



Fabrication of gold nanoparticles in confined spaces using solid-phase reduction: Significant enhancement of dispersion degree and catalytic activity



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ARTICLE INFO

Keywords:

Dispersion
Gold nanoparticles
Confined spaces
Solid-phase reduction
Catalytic reduction

ABSTRACT

Au-containing catalysts are highly active in diverse reactions, and their activity strongly depends on the dispersion degree of Au. Here we report for the first time a solid-phase reduction strategy to promote Au dispersion in template-occluded SBA-15 (AS) by fully considering three crucial factors, namely (i) the interaction between Au and supports, (ii) the space where Au precursors locate during reduction, and (iii) the reduction method. *First*, both template and silica walls in AS offer interaction with Au species. *Second*, AS presents confined spaces between template and silica walls. *Third*, the reduction in solid phase avoids the competitive adsorption of solvent molecules. The results show Au-containing AS has a better dispersion of Au than its counterpart prepared from template-free SBA-15 (CS). Moreover, the obtained materials exhibit excellent catalytic activity in reduction reactions and that the organic template retained in mesopores promotes the reactions greatly.

1. Introduction

Due to their unique physicochemical properties and excellent catalytic activity, noble metal nanoparticles have attracted much attention in recent years (Azubel et al., 2014; Ciraci et al., 2012; Savage et al., 2012; Valente et al., 2012; Wang et al., 2009). As one of the most concerned noble metal systems, gold nanoparticles (Au NPs), in contrast to the chemical inertness of pure Au films or bullion, are extensively studied (Boscoboinik et al., 2015; Yatabe et al., 2015). Au NPs have been demonstrated to be good catalysts for a variety of reactions such as oxidation (Wang et al., 2015), reduction (Mistry et al., 2014; Zhu et al., 2013), and dissociation (Lin et al., 2015). Because only those active species dispersed on the outermost layer are accessible to reactant molecules, the catalytic activity is strongly dependent on the dispersion degree of Au. An exponential increase in catalytic activity with the decrease of particle sizes has been observed (Lee et al., 2014; Lin et al., 2015). Unfortunately, noble metal nanoparticles are easily mobile on the surface of supports, often leading to severe aggregation and subsequent decrease/loss of catalytic activity after exposure to reaction conditions. As a kind of material with ordered pore structure, mesoporous silica shows high surface area and large pore volume, and is an ideal choice of support for Au dispersion.

Although various methods including ion implantation (Guczi et al., 2003), sol-gel process (Fang et al., 2011), and sputtering (Raghuwanshi et al., 2014) have been reported to disperse Au on mesoporous silica, Au NPs still suffer from considerable aggregation between nanoparticles in close proximity owing to high specific surface energy. So far the development of a facile, efficient method to disperse and stabilize Au NPs has remained a great challenge.

On the basis of previous reports and deep analysis, three factors are believed to correlate closely with the dispersion of Au, namely (i) the interaction between Au and supports, (ii) the space where Au precursors locate during reduction, and (iii) the reduction method for Au precursors. For the *first* factor, functional groups (e.g. $-\text{NH}_2$ (Dhar et al., 2009; Yoon et al., 2013), $-\text{SH}$ (Mayeda et al., 2012), and $-\text{SO}_3\text{H}$ (Rombi et al., 2012; Tschulik et al., 2015)) are usually grafted onto mesoporous silica to promote the interaction between Au and supports. A case in point is Wang's work (Wang et al., 2010), where mesoporous silica SBA-15 was functionalized with amino groups prior to the introduction of Au. A monolayer of charged organic groups were attached on the surface of mesopores, which can adsorb and interact strongly with oppositely charged metal precursors to fabricate dispersed Au NPs. Albeit interesting, complicated surface functionalization is unavoidable by using this traditional method. For the *second*

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factor, Au precursors always locate in template-free mesopores during reduction. In other words, only after the complete removal of template, Au precursors are introduced and subsequently reduced. Nevertheless, there exists a special micro-environment between template and silica walls in template-occluded mesoporous silica. This micro-environment has been proven by Zhu and coworkers (Yue et al., 2008). They created a new kind of CO₂ capturer by incorporating amino group into template-occluded MCM41, which is highly efficient in the adsorption of CO₂. If Au precursors located in this special micro-environment during reduction, the confined effect may favor the dispersion of resultant Au NPs. For the *third* factor, a liquid-phase method is frequently used for the reduction of Au precursors to metallic Au, namely, the reduction process is performed in solutions (Yang et al., 2013). Taking account of the competitive adsorption of solvent molecules, the dispersion degree of resultant Au NPs by use of such a liquid-phase method is questionable (Wang et al., 2004). Moreover, the solubility makes precursors diffuse easily in both internal and external surfaces of supports, and the formation of aggregated nanoparticles becomes possible. In this regard, a new reduction method based on solid phase should benefit the formation of well dispersed Au NPs. Despite great efforts, the fabrication of Au NPs by fully considering the abovementioned three factors has never been reported up to now.

Here, we report for the first time a solid-phase reduction (SPR) strategy to fabricate Au NPs in template-occluded mesoporous silica by fully considering the abovementioned three factors. The Au precursor (HAuCl₄) was incorporated into the template-occluded SBA-15 (AS) by grinding, followed by the addition of reductant NaBH₄ to grind for another 10 min during which the precursor can be converted to metallic Au completely (Scheme 1). *First*, our strategy avoids the complicated surface functionalization, while both template (with plenty of hydroxyl groups) and internal surface (containing more silanols than calcined SBA-15, CS) in the template-occluded support possess interaction with Au species. *Second*, the AS support provides a confined space between template and silica walls, which hinders the aggregation of Au during reduction and maintains the catalytic activity during reactions by limiting the movement of Au species. *Third*, the reduction in solid phase evades the competitive adsorption of solvent molecules and restricts the diffusion of Au species, which is beneficial to the dispersion of resultant Au NPs. The results show that our strategy is highly efficient in fabricating dispersed Au NPs, and the size of Au NPs is only 3.8 nm for the material containing 1.0 wt% of Au (1.0AuAS), which is much smaller than its counterpart prepared from template-free SBA-15 (1.0AuCS, possessing an Au size of 11.5 nm). We also demonstrate that the obtained materials exhibit excellent catalytic activity in the reduction of organics. Taking catalytic reduction of methylene blue (MB) as an example, 1.0AuAS can convert 100% of MB within 5 min, whereas only 35% of MB was converted even after 60 min over its counterpart 1.0AuCS. Similarly, the reduction of 4-aminophenol (4-NP) was finished quickly within 24 min over 1.0AuAS;

however, only 22% of 4-NP was converted even after 60 min over 1.0AuCS. It is interesting to note that the organic template retained in mesopores is capable of enriching organic reactants during reactions, which favors the subsequent catalytic reactions greatly. The preservation of template is thus beneficial to not only the dispersion of Au NPs, but also the improvement of catalytic activity of resultant materials.

2. Experimental section

2.1. Chemicals

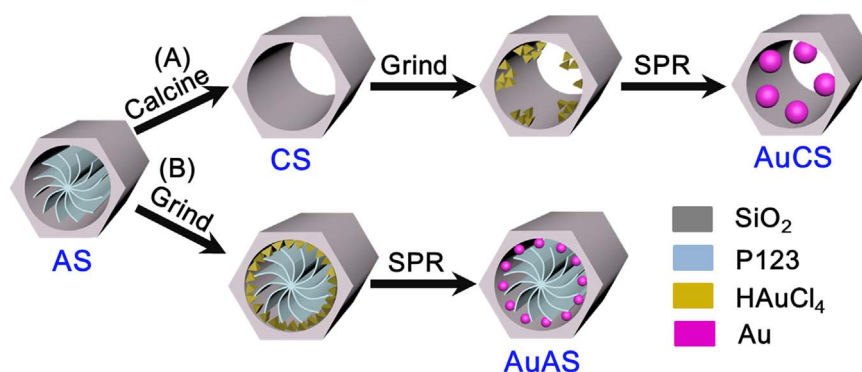
Pluronic 123 (P123), sodium borohydride (NaBH₄), 4-nitrophenol (4-NP), and methylene blue (MB) were obtained from Aldrich. Tetraethylorthosilicate (TEOS) were obtained from Sinopharm. Hydrochloric acid (HCl) were obtained from Shanghai Ling Feng. Chloroauric acid (HAuCl₄·3H₂O) were obtained from Adamas. All reagents were used as received without further purification.

2.2. Materials synthesis

Mesoporous silica SBA-15 was synthesized according to the reported method (Zhao et al., 1998b). In a typical synthesis, 2 g of Pluronic P123 was firstly dissolved in 75 g of aqueous HCl solution (1.6 M). Then 4.25 g of silica source tetraethylorthosilicate (TEOS) was added to the homogeneous solution and stirred at 40 °C for 24 h, followed by hydrothermal treatment at 100 °C for 24 h. The template-occluded mesoporous silica SBA-15 (denoted as AS) was recovered by filtration and dried under ambient conditions. After calcination in flowing air at 550 °C for 5 h, the template P123 was removed and template-free mesoporous silica SBA-15 (denoted as CS) was obtained.

The Au precursor HAuCl₄·3H₂O was introduced to AS by grinding under ambient conditions, then the obtained solids were reduced by a SPR strategy. The SPR strategy means that Au precursor was reduced by grinding with the reductant under the free-solvent condition. The obtained samples were denoted as *n*AuAS (*n* represents the weight percent of Au per gram of the obtained samples). Typically, 0.0106 g of HAuCl₄·3H₂O was introduced to 0.5 g of AS by grinding under ambient conditions for 30 min. Then 0.0152 g of NaBH₄ was added to the above mixtures and ground for another 10 min (the Au/NaBH₄ molar ratio was 1:15). The color of mixtures turned red quickly. After reduction, the obtained solids were washed with deionized water sufficiently so that excess amounts of reagents including reductant NaBH₄, and byproduct such as NaCl can be removed. The obtained sample was denoted as 1.0AuAS. By changing the amount of Au precursor, it can obtain other samples which have the different Au content. For comparison, HAuCl₄·3H₂O was also introduced to CS in a similar process as described above. The obtained samples were denoted as *n*AuCS (*n* represents the weight percent of Au per gram of the obtained samples).

In a typical solution phase syntheses, 0.0106 g of HAuCl₄·3H₂O,



Scheme 1. The SPR strategy for fabrication of (A) aggregated Au NPs in conventional mesopores and (B) well-dispersed Au NPs in confined spaces (template-occluded mesopores).

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