



Ag nanoparticle incorporation in mesoporous silica synthesized by solution plasma and their catalysis for oleic acid hydrogenation

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ABSTRACT

The incorporation of Ag nanoparticles on mesoporous silica as the supporting material and their catalysis for oleic acid hydrogenation were described in this study. The template removal and Ag nanoparticle incorporation were concurrently taken place in the novel glow discharge in a solution, namely solution plasma process under controlled conditions. With only 15 min of discharge time, Ag nanoparticles were incorporated on the mesoporous silica matrix confirmed by the evidences of XRD and TEM and the template inside mesopores was mostly removed confirmed by FTIR spectra. The hydrogenation catalysis of oleic acid was preliminarily tested using UV–VIS spectroscopy after oxidation using permanganate ions (MnO_4^-). It was found that the conversion was observed to be 12.83% in the butanol system and reached to 90.56% in ethanol.

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1. Introduction

The solution plasma process (SPP) has been demonstrated as a versatile process with high performance for many applications including nanoparticle synthesis, water purification, organic compound decomposition as well as sterilization. This method offers many benefits by the presence of active species and radiation. The active species (e.g. H^\cdot , O^\cdot , OH^\cdot , and HO_2^\cdot), high energy electrons, and UV radiation are produced during discharge providing high reaction rates and different effective chemical reaction paths [1]. SPP is superior to other conventional methods, owing to its properties such as ease of handling, no need of pressure and temperature, short consumption time, and variation in a wide range of chemical use. For instance, in a previous report, the organic template inside mesoporous silica was decomposed via oxidation by the generated OH^\cdot after SPP only 15 min without the influence on mesopore morphology [2]. Gold nanoparticles were successfully synthesized through reduction of H^\cdot without addition of any reducing agent [3].

In the nanoparticle field, Ag nanoparticles (AgNPs) are extensively investigated considering their significant physicochemical characteristics. AgNPs are widely applied in various advantages for instance microbial inhibition, sensors, and optical and electronic devices [4–6]. Typically, AgNPs are synthesized by a chemical reaction of Ag^+ solution (e.g. AgNO_3) and reducing agents (e.g. NaBH_4). Moreover, the laser ablation containing Ag nanowire and sodium citrate and the γ -irradiation in ethanol containing AgNO_3 and sodium citrate were

reported to be the reliable pathways for AgNP synthesis [4,7]. In terms of catalytic application, AgNPs incorporated in various types of supporting material have been studied. The highly dispersed AgNPs on Aerosil-200 silica for ethylene hydrogenation at temperature over 550 K and AgNPs on silica for chloronitrobenzene hydrogenation with high activity and selectivity were reported [8,9].

Herein, mesoporous silica used as a supporting material was prepared via the sol–gel method in an acid solution. To incorporate AgNPs and remove template inside mesopores without addition of reducing and oxidizing agents, SPP was employed at only 15 min of processing time. The obtained materials after discharge were characterized and referred to the role of SPP for Ag incorporation and template removal ability. Moreover, use of the obtained materials as a catalyst for hydrogenation of the unsaturated oleic acid was also evaluated.

2. Experimental

2.1. AgNP-incorporated mesoporous silica synthesis and its catalytic test

In a synthesis, the surfactant system containing 0.5 g triblock-copolymer P123 ($\text{EO}_{20}\text{PO}_{69}\text{EO}_{20}$), 0.1 g 1,1,2,2,3,3,4,4,4-nonafluoro-1-butane sulfonate (NFBS), and 0.084 g sodium dodecylbenzene sulfonate (SDBS) was dissolved in a 3 M hydrochloric acid (HCl) solution and continuously stirred until it becomes a homogeneous solution. Consequently, 2.15 g tetraethyl orthosilicate (TEOS) was added and the mixture was kept at an ambient temperature for 24 h to form the white precipitate. To incorporate AgNPs, 150 ml of 0.5 mM (1 and 5 mM) silver nitrate (AgNO_3) solution and 0.15 g P123 were prepared. 1 g of as-synthesized silica was added in the solution and the discharge

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was further processed for 15 min by bipolar pulsed power supply using 1.6 kV, 15 kHz, 2 μ s, and 0.3 mm of voltage, pulse frequency, pulse width, and electrode distance, respectively. For the preliminary catalytic test, a mixture of 1.5 g oleic acid, 40 ml ethanol (butanol), and 20 mg AgNP-incorporated mesoporous silica was prepared in a round-bottom flask. This mixture was purged by H₂ for 15 min and heated at 50 °C for 1 h. The hydrogenated outcome was dropped by the 0.5 M potassium permanganate (KMnO₄) solution. The oxidized solution determined the remained permanganate species using UV–VIS spectrophotometer.

2.2. Characterization

The samples were studied by X-ray diffraction which was carried out on XRD Rigaku Smartlab with Cu K α radiation ($\lambda = 0.154$ nm). Transmission electron microscope (TEM) and energy-dispersive X-ray (EDX) investigations were performed on JEM-2500SE with an acceleration voltage of 200 kV. Fourier transform infrared (FTIR) spectra were measured on a Digilab FTS-7000 series in a range of 4000–400 cm^{-1} . Surface area and pore diameter were calculated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods from N₂ adsorption–desorption isotherm measured on Belsorp-mini II. For the catalytic test, UV–VIS spectra were recorded with Shimadzu UV-3600 UV–VIS–NIR spectrophotometer by scanning from 200–700 nm.

3. Results and discussion

The formation of AgNPs on mesoporous silica after SPP for 15 min in various AgNO₃ concentrations was found in XRD patterns as shown in Fig. 1. XRD patterns were divided into two regions. Firstly around 0.8°, the broad diffraction peaks were detected without any higher diffraction peak (Fig. 1A). This feature was referring to the worm-like mesopore characteristic similar to the report of Y. Wang [10]. In the second region (Fig. 1B), we observed three peaks at 38, 44, and 64° corresponding to (111), (200), and (220) plane reflections of the face-center cubic (fcc) structure of AgNPs [11]. Moreover, the difference in intensity which referred to the AgNP amount was presented. It suggests that the AgNP amount was proportional to AgNO₃ concentration.

Fig. 2(a, b, and c) shows the TEM images of the dispersed AgNPs on mesoporous silica with the average sizes about 5.76, 15.66, and 32.31 nm after discharge in the use of 0.5, 1, and 5 mM AgNO₃, respectively. The AgNP contents calculated by a wide-area scanning of EDX were 9.89, 13.57, and 25.78%, respectively. The high-resolution TEM image (Fig. 2d) reveals fcc structure of AgNPs attached on the worm-like silica matrix. This evidence could not observe the ordered arrangement and it hardly confirmed the interplane diffraction of silica in XRD, even if well-ordered mesopores were constructed [12].

FTIR spectra pay regard to the feasibility of SPP for template decomposition as shown in Fig. 3. In as-synthesized silica, the vibrational peaks were observed at 3100–3700 (O–H stretching), 2800–3000 (C–H stretching), 1730 (O–H bending), 1480 (C=C stretching), 1380 (SO₃ stretching), and 1150–1250 cm^{-1} (unclear band of C–F stretching) corresponding to the organic surfactant [13,14]. The silica backbone was confirmed in a range of 1000–1250 and 800 cm^{-1} [10]. After SPP, only peaks of O–H stretching and bending and Si–O stretching remained belonging to silica framework and absorbed moisture inside mesopores. The results note that template was discarded by SPP which was comparable to the result using thermal calcination [2].

BET surface area and pore diameter pay attention to the use of mesoporous silica as a catalyst and they were calculated from N₂ adsorption–desorption isotherms. BET surface area and pore diameter were reported to be 675, 639, and 581 m^2g^{-1} and 3.3, 3.2, and 2.9 nm for 0.5, 1, and 5 mM AgNO₃, respectively (data not shown). The increase in

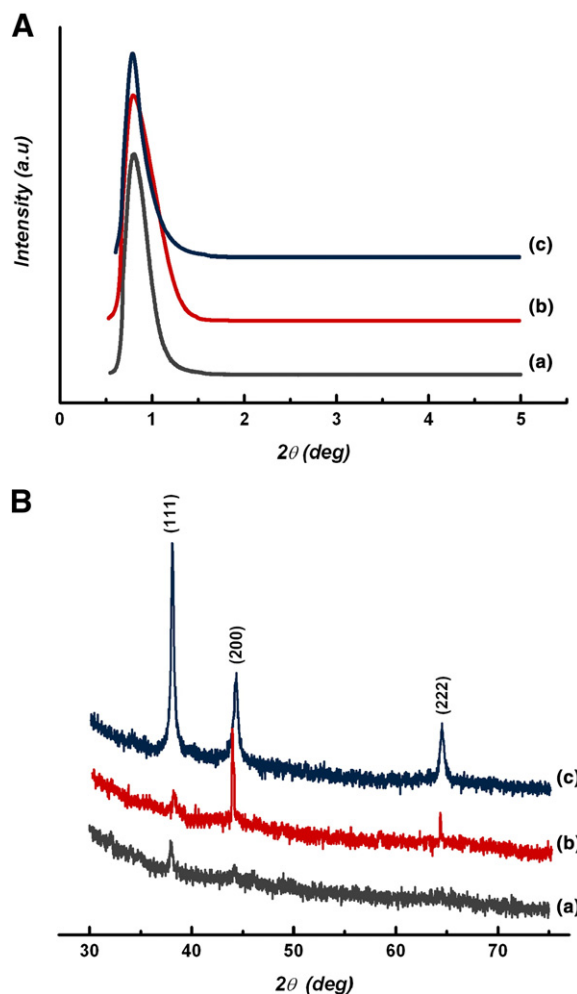


Fig. 1. XRD patterns of AgNP-incorporated mesoporous silica after SPP for 15 min in (a) 0.5 mM, (b) 1 mM, and (c) 5 mM AgNO₃: (A) Si region and (B) AgNP region.

AgNO₃ concentration resulted to the increases in nucleation and particle growth to obstruct the gas adsorption.

The reduction and oxidation to form AgNPs and decompose template by H[•] and OH[•] can be explained by following reactions,



The H₂O molecule was dissociated and excited by plasma energy (1), and consequently radicals were transferred into a liquid phase. The propagation of dissociation and excitation in liquid occurred to generated active species (2). H[•] is an initiator of reduction to convert Ag⁺ to AgNPs (3). Moreover, OH[•] is an initiator for oxidation to decompose the template to be small organic compounds [2].

To investigate the preliminary catalytic test for oleic acid hydrogenation, the sample prepared using 1 mM AgNO₃ was employed as a catalyst, owing to the balance of the AgNP content

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