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A simple one pot synthesis of mesoporous silica hosted silver catalyst and its low-temperature CO oxidation

Zhenping Qu *,[1], Xiaodong Zhang [1], Fangli Yu, Jingxuan Jia

Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, China

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ABSTRACT

A novel and simple one pot synthesis approach using dodecylamine (DDA) as capping agent and structure director has been employed to synthesize the silica-supported Ag nanoparticles. The catalysts were characterized by XRD, N_2 adsorption–desorption isotherms, TEM and TG-DTA. It was found that the loading and particle size of Ag were strongly related to the surfactant DDA. In addition, the formed local reductive environmental due to the decomposition of DDA during thermal treatment procedure could prevent the aggregation of Ag nanoparticles and be benefit for the formation of uniformly dispersed Ag nanoparticles on the HMS support (1.5–4.5 nm). The excellent catalytic activity for CO oxidation (T_{98}(CO) = 20 °C) demonstrated that the method was effective for synthesizing the highly dispersed nano-silver catalyst.

1. Introduction

Noble metal nanoparticles in the nanometer size range have received considerable interest in recent years [1,2]. Metal nanoparticles possess unique physical and chemical properties, such as magnetic, optical and electrical properties, which are intensely dependent on the particle size and shape [3,4]. They have wide applications in catalysis, optics, microelectronics, biology, medicine and surface-enhanced Raman spectroscopy [5–9]. Remarkably, size affords crucial control over physical and chemical properties of nano-materials including conductivity, luminescence and catalytic activity [10,11]. Importantly, in catalytic reaction, the dispersion and thermal stability of metal nanoparticles strongly affect their activities [12–14]. Therefore, the research is focused on the preparation of highly dispersed Ag nanoparticles with small size.

Capping agents were usually used in the preparation of metallic nanoparticles by wet chemistry [15]. Their functions are to avoid the aggregation of the nanoparticles in solution and to control the size and shape at the crystallographic level [16,17]. The studies showed the dodecylamine (DDA) was a better capping agent to form a self-assembled layer on the gold particle by a weak covalent bond between the amine group and gold [18]. However, capping agents could compete with reactants and products for the adsorption sites, consequently leading to the decrease of the catalytic activity [19]. On the other hand, capping agent DDA was also used as the surfactant to synthesize a hexagonal molecular sieve (HMS). HMS possesses small crystallite size of primary particles and complementary textural porosity to provide better transport channels for reactants and products [20–22]. Recently, Liu et al. reported that one-pot synthesis approach using HCHO as a reducing agent has been successfully used to synthesize highly dispersed Ag nanoparticles supported on HMS [21]. However, the relatively poor uniformity of Ag nanoparticles (2–7 nm) was observed. Tian et al. also reported *in situ* reduction with HCHO led to the agglomeration of Ag nanoparticles [23]. In our previous works, we found that DDA could coordinate with Ag^+, depending on the affinity between the metal ions and the functional group of DDA [24]. Here, a novel and simple one pot method was developed to synthesize highly dispersed uniformly sized Ag nanoparticles. In this method, DDA was used as capping agent and structure director to synthesize the HMS-supported Ag nanoparticles. Above all, Ag^+ was directly calcined to obtain Ag nanoparticles. Meanwhile, DDA was completely decomposed. It was found that highly dispersed uniformly sized Ag nanoparticles on the mesoporous silica were synthesized due to the protection of reductive gas resulted from the decomposition of DDA in thermal treatment procedure. The catalytic activity of Ag catalysts for low-temperature CO oxidation was tested. Surprisingly, highly dispersed Ag nanoparticles with narrow size distribution were activated and exhibited 98% CO conversion at 20 °C. In order to well study the formation mechanism of highly dispersed uniformly sized Ag nanoparticles, the silver

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* Corresponding author. Tel./fax: +86 411 84708083.
E-mail address: quzhenping@dlut.edu.cn (Z. Qu).

[1] These authors contributed equally to this work.

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catalysts were also prepared via direct synthesis extraction (DSE) method and excessive impregnation (EI) method.

2. Experimental

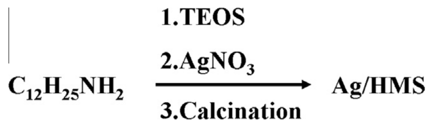
2.1. Catalysts preparation

Ag/HMS catalyst was prepared by one pot method (DSC, direct synthesis calcination method). DDA (2.5 g) was dissolved in 10 ml of ethanol, and then 10 ml of H_2O was added to the solution. The synthesis was carried out at 25 °C. 10 ml of TEOS was added to the surfactant solution to obtain the mixture solution. After the stirring of the mixture solution for 1 h silver nitrate was directly added to the above solution. Afterward, the synthesis solution was aged at 25 °C under stirring for 24 h. The formed solid was filtered, washed, and dried at 100 °C overnight to obtain as-prepared Ag/HMS catalyst. Then, the as-prepared Ag/HMS catalyst was subjected to thermal treatment in air at 600 °C for 5 h to remove DDA and decompose silver nitrate. The obtained sample was defined as the Ag/HMS (DSC). The formation route of Ag/HMS (DSC) catalyst by one pot synthesis method was shown in Scheme 1. The molar composition of this synthesis solution was $TEOS:C_{12}H_{25}NH_2:C_2H_5OH:H_2O:AgNO_3 = 1:0.2965:7.593:24.58:0.0221$. In addition, another method to remove template DDA was carried out by direct synthesis extraction method (DSE). The as-prepared Ag/HMS catalyst was extracted by ethanol for 12 h at 80 °C, followed by drying at 100 °C overnight. Then the catalyst was subjected to thermal treatment in air at 600 °C for 2 h to decompose silver nitrate. The obtained sample was named as Ag/HMS (DSE).

HMS-supported silver catalyst was also prepared by excessive impregnation method. Mesoporous silica HMS was prepared by the above procedure, but without the addition of silver nitrate. The prepared HMS (1 g) was immersed into excessive silver nitrate aqueous solution (0.0185 M), and followed by aging at 25 °C for 12 h. Afterward, the solid was filtered, dried at 100 °C overnight and calcined at 600 °C for 2 h to decompose silver nitrate, and then to obtain the Ag/HMS (EI) catalyst.

2.2. Characterization

Routine X-ray powder diffraction (XRD) experiments were carried out on a Rigaku D/max-γb X-ray diffractometer with monochromatic detector. Copper Kα radiation was used, with a power setting of 40 kV and 100 mA, and a scan rate of 5°/min (40 kV, 30 mA, and a scan rate of 2°/min for small-angle X-ray scanning). TEM experiments were performed with the JEM-2000EX microscope, using an accelerating voltage of 100 kV. For the TEM analysis, a sample was dispersed in absolute alcohol by an ultrasonic bath and deposited on a Formvar coated 200 mesh Cu grids. SEM images were taken on the Hitachi S-5500 scanning electron microscopes. The ICP-AES was used to determine the content of silver in the synthesized samples, which was performed on an OPTIMA 2000. Before any measurements were taken, the solid sample was dissolved in dilute HNO_3 solution with a small amount of HF. The N_2 adsorption/desorption isotherms at about -196 °C were measured using a Quantachrome SI gas sorption analyzer. The specific surface area was calculated by using the BET (Brunauer–Emmett–Teller) model. The pore size distributions were determined by the BJH (Barrett–Joyner–Halenda) method using the desorption branch of the isotherms. Uncalcined HMS support and Ag/HMS catalyst were analyzed by a thermogravimetric-differential thermal analyzer (TG-DTA, X-DSC6300). Temperature programmed decomposition in air gas stream (30 ml/min) was measured on the flowing reaction system using a mass spectrometer (Ametek, LC-D200 M) as the detector by heating 10 °C/min to 600 °C and maintaining that temperature for 5 h.



Scheme 1. The formation route of Ag/HMS catalyst by the one pot synthesis method.

2.3. Catalytic activity test

CO oxidation activity measurements were carried out in a fixed-bed flow reactor (4 mm inner diameter, 6 mm outside diameter) at atmospheric pressure and with 0.2 g of catalyst. Before the reaction, the catalyst was activated with H_2 at 300 °C for 1 h at a flow rate of 30 ml/min. The reaction was performed from the low temperature (5 °C) to high temperature (150 °C) with flowing gases. The reactant gases were fed with a volume ratio of $He/CO/O_2 = 79/1/20$ at a total flow rate of 30 ml/min. Each reaction temperature was kept 30 min to get the value of CO conversion. On-line gas chromatograph (GC 7890II) with a TCD detector was employed to measure the reactor inlet and outlet effluent gas streams. 5A molecular sieves column (3 m × 3 mm) was used to separate oxygen, carbon monoxide. In this paper, the CO conversion was calculated from the change of the CO concentration:

$$\text{CO conversion} = ([\text{CO}]_{\text{in}} - [\text{CO}]_{out})/[\text{CO}]_{in} \times 100\%$$

where $[\text{CO}]_{\text{in}}$ is the inlet CO concentration and $[\text{CO}]_{\text{out}}$ is the outlet CO concentration.

3. Results and discussion

3.1. Synthetic method of highly dispersed uniformly sized Ag nanoparticles

Fig. 1 shows the low angle and wide angle XRD patterns of Ag/HMS catalysts. A broad diffraction peak at 2θ of 1.5–3 ° is clearly observed in the low angle XRD pattern for all catalysts (Fig. 1(a)). This peak is characteristic of wormhole structures, assembled from neutral, long alkyl chain amines, which possess short-range ordered pore network [20,25,26]. The low angle XRD peaks of Ag/HMS (DSC) and Ag/HMS (EI) catalysts are virtually similar. However, the low angle diffraction peak of Ag/HMS (DSE) catalyst becomes weaker, indicating that short-range ordered structure is deteriorated. In addition, no obvious diffraction peaks of silver or silver compounds are detected on Ag/HMS (DSE) catalyst (Fig. 1(b)). The absence of diffraction peaks of silver species may be due to two possibilities: (i) The low content of Ag. The ICP results reveal that the Ag loading is only 0.7 wt% (Table 1). (ii) The small particles with size lower than the detection limit of XRD, which is consistent with TEM result (Fig. S1). Difference from Ag/HMS (DSE) catalyst, Ag/HMS (DSC) and Ag/HMS (EI) catalysts exhibit four obvious peaks, which correspond to the (111), (200), (220), (311) lattice planes of metallic Ag, respectively [27]. A broad peak at about $2\theta = 22$ ° is observed, corresponding to the amorphous part of the support silica [27].

In order to have a deep insight into silver nanoparticles distribution, Ag/HMS (DSC) and Ag/HMS (EI) catalysts are further characterized by TEM micrographs. As seen in Fig. 2(a), Ag nanoparticles with a uniform size of around 3–6 nm and are well dispersed on the HMS support for Ag/HMS (DSC) catalyst. However, for Ag/HMS (EI) catalyst, the average particle size of Ag nanoparticles increases from 5 nm to 14 nm; moreover the particle size