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Short communication

Heterogeneous nucleation/growth of silver nanoparticles onto oxygenated mesoporous carbon: Alcohol effect and catalytic property☆

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ABSTRACT

Alcohols (methanol, ethanol and isopropanol) have been found to affect the heterogeneous nucleation and growth of Ag nanoparticles onto oxygenated mesoporous carbon support and the corresponding catalytic property of Ag/Carbon nanocomposite in nitroaromatics (4-nitrophenol and 2-nitroaniline) reduction reactions. Ethanol exhibits unique capability to regenerate reactive —CH_2OH groups on carbon surface and successfully control Ag particle size through extending the nucleation process. Catalyst prepared with ethanol shows well-controlled particle size and dispersion and thus the highest catalytic activity in reduction reactions. The mechanism of catalyst structure control by alcohols is also investigated in this work.

1. Introduction

Nanomaterial structure design, synthesis and application have aroused great interest in the past decades due to their unprecedented physicochemical properties compared to conventional materials [1–6]. Nanomaterial size and morphology are important factors those influence the material property, which can be well controlled through adjusting the reaction conditions [7,8]. Among the reported synthetic methods, wet-chemical synthesis is mostly studied due to its better reaction control, lower cost and easier scale-up production [9,10] compared to other methods such as chemical/physical vapor deposition, electrochemical deposition and etc. Among the various parameters in wet-chemical reaction including the selection of solvent, surfactant, precursor and input energy source (microwave, sono-energy, thermal heat and light radiation), the effect of solvent on nanostructure control has been well recognized and intensively investigated over last a few decades. The role of solvent in nanostructure control could be briefly summarized as follows: (1) adjust reactant solubility in solvent to accelerate/decelerate the reaction (polymerization, hydrolysis and etc.) rate [11–13]; (2) tune solvent hydrophilicity/hydrophobicity property to increase/decrease the reaction interface of each reactant [14,15]; and (3) control the saturated vapor pressure of solvent to reach desired match of system temperature and pressure especially in hydrothermal and solvothermal reactions [16,17]. Until now, most of the existing research focuses on the control of nucleation and growth of nanostructures in homogeneous solutions. The solvent effect on heterogeneous nucleation and growth onto desired substrate (form nanocomposites) is less investigated. However, nanostructure control on desired supports is becoming increasingly important in emerging catalytic, energy storage and environmental applications [5,18–20]. Not only synergistically enhanced properties can be obtained, but also new properties have been found in a wide range of nanocomposite materials [21].

Nanocomposite catalyst, with active metallic/oxide nanoparticles supported on mostly porous substrate, is one of the most studied materials in catalysis taking advantages of the large surface area of support for particle dispersion control [22,23]. Among the various factors, particle size seems the most influential parameter that affects the catalyst activity tremendously. To control particle size, mixture solvent has been previously investigated in the preparation of supported noble nanocatalysts [20,24–26]. The idea is to control the nucleus density, nucleation rate and growth rate through tuning solvent property. For instance, Zhang et al. [27] successfully controlled the Ru nanoparticle size by adjusting the ratio of ethanol and super critical CO_2. Some other previous research reported that Ag nanoparticle size can be well controlled by conducting the $Ag(NH_3)_2NO_3 \rightarrow Ag^0$ reduction reaction in ethanol/water mixture solvent rather than pure water [28,29]. So far, the role of ethanol in the mixture solvent during nanoparticle

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formation is still not clear, which makes the particle size control process more likely empirical rather than theory guided.

In this work, the alcohol solvent effect on heterogeneous nucleation/growth of Ag nanoparticles onto oxygenated mesoporous carbon (OMC) support and the corresponding catalytic property of Ag/OMC in nitroaromatics reduction reactions are investigated. Specifically, three regular alcohols, methanol (Me), ethanol (Et) and isopropanol (iPr), were mixed with water and served as liquid reaction media. $Ag(NH_3)_2NO_3$ was in-situ reduced onto OMC with the presence of the alcohol/water liquid mixtures and the products were denoted as Ag/OMC-Me, Ag/OMC-Et and Ag/OMC-iPr, respectively. Pure liquid water was used as reaction media to synthesize Ag/OMC-H_2O as a control to explore the alcohol effect.

2. Experimental section

2.1. Materials

Silver nitrate ($AgNO_3$, ≥99%), 4-nitrophenol (4-NP, ≥99%), 2-nitroaniline (2-NA, 98%), methanol (99.8%) and isopropanol (99.8%) were purchased from Sigma Aldrich. Sodium borohydride ($NaBH_4$, ≥99%) was purchased from Fluka Chemical Corp. Ammonium hydroxide (NH_4OH, 28–30%) was purchased from BDH Chemistry. Ethanol (99.9%) was purchased from Decon laboratories, Inc. Cotton fabric was cut from a commercially available T-Shirt (100% cotton). All the chemicals were used as received without further purification. Deionized water (Millipore) was used throughout the experiment.

2.2. Synthesis of Ag/oxygenated mesoporous carbon (Ag/OMC)

Oxygenated mesoporous carbon support (OMC) was prepared from cotton fabric with carbonization at 800 °C and oxidation at 370 °C, detailed procedures refer to our previous publication [30]. Fresh Tollen agent ($Ag(NH_3)_2NO_3$, 5 mM) was prepared by dropwise addition of 10 wt% aqueous ammonia into 20.0 mL $AgNO_3$ aqueous solution until the solution become pellucid. In order to study the alcohol effect, three alcohols were selected those are methanol (MeOH), ethanol (EtOH) and isopropanol (iPrOH). Mixture solutions were prepared by mixing alcohols and 5 mM $Ag(NH_3)_2NO_3$ with volume ratio of 1:4. Then 0.4 g OMC was added into 20.0 mL mixture solution and stirred at 40 °C for 30 min. The products were filtered, rinsed with 500 mL deionized water and dried at 70 °C for 12 h, which were named as Ag/OMC-Me, Ag/OMC-Et and Ag/OMC-iPr respectively synthesized from H_2O/MeOH, H_2O/EtOH and H_2O/iPrOH solvents. In order to explore the effect of alcohol in the mixture solvent, Ag/OMC synthesized by pure water without alcohols was also comparatively studied, denoted as Ag/C370-H_2O.

2.3. Characterization

The sample morphology was characterized by scanning electron microscopy (SEM, JEOL-7401) with a sputter-coated gold layer on sample surface. Ag nanoparticle size and morphology was further characterized by transmission electron microscopy (FEI TEM). Samples for TEM characterization were prepared by drying a drop of sample powder ethanol suspension on carbon-coated copper TEM grids. The powder X-ray diffraction analysis was carried out with a Bruker AXS D8 Discover diffractometer with GADDS (General Area Detector Diffraction System) operating with a Cu-K α radiation source filtered with a graphite monochromator (λ = 1.541 Å). The Ag nanoparticle loading was determined by thermogravimetric analysis (TGA, TA instrument Q500) in air from 20 to 800 °C with a heating rate of 10 °C/min. Fourier transform infrared (FT-IR) spectra were recorded with a Digilab Excalibur FTS 3000 series FT-IR Spectrometer using KBr pellets. A UV-1800 Shimadzu spectrophotometer was used to monitor the catalytic reaction for kinetic study.

3. Results and discussion

TEM micrographs reveal the Ag nanoparticle size and dispersion on OMC support, Fig. 1. All the samples show uniform particle distribution but different in particle size. The inset figures depict the statistical particle size distribution based on a sample size of >500 Ag nanoparticles in each material. The average Ag nanoparticle size is about 3.0 nm in Ag/OMC-Et with narrow size distribution, Fig. 1a. However, larger Ag nanoparticles were observed in the Ag/OMC-Me and Ag/OMC-iPr, Fig. 1b & c. The average particle size obtained from the Ag/OMC-Me and Ag/OMC-iPr is 5.1 and 3.9 nm, respectively. The different particle size is attributed to the different nucleation and growth processes in the alcohol/H_2O reaction systems. In pure aqueous solvent, Ag/OMC-H_2O has the same average particle size of 3.9 nm as Ag/OMC-iPrOH, Fig. 1d. However, broader particle size distribution is observed compared to Ag/OMC-Et and Ag/OMC-iPr. It is worth mentioning that much larger Ag particles (>100 nm) were also observed in Ag/OMC-H_2O. Without alcohol molecules in the reaction solution, the nucleation and growth processes seem less controlled, which further confirms the active role of alcohol molecules in the heterogeneous reduction reactions. More TEM images on Ag particle distribution have been provided in Figs. S1 & S2 in ESI. X-ray diffraction analysis (Fig. S3 in ESI) confirms the same face centered-cubic crystalline structure of Ag nanoparticles (JCPDS card no. 4-783) in all the Ag/OMC samples. Meanwhile, the same Ag nanoparticle loading of 2.5 wt% is obtained in all the Ag/OMC samples as evidence by TGA results in Fig. S4 in ESI.

To reveal the function of different alcohols during Ag nanoparticle formation, IR spectrum was collected to analyze the surface group evolution before and after Ag reduction process. As reported in our previous work [30], oxygen-containing functional groups (—OH, —C═O and —COOH) exist on the OMC surface. These groups are responsible for the reduction of $Ag(NH_3)_2NO_3$ to Ag nanoparticles. With increasing initial concentration of $Ag(NH_3)_2NO_3$, the adsorption peaks at 3400 and 2800 cm^{-1}, corresponding to the O—H and C—H stretching vibration, decreased gradually. It suggested that —CH_2OH groups on carbon surface directly involved in the redox reaction for Ag nanoparticle formation [30]. Furthermore, the peak at ~1100 cm^{-1} (C—O bond) shifted to 1220 cm^{-1}, Fig. S5 in ESI, indicating the transition from primary and secondary alcohols to tertiary and aromatic alcohols [31]. With the increase of silver loading, more primary alcohol groups transfer to tertiary alcohol groups. When the Ag loading increases to 13.6 wt%, tertiary and aromatic alcohols are dominated on the carbon surface. Knowing the fact that the tertiary alcohol group is non-reactive to Ag precursor, it is not surprising to observe the formation of relatively larger particles due to the dominant role of growth on existing nucleus.

Fig. 2 shows the IR spectrum of pure OMC and Ag/OMC samples prepared from different alcohol/H_2O solvent systems. Comparing the IR spectrum from pure OMC and Ag/OMC-H_2O, the peaks at 3400 and 2800 cm^{-1} disappeared after growing Ag nanoparticles, Fig. 2a-V. Meanwhile, the C—O adsorption peak shifted from 1100 to 1220 cm^{-1}, indicating the transformation of alcohol groups from primary position to tertiary position. This peak shift after incorporating Ag nanoparticles was observed in other alcohol/H_2O mixture solvent except ethanol/H_2O. In fact, the pure OMC and Ag/OMC-Et exhibit very similar IR spectrum (Fig. 2a-I & a-II), which reveals that ethanol may have a unique function among the alcohols that affects the silver nucleation and growth on OMC. Fig. 2c shows a proposed mechanism that describes the change of the surface groups on carbon surface when exposed to silver precursor. During the $Ag(NH_3)_2NO_3 \rightarrow Ag^0$ reduction process, the removal of —CH_2OH groups at the surface creates vacant active sites those tend to be stabilized by surrounding water molecules via C—H bond formation, Fig. 2c-V. When alcohol molecules present in the solvent system, different alcohol molecules will be involved in the rearrangement of surface radicals and form different surface groups. These vacant active sites on the carbon surface will be occupied by rearranged functional groups