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In situ preparation and catalytic activation of copper nanoparticles from acetylide molecules

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ABSTRACT

Because metal nanoparticles have a high surface area to volume ratio, they can be highly reactive, cost-effective catalysts. However, metallic surfaces are usually too reactive to maintain their metallic character in the presence of oxygen and/or water vapor. Metal nanoparticle catalysts must be handled carefully to avoid oxidation and inactivation. Here, we suggest a facile in situ preparation method for metal nanoparticle catalysts. Copper acetylide and copper methyl-acetylide molecules are based on ionic bonding, and are relatively stable in air. They can be used as a precursor of copper nanoparticles. Due to their instability at increased temperatures, subsequent annealing promotes a segregation reaction into elemental copper and carbon. Transmission electron microscopy and powder X-ray diffraction revealed that the average diameters of the Cu nanoparticles thus formed were 13.3 and 4.4 nm for C_2Cu_2 and $CuCC–CH_3$ precursors, respectively. This suggests that the substitution of acetylide molecules can control the size of the resulting copper nanoparticles. The primary advantage of this preparation method is that the functional acetylide group can reduce copper cations. No additional reducing agent is required, so no further separation process is necessary. This presents in situ preparation process. The catalytic activity of the resulting Cu nanoparticles was confirmed for a hydrogen storage system.

1. Introduction

Metallic nanoparticles have attracted widespread attention due to their fascinating optical, electronic, and catalytic properties [1–3]. For many applications, small nanoparticles are preferable to larger ones, because of their higher surface area to volume ratio. However, as the size of the nanoparticles decreases, the surface energy increases, favoring the aggregation of small particles or their growth into larger particles. It is difficult to keep small nanoparticles separated. In addition to their surface energy, the chemical reactivity of nanoparticles also depends upon their sizes, and smaller particles are generally much more chemically reactive than larger particles. This tendency interferes with the preparation of small metallic nanoparticles.

Over the past two decades, a substantial body of research has been directed toward the synthesis and application of small Au and Ag nanoparticles [1,4,5]. Brilliant achievements have been reported toward the successful control of nanoparticle size and shape [4,6,7], as well as broad applications in sensors [8], catalysis [9], and substrates for surface-enhanced Raman scattering [10]. Copper is a highly conductive, cheap, and widely-used industrial material, with a valence electron structure similar to the other coinage metals, Au and Ag. Nevertheless, over the years, the fabrication of Cu nanoparticles has attracted less attention than that of Au and Ag nanoparticles, and remains open for more intensive investigation.

The reason for the reduced attention to the fabrication of Cu nanoparticles is that Cu is much more reactive than Au or Ag. For example, the standard electrode potential of Cu^{2+}/Cu is +0.34 V, and the potentials of Ag^{+}/Ag and Au^{+}/Au are +0.80 V and +1.69 V, respectively. Therefore, Cu nanoparticles are much more easily oxidized than Au or Ag nanoparticles. However, the higher reactivity of Cu nanoparticles gives them a tremendous potential for applications in catalysis [11–14]. Several methods have been developed for the preparation of Cu nanoparticles, including the reverse micelle method [15], polyol reduction [16], microwave-assisted synthesis [17], thermal reduction [18–20], a sputtering aggregation source in the gas phase [21], and capping ligand protection techniques [22,23]. Very recently, Barron et al. reported ultra-small Cu nanoparticle production, controlled by a surfactant template and carbon nanotubes [24]. Elemental analysis by powder X-ray diffraction (XRD) [25] and X-ray photoelectron spectroscopy (XPS) [24] in those studies showed oxide contamination peaks caused by partial

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oxidation of the Cu nanoparticles. In most of the above methods, it was quite difficult to prevent the Cu nanoparticles from oxidizing. Yang et al. made use of this oxidation tendency to produce core–shell and hollow nanostructures of copper and copper oxide [26].

In this study, we suggest a facile method of preparing metallic Cu nanoparticles for application in catalysis. Copper acetylide (C_2Cu_2) molecules and copper methyl-acetylide ($CuCC–CH_3$) molecules can be used as precursors of Cu nanoparticles. Due to their instability at higher temperatures, annealing at 200 °C causes a segregation reaction into copper and amorphous carbon. Transmission electron microscopy (TEM) and XRD measurements revealed that the average diameter of the Cu nanoparticles produced were 13.3 and 4.4 nm from C_2Cu_2 and $CuCC–CH_3$ precursors, respectively. This indicates that the substituent of the acetylide molecules can be used to control the size of the nanoparticles. An advantage of this preparation method is that the acetylide functional groups can reduce copper cations. Therefore, an additional reducing agent is not required, removing the necessity of an additional separation process, making in situ preparation possible. The preparation of reactive Cu nanoparticles promises new applications for chemical reactions such as catalysis.

2. Experimental

2.1. Preparation of precursors

Copper(I) chloride (CuCl, 1 g, >95%, Kanto Chemical Co. Inc.) was dissolved in 5% aqueous ammonia (NH_3, 100 mL, Kanto Chemical Co. Inc.) solution in a separable flask of 500 mL inner volume. First, pure Ar gas was bubbled through the solution at a flow rate of 50 mL/min for 30 min in order to reduce the residual oxygen in the solution and in the gaseous space of the flask. Then, 1% acetylene (C_2H_2) gas or 10% methyl-acetylene, propyne ($HCC-CH_3$) gas in Ar was introduced into the reactor at an extremely slow flow rate (5 mL/min). The gas flow was controlled using a digital mass flow controller (CMQ9200, Yamatake Corp.). The solution was stirred at 300 rpm continuously during gas injection. A dark-brown (C_2Cu_2) or light-yellow ($CuCC–CH_3$) precipitate was produced after 3 h. The solid product was suction-filtered and washed with distilled water and methanol. The obtained precipitate was suspended in 50 mL of methanol in an ultrasonic bath, and was filtered again. Subsequently the precipitate was dried in a vacuum desiccator (yields ~50 mg). Caution: the C_2Cu_2 product is highly explosive. On drying, the sample becomes much more dangerous. Do not handle large amounts of C_2Cu_2.

2.2. Conversion to Cu nanoparticles

The acetylide product (C_2Cu_2 or $CuCC–CH_3$) was placed in a quartz glass tube (inner diameter 30 mm), and the tube was evacuated by a turbo molecular pump (TSU 071, Pfeiffer). Under high vacuum (below 10^{-4} Pa), the acetylides were annealed at 100–200 °C for 12–24 h in an electric tube furnace (FUT552FA, ADVANTEC Toyo Corp.). The segregation reaction during annealing formed Cu nanoparticles covered with amorphous carbon polymers.

2.3. Characterization

The obtained Cu nanoparticles were examined by transmission electron microscopy (TEM), X-ray diffraction (XRD), and UV–visible absorption spectroscopy. TEM imaging and electron energy loss spectroscopy (EELS) were carried out using a TEM apparatus with a 300 kV electron beam (JEM-3200FS, JEOL). XRD was performed with a Mo Kα line irradiated upon a glass capillary containing a powder sample (Mercury CCD-1 R-AXIS IV, Rigaku). UV–visible absorption spectra were obtained using an integrating sphere with a sample suspended in chloroform (UV-3600, Shimazu).

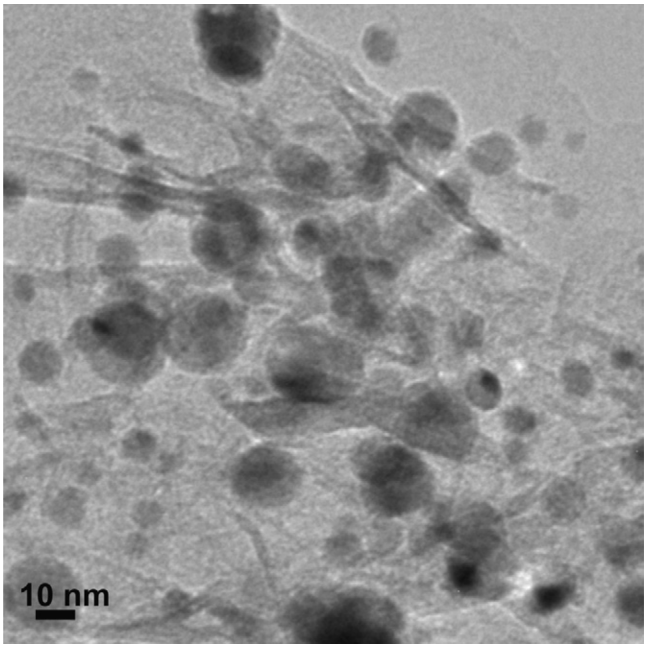

Fig. 1. TEM image of annealed C_2Cu_2. The annealing of acetylide molecules in a vacuum causes a segregation reaction to form copper and carbon. The resulting Cu nanoparticles were observed to have a spherical shape.

2.4. Catalytic activity

The Cu nanoparticles were evaluated as a catalyst for hydrogen storage materials. Magnesium hydride (MgH_2) and 10 wt.% of the Cu nanoparticles were mixed by milling with stainless steel balls for 24 h. Hydrogen absorption and desorption rates were measured using a PCT measurement system (PCT-2SDWIN, Suzuki Shokan). A reference measurement was made for a sample of only MgH_2 without Cu nanoparticles, in order to extract the catalytic enhancement from the particle size dependence of the absorption and desorption rates.

3. Results and discussion

Fig. 1 shows a TEM image of annealed C_2Cu_2 product. Our previous study revealed that C_2Cu_2 molecules self-assemble into a nanowire morphology, and annealing at 80–100 °C promotes a segregation reaction into copper and carbon elements [27–30]. The morphology of homogenous C_2Cu_2 nanowires was converted to inhomogeneous nanocables, which were metallic Cu nanowires covered with amorphous carbon [27]. In this study, C_2Cu_2 acetylide nanowires were heated to 200 °C, at which the shape of the metallic Cu nanowires could not be maintained. Spherical Cu nanoparticles were observed as dark spots, as shown in Fig. 1. The initial structure of the nanowires remained in the TEM image as brighter regions, which can be considered as carbon fibers. Because the covalent carbon bond has a binding direction, this morphology could be maintained at the annealing temperature.

The substituent effect of acetylide molecules was examined for the nanofabrication by changing the substituent from acetylene to methyl-acetylene. Fig. 2 shows a TEM image of annealed $CuCC–CH_3$ product. Because some of the Cu nanoparticles could migrate on the surface of the TEM grid, the image shown in Fig. 2 contained no carbon fibers like those shown in Fig. 1. The diameters of the