

PREPARATION OF Au/SULFONATED POLYSTYRENE CATALYSTS FOR LOW-TEMPERATURE CO OXIDATION*

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Abstract Supported Au catalysts for low-temperature CO oxidation were prepared by solvated metal atom impregnation (SMAI) and conventional impregnation (CI). X-ray photoelectron spectroscopy (XPS) investigations indicated that the elemental gold in all the samples was in the metallic state. XRD measurements showed that the mean diameters of Au particles prepared by SMAI were smaller than those prepared by CI with the same gold content. Catalytic tests showed that the SMAI catalyst had higher CO oxidation activity than the CI catalyst with the same compositions. Both SMAI and CI catalysts exhibited high activity in low temperature CO oxidation. Full CO conversion was obtained at 323–383K.

Keywords CO oxidation, Gold catalysts, Solvated metal atom impregnations, Conventional impregnation, Sulfonated polystyrene

INTRODUCTION

Low-temperature CO oxidation has been extensively studied because it plays an important role in gas purification of CO₂ lasers, CO gas sensors, air-purification devices for respiratory protection, pollution control devices for reducing industrial and environmental emissions and removing a trace quantity of CO from the ambient air in enclosed atmospheres such as in submarines and in spacecraft. It has been reported that gold nanoparticles deposited on metal oxides, such as TiO₂, Fe₂O₃, Co₃O₄ and NiO, exhibit high catalytic activity in low temperature CO oxidation^[1-3], whereas the support alone, bulk gold and gold particles of about 20 nm in diameter are known to be rather inactive up to temperature of about 573 K^[4, 5]. Granwaldt suggested that no strong interfacial contact between gold and oxide seems to be necessary, as follows from the fact that the uncalcined Au/TiO₂ catalyst shows significant activity^[6]. The catalytic performance of gold is supposed to depend markedly on particle size, the nature of the support, and the preparation methods. Many experimental results have demonstrated that gold particle size significantly affects the activity of gold catalysts. Harceta reported that the CO oxidation activity of a gold catalyst increases with decreasing size of the Au particles^[4]. For potential application in catalysis smaller gold particles need to be synthesized. Designing a good preparation method to obtain ultrafine gold particles is a challenging task.

Here we report the preparation of resin supported gold catalysts via solvated metal atom impregnation (SMAI) and conventional impregnation (CI). One of the features of this SMAI technique is that it can directly immobilize the zero-valent metal on a support without needing high-temperature calcination and reduction which might cause the metal particles to aggregate to form larger ones. The SMAI method is especially useful for preparing polymer supported metal catalysts because organic polymers are generally of poor thermal stability. Our earlier work^[7, 8] showed that the supported metal particles prepared via SMAI were very small with mean diameter generally in the range of 1–5 nm, and showed high activities in many reactions. Therefore, the

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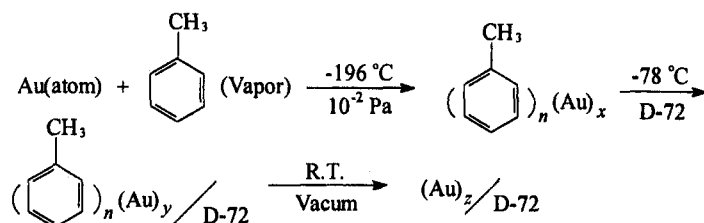
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preparation of gold catalysts via the SMAI method and comparing it with the CI method is a useful strategy to gain more detailed understanding of the influence of particle size on CO oxidation activity.

EXPERIMENTAL

Preparation of Catalyst

The procedures for preparing Au/sulfonated polystyrene catalysts by the SMAI method are as follows:



The support D-72 is a macroporous sulfonated polystyrene (produced by the Chemical Plant of Nankai University) with an exchange capacity ≥ 4.0 mmol/g, diameter of aperture 300 nm and specific area $15 \text{ cm}^2/\text{g}$. The highest use temperature of the resin is 393 K. It was converted into Na type and dehydrated under vacuum (1.3×10^{-2} Pa) at 100°C for 8 h before use. Toluene used as the solvating medium was carefully dehydrated and degassed by a "freeze-thaw" process. The design of the static metal atom reactor for the preparation of the precursor solution of bis(toluene) gold(O) has been described elsewhere^[9]. In a typical experiment, approximately 1 g of gold (99.9%) was evaporated and cocondensed with 130 mL of toluene at -196°C under a dynamic vacuum of less than 1.33×10^{-2} Pa over a period of about 1 h. After finishing the cocondensation, the cocondensate was warmed up to -78°C and melted down to the bottom of the reactor. The bis(toluene) gold(O) complex prepared in this way is extremely air sensitive and thermally unstable, and decomposes into gold(O) and toluene at about -100°C . The precursor solution was transferred to the precooled (-78°C) D-72 resin through a stainless steel tube. The D-72 resin was impregnated with solvated Au atom(cluster) solution for 5 h at -78°C under stirring. Then the Au-toluene/resin slurry was gradually warmed to room temperature. The excess toluene was removed by a syringe and the Au/D-72 catalyst was dried under vacuum at room temperature for several hours. The dry samples were stored and handled in the glovebox filled with N_2 .

The CI Au/D-72 catalysts were prepared by the reduction of HAuCl_4 with diammonium citrate in an aqueous dispersion of D-72 resin under stirring for 4 h. The catalyst precipitates were repeatedly washed with distilled water until no Cl^- was detected in the filtrates. This catalyst was finally dried under vacuum at 100°C .

Characterization of the Catalyst

XRD

X-ray diffraction measurement of the supported gold particles was performed on a D/MAX-III A X-ray diffraction spectrometer. The diffraction patterns were recorded with $\text{CuK}\alpha$ radiation and graphite monochromator over a 2θ range of 20° to 70° . The working voltage and current of the X-ray tube were maintained at 45 kV and 170 mA.

XPS

The XPS spectra were recorded on a PHI-5300 spectrometer using $\text{MgK}\alpha$ radiation to excite photoelectrons. The instrument was operated at pressure below 1×10^{-6} Pa and at 150 eV. Samples were mounted on the holder using double-sided adhesive tape. The binding energy was calibrated versus $\text{Au}_{4f_{7/2}}$ at 84.0 eV.

Catalytic test

Steady-state catalytic tests were carried out in a fixed-bed flow microreactor. The catalyst powder was embedded between the glass wool plug in a glass tube reactor having an internal diameter of 8 mm. Experiments were

performed in the temperature range of 273–393 K and at atmospheric pressure. For each experiment, 200 mg catalyst was transferred into the reactor under the protection of N₂ gas flow. The reaction gases contain 1.0% CO balanced with air purified through a molecular sieve column passed through the catalyst bed at a flow rate of 67 mL/min (*sv* = 20000 mL/h/g). Kinetic data were taken after 10 or 20 min on stream under specified conditions. The products were analyzed by a SP-501 gas chromatograph.

RESULTS AND DISCUSSION

Characterization of XRD and XPS

Figure 1 shows the XRD patterns for 4.3 wt% Au/D-72 (SMAI) and 4.3 wt% Au/D-72 (CI) catalysts. The intensity of the diffraction peaks at $2\theta = 38.2^\circ$ for Au (III), $2\theta = 44.4^\circ$ for Au (200) and $2\theta = 64.6^\circ$ for Au (220) depended on the methods of catalyst preparations. There are no Au diffraction peaks observed on the samples prepared by the SMAI method. This is because the Au particles in this sample are so small that they go beyond the limit of the instrument sensitivity (≈ 2.5 nm). However, it can be seen there are Au(III) diffraction peaks in the spectra of the CI samples. The average crystallite diameter can be obtained according to Scherrers equation $dv = K\lambda/\beta \cos\theta$. The results are listed in Table 1.

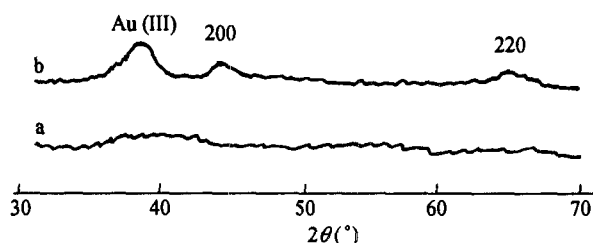


Fig. 1 XRD patterns of Au/D-72 catalysts

a) 4.3 wt% Au/D-72 (SMAI)

b) 4.3 wt% Au/D-72 (CI)

Table 1. Particle sizes of Au/D-72 resin catalysts

Catalyst	Preparation method	Particle size (nm)
4.3 wt% Au/D-72	SMAI	< 2.5
4.3 wt% Au/D-72	CI	3.8

XPS spectra of D-72 supported gold catalysts are shown in Fig. 2. The detected Au_{4f} peaks did not exhibit any appreciable shift in the binding energies from those of bulk gold, indicating that gold particles of all the samples were in the metallic state.

The Au concentration (at%) on the surface of the samples was determined from Au_{4f} peak area of the corresponding lines using a Shirley-type background and empirical cross section factor for XPS^[10, 11]. The Au surface concentrations were found to be 3.5 at% for 4.3 wt% Au/D-72 (SMAI) and 1.1 at% for 4.3 wt% Au/D-72 (CI)

Catalytic Activity in CO Oxidation

Table 2 shows a comparison of the catalytic activity of SMAI and CI gold catalysts for CO oxidation. The 4.3 wt% Au/D-72 catalyst prepared by the SMAI method exhibited higher activity in CO oxidation at low temperature, giving 50% CO conversion at 313 K and 100% CO conversion at 373 K. In contrast, the 4.3 wt% Au/D-72 catalysts prepared by the CI method showed lower activities than the SMAI catalysts with the same composition.

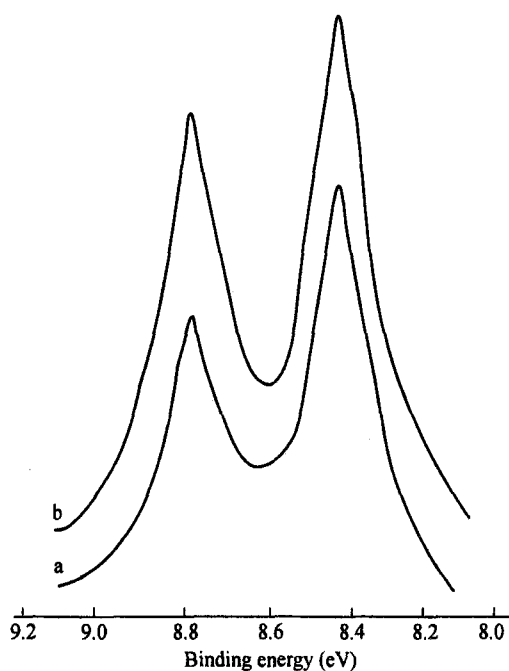


Fig. 2 Au_{4f} XP spectra of the gold catalysts

a) 4.3 wt% Au/D-72 (SMAI)

b) 4.3 wt% Au/D-72 (CI)

Table 2. Catalytic activity of various gold catalysts in CO oxidation

Catalyst	Preparation method	T_s (K)	$T_{50\%}$ (K)	$T_{100\%}$ (K)
4.3 wt% Au/D-72	SMAI	283	313	373
4.3 wt% Au/D-72	CI	303	333	393

Note: T_s , temperature for co oxidation to start; $T_{50\%}$, temperature for 50% conversion; $T_{100\%}$, temperature for 100% conversion

Figure 3 depicts the catalytic activity (CO conversion) of the gold catalysts in CO oxidation as a function of reaction time. It is to be noted that the CO conversion increases with increasing temperature for all the samples under the present reaction condition. But the CO conversion data differ significantly for SMAI and CI catalysts. The 4.3 wt% Au/D-72 catalyst prepared by SMAI method is more active than the CI catalysts.

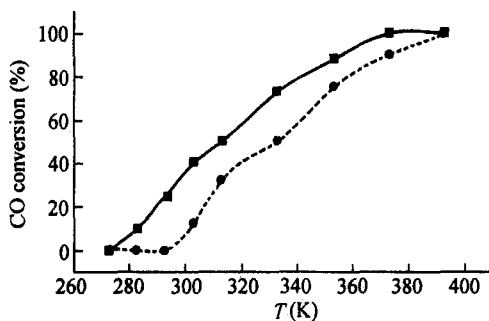


Fig. 3 Catalytic activity of gold catalysts in CO oxidation as a functional of reaction temperature

■ 4.3 wt% Au/D-72 (SMAI); ● 4.3 wt% Au/D-72 (CI)

An interesting result of the present work is that the gold particles supported on resin are active for low temperature CO oxidation. It has been known from our previous work^[12] that the interaction between the metal particles and resin is so weak that the metal particles can peel off during the reaction time. This result proves that no strong structural gold/support interaction is necessary for the low temperature CO oxidation.

CONCLUSIONS

The preparation of supported gold particles via solvated metal atom impregnation affords highly active catalysts for the low temperature oxidation. SMAI is a very intriguing technique for preparing highly dispersed gold particles which is the key factor in low temperature CO oxidation. The SMAI catalysts show higher activity of CO oxidation than the CI catalysts with the same composition.

No strong gold/support interaction is necessary for the significant activity. The experimental results show an overall trend that the CO oxidation activity increases with decreasing size of the Au particles.

Catalyst preparation via SMAI offers a way to tailor the particle size through the change of the metal evaporation rate, the molar ratio of metal atom to solvent and the impregnation temperature. Moreover, this method can also be used for gold immobilization on supports such as resin, where conventional preparation methods have considerable limitations. This could give a valuable insight into the role of the particle size and supports in low temperature CO oxidation.

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