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Nanoengineering Supports for Gold Catalysts via Selective Surface Functionalization

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Introduction

We have been interested in the development of layer-by-layer functionalization techniques to tailor the surfaces of mesoporous materials for catalysis applications and recently reported a surface sol-gel process technique to accomplish the formation of gold nanoparticles on ordered mesoporous silica materials via the deposition-precipitation (DP) method without the constraint of the low isoelectric point (IEP) of SiO₂ surfaces.[1-3] The essence of this methodology involves the introduction of a high-IEP oxide component on mesoporous silica surfaces to decrease the negative charges of silica surfaces. The surface sol-gel process (SSP) was originally developed by Kunitake and co-workers.[4] This novel technology enables the molecular-scale control of film thickness over a large 2D substrate area and can be viewed as a solution-based methodology for atomic layer deposition (ALD) synthesis.[5] The SSP technique generally consists of two half reactions: (a) nonaqueous condensation of metal-alkoxide precursor molecules with surface hydroxyl groups and (b) aqueous hydrolysis of the adsorbed metal-alkoxide species to regenerate surface hydroxyls. The iteration of the above sequential condensation and hydrolysis reactions allows the layer-by-layer coating of a selected metal oxide on a hydroxyl-terminated surface. The key advantages of this layer-by-layer approach are (a) conformity, (b) monolayer precision, and (c) diverse composition. Here, we report our recent work on the extension of SSP to the 3-D modification of silica surfaces for preparation of highly stable gold nanocatalysts for CO and other oxidation reactions.

Materials and Methods

Gold nanoparticles were introduced on nanoparticles of TiO₂ (P25) via a DP procedure based on the method developed by Haruta.[6] Typically, the pH value of a 0.015 M aqueous solution (150 ml) of HAuCl₄·3H₂O was adjusted to 10.0 with a 1 M NaOH aqueous solution. To this solution, 4 g of TiO₂ nanoparticles were added and magnetically stirred at 70°C for 2 h. The particles were washed with distilled water, dried, and calcined at 300°C for 3 h in air (Au/TiO₂: 3.2 wt%). Two methodologies were developed to encapsulate the resulting Au/TiO₂ catalyst with porous silica coatings.

The first methodology involves an efficient surface-catalyzed SSP on the surface of Au/TiO₂. [7-8] The multilayers of silica were conformally grown on the surface of TiO₂ nanoparticles. Briefly, a pre-weighed Au/TiO₂ powder sample was loaded into a reflux flask and dried at 125°C for 16 h. Subsequently, tris(tert-butoxy)silanol and anhydrous toluene were transferred into the reflux flask. The resulting solution was refluxed for 3 h. The final product was filtered, washed, hydrolyzed, and dried at 80°C overnight.

The second encapsulation methodology involves the direct coating of a mesoporous layer on the surface of the Au/TiO₂ catalyst. Briefly, the calcined Au/TiO₂ catalyst (0.5 g) was

dispersed into an ethanol solution (150 ml) containing 3.04g TMOS, 1.5g H₂O, 1.7g Brij 30. The resulting mixture was stirred for 15h, filtered, washed, and dried oven at 70 °C.

Results and Discussion

Our overall objective was to create complex surface structures for stabilizing gold nanoparticles without degradation of catalytic activities. The stability of nanoparticles depends not only on 2-D surface structures but also on 3-D surface structures. We have exploited the selective surface modification of active catalytic systems via a catalyzed SSP process. **Scheme I** gives a schematic diagram of the SSP process for the modification of active sites. The essence of our method is to make use of selective and catalyzed deposition of oxides via SSP on TiO₂ surfaces without affecting metallic gold nanoparticles. This selective SSP process will lead to 3-D oxide cavities for the immobilization of gold nanoparticles, which can enhance the stabilities of the resulting catalysts against sintering and aggregation. The activity of the gold catalysts for CO oxidation was characterized using a plug-flow reactor. The comparison of the gold catalyst stabilized via the SSP method with that derived from the direct coating of the mesoporous layers was made. The dependence of the catalysis activities on surface topologies was investigated. Considerably enhanced stabilities of gold nanoparticles against sintering were found for both catalyst systems.

Significance

In conclusion, both SSP and direct coating methods have been demonstrated to be very effective in creating complex support surfaces with 3-D structures for enhancing stabilities and activities of gold catalysts. This research opens up a new avenue in rational design of catalyst supports.

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Scheme I

