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Article

Gold nanoparticle stabilization within tailored cubic mesoporous silica: Optimizing alcohol oxidation activity

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ABSTRACT

Stabilizing gold nanoparticles (AuNPs) within a desired size range is critical to realize their promising catalytic performance in many important reactions. Herein, we investigate the anti-sintering properties of cubic mesoporous silica (FDU-12) as a function of pore entrance size. Simple adjustments to the type of organic template and reaction temperature enable the successful synthesis of FDU-12 with controllable entrance sizes (< 3, 3–5 and 7 nm). Excellent anti-sintering properties are observed for FDU-12 with a sub-5-nm entrance size (3–5 nm) over a wide loading concentration (1.0–8.3 wt%) and the AuNPs can be stabilized within a 4.5–5.0-nm range after calcination at 550 °C in air for 5 h. Smaller entrance size (< 3 nm) prevents ingress of 3-nm AuNPs to the mesopores and results in low loading capacity and sintering. Conversely, FDU-12 possessing a larger entrance size (7 nm) shows promising anti-sintering properties at high loading concentrations, although catalytic performance is significantly lost at lower concentrations (e.g. 2.1 wt%, 14.2 ± 5.5 nm). Different anti-sintering mechanisms are proposed for each of the different FDU-12 entrance sizes. Additionally, catalytic data indicates that the obtained 4.5-nm AuNPs supported on FDU-12 with a sub-5-nm entrance size exhibit excellent mass-specific activity (1544 mmol g_{Au}^{-1} h^{-1}) and selectivity (> 99%) at 230 °C for the gas-phase selective oxidation of cyclohexanol.

1. Introduction

Gold nanoparticles (AuNPs) have attracted great interest owing to their valuable potential in many important catalytic reactions, such as hydrogenation of olefins, water gas shift reaction, direct synthesis of hydrogen peroxide and selective alcohol oxidation [1]. The catalytic activities of AuNPs are largely associated with their sizes, atom-packing configuration, crystal facets, and the interface types with supports [2,3]. However, the thermodynamic tendency of AuNPs to grow into larger crystallites, which minimizes their surface energy, is a key obstacle to achieving efficient and sustainable catalytic activity [4–9]. To maintain AuNPs within the desired size range at high temperatures (generally > 300 °C), both atom migration (Ostwald ripening) and particle migration need to be controlled during thermal treatment [10,11].

Porous materials have long been used as supports for the preparation of supported AuNP catalysts to improve their thermal stability. There are numerous proposed methods directed at hindering sintering effects caused by particle or atom

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migration [12–23]. Generally, the narrow pore dimensions of porous supports enhance the physical barriers that mitigate the rate of particle growth of supported AuNPs [14,24,25]. Additionally, high metal loading should be avoided to suppress particle aggregation by increasing inter-particle distances [26]. Conversely, pore connectivity and structure have been reported to significantly impact NP stability [14,27,28]. It has been shown that one-dimensional (1-D) pores are more efficient in restricting particle growth than three-dimension (3-D) pore systems by restraining metal NP transportation [26,27]. However, mass diffusion limitations and pore blockage are more of an issue in 1-D porous systems than their 3-D counterparts.

Prior to this work, we have shown that excellent anti-sintering properties can be achieved at high AuNP loading levels when using the extra-large mesoporous silica, EP-FDU-12 (cage size > 25 nm), as the support [29]. The 3-D porous structure of EP-FDU-12 allows two or more AuNPs to reside in every extra-large mesopore at high loading concentrations (> 9 wt%). Thus, inter-particle interactions are remarkably strengthened *via* significant overlapping of the diffusion-spheres of AuNPs and local vapor-particle equilibrium in each cage is possible. In this case, a self-focusing mechanism dominates the particle growth, leading to an obvious suppression of atom migration and therefore outstanding anti-sintering properties. Nevertheless, traditional EP-FDU-12 having larger entrance sizes (> 7 nm) is not able to suppress sintering at low loading concentrations. Following the classic Ostwald ripening mechanism, the AuNPs grow larger after high-temperature calcination.

Herein, we study the sintering resistance properties as a function of FDU-12 pore entrance size. Simple adjustments to the type of organic template and reaction temperature enable the successful synthesis of FDU-12 with controllable entrance sizes (< 3, 3–5 and 7 nm). Different NP growth mechanisms are proposed for each of the different entrance sizes. It is worth noting that stabilized AuNPs having the desired size range over a narrow distribution (4.5–5.0 nm) form after calcination (550 °C in air for 5 h) when supported on FDU-12 having a sub-5-nm entrance size. This stabilization is achieved over a wide loading concentration (1.0–8.3 wt%) in contrast to EP-FDU-12 having a larger entrance size (7 nm). Catalytic performance of the supported AuNPs is evaluated from gas-phase alcohol selective oxidation reactions. It is shown that the supported Au catalysts with the desired uniform size distribution exhibit excellent mass-specific activity (1544 mmol g_{Au}^{-1} h^{-1}) and selectivity (> 99%) at 230 °C for the gas-phase selective oxidation of cyclohexanol, which significantly surpasses previously reported Ag- or Mn-based catalysts (784 mmol g_{Ag}^{-1} h^{-1}, 50% selectivity and 879 mmol g_{Mn}^{-1} h^{-1}, 70% selectivity, respectively) [30,31]. Furthermore, AuNP/FDU-12 catalysts show superior long-term stability under the applied reaction conditions.

2. Experimental

2.1. Material preparation

2.1.1. Preparation of FDU-12

Cubic mesoporous silica (FDU-12) with controllable sub-5-nm entrance sizes was synthesized as a function of changes to the type of organic template and synthesis temperature, following previously reported methods [32,33]. In a typical synthesis, 0.50 g of triblock copolymer $EO_{132}PO_{50}EO_{132}$ (Pluronic F108, BASF), 0.60 g of 1,3,5-trimethylbenzene (TMB, CP grade, Sinopharm Chemical Reagent Co. Ltd.) and 1.25 g of KCl (AR grade, Sinopharm) were dissolved in 50 mL of 1 mol/L hydrochloric acid at 25 ± 0.1 °C. After stirring for 1 h, 2.08 g of tetraethyl orthosilicate (TEOS, AR grade, Sinopharm) was added to give a molar sol-gel ratio of 0.00136 F108 : 0.62 KCl : 0.37 TEOS : 0.185 TMB : 1.85 HCl : 100 H_2O. After stirring for 24 h at 25 ± 0.1 °C, the mixture was transferred into an autoclave and heated at a desired temperature for 24 h. For FDU-12(18, 4) (18 and 4 indicate the pore and entrance size, respectively), the hydrothermal temperature was set to 140 °C and lowered to 100 °C for FDU-12(15, <3). The as-made product was obtained by filtration and air-dried at room temperature. The organic template was removed by calcination in air at 350 °C for 5 h. EP-FDU-12 having larger entrance sizes was synthesized according to our previous report [29].

2.1.2. Preparation of AuNPs

The synthesis of AuNPs was similar to the reported method [34]. In a typical synthesis, 100 mg of $AuPPh_3Cl$ was mixed with 400 μL of dodecanethiol (≥ 98%, Sigma-Aldrich) in 20 mL of toluene (AR grade, Sinopharm) to form a clear solution, to which 84 mg of $NaBH_4$ (96%, Sinopharm) was added in one portion. The mixture was heated with stirring at 55 °C for 7 h before the reaction system was cooled to room temperature. AuNPs were precipitated out from the reaction mixture as a black solid powder by addition of 40 mL of ethanol. The precipitate was separated by centrifugation before washing with ethanol and natural drying.

2.1.3. Preparation of AuNP/mesoporous silica and AuNP/γ-Al_2O_3

AuNPs were loaded into mesoporous silicas by a colloid deposition method [35]. The desired amount of AuNPs was suspended in 25 mL of chloroform. To this solution, the desired amount of mesoporous silica was added. After stirring for 1–24 h, the solid product was centrifuged and air-dried. The AuNP/mesoporous silica samples were thermally treated at 550 °C in air for 5 h to evaluate their anti-sintering properties and catalytic performance. The preparation of AuNPs on a commercial γ-Al_2O_3 (99.9%, Aladdin) was identical to the AuNP/mesoporous silica method, except that the calcination temperature was lowered to 350 °C. AuNP particle size was analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurements.

2.2. Catalytic oxidation of cyclohexanol

The oxidation of cyclohexanol was performed within an electronically controlled furnace in a fixed bed vertical glass reactor (length = 250 mm, i.d. = 12 mm), fitted with a glass frit carrying the catalyst mixed with quartz sand. The oxygen stream (4 mL/min) was controlled by a mass flow instrument