obtained from a Milli-Q system (Millipore, Bedford, MA, USA) was used in all experiments. O_2 (>99.99%) and CO (>99.99%) were supplied by the Beijing ZG Special Gases Science&Technology Co., Ltd.

2.2. Catalyst preparation

2.2.1. Preparation of resol precursors

The resol precursor was prepared according to procedures reported in the literature [30]. In a typical procedure, 6.10 g of phenol was melted at 40–42 °C in a flask and mixed with 1.30 g of a 20 wt% NaOH aqueous solution under stirring. After 15 min, 10.50 g of formaldehyde solution (37 wt%) were added dropwise below 50 °C. Following further stirring for 1 h at 70–75 °C, the mixture was cooled to room temperature (RT) and the pH value was adjusted to about 7.0 by adding a 2.0 mol/L HCl solution. Water was then removed by vacuum distillation below 50 °C and the final product was redispersed in 65 g of ethanol. The NaCl precipitate was separated by filtration, and the filtrate, the resol precursor with a concentration of 20 wt% in ethanol, was collected.

2.2.2. Preparation of ordered mesoporous silica-carbon nanocomposites

The ordered MSC supports were synthesized via a surfactant-templating method by triconstituent co-assembly of resol, oligomer silicates from TEOS, and copolymer Pluronic F127 template [31]. In a typical synthesis, 1.6 g of triblock copolymer F127 were dissolved in 8.0 g of ethanol solution with 1.0 g of 0.2 mol/L HCl and stirred for 1 h at 315 K to afford a clear solution to which 2.08 g of TEOS and 5.0 g of resol precursor solution (containing 1.0 g of resol) were then added in sequence. After being stirred for 2 h, the mixture was casted onto several dishes. After ethanol evaporation at RT for 5–8 h and thermopolymerization at 100 °C for 24 h, the as-made products, flaxen and transparent membranes were scraped from the dishes and grounded into fine powders. Calcination was carried out in a tubular furnace at 900 °C for 2 h under N_2 flow to get the MSCs. The heating rate was 1 °C /min below 600 °C and 3 °C /min above 600 °C.

2.2.3. Preparation of ordered mesoporous carbon nanocomposites

The MC support was prepared by a solvent evaporation-induced self-assembly (EISA) method [30]. In a typical preparation, 1.0 g F127 was dissolved in 20.0 g of ethanol and 5.0 g of 20 wt% resols ethanol solution were added under stirring for 10 min. The following procedure was the same as that adopted for MSC. The as-made product was calcined at 900 °C in N_2 to get MC.

2.2.4. Preparation of Cu catalyst

Supported Cu catalysts loaded on different carriers with a Cu content of 5 wt% through excessive wetness impregnation. Typically, 30 mL of distilled water containing 0.1 g $Cu(NO_3)_2 \cdot 3H_2O$ were impregnated with 0.5 g of dry mesoporous carrier. The mixture was heated to 70 °C and constantly stirred until complete evaporation; it was then dried at 120 °C overnight. The catalyst was heated at a rate of 3 °C/min up to 450 °C and reduced for 2 h by a 10 vol% H_2/N_2 stream. At the end of this procedure, the Cu/MSC and Cu/MC catalysts were obtained.

2.3. Characterization

Transmission electron microscopy (TEM) analysis was carried out on a JEM 2100 F field emission transmission electron microscope (JEOL, Tokyo, Japan) equipped with an associated energy-