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Full Length Article

Cu nanoparticles encapsulated with hollow carbon spheres for methanol oxidative carbonylation: Tuning of the catalytic properties by particle size control

Ruina Shi, Juan Wang, Jinxian Zhao, Shusen Liu, Panpan Hao, Zhong Li, Jun Ren*

Key Laboratory of Coal Science and Technology (Taiyuan University of Technology), Ministry of Education and Shanxi Province, 030024 Taiyuan, China

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ABSTRACT

Cu nanoparticles (NPs) encapsulated within a hollow carbon spheres (Cu@HCS) is an effective catalyst with optimal structural design for the oxidative carbonylation of methanol to dimethyl carbonate (DMC). Control of the structural properties of both the shell and the core plays a vital role in determining the catalytic properties. In this study, mesoporous HCS with an average diameter of 190 nm and a shell thickness of 15 nm were obtained using silica microspheres as a hard template and by tuning the amount of resorcinol and formaldehyde. Cu@HCS catalysts were fabricated by hydrothermal impregnation followed by hydrogen reduction, and the size of Cu NPs was delicately controlled by varying heating rate of reduction process. The results show that a thin mesoporous carbon shell of Cu@HCS is beneficial to the diffusion of reactants and products, and that Cu NPs with very small size can provide a large active specific surface area. In comparison with the commercial CuCl catalyst, the Cu@HCS-5 catalyst displays superior catalytic activity; its turnover frequency and apparent activation energy reaches 23.1 h^{-1} and 20.5 $kJ{\cdot}mol^{-1}$, respectively. In addition, it exhibits higher stability than that of CuCl because the carbon shell prevents the aggregation and leaching of copper NPs during the reaction. With the advantages in catalytic activity, corrosion effect, and recovery performance, the Cu@HCS catalyst has a promising potential for realizing the cleaner production of DMC.

1. Introduction

The production volume of the green chemical dimethyl carbonate (DMC) has increased due to its applicability as an intermediate in organic synthesis, a high-quality solvent, as well as a gasoline additive [1–5]. Among the various synthetic routes, the oxidative carbonylation of methanol (MeOH) is considered a promising process for the DMC production. Cuprous chloride (CuCl) is employed as a commercial catalyst for DMC synthesis via the liquid-phase process, which was firstly developed by Enichem Company in 1983 [6]. However, the CuCl catalyst suffers from serious corrosion and deactivation owing to the loss of chloride during the reaction. The development of an alternative catalyst has been widely attempted using different strategies. Nam and coworkers [7] supported CuCl on Y-zeolite to lessen the dissolution of active copper species in the reaction system. Fan et al. [8] immobilized CuCl on diamide-modified SBA-15, in which the strong copper-amide ligand interaction increase the reaction efficiency and stability. Mo et al. [9–12] stabilized CuCl using polymeric ligands through the copper-organonitrogen coordination interaction. Dong et al. [13,14] used ionic liquids as reaction media to improve the activity and stability of CuCl catalyst. In general, the problem of equipment corrosion and catalyst deactivation is alleviated to some extent with these methods, but it is far from solved since chlorine still exists in the catalyst or the reaction system. In our opinion, the most promising strategy is to explore chlorine-free catalysts for the synthesis of DMC via liquid-phase oxidative carbonylation of MeOH.

Copper catalysts supported on a variety of carbonaceous materials for DMC synthesis have been intensively studied [15–22]. Activated carbon supported Cu nanoparticles (NPs) are highly active in this reaction [22,23]; however, the highly dispersed copper NPs have high surface energy and therefore tend to aggregate with each other, leading to a decline of the catalytic activity during the reaction. As a novel carbon material, hollow carbon spheres (HCS) have attracted great attention over the last decade because of their outstanding properties including high surface area snd pore volume, porous shells, and accessible interior space [24,25]. Bin et al. [26] synthesized HCS with designated styles of inner constitutional inhomogeneity by controlling the molecular/environmental variables, and it could act as a promising

* Corresponding author at: No. 79 Yingze West Street, Taiyuan 030024, China.
E-mail address: renjun@tyut.edu.cn (J. Ren).

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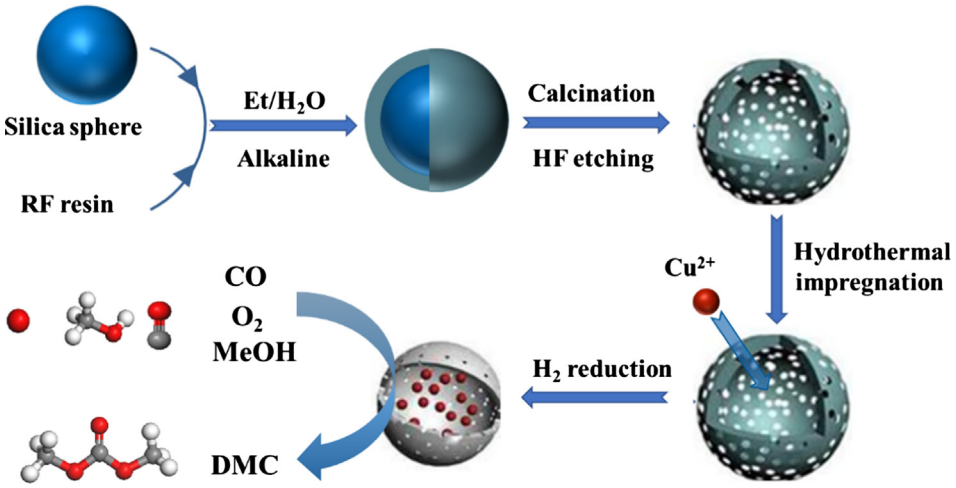

Scheme 1. Procedure for the preparation and application of the catalyst of Cu@HCS.

potential anode material for potassium-ion battery. Liu and coworkers [27] reported HCS with nanoporous shells via annealing precursors under hydrogen contained inert gas, which was used as sulfur host to realize ultralong cycle life of lithium sulfur battery. Peng et al. [28] prepared N-doped HCS (NHCS) through a simple "one-pot" method by appropriately controlling the polymerization of tetraethoxysilane and resorcinol/formaldehyde, and it showed excellent electrocatalytic properties for sensitive H_2O_2 sensing in human serum.

A promising core-shell structure can be further formed by introducing metal NPs into the cavities of the HCS, which has been extensively investigated in heterogeneous catalysis [29,30]. Such a carbon shell can function as a barrier for preventing encapsulated NP from aggregation and can enhance the chemical and thermal stability of active metals in the reaction. Chen et al. [31] assembled a zinc-air battery based on the Co-NHCS nanocomposite via a facile emulsion approach followed by carbonization, which outperformed commercial Pt-C. Zhang and coworkers [32] synthesized SnO_2@HCS via a confined Friedel-Crafts crosslinking of a novel metal-organic compound on the surface of difference-sized SiO_2 template, and it was certified as a high-performance anode material in Li-ion batteries. Huang et al. [33] fabricated a highly active Fe_2C@HCS catalyst for Fischer–Tropsch synthesis, and they found that the products distribution could be manipulated by changing the geometric diameters of HCS.

In our previous work [20], Cu@C catalysts with a core radius of ~20 nm and shell thickness of ~70 nm were prepared by a one-pot synthesis method. They exhibited promising catalytic stability in DMC synthesis. However, the activity is not comparable to that of CuCl catalyst. A pore size of around 4.0 nm for the carbon shell is probably suitable for the reaction; however, the catalytic activity can be greatly limited by a thicker carbon shell, which affects the diffusion of the reactants and products and by the lower active specific areas derived from larger copper NPs. As a result, it is believed that controlling the thickness of carbon shell and the particle size of copper cores may play an important role in improving the catalytic activity of Cu@C in the DMC synthesis [34]. This has been evidenced by a recent study by our group [16]; whereby enhanced catalytic properties were achieved by introducing nitrogen into the carbon shell.

In fact, the hard-template process is more frequently used for the synthesis of HCS as compared with the soft-template method [17,20]. It has certain advantages, such as the tunability of the cavity size and the thickness of the carbon shell [35–37].The wall thickness has reported to be easily controlled by simple change of the amounts of resorcinol (R) and formaldehyde (F) [34].

In the present work, mesoporous HCS with thin carbon shell was synthesized by hard-template method to encapsulate Cu NPs to prepare a potential catalyst, which was tested in the oxidative carbonylation of MeOH to DMC. The particles size of Cu cores was finely controlled by varying the heating rate in the hydrogen reduction process. The structual properties of the HCS and the Cu@HCS catalysts were systematically studied using a combination of advanced characterization techniques. The catalytic performance of CuCl was also tested to present a comparative evaluation with the Cu@HCS catalyst. It is believed that our strategy can be further extended to the optimization of the catalytic performance of various metal@carbon core-shell structures by tuning of the structural parameters of the special host-guest system.

2. Experimental section

2.1. Catalyst preparation

2.1.1. Synthesis of HCS

HCS was prepared using silica primary spheres generated in situ as templates via a simple one-pot process [38]. SiO_2 spheres were previously synthesized through the Stöber method [39]. Typically, tetraethyl orthosilicate (TEOS, Tianjin Kemiou Chemical Reagent Co., Ltd) was mixed with a solution of ethanol, $NH_3{\cdot}H_2O$, and H_2O under vigorous stirring at 25 °C. After 30 min, R and F (Sinopharm Chemical Reagent Co., Ltd) were added and the system was kept stirring all day at room temperature (RT). The precipitates were separated by centrifugation, washed with water and ethanol, and dried at 50 °C overnight. HCS was obtained after carbonization for 5 h at 700 °C under N_2 atmosphere and removal of SiO_2 by 20 wt% HF solution.

2.1.2. Synthesis of Cu@HCS core-shell nanospheres

The catalysts were prepared by ship-in-bottle method, and Cu NPs were introduced through hydrothermal impregnation. Typically, 50 mg of HCS were dispersed in 30 mL of copper nitrate solution (0.24 M). The mixture was hydrothermally treated for 24 h at 120 °C. When the resulting precipitate was cooled to RT, it was collected by centrifugation, washed with ethanol, and dried for 6 h at 50 °C. The obtained solid powder was then calcined under 10 vol% H_2/N_2 atmoshpere for 2 h at 400 °C to obtain Cu@HCS. Similarly, Cu@HCS-1, Cu@HCS-5, and Cu@HCS-10 were fabricated using the heating rates of 1, 5, and 10 °C·min^{-1}, respectively. The strategy for synthesizing Cu@HCS is schematically depicted in Scheme 1.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were recorded at a scanning speed of 2°·min^{-1} in the scanning region from 5° to 85° on a Rigaku D/max 2500 with using Cu Kα radiation (λ = 1.54056 Å). The morphology and structure of the samples were investigated by scanning electron