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Size-controllable gold nanoparticles prepared from immobilized gold-containing ionic liquids on SBA-15

Etty N. Kusumawati[a], Daisuke Nishio-Hamane[b], Takehiko Sasaki[c,*]

[a] Department of Chemistry, Graduate School of Science, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan
[b] Institute of Solid State Physics, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
[c] Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan

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ABSTRACT

A series of gold nanoparticles (AuNPs) with controllable size were prepared from immobilized gold-containing ionic liquid on SBA-15 (AuCl_me-Im@SBA-15) at room temperature. AuNPs size and shape could be controlled inside porous SBA-15 in the presence of immobilized 1-methyl-3-(3-trimethoxysilyl- propyl)-imidazolium chloride by controlling a concentration and a feed rate of a reducing agent $NaBH_4$. The smallest AuNPs with the average size of 1.6 nm was obtained at a fixed feed rate of 0.2 ml/min with 4 mM $NaBH_4$. The transformation of AuNPs shape from spherical to capsule-like NPs was observed at low feed rate of 0.04 ml/min. The prepared AuNPs catalysts were characterized by TEM, XPS, FTIR, and XRD. The catalyst with the smallest NPs, AuNP (1.6 nm)_me-Im@SBA-15, exhibited the highest catalytic performance in *p*-nitrophenol hydrogenation reaction at room temperature. Moreover this catalyst was reusable up to four recycle processes.

1. Introduction

Gold nanoparticles (AuNPs) are one of the most promising materials as catalyst for various organic reactions [1–4]. Moreover, supported AuNPs catalysts have recently attracted tremendous attention due to their unique catalysis in selective hydrogenation of nitro-compounds [5–7]. Their catalytic activities strongly depend on the particle size and shape, morphologies, metal additives, nature of the supports, and the preparation methods [8–10]. In this study mesoporous silica SBA-15 was selected as a support. SBA-15 is the most well-known mesoporous silica with well ordered hexagonal structure from its family, Santa Barbara Amorphous (SBA) materials [11]. Compared to metal oxides or other materials, SBA-15 offers many advantages as support due to its high surface area, large pore size and uniform pore distribution. These properties allow it to be designed with more flexibility to meet the requirements for various applications. On the other hand, ionic liquids (ILs) or molten salts composed solely of ions, have versatile functionalities and when it is immobilized on solid support finds new opportunities in catalysis. Our research group has reported successful immobilization of metal ion-containing ionic liquids salt and metal ion-containing ILs on silica Aerosil 300 and SBA-15 frameworks for various catalytic reactions [12–18]. In this study we prepared AuCl containing ILs on SBA-15 as a precursor for AuNPs catalysts.

The size of NPs is an important issue. For example, large NPs on porous materials would be an obstacle for the reactant to reach more active sites deeper into porous channel by blocking pores. Therefore, small NPs may be more favourable to optimize the catalytic performance. In many cases catalytic activities of metal nanoparticles depend on particle size and shape [19,20]. Therefore, it is important to control these parameters.

NPs synthesis process contains the reduction of metal precursor with a reducing agent such as sodium borohydride. Many approaches for controlling NPs size have been adopted by controlling the concentration of the ratio between reducing agent and the metal precursor, pH of solution, temperature of synthesis, and by the presence of a stabilizing agent, such as polymer PVP (polyvinylpyrrolidone), PVA (polyvinyl alcohol), ionic liquids, surfactants and dendrimers [21–25]. To manipulate size, shape and structure of NPs, one should understand the particle growth process. Privman described the nucleation and growth of NPs as a model consisting of two-steps: a burst nucleation step, followed by an aggregation of primary particles into micron-sized colloidal agglomerates [26]. Meanwhile, Polte and co-workers studied the metal colloidal growth by the reduction of AuNPs using $NaBH_4$. In those systems, the reduction process is much faster than the actual growth, and the growth mechanisms are always governed by coalescence [27,28].

* Corresponding author.
E-mail address: takehiko@k.u-tokyo.ac.jp (T. Sasaki).

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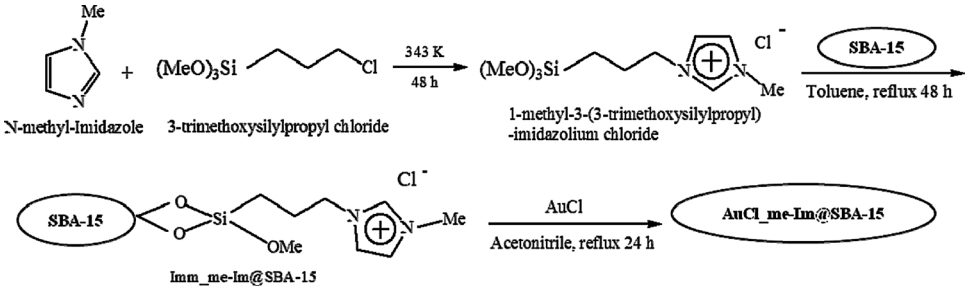

Scheme 1. Preparation steps for AuCl_me-Im@SBA-15.

In this study, we focus on controlling the NPs size and shape by varying the concentration of reducing agent at different rates on SBA-15 with immobilized ionic liquid. We found small NPs with narrow size distribution were obtained at the feed rate of $NaBH_4$ at 0.2 ml/min, whereas at slower feed rates the transformation of spherical into larger capsule-like NPs was observed. The metal precursor AuCl was immobilized on SBA-15 to form $AuCl_x$ anionic species by reacting with Cl^-. These gold chloride complexes were reduced by $NaBH_4$ to obtain Au NPs. The catalytic performance of the synthesized materials was monitored by the reduction of *p*-nitrophenol.

2. Experimental

All chemicals were used without further purification. Tetraethyl orthosilicate (TEOS, 95%) was used as silica source and was purchased from WAKO. Gold (I) chloride (AuCl, 98.5%) and amphiphilic triblock copolymer poly(ethylene oxide)-poly(propylene oxide)–poly(ethylene oxide) Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800) was purchased from Sigma-Aldrich. 1-Methylimidazole ($CH_3C_3H_3N_2$), and 3-trimethoxysilyl-propyl chloride ($C_6H_{15}ClO_3Si$), hydrogen tetrachloroaurate ($HAuCl_4{\cdot}4H_2O$, 99%), *p*-Nitrophenol ($C_6H_5NO_3$, 98.0%), sodium borohydride ($NaBH_4$, 95%), sodium hydroxide (NaOH, 96.0%), hydrochloride acid (HCl, 35.0–37.0%), acetone (C_3H_6O, 99.0%), dehydrated toluene (C_7H_8, 99.5%), dichloromethane (CH_2Cl_2, 99.5%), acetonitrile (C_2H_3N, 99.5%), were purchased from WAKO.

2.1. Synthesis of mesoporous SBA-15

SBA-15 was synthesized according to the procedure reported by Zhao et al. [29], using Pluronic 123 triblock copolymer (P123) as structure-directing amphiphilic agent and TEOS as silica source. 4 g of P123 was first dissolved in the hydrochloride acid solution until a solution became clear, and then TEOS was added drop-wise under stirring at room temperature. The chemical composition of the reaction mixture was 4 g P123:0.041 mol TEOS:0.24 mol HCl:6.67 mol H_2O. The mixture was then stirred to react at 35 °C for 20 h followed by heating at 100 °C for 48 h under static condition in PP bottle. The material was filtered, washed with distilled water and dried at room temperature. As-synthesized SBA-15 was obtained after calcination, in which it was heated to 500 °C at a ramping rate of 1 °C/min and kept at 500 °C for 6 h in air.

2.2. Preparation of ionic liquid

Immobilized ionic liquid on mesoporous silica SBA-15 were prepared using 1-methyl-3-(3-trimethoxysilylpropyl)-imidazolium chloride (MTI). The procedure is based on our previous report [12]. In a typical reaction, the mixture of 1-methyl-imidazole and 3-trimethoxysilylpropyl chloride was refluxed at 70 °C for 48 h under N_2 atmosphere.

2.3. Immobilization of gold ions-containing ionic liquid on SBA-15

In a typical synthesis, 1 g of SBA-15 was reacted with 1.3 g MTI in separable flask with dehydrated toluene. The mixtures were refluxed at 111 °C for 48 h under N_2 atmosphere. After separation and fully washed, the solid product after drying under reduced pressure, was denoted as Imm_me-Im@SBA-15 [16,17]. Two molecules of MTI were immobilized on 1 nm^2 of SBA-15 surface area as confirmed by elemental analysis.

40 mg of AuCl and 2 g of Imm_me-Im@SBA-15 in 250 ml of acetonitrile were refluxed at 82 °C for 24 h under nitrogen atmosphere in a separable flask. After filtration, fully washed with acetone, the solid was dried under reduced pressure. The white powder material was denoted as AuCl_me-Im@SBA-15 with 2 wt% loading of Au.

2.4. Synthesis of AuNPs_me-IL@SBA-15

In a typical reduction process, 0.1 g of AuCl_me-Im@SBA-15 in 10 ml distilled water was reduced by 10 ml of $NaBH_4$ solution under stirring using an automatic syringe pump with a controlled feed rate under N_2 flow. The effects of reducing agent concentration ($NaBH_4$) were studied by varying the molar concentration of $NaBH_4$ solution from 1 mM to 100 mM at a constant feed rate of 1.6 ml/min. On the other hand, the concentration of $NaBH_4$ was fixed to 4 mM to study the effect of feed rate which varied from 0.04 ml/min to 1.6 ml/min. The reduction was conducted at room temperature under N_2 flow. The pinkish solid was separated from the mixture by filtration, after fully washed with distilled water and acetone. Finally, the solid product was then dried at reduced pressure overnight. The resulting materials were denoted according to their size, such as AuNP(1.6 nm)_me-Im@SBA-15 as determined after TEM observations (Scheme 1)istilled water was reduced b.

2.5. Synthesis of Au/SBA-15

Au supported on as-prepared SBA-15 denoted as Au/SBA-15 was synthesized as a reference catalyst according to C.Y. Ma et al. [30] via impregnation method with modification as described below. 4 mg of $HAuCl_4{\cdot}4H_2O$ was dissolved in 0.25 ml distilled water followed by the addition of 0.5 M NaOH to adjust the pH solution. Then 0.2 g of SBA-15 was added into the solution and kept stirring at room temperature for 12 h under N_2 atmosphere. After drying at 70 °C for 5 h, the wet powder was calcined at 200 °C for 2 h.

2.6. Transfer hydrogenation of p-nitrophenol

The catalytic activities of prepared Au NPs catalysts were investigated by the catalytic hydrogenation of *p*-nitrophenol (PNP) with $NaBH_4$ in a quartz cuvette with magnetic stirrer at room temperature using UV–vis spectroscopy (Jasco V-630 BIO). The catalyst suspension in water was sonicated for 20 min before the catalytic test. In a typical reaction, 0.3 mg/ml of catalyst in water was added to 1.0 ml of aqueous PNP solution (0.3 mM or 1 mM), and 1.0 ml of fresh $NaBH_4$ solution (15 mM or 50 mM) in a quartz cuvette. The cuvette with 3 ml mixture of Au:PNP:$NaBH_4$ = 1:10:500 was quickly inserted in UV–vis spectrometer and the reaction progress was monitored at 1 min interval under stirring at room temperature (20 °C). The initial absorbance (C_0) of the high concentration of PNP (1 mM) was determined by the extrapolation