

Preparation of Ag/SBA-15 Nanocomposites Using a Supercritical Fluid Deposition Method

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Abstract: Ag/SBA-15 nanocomposites were synthesized using a supercritical fluid deposition method. Using ethanol or ethylene glycol and ethanol as cosolvent, the silver nitrate was dissolved in supercritical carbon dioxide and deposited into the channels of SBA-15 at 50 °C, 20-26 MPa, and converted to its metallic form through calcined in air at 400 °C for 6 h and reduction in H₂ at 400 °C for 1 h. The obtained composites were characterized by XRD, TEM and EDXS. The average diameter of the Ag nanowire is 6.7 nm, the length varied from several nanometers to several micrometers, and the nanowires grow and curve along the channels of SBA-15. Meanwhile, Ag nanoparticles with the diameter of 3-7 nm were highly dispersed in the channels. The size and distribution of the nanoparticles or nanowires are affected by the precursor concentration, the deposition time, and the cosolvent. We also investigated the catalytic activity of the composite and the Ag nanowires in the composites which removed the substrate.

Keywords: supercritical fluid deposition; nanocomposites; silver; SBA-15

1 Introduction

In recent years, the synthesis of supported metal nanocomposites have been attracted a great deal of attention for their unusual optical, electronic, electrochemical and catalytic properties^[1-4]. Nanometer-scale silver have attracted extensive attention due to their potential utility in electrocatalysis, chemical sensors, and optical devices^[5-6], and its unusual properties depend on the size and shape of the nanoparticle^[7]. There are several ways to synthesize supported nanoparticles, including impregnation^[8], sol-gel processing^[9] and chemical vapor impregnation^[10] et al. However, control over particle size, distribution, and metal concentration in the composite is challenging.

Supercritical Fluid Deposition (SCFD) is a new way to synthesize supported nanocomposites recently^[11-12]. A Supercritical Fluid (SCF) is a fluid that has been heated and compressed above its critical temperature and pressure. The thermophysical properties of a SCF are intermediate between those of a gas and a liquid and can be adjusted by slightly changes in temperature and /or pressure. Among the SCFs, supercritical CO₂ (SCCO₂) is particularly attractive for a wide variety of applications for its nontoxic, chemically inert, environment benign, very cheap and the modest critical condition ($P_c=7.38$ MPa, $T_c=31.1$ °C).

The SCFD process involves the dissolution of a metallic precursor or precursor/cosolvent solution in a SCF and the expose of the substrate to this solution. And the metallic precursor converts to its metal form by injecting a reducing agent such as hydrogen into the supercritical solution^[13], or by first depressurizing the supercritical solution and then subjecting the precursor/substrate composite to heat treatment (sometimes under inert atmosphere) and/or hydrogen^[14-15]. Many researchers have been using this method to prepare high-purity supported metallic nanoparticles, deposit thin metal films onto a wide range of surfaces, and incorporate

metallic nanoparticles into different inorganic and organic substrates [16-17].

In this paper, we synthesized Ag/SBA-15 nanocomposites with the SCFD method. Generally, precursors used in SCFD are organic metallic compounds which have relatively large solubility in SCF. But these precursors are expensive and some are usually poisonous. So we used inorganic salt AgNO₃ as the precursor in our experiment. Because AgNO₃ can't dissolve in SCCO₂, we used ethanol or ethylene glycol as the cosolvent. The obtained Ag/SBA-15 nanocomposites were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy-dispersed X-ray spectrometer (EDXS).

2 Experimental Sections

2.1 Materials

SBA-15 was prepared by a method similar to that reported by Zhao et al. [18]. P123 was used as structure-directing agent. Tetraethyl orthosilicate (TEOS, 17.0 g) was added to an aqueous solution of P123 (8.0 g) and HCl (2 mol/L, 240 ml). The mixture was stirred at 40 °C for 24 h and then at 100 °C for 48 h. The precipitate was filtered, washed with water, and then dried at 100 °C overnight to get a sample denoted SBA-15-as. To remove the structure-directing agent, the dried precipitate was calcined in air at 550 °C for 6 h, to finally get the SBA-15 with the BET surface area of 815 m²/g, total pore volume of 1.20 cm³/g and average pore diameter of 6.9 nm. AgNO₃ was purchased from the Shepherd Chemical Company (BeiJing, China). Carbon dioxide (>99%) was obtained from GuangMing gas Co. Ltd. (DaLian, China). Ethanol and ethylene glycol of analytical grade were supplied by FuYu fine chemicals Co. Ltd. (TianJin, China).

2.2 Preparation of Supported Nanocomposites

For a typical experiment, 13 mL ethanol (or ethanol 1.5 mL + ethylene glycol 1.5 mL) and AgNO₃ (300 mg) were placed into a stainless steel autoclave (84 mL). A stainless steel basket containing SBA-15 (300 mg) was then fixed in the upper part of the autoclave which did not contact with the ethanol solvent. The sealed autoclave was heated to 50 °C and then charged with CO₂ to the required pressure (20-26 MPa) while the solution in it was magnetically stirred continuously. After the pressure and temperature were kept for a required time (0.5-24 h), the autoclave was depressurized slowly. The amount of precursor adsorbed was determined by the weight change of the substrate using an analytical balance (Adventue model AR2140) accurate to 1 mg. Subsequently, the AgNO₃/SBA-15 composite was calcined in air at 400 °C for 6 h and reduced in H₂ at 400 °C for 1 h to obtain the SBA-15 supported Ag nanoparticles or nanowires. The morphology of Ag that obtained by removed the substrate from the Ag/SBA-15 nanocomposites was investigated. The composite was firstly placed in 20 ml NaOH solution (2 mol/L), then the solution was heated to 60 °C and kept this condition for 2 h while stirred continuously. The solid was recovered by centrifugal machine. And then repeat the steps as described above for two times. In the end, the product was recovered. The catalytic performance of the Ag/SBA-15 composite was evaluated in a fixed-bed flow reactor at atmospheric pressure using 100 mg of a catalyst diluted with SiC. A reaction gas containing 2 vol % CO, 1 vol % O₂, and 40 vol % H₂ in He was allowed to pass through the reactor at a flow rate of 67 cm³·min⁻¹, corresponding to a space velocity of 40000 mL·h⁻¹·g⁻¹Cat. The effluent gas was analyzed using an online gas chromatograph system (Agilent GC-8800) equipped with a thermal conductivity detector.

2.3 Characterization

Power X-ray diffraction (XRD) patterns were collected with a D/Max-βb diffractometer

using a Cu K_{α} radiation source ($\lambda = 0.15432$ nm), operated at 40 kV and 30 mA. A continuous mode was used for collecting data from 20° to 80° of 2θ at a scanning speed of $5^{\circ}/\text{min}$. The morphology of the Ag/SBA-15 nanocomposites and the nanowires which removed the substrate were examined by transmission electron microscopy (TEM) on a JEOL 2000EX electron microscope operating at an accelerating voltage of 120 kV. The EDXS was also obtained on this equipment.

3 Results and Discussion

The details of the preparation conditions are listed in Table 1, and all the experiments are carried out at 50°C , 20 - 26 MPa. The uptake of the precursor was determined from the change in the mass of the material. From the uptake of the materials, we can know that the AgNO_3 partitions favorably to the substrate phase.

sample	support	AgNO_3 amount /mg	cosolvent /ml		deposition time /h	uptake / mg
	SBA-15 amount /mg		ethanol	glycol		
1	300	300	13	0	19	112
2	300	300	13	0	6	92
3	300	150	13	0	19	69
4	300	300	1.5	1.5	24	157
5	300	300	1.5	1.5	0.5	132

The nature and crystallinity of the deposited Ag of the Ag/SBA-15 composite were confirmed by XRD spectra, as shown in figure 1 and 2. The (111), (200), (220) and (311) peaks in the figures are the peaks for elemental Ag that we are expected. When using ethanol as the cosolvent, as shown in Figure 1, the character peaks are relatively broad, which is indicative of small crystallite size. When using ethanol and glycol as the cosolvent, a respective XRD image is shown is Figure 2. We can know that the Ag character peaks are very strong and sharp, which indicate large crystallite size. The crystallite size of sample 1 was estimated using Scherrer's formula and the (111) reflection is 5.6 nm, in close agreement with the TEM data.

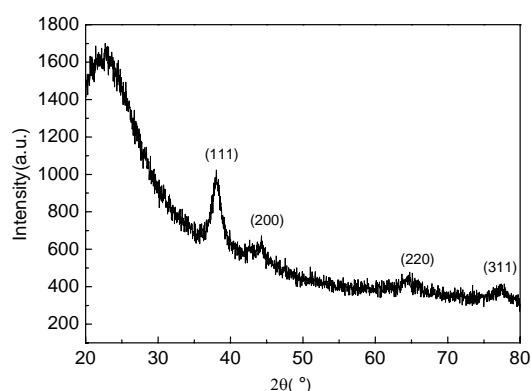


Fig. 1 The XRD image of sample 1 prepared at 50°C , 20.5-24.1 MPa, 19 h, with ethanol as the cosolvent

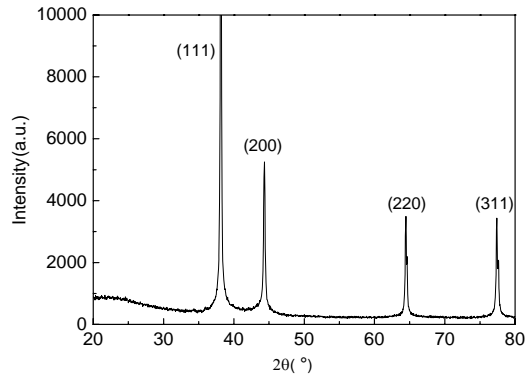


Fig. 2 The XRD image of sample 5 prepared at 50 °C, 23.3-23.5 MPa, 0.5 h, with ethanol and glycol as the cosolvent

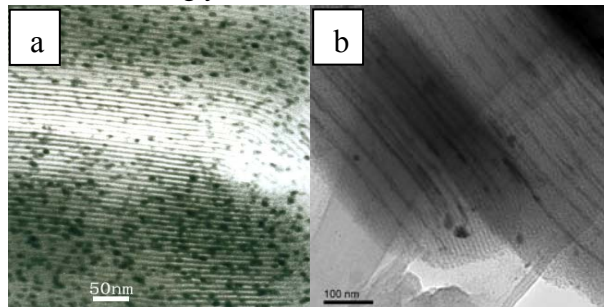


Fig. 3 The TEM image prepared at 50 °C, with ethanol as the cosolvent (a) sample 1, 20.5-24.1 MPa, 19 h; (b) sample 2, 23.3-25.8 MPa, 6 h.

Fig. 3 shows the TEM data obtained from sample 1 and 2. The image reveals that highly dispersed Ag nanoparticles dispersed in the channels of SBA-15 (Fig. 3a), no coalescence of the metal nanoparticles was observed, and uniformly dispersed metal nanoparticles with a mean particle size of 5.6 nm and a narrow particle size distribution. When the deposition time is shorter (sample 2), the morphology of Ag is nanowires, and the diameter is 6.7 nm, the length can change from 100 nm to 800 nm.

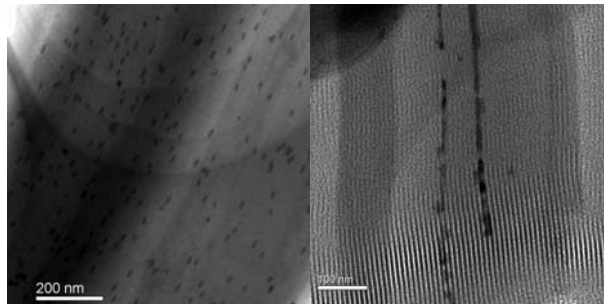


Fig. 4 The TEM image of sample 3 prepared at 50 °C, 23.2-24.0 MPa, 19 h, with ethanol as the cosolvent

When the concentration of precursor is different (sample 1, 3), the morphology of the composite can vary a lot, as shown in Fig. 3a and Fig. 4. Also, the uptake is different, listed in Table 1. Maybe the concentration is larger, the diffusion of the precursor from the solution to the substrate is more easily. At the same deposition time, more precursor can diffused into the channels of the substrate, resulting in the larger uptake, and more Ag nanoparticles dispersed in the channels of the SBA-15. This is not unexpected given that a higher metal content results in a larger number of nanoparticles per unit area.

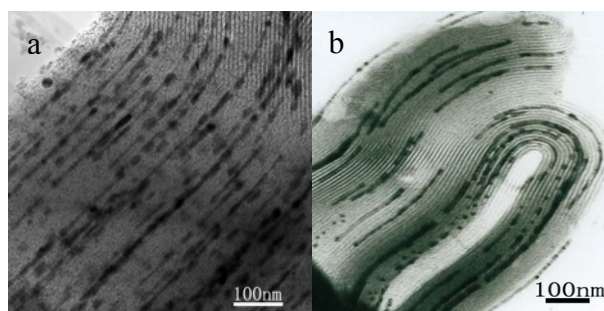


Fig. 5 The TEM image prepared at 50 °C, with ethanol and glycol as the cosolvent. (a) sample 4, 23.4-23.7 MPa, 24 h; (b) sample 5, 23.3-23.5 MPa, 0.5 h.

Examples of typical TEM micrographs obtained from the samples using ethanol and ethylene glycol as the cosolvent are shown in Fig. 5. In each case, the uptake and the size of the nanowire are very larger. To be sure the equilibrium can be achieved, the deposition time of 24 h is used. When the deposition time is only 0.5 h, the uptake can be achieved 84% of that at equilibrium. The morphology of Ag is nanowire. Comparison of the micrographs of samples 4 and 5, as well as sample 2, shows that the obtained Ag nanowires are larger and have broader size distributions when using glycol and ethanol as cosolvent, and the deposition time is obviously shorter. These observations indicated that ethylene glycol facilitates the diffusion of $\text{Ag}(\text{NO}_3)_2$ from the solution to the channels of SBA-15, and the formation of nanowires.

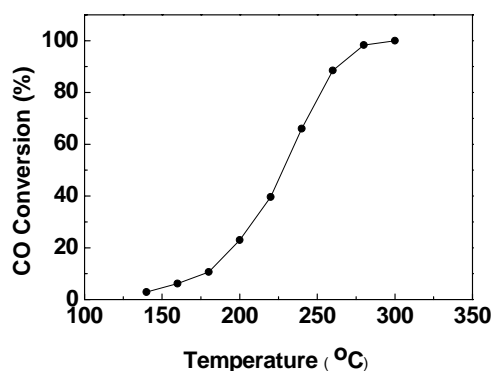


Fig. 6 Catalytic performance of Ag/SBA-15 for CO selective oxidation

The catalytic activity of the composite is characterized by the experiment of CO oxidation. Fig. 6 illustrates the CO conversion as a function of the reaction temperature. It can be seen that when the temperature less than 200 °C, the conversion is very low. The conversion reached to about 89% while the temperature is 260 °C, and 100% when the temperature increased to 300 °C.

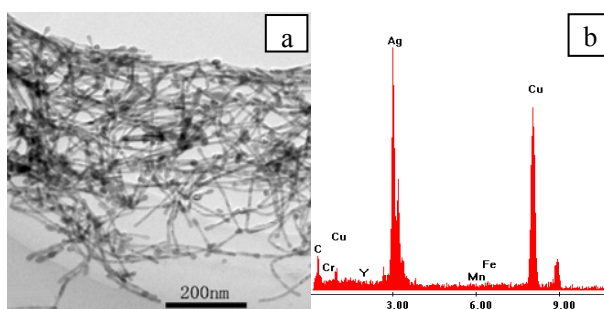


Fig. 7 The TEM and EDXS image of Ag nanowire

We also investigated the morphology of Ag nanowire of sample 2 which removed the substrate. The TEM and EDXS images are shown in Fig. 7. The character of these nanowires was

confirmed using EDXS, and an example of a typical spectrum is shown in Fig. 7b. The spectrum contains strong characteristic Ag X-ray peaks as expected, together with additional peak corresponding to Cu and C. This latter peak is artifact that arises from the Cu grid on which the TEM sample is supported. The obtained nanowires can be used as conductive nanowire in the microelectron area. The diameter of nanowires sometimes can reach to 20 nm, this maybe due to several Ag nanowires coalesced together without limitation of the substrate.

4 Conclusions

Ag/SBA-15 nanocomposites were synthesized using a SCFD method. In this study, we used the AgNO₃ as the precursor rather than the organic metallic compound. The Ag loading is very high in the composites, and the nanoparticles or nanowires were highly dispersed in the channels of SBA-15. The morphology of Ag can be controlled to a certain extent by the preparation conditions. When the concentration of the precursor is low, the uptake is low and the nanoparticles or nanowires are fewer; when the deposition time is different, resulting different uptake, the morphology of Ag can be particles or wires; when using ethanol and glycol as cosolvent, the deposition time can be very short, the uptake is large, and the size of the obtained nanowires is larger. Ag nanowires were obtained from removed the substrate of the Ag nanowire/SBA-15 composites. The composite also performed well catalytic activity in the CO oxidation experiment. From the experiments in this study, we can see that the supercritical fluid route is an effective way to preparing nanocomposites.

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