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MOF derived porous carbon supported Cu/Cu_2O composite as high performance non-noble catalyst

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ABSTRACT

Porous carbon supported copper composite ($Cu/Cu_2O/C$) was synthesized with a facile, low cost and novel method and used as non-noble-metal catalyst for reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by $NaBH_4$. In the synthetic strategy, metal organic framework $Cu_3(BTC)_2$ (also denoted as HKUST-1) was used as both sacrificial template and copper precursor, and phenol formaldehyde resin as carbon precursor. The catalytic Cu/Cu_2O nanoparticles (Cu/Cu_2O NPs) about 40 nm-in-diameter distributed uniformly both on the internal and external surface of the porous carbon flakes, and took up 33.38–37.56 wt% of the $Cu/Cu_2O/C$ composite. Compared with noble metal catalysts, the prepared composite showed comparable high catalytic activity, which was mainly due to their porous structure facilitating diffusion of reactants and products, and the high dispersion of accessible catalytic Cu/Cu_2O NPs on porous carbon. Moreover, the synthesized catalyst can be reused for at least five cycles due to its good stability. These results confirmed that the as-prepared $Cu/Cu_2O/C$ is promising candidate to replace noble metal for catalytic application.

1. Introduction

In catalysis, noble metal catalysts (Au, Ag, etc) have been widely used due to their high selectivity and catalytic efficiency [1,2]. Despite the great progress achieved by far, the scarce and high-cost of noble metal resources make them uneconomic for practical application. With growing emphasis on economical, effective and sustainable development, increasing importance has been placed on utilizing non-noble metal materials for substitute. So far, various metal nanoparticles (NPs) such as copper, aluminum, magnesium, zinc and their oxides have been proved to be applicable in different types of reactions [3–5].

Metal NPs with nanometer scale dimensions are unstable and get self-aggregation easily because of their high surface energy and large specific surface area, which may lead to the deterioration of catalytic efficiency and influent their recycling. Therefore, increasing efforts have been made by loading metal NPs on various supports [6–8]. The supporting matrices reported in literature generally possess low surface areas, and the NPs are usually imbedded into the supports, which results in the poor accessibility of catalysts towards targets [9]. Thereby, supporting materials, with high porous structure, may provide multiple accessible channels for diffusion and transport to take full advantage of the excellent catalytic functionalities of metal NPs.

In recent years, metal-organic frameworks (MOFs) have emerged as a particular class of multifunctional materials due to their modularity, hybrid composition, high surface area, tunable porosity, and various potential applications in different fields [10–12]. Over the past decade, research works have been mostly focused on preparing new MOFs and exploring their applications in gas adsorption and separation. So far, the research on synthesis of inorganic functional materials derived from MOFs is still in early stage [13–15].

Recently, W. Bak et al. have synthesized Cu/Cu_2O@C composite materials from MOF through vapor phase polymerization of phenolic resin inside the nanopores of the MOFs followed by thermolysis under an inert atmosphere [16]. The as-prepared composites preserved the morphology of MOF with micropores.

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Herein we present a different and facile method to obtain porous carbon supported Cu/Cu_2O composite architecture (Cu/Cu_2O/C) by using $Cu_3(BTC)_2$ (also denoted as HKUST-1) as sacrificial template and phenol formaldehyde resin as carbon precursor. The Cu/Cu_2O/C composites possess different pore sizes ranging from micro-to macro-pores, and the Cu/Cu_2O particles 40 nm-in-diameter distributed evenly on the internal and external surface of the porous carbon flakes, which allow the accessibility of the catalytic active sites (Cu/Cu_2O NPs). The resulted Cu/Cu_2O/C materials are employed as catalysts for the reduction of 4-nitrophenol (4-NP) with $NaBH_4$ and shows excellent catalytic performance. Compared with previous noble metal-based systems, copper is several orders of magnitude cheaper than noble metal. To the best of our knowledge, this is the first report on the synthesis of porous carbon supported non-noble Cu/Cu_2O hybrid material by using MOF as both sacrificial template and metal NPs precursor.

2. Experimental

2.1. Chemicals and materials

All reagents were of analytical reagent grade and used without further purification. Copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), anhydrous methanol (CH_3OH), and ammonia ($NH_3 \cdot H_2O$, 25%) were purchased from J&K Chemical Ltd. (Beijing, China). Phenol, 4-nitrophenol (4-NP), benzene-1,3,5-tricarboxylic acid ($C_6H_3(COOH)_3$), and aqueous formaldehyde solution (37%) were obtained from Sinopharm Chemistry Reagent Co., Ltd. (Beijing, China).

2.1.1. Synthesis of HKUST-1

The HKUST-1 was prepared via a method as described previously [17]. In brief, copper nitrate (1.82 g) and benzene-1,3,5-tricarboxylic acid (BTC) (0.875 g) were dissolved in 50 mL anhydrous methanol, respectively. Then, the copper nitrate solution was transferred into the tricarboxylic acid solution followed by continuous magnetic stirring for 2 h at room temperature. The blue precipitate was retrieved by centrifugation and washed with methanol twice, and dried at 50 °C under vacuum.

2.1.2. Synthesis of carbon supported Cu/Cu_2O

Typically, 0.2 g HKUST-1 and 125 mL deionized water were added into a 250 mL three-necked round bottomed flask and ultrasonicated for 10 min. Then, 0.15 mL $NH_3 \cdot H_2O$ and 0.2 g resorcinol were added into the mixture under mechanical stirring for more than 1 h at 30 °C. Subsequently, 0.1 mL formaldehyde solution was added to the reaction solution and stirred for 8 h. After that, the mixture was heated at 80 °C for another 10 h under stirring. The solid product was recovered by centrifugation, dried at 50 °C under vacuum, and finally heated under a N_2 atmosphere to 600 °C (kept for 4 h) for carbonization. The obtained sample was denoted as Cu/Cu_2O/C.

2.1.3. Catalytic reduction of 4-nitrophenol

The reduction of 4-nitrophenol (4-NP) in the presence of $NaBH_4$ was carried out to investigate the catalytic activity and reusability of the Cu/Cu_2O/C catalyst. Typically, 2 mL of deionized water, 0.1 mL 4-nitrophenol solution (5×10^{-3} M), and 1.0 mL of fresh $NaBH_4$ (0.2 M) were added into a quartz cuvette in sequence, followed by the addition of 0.04 mg of catalyst to the mixture. The mixture was quickly subjected to UV–Vis measurements and scanned at a certain time interval. To determine the reusability, the amounts of 4-NP and catalyst were increased to 10 times of the above typical reduction. When the reduction process was completed, the catalysts were isolated by centrifugation and reused in next cycle.

2.2. Characterization

The size and morphology of the synthesized materials were investigated by using a transmission electron microscope (TEM) of

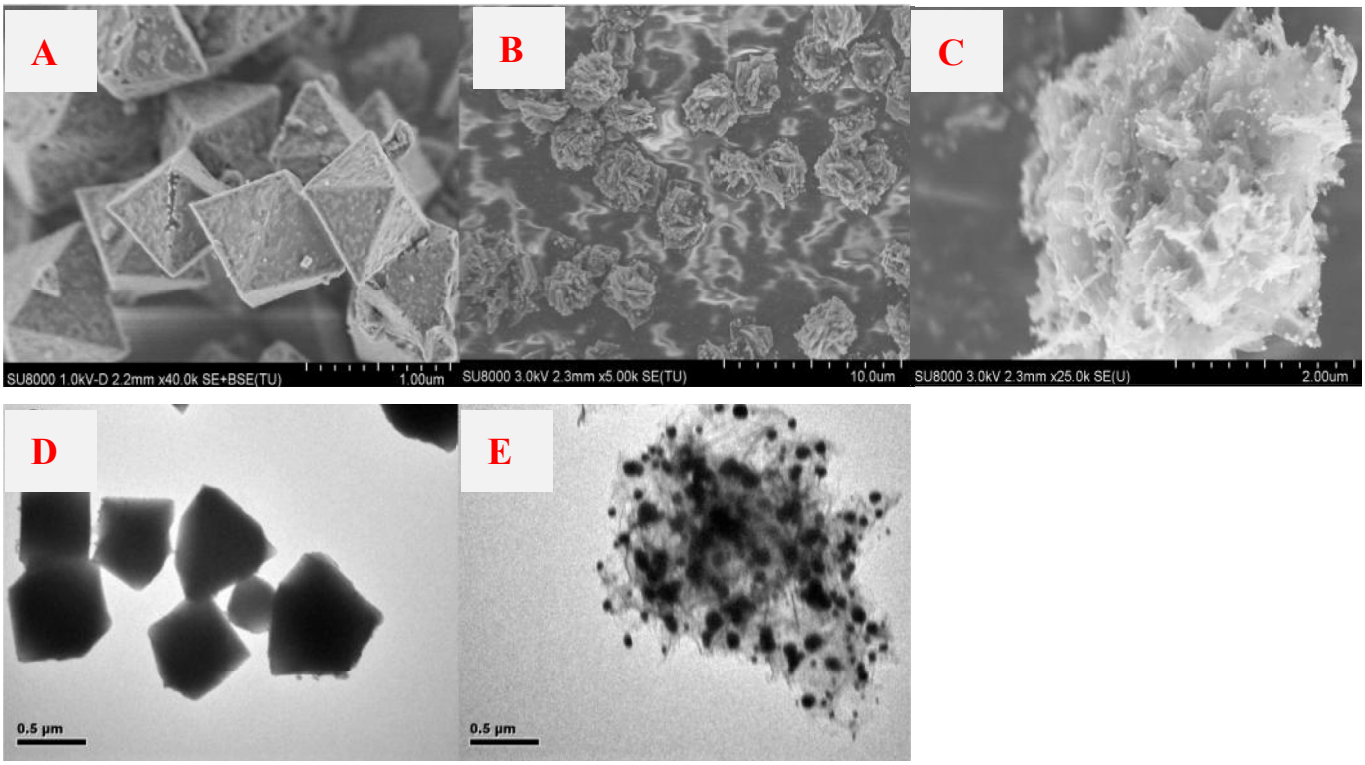

Fig. 1. SEM and TEM images of HKUST-1 (A, D), and Cu/Cu_2O/C composite (B, C, E).