Nanosized Au/C Catalyst Obtained from a Tetraamminegold(III) Precursor: Synthesis, Characterization, and Catalytic Activity in Low-Temperature CO Oxidation

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Abstract—A method in which the water-soluble complex [Au(NH₃)₄](NO₃)₃ is used as the active-component precursor is suggested for preparing nanosized Au/C catalysts (C = Sibunit, a mesoporous carbon material). The complex is unreadily reducible by the carbon matrix and can be involved in cation exchange with proton-containing groups of the support. This method is referred to as cationic adsorption. It has been demonstrated by X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy that the catalyst prepared in this way and treated with H₂ at 400°C contains size-uniform gold metal particles with a dominant diameter of <5 nm. The greater part of the gold particles is located on the outer surface of the Sibunit granules; that is, an egg shell-type distribution of the active component takes place. The catalyst containing 1.3 wt % Au shows high activity in CO oxidation with excess humid air at 40°C. In this respect, it is far superior to the Au/C catalysts prepared by conventional methods (deposition–precipitation and impregnation), in which the typical gold particle size is several tens of nanometers.

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Gold particles smaller than 5 nm in diameter are catalytically very active in some reactions, particularly in low-temperature CO oxidation [1]. In recent years, several methods have been suggested for preparing nanosized Au/EOₓ catalysts (EOₓ = TiO₂, CeO₂, Fe₂O₃, Al₂O₃, MgO, etc.) [2–6]. The gold catalysts prepared by these methods have been tested in the removal of CO from air, industrial gas emissions, and automotive exhaust [5]. For many potential applications of gold catalysts ( household and industrial air cleaners, gas masks, respirators, gas sensors, fuel cells, catalytic reactors for liquid-phase reactions), preferable supports are carbon materials owing to their excellent texture and sorption properties, high resistance to acidic and alkaline media, availability, and low cost, as well as the possibility of recovering gold from the spent catalyst by burning the support [7]. Nevertheless, there are still no convenient methods for obtaining ultrafine gold particles on carbon supports.

Nanosized gold catalysts on oxide supports are usually prepared by deposition–precipitation technique via adsorption of anionic Au⁺⁺⁺ hydroxochloro complexes from an alkalified HAuCl₄ solution and calcination of the product at a high temperature or via impregnation of the support with an aqueous HAuCl₄ solution followed by reducing the supported component with hydrogen [1, 6]. However, gold deposition on carbon support by these methods mainly yields large Au⁰ crystallites, supposedly because anionic Au⁺⁺⁺ chloro and hydroxochloro complexes in the aqueous medium are readily reduced by carbon to gold metal, which deposits on the outer surface of the support granules [8–12]. To avoid this situation, it is suggested to impregnate the carbon support with a beforehand prepared Au⁰ sol with the necessary particle size [13]. However, this method does not provide sufficient reproducibility because the size of colloidal particles is very sensitive to the synthesis conditions. In addition, the reductants and the macromolecular organic stabilizers that are added to sols in order to prevent colloidal particles from coagulation, as well as their thermal decomposition products, can block the catalyst surface and cause a considerable decrease in catalytic activity.

We think that a more promising strategy is to use, as the active component precursor, a gold complex that is unreadily reducible by carbon but can be involved in an ion- or ligand-exchange reaction with functional groups of the carbon surface. In this case, provided that the precursor and precursor–support interaction conditions are optimal, it is possible to obtain the active component in the molecular (or near-molecular) disperse state and to ensure strong bonding between the active component and the support. Possible precursors for this technology are cationic gold complexes with stable N-, P-, or S-donor ligands that have a low redox potential and can be exchanged for protons of the surface groups of carbon. The only example of implementing this strategy was reported by Bulushev et al. [14], who deposited the gold ethylene-
diamine (en) complex [Au(en)\textsubscript{3}]Cl\textsubscript{3} on activated carbon filaments with a microporous structure via a cation-exchange reaction between the complex and surface phenol groups followed by reduction of the product with H\textsubscript{2}. This method can be called cationic adsorption. Because a considerable part of the Au\textsuperscript{III} ions did interact with the carbon surface to yield gold metal under these deposition conditions, the resulting samples had a broad Au particle size distribution covering the range from 2–5 nm to several tens of nanometers. Fairly high CO oxidation activity was shown only by catalysts prepared by deposition of [Au(en)\textsubscript{3}]Cl\textsubscript{3} on activated carbon fibers that had been subjected to drastic pretreatment (boiling in aqueous HNO\textsubscript{3} followed by calcination in flowing helium at 700°C). However, this pretreatment exerted an adverse effect on the adsorption properties of the support. Unfortunately, Bulushev et al. [14] did not reported any quantitative data concerning the proportions of small and large particles in the resulting catalysts, so it is impossible to judge the actual uniformity of the Au particle size distribution in these catalysts.

Here, we demonstrate that a highly dispersed Au/C catalyst can be obtained by adsorbing [Au(NH\textsubscript{3})\textsubscript{4}](NO\textsubscript{3})\textsubscript{3}, another cationic gold complex, on the surface of a granular carbon support without subjecting the latter to any thermal or chemical pre-treatment. The Au/C catalyst that was prepared using this complex and was treated with H\textsubscript{2} at 400°C contained predominantly <5-nm gold particles and showed high activity in the removal of CO from a humid air stream at 40°C. Its activity was comparable with the activity of the highly dispersed Au/Al\textsubscript{2}O\textsubscript{3} catalyst prepared by the deposition–precipitation method.

**EXPERIMENTAL**

**Catalyst Preparation**

HAuCl\textsubscript{4} ⋅ nH\textsubscript{2}O (reagent grade) contained 49.47 wt % Au (Aurat Company, Specifications TU 6–09–05–1075–89). [Au(NH\textsubscript{3})\textsubscript{4}](NO\textsubscript{3})\textsubscript{3} was obtained by reacting HAuCl\textsubscript{4} with NH\textsubscript{3} ⋅ H\textsubscript{2}O in a saturated NH\textsubscript{4}NO\textsubscript{3} solution. The complex was isolated from the solution and was purified from Cl\textsuperscript{−} by recrystallization using a procedure described in the literature [15, 16]. The other chemicals were used as received.

The support was mesoporous, graphite-like carbon Sibunit [17] with a particle size of 0.2–0.5 mm, a BET surface area of 281 m\textsuperscript{2}/g, and a total pore volume of 0.39 cm\textsuperscript{3}/g. The support mostly 3–10 nm and no micropores (the mean pore diameter was 5.5 nm). The support was used without any pretreatment.

**Preparation of an Au/C catalyst by cationic adsorption.** Sibunit granules (1 g) were stirred in distilled water (4 ml) at room temperature for 30 min. Thereafter, the water was decanted and an aqueous solution of [Au(NH\textsubscript{3})\textsubscript{4}](NO\textsubscript{3})\textsubscript{3} (40 ml, 2.55 mmol/l) was added.

The resulting suspension was stirred for 2 h and then filtered. The solid was washed on the filter with water, outgassed to a residual pressure of 0.05 Torr using a vacuum system, and calcined in flowing H\textsubscript{2} (80 ml/min) at 400°C for 4 h.

**Preparation of reference catalysts.** The Au/C catalysts to be used as reference samples were prepared by incipient-wetness impregnation and deposition–precipitation methods. In the first method, an aqueous HAuCl\textsubscript{4} solution (0.11 mmol/l, pH ≈1) was added to a Sibunit sample. The volume of the solution was 10% larger than the water-filled pore volume of the support. The resulting paste was mixed for 1 h and was left in air for water evaporation. In the second method, Sibunit (1 g) was treated at 70°C with an HAuCl\textsubscript{4} solution (40 ml, 2.55 mmol/l) alkalified with NaOH to pH ≈ 7. The process was performed in a shaker reactor for 1 h. Thereafter, the solid was filtered and was washed on the filter with warm distilled water. The samples prepared by incipient-wetness impregnation and deposition–precipitation methods were dried in air at 80–100°C for 6 h and were then reduced with flowing H\textsubscript{2} at 400°C for 4 h.

Hereafter, the Au/C catalysts prepared by cationic adsorption, deposition–precipitation, and impregnation are designated Au(CA)/C, Au(DP)/C, and Au(Imp)/C, respectively. (These abbreviations originate from universally accepted names of catalyst preparation techniques: CA = cationic adsorption, DP = deposition–precipitation, and Imp = impregnation.)

**Catalyst Characterization**

The X-ray fluorescence analysis of catalysts for Au and Cl was carried out using a VRA-30 instrument with a Cr-anode X-ray tube.

X-ray diffraction patterns were obtained on an HZG-4C diffractometer using CuK\textsubscript{α} radiation (λ = 0.15418 nm) with a graphite monochromator in the diffracted beam. Diffraction patterns were recorded by point scanning in the 2θ = 15°–50° range with 0.05° increments and a counting time of 5 s per point. The mean Au crystallite size (d\textsubscript{111}) was determined by measuring the integrated half-width of the Au(111) reflection (ratio of the integrated intensity of the reflection to its height) after subtraction of the background due to the support and was calculated by the Scherrer formula [18] with the instrumental line width taken into account.

Transmission electron microscopic (TEM) examination of catalysts was carried out on a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV with 0.14 nm resolution. Ground samples as an ethanolic suspension were applied on a perforated carbon substrate secured on a copper grid. The average size of gold particles was determined by statistical processing of the results of measuring particle diameters on TEM images. The diameters of at least 500 particles were measured for each specimen.