Silver Nanoparticles Confined in SBA-15 Mesoporous Silica and the Application as a Catalyst for Glucose Oxidation*

Bui Thi Thanh Ha, Nguyen Thi Minh Thu, Giang Thi Phuong Ly, Nguyen Thanh Binh, Le Thanh Son, and Tran Thi Nhu Mai†
Faculty of Chemistry, Hanoi University of Science, 334 Nguyen Trai Road, Thanh Xuan, Hanoi, Vietnam
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In this paper, the dispersion of Ag metal nanoparticles on SBA-15 mesoporous silica and its catalytic performance to oxidize glucose to gluconic acid were studied. Mesoporous silica SBA-15 materials were synthesized using the triblock copolymer Pluronic P123 as a template in acid condition. Ag nanoparticles were prepared using impregnation method inside the pores of the support by controlled reduction of AgNO3 with sodium borohydride (NaBH4). The XRD, TEM, EDS, BET techniques were used for characterization of materials. Silver nanoparticle formation is confirmed by TEM. The efficiency of glucose oxidation to gluconic acid is determined by HPLC-RID and LC-MS. Obtained results showed that it can prepare silver nanoparticles with particle diameter about 5 nm; and catalyst based on these particles has quite efficiency in glucose oxidation to gluconic acid.


Keywords: Ag nanoparticles; SBA-15; Glucose oxidation

I. INTRODUCTION

Recently, the discovery of mesoporous silicas, such as M41S and SBA-15, has stimulated intensive studies of “host-guest” chemistry inside the channels of mesoporous silicas, which have potential applications in catalysis, selective adsorbents, medical, sensors, and nanomaterials fabrications [1–3]. Thanks to their uniform mesostructures, high surface areas, and tunable pore sizes, these ordered mesoporous silicas have been used as the promising templates to control the shape and size of metal nanoparticles. Many published works gave the relation between nanoparticles confined in various molecular sieves and their properties. Moreover, the surface of these ordered mesoporous silicas are also modified for many potential applications. For modifying the mesoporous materials through covalent linkage between functional groups and silica framework, two major methods, grafting (post synthesis) and cocondensation (direct incorporation), have been traditionally explored. The distribution and concentration of functional groups are influenced by reactivity of the organosilane and their accessibility to surface silanols, which are limited by diffusion and steric factors.

Many scientist prepared SBA-15 functionalized with (CH3O)3Si(CH2)3N(CH3)3Cl (TPTAC) and further synthesized metal nanoparticles by anion exchange between grafted SBA-15 and metal precursors inside the channels as well as upon reduction of precursors. The amount of metal loading as well as the morphology of metal in host SBA-15 can be rationally controlled through repeating ion-exchange/reduction cycles in the TPTAC-SBA-15 silica host. They used the same method to prepare Au nanoparticles and found that the size and morphology of Au nanoparticles in mesoporous SBA-15 are controllable by the preparation methods.

However, above-mentioned grafting methods basically allow introduction of functionalization at both intrapore and extrapore media, which led the nanoparticles form at both surfaces. Therefore, large metal particles aggregate would form on the external surface of the host materials. To overcome this disadvantage, we can synthesized Pt nanoclusters within the pore channels of selectively modified mesoporous silica SBA-15 by a new in situ reduction process [5–8]. The silanols on the external surface of SBA-15 were capped with –Si(CH3)3 groups, thus effectively avoiding the formation of large particles outside the channels. On the other hand, the inner surface of the channel was functionalized with highly reducing Si–H bonds. Pt nanoclusters were formed inside the channels of SBA-15 from H2PtCl6 by in situ reduction with Si–H bonds. Like Pt, silver nanoparticles confined inside the channels of SBA-15 resulted in an unusual thermal stability.

In this paper, the stabilizer-free and confined silver nanoparticles inside the channels of selectively grafted mesoporous silica SBA-15 by an in situ reduction process were synthesized. The catalytic activity of silver nanoparticles confined in the mesoporous silica SBA-15 to the reduction of glucose was studied.

II. EXPERIMENTAL

A. Synthesis of Ag-SBA-15

Mesoporous silica SBA-15 was synthesized following the published procedure [1–3] using the triblock copolymer Pluronic P123 as a template in acid conditions. Typically, a 1 g Pluronic P123 template was dissolved with stirring in a solution of 9.7 g HCl 12 M at 313 K, and 2.1 g of tetraethyl orthosilicate (TEOS) was then added. The resulting mixture was stirred at 313 K for 24 hours, and then aged in air for 48 hours under static condition. The recovered solid was extensively washed with deionized water and drying at 353 K for 12 hours yielded as-SBA-15. To get calcinated SBA-15 (cal-SBA-15), the surfactant template of as-SBA-15 was removed by calcination in air.

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†Corresponding author: namtranhhuy@yahoo.com

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at 823 K for 6 hours.

About 1 wt.% Ag catalyst was synthesized as follows: one certain amount silver nitrate was dissolved on absolute alcohol. 1 g of SBA-15 was stirring on the AgNO$_3$/C$_2$H$_5$OH solution in 2 hours, and then an solution of NaBH$_4$/C$_2$H$_5$OH was added dropwise. The solution is stirring in 3 hours at 343 K until form a brown solution. The recovered solid was extensively washed with deionized water and drying at 333 K.

B. Characterization methods

SBA-15 mesoporous silica was characterized by a combination of physical techniques. X-ray diffraction (XRD) patterns were recorded using a Siemens, XRD 5005 powder diffractometer system with CuK$\alpha$ radiation (K$\alpha$ = 1.5406 Å) with 0.2 step size and 1 s step time over the range 0 < 2$\theta$ < 10. The transmission electron microscopy (TEM) with a JEOL 3010 microscope. BET (Brunauer, Emmett and Teller) specific surface areas were obtained from the nitrogen adsorption experiments measured at 77.35 K after degassing the samples below 10$^{-3}$ Torr at 473 K for 2 h using an Autosorb-1C (Quantachrome) unit. The pore size distribution was determined from the desorption branch of the isotherm by BJH (Barrett-Joyner-Halenda) method. The total pore volume was calculated as the amount of nitrogen adsorbed at the relative pressure until 0.99. Pore wall thickness was calculated as: 

\[ \text{Pore wall thickness} = d(100) \times 2/\sqrt{3} \] 

where \( d(100) \times 2/\sqrt{3} \) represents the unit cell parameter and \( d(100) \) is the d-spacing value of the (100) diffraction peak in XRD patterns of the samples. Chemical composition analysis was performed with Varian Vista Ax inductively coupled plasma-atomic emission spectroscopy (ICP-AES) spectrometer.

C. Catalytic reaction procedure

Catalytic reactions were performed in a polypropylene copolymer (PPCO) batch reactor (40 mL) equipped with two tubes for gas inlet and gas outlet of the reflux condenser. The typical reaction procedure was as follows:

20 ml Glucose 1.6 M solution and 0.1 g catalyst were introduced in the reaction simultaneously. The solution was stirred with a magnetic stirrer at about 700 rpm and then it was bubbled by flowing air, and the reaction was started. After the reaction, the aqueous solution was separated from the solid catalyst by filtration and cooled in an ice bath.

D. Products analysis

The resultant aqueous solution was analyzed with two high performance liquid chromatography (HPLC) systems. The HPLC measurement employed a post-column method using bromothymol blue (BTB) equipped with an Hitachi L-2420 UV-vis detector (wavelength 440 nm), two Hitachi L-2130 HPLC pumps and double columns of Shodex RSpack KC-811 using 3 mmol L$^{-1}$ HClO$_4$ as eluent at a flow rate of 1.0 mL min$^{-1}$ at 313 K for the determination of carboxylic acids. The other HPLC system was equipped with a Hitachi L-7490 RI detector, a Hitachi L-6200 HPLC pump and a column of Shodex Sugar 0810 using water as eluent at a flow rate of 1.0 mL min$^{-1}$ at 353 K for the determination of sugars and alcohols. The products were determined based on the standard solutions prepared by dissolving each commercial sodium carboxylate, sugars, and alcohols in distilled deionized water.

III. RESULTS AND DISCUSSIONS

A. Characterization

Figure 1 shows low angle X-ray diffraction patterns of the calcined porous silica host and the calcined doped sample with 1.0 wt.% Ag. The SBA-15 sample have a strong peak in \( d(100) \) plane with 2 is about 0.90, and two weak peak are corresponded to \( d(110) \) and \( d(200) \) planes, indicating ordered pore structure of SBA-15. With the calcined doped sample with 1.0 wt.% Ag, 3 peaks appearing at low angle (2 =0.9, 1.6, 1.9) correspond to \( (100), (110), (200) \) planes of SBA-15 indicating ordered pore structure of SBA-15, which suggests that the hexagonal pore structure of SBA-15 should be retained after being
incorporated with Ag.

B. TEM and EDS images

The TEM images of the calcined porous silica host SBA-15 and calcined Ag/SBA-15 samples are shown in Figs. 2(a), (b) and (c). In agreement with the above SAXRD results, the synthesized sample is of hexagonal mesostructure and remains intact after supported with Ag. The simultaneous EDS analysis, as shown in Fig. 2(d), indicates that Ag element exists on the mesoporous host.

C. N$_2$ sorption isotherms

Figure 3 presents the N$_2$ adsorption/desorption isotherm of the SBA-15 and Ag/SBA-15 samples. The Ag/SBA-15 sample exhibits a typical adsorption curve of type IV, which is the characteristic of nanostructured materials with uniform mesopores. The adsorption and desorption isotherms show a large increase in the relative pressure ($P/P_0$) range from 0.64 to 0.86 (Fig. 3(a)) and 0.45 to 0.8 (Fig. 3(b)), which is due to the capillary condensation of nitrogen within the mesopores. The sharpness of the inflection step reflects the uniform pore size distribution of the Ag/SBA-15 sample. In consonance with results of XRD, the N$_2$ adsorption/desorption isotherm also confirm that the Ag/SBA-15 sample possess high structural integrity.

Table I shows $S_{BET}$, $V_{BJH}$, $t$ (pore wall thickness) values. The total pore volume of SBA-15 sample is double higher than the value of the Ag/SBA-15 sample. It proves that there is presence of silver nanoparticles in mesoporous pore. Beside, the pore wall thickness of Ag/SBA-15 sample is higher than the value of the SBA-15 sample, indicated that incorporation with Ag in pores would increase stability of the host material.

D. Catalytic activity

The catalytic performance of prepared Ag/SBA-15 sample for the glucose oxidation was investigated. The...
FIG. 3: N₂ sorption/desorption isotherms for (a) SBA-15 sample and (b) Ag/SBA-15 sample.

results are presented in Fig. 4. In Fig. 4, we can see that glucose is oxidized to acid gluconic, and a small part is isomerized to fructose because the reaction condition is base one.

IV. CONCLUSION

Nano-scale silver supported mesoporous molecular sieve Ag/SBA-15 was directly prepared by one-pot synthesis method using hexadecyltrimethylammonium bromide (CTAB) as both a stabilizing agent for Ag nanoparticles and a template for SBA-15 host. XRD result shows that there was no appreciable incorporation of silver into the mesoporous matrix, silver nanoparticles present inside the channels or deposits on the external surface of SBA-15. Ag/SBA-15 is found to be an effective catalyst for the glucose oxidation to acid gluconic.

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