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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 $[Au(NH_3)_4](NO_3)_3$ 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 H_2 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/EO_x catalysts (EO_x = TiO_2, CeO_2, Fe_2O_3, Al_2O_3, 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^{III} hydroxochloro complexes from an alkalified $HAuCl_4$ solution and calcination of the product at a high temperature or via impregnation of the support with an aqueous $HAuCl_4$ solution followed by reducing the supported component with hydrogen [1, 6]. However, gold deposition on carbon support by these methods mainly yields large Au^0 crystallites, supposedly because anionic Au^{III} 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 Au^0 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 $[Au(en)_2]Cl_3$ 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_2. This method can be called cationic adsorption. Because a considerable part of the Au^{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 $[Au(en)_2]Cl_3$ on activated carbon fibers that had been subjected to drastic pretreatment (boiling in aqueous HNO_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 $[Au(NH_3)_4](NO_3)_3$, another cationic gold complex, on the surface of a granular carbon support without subjecting the latter to any thermal or chemical pretreatment. The Au/C catalyst that was prepared using this complex and was treated with H_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_2O_3 catalyst prepared by the deposition–precipitation method.

EXPERIMENTAL

Catalyst Preparation

$HAuCl_4 \cdot nH_2O$ (reagent grade) contained 49.47 wt % Au (Aurat Company, Specifications TU 6-09-05-1075-89). $[Au(NH_3)_4](NO_3)_3$ was obtained by reacting $HAuCl_4$ with $NH_3 \cdot H_2O$ in a saturated NH_4NO_3 solution. The complex was isolated from the solution and was purified from Cl^- 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^2/g, and a total pore volume of 0.39 cm^3/g. It contained 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 $[Au(NH_3)_4](NO_3)_3$ (40 ml, 2.55 mmol/l) was added. The resulting suspension was stirred for 2 h and was 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_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 $HAuCl_4$ 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 $HAuCl_4$ 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_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_α radiation (λ = 0.15418 nm) with a graphite monochromator in the diffracted beam. Diffraction patterns were recorded by point scanning in the $2\theta = 15°–50°$ range with 0.05° increments and a counting time of 5 s per point. The mean Au crystallite size (d_{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 Selyakov–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.

Table 1. Elemental analysis, TEM, X-ray diffraction, and XPS data for Au/C catalysts prepared by cationic adsorption (CA), impregnation (Imp), and deposition–precipitation (DP) techniques

Method	[Au], wt %	η, %	Average Au particle diameter, nm				XPS data*	
			$d_l \pm \sigma$	d_{vs}	d_m	d_{111} (W, %)	binding energy of Au $4f_{7/2}$ electrons, eV	Au : C, atom/atom
CA	1.3	65	3.2 ± 1.2	4.3	5.0	6 (90)	84.1 (84.2)	0.0187 (0.0012)
Imp	1.9	95	11.7 ± 11.9**	32.3	35.5	26 (90)	84.1 (84.2)	0.0057 (0.0007)
DP	1.5	75	Polydisperse sample (d_i = 10–500 nm)			25 (100)	84.1 (84.1)	0.0128 (0.0010)

Note: η is the degree of completeness of gold deposition; $d_l = \Sigma d_i/N$, $d_{vs} = \Sigma d_i^3/\Sigma d_i^2$, and $d_m = \Sigma d_i^4/\Sigma d_i^3$, where d_i is the diameter of an Au particle measured by TEM and N is the total number of particles; σ is the standard deviation; d_{111} is the crystallite size derived from the integrated half-width of the Au(111) reflection; W is the mass fraction of the metal detectable by X-ray diffraction.

* The numbers in parentheses are data obtained for ground samples.

** Bimodal particle size distribution (maxima at 5.7 and 31 nm).

X-ray photoelectron spectra were recorded on a VG ESCALAB HP spectrometer using nonmonochromated AlK_α radiation ($E_{h\nu}$ = 1486.6 eV, 200 W). The binding energy (BE) scale was calibrated against the Au $4f_{7/2}$ (BE = 84.0 eV) and Cu $2p_{3/2}$ (BE = 932.6 eV) peaks from polycrystalline gold and copper foil, respectively. The samples as granules or powder were secured on a double-sided copper, conductive, adhesive tape. For correct calibration of photoelectron emission lines, we used the C 1*s* line of the support (BE = 284.5 eV) as the internal standard. Atomic concentrations were derived from the areas of photoelectron emission peaks after subtracting the background by the Shirley method taking into account the corresponding sensitivity factors [19].

Catalytic Activity Measurements

The catalytic activity of Au/C catalysts in CO oxidation with excess humid air was determined in a flow glass reactor at 40°C and atmospheric pressure. The reaction mixture, which consisted of 1.0 vol % CO, 20.0 vol % O_2, 2.4 vol % H_2O, and N_2 as the balance gas, was fed into the reactor at GHSV = 60000 h^{-1}. The catalyst (40–42 mg) was diluted with quartz sand. Samples of the initial and final reaction mixtures (upstream and downstream of the catalyst bed, respectively) were analyzed on-line using a PEM-2M optical analyzer (Promanalitpribor, Russia), and the CO and CO_2 mole fractions in the initial and final reaction mixtures (hereafter, IRM and FRM, respectively) were determined from analysis data. The CO conversion (X, %) was calculated as the ratio of the difference between the CO mole fractions in the IRM and FRM to the CO mole fraction in the IRM. Catalytic activity (A) was calculated as the CO_2 mole fraction in the FRM divided by the residence time of the reaction mixture and by the mass of Au in the catalyst bed. The carbon balance between the IRM and FRM was 100 ± 3% in all runs.

RESULTS AND DISCUSSION

Chloroauric acid is known to be a strong acid almost entirely dissociated in aqueous solutions. At pH ≤ 2.5, dilute aqueous solutions of $HAuCl_4$ are dominated by $[AuCl_4]^-$ ions. Upon the alkalization of the solution to pH ≈ 7, these ions hydrolyze mainly into $[AuCl_2(OH)_2]^-$ and $[AuCl(OH)_3]^-$ [20]. As an $HAuCl_4$ or $HAuCl_4$ + NaOH solution was added to Sibunit granules, the formation of gas bubbles (CO, CO_2) was observed and the outer surface of the support was metallized rapidly (the carbon granules were covered by a rust-colored or yellow island film with metallic luster). As an $[Au(NH_3)_4](NO_3)_3$ solution was added to Sibunit, no gas evolution took place and the carbon granules looked unchanged throughout the time they were in contact with solution and after their filtration and drying.

Below, we present the results of our physicochemical study of the Au/C catalyst prepared using the tetraamminegold(III) cationic complex and compare these results with the data obtained for catalysts prepared from conventional precursors—$[AuCl_{4-x}(OH)_x]^-$ anionic complexes.

Elemental Analysis

According to X-ray fluorescence data (Table 1), the amount of supported gold (η) in the Au/C catalysts prepared by the sorption methods (CA and DP) is, respectively 65 and 75% of the initial share of gold in the precursor solution. Note that the share of gold supported on Sibunit by CA can be increased to 90% by raising the $[Au(NH_3)_4](NO_3)_3$ concentration in the solution from 2.5 to 12.75 mmol/l and by extending

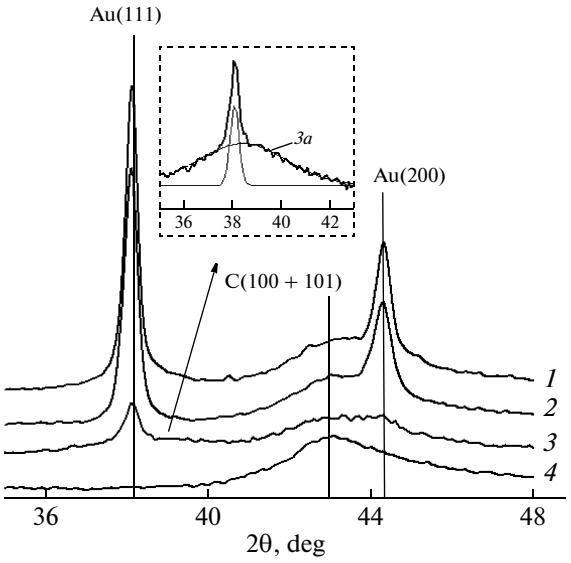

Fig. 1. Fragments of the X-ray diffraction patterns of (*1*) 1.9% Au(Imp)/C, (*2*) 1.5% Au(DP)/C, (*3*) 1.3% Au(CA)/C ((*3a*) enlarged fragment of diffraction pattern *3* around the Au(111) reflection with the background due to the support subtracted), and (*4*) initial Sibunit.

the solution–support contact time from 2 to 15 h. The Cl content of the Au(CA)/C and Au(DP)/C samples (100–200 ppm) is close to the sensitivity limit of X-ray fluorescence analysis and is far below the Cl content of Au(Imp)/C (3000–5000 ppm).

X-Ray Diffraction Data

The X-ray diffraction patterns of the Au/C catalysts reduced with H_2 at 400°C (Fig. 1) show reflections from Sibunit and broadened reflections from gold metal. The diffraction pattern of the Au(CA)/C catalyst shows, under the strongest reflection Au(111) at $2\theta = 38.2°$, a well-defined halo, which indicates the presence of small metal crystallites with a size of <3 nm [10]. In the diffraction pattern of the Au(Imp)/C catalyst, the halo is weak (<10% of the integrated reflection intensity). In the diffraction pattern of Au(DP)/C, there is practically no halo.

The mass fraction of gold metal detectable by X-ray diffraction (W, %) was determined from the integrated intensity of the Au(111) reflection measured after subtraction of the Sibunit background and normalized to the integral intensity of the C(002) peak from the same sample. This peak served as the internal standard as well. The value of W was determined using the calibration line obtained within a set of (1–2% Au)/C standard samples. They were prepared by impregnating Sibunit with a gold metal sol [13] and, according to TEM data, comprised Au particles with diameters ranging from 8 to 35 nm ($d_{111} = 22 \pm 0.5$ nm). We determined in this way that the mass fraction of gold metal detectable by X-ray diffraction in the Au(Imp)/C and Au(DP)/C catalysts exceeds 90% of their total gold content (Table 1). Therefore, the average gold crystallite size calculated from the integrated half-width of the Au(111) reflection, which is ~25 nm, characterizes practically the entire amount of gold in Au(Imp)/C and Au(DP)/C. The average Au crystallite size in Au(CA)/C determined in the same way has a much smaller value of $d_{111} = 6$ nm. In this case, we separated the contributions from large and small Au crystallites to the observed integrated intensity of the Au(111) reflection. This was done by decomposing this reflection into its narrow part, which referred to coarse metal crystallites ($d_{111} \approx 30$ nm), and the halo (Fig. 1, curve *3a*). We found that halo, which was due to the small Au crystallites with $d_{111} < 3$ nm, accounted for ~80% of the observed integrated intensity of the Au(111) reflection. Therefore, the mass fraction of these particles in Au(CA)/C was much larger than that of the coarse component.

TEM Data

The transmission electron micrographs of the Au(CA)/C catalyst made at medium magnification show contrast images of spherical or near-spherical Au particles with an apparent diameter of $d_i = 0.5–10$ nm, mainly between 1.5 and 5.5 nm (Fig. 2a). The Au particle size distribution in this sample (Fig. 2a, inset) is near-lognormal, with a maximum near 3 nm. The values of the average linear diameter (d_l), average volume/surface area diameter (d_{vs}), and mass-average diameter (d_m) of the Au particles calculated from this distribution are listed in Table 1. The TEM images of Au(CA)/C made at low magnification revealed isolated, very large, 100- to 300-nm gold aggregates consisting of 10- to 40-nm crystal blocks (Fig. 2b). Each of these blocks must participate in diffraction as a separate particle. It is likely due to the presence of these aggregates that there are weak narrow reflections from Au^0 against the background of an intense halo in the diffraction pattern of Au(CA)/C. These aggregates were excluded from the Au particle size distribution from which d_l, d_{vs}, and d_m were to be calculated. In view of this, the approximate coincidence between the mass-average diameter derived from TEM data (d_m = 5 nm) and the average crystallite size ($d_{111} = 6$ nm) is further evidence that the mass fraction of large Au crystallites in the Au(CA)/C catalyst is very small.

The TEM images of the Au(Imp)/C reference catalyst (Fig. 2c) show, along with relatively small Au particles ($d_i = 2–15$ nm), numerous large crystallites 20 to 45 nm in size. The Au particle size distribution in this case is bimodal, with maxima at 5.7 and 31 nm. This is in agreement with the reports according to which activated carbons impregnated with an $HAuCl_4$ solution at low pH and then subjected to reduction with HCOOH [10] or H_2 [13, 14] contain both large and small gold particles. At the same time, the d_m value determined for the Au(Imp)/C catalyst is 7 time larger

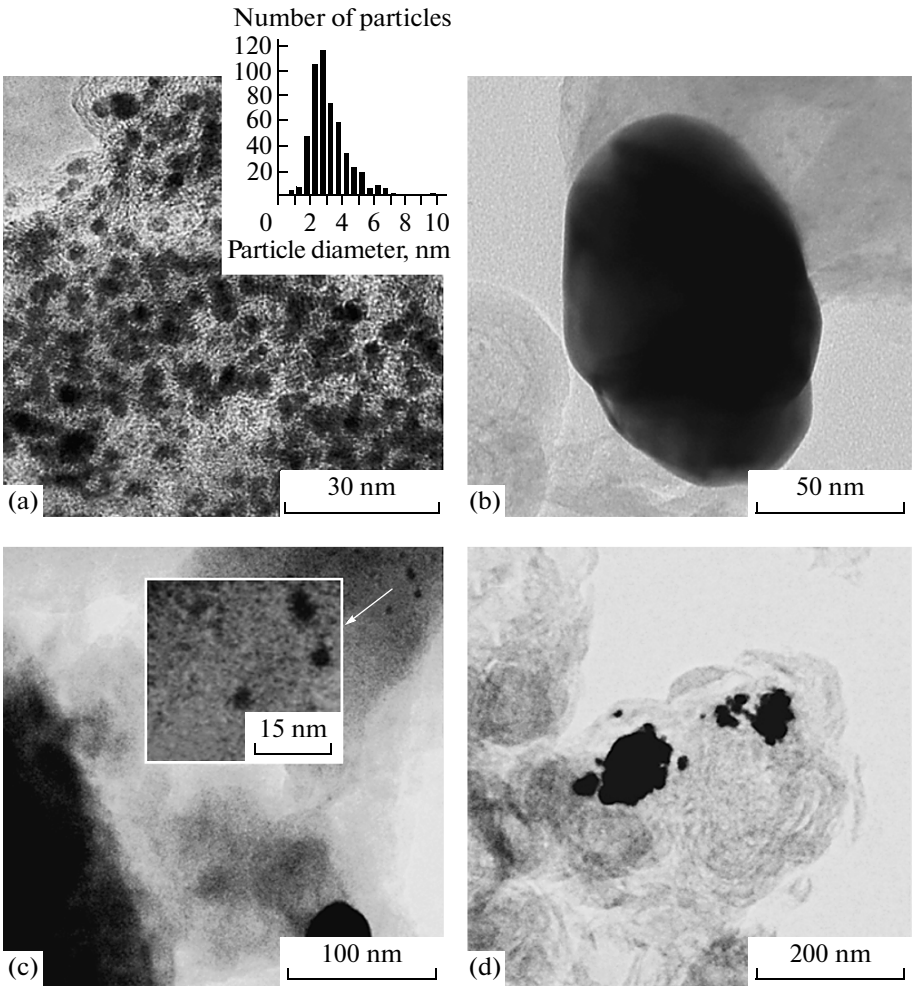

Fig. 2. TEM data for Au/C catalysts: (a) typical image of 1.3% Au(CA)/C and gold particle size distribution for this catalyst (the average particle diameters calculated from this distribution are listed in Table 1); (b) large gold particle with a multiple twinned substructure on the surface of the 1.3% Au(CA)/C catalyst; (c) typical image of 1.9% Au(Imp)/C; (d) typical image of 1.5% Au(DP)/C.

than the same value for the Au(CA)/C catalyst. Therefore, the mass fraction of Au particles several tens of nanometers in diameter in the catalyst prepared by impregnation is much larger than in the catalyst obtained by the CA method. The TEM images of Au(DP)/C (Fig. 2d), the other reference catalyst, shows no metal particles with $d_i < 10$ nm. It is impossible to determine d_l, d_{vs}, and d_m in this case because the particle are extremely nonuniform in size and there are a great number of very large, irregularly shaped particles up to 500 nm in size, each consisting of twinned crystallites several tens of nanometers in size.

X-Ray Photoelectron Spectra

The survey X-ray photoelectron spectra of all of the Au/C catalysts examined in this study contain core-level lines characteristic of the support (C 1*s* and O 1*s* at BE = 284.5 and 532.0 eV, respectively) and gold (Au 4*f*). The spectrum of the catalyst prepared by impregnation exhibits a distinct Cl 2*p* peak at BE = 198.7 eV, which is characteristic of the Cl^- ion [21]. In the spectra of the catalysts obtained by the other methods, the intensity of this line is on the noise level. In the spectrum of the catalyst prepared using $[Au(NH_3)_4](NO_3)_3$, there is no significant N 1*s* line characteristic of the NH_3 molecule and NO_3^- ion in the BE = 390–415 eV range [21]. Therefore, the ammine ligands and nitrate ions of the supported complex are entirely removed from the catalyst surface as the catalyst is treated with H_2 at 400°C.

Figure 3 shows typical Au 4*f* spectra of the Au(CA)/C and reference catalysts. In all cases, the spectra are fitted well by a single doublet consisting of Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks arising from spin–orbit coupling. The binding energy corresponding to the stronger, Au $4f_{7/2}$ peak (BE = 84.0–84.2 eV) almost coincides with the tabulated binding energy value for

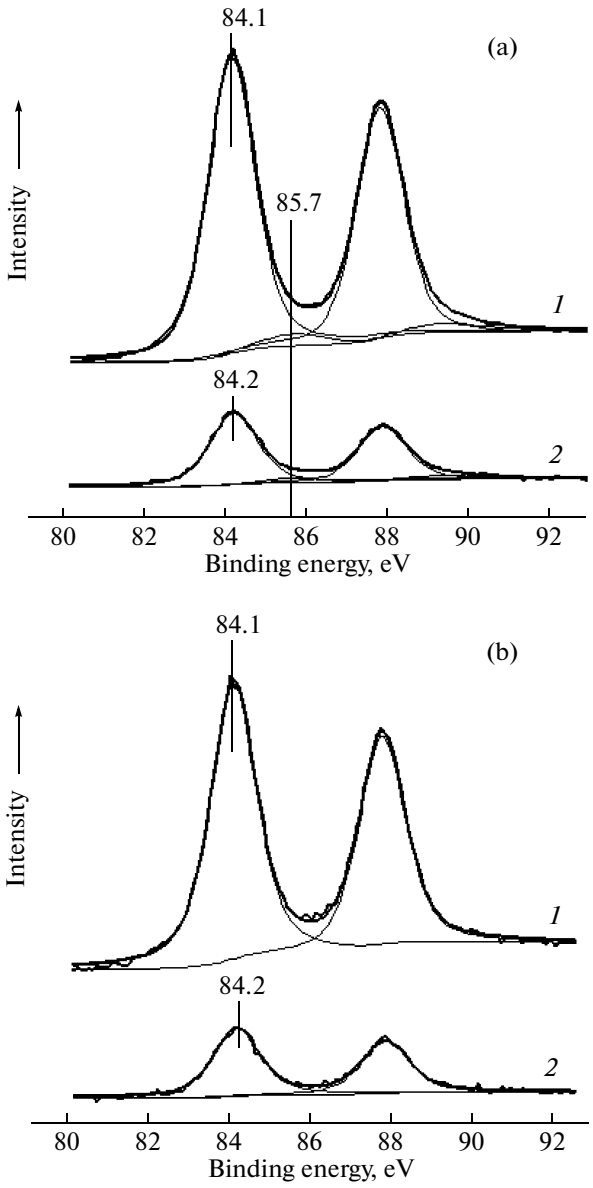

Fig. 3. X-ray photoelectron spectra in the Au 4*f* region for the (*1*) granular and (*2*) ground (a) 1.3% Au(CA)/C and (b) 1.9% Au(Imp)/C catalysts.

gold metal (BE = 84.0 eV) [21]. The spectrum of the Au(CA)/C catalyst (Fig. 3a) is somewhat asymmetric, suggesting the existence of different charge states of gold in the surface layer. The decomposition of this spectrum into individual components reveals an additional spin doublet at higher BEs, whose intensity does not exceed 5% of the total intensity of the Au 4*f* spectrum. This line is likely due to the oxidized Au species that remain on the sample surface after the treatment of the sample with hydrogen.

It is also clear from Fig. 3 that the intensity of the Au $4f_{7/2}$ peak depends strongly on how finely the sample was ground before taking its spectrum. Grinding all Au/C catalysts with a granule size of 200–500 μm into a powder with a particle size of a few micrometers causes a considerable decrease in the integrated intensity of the Au $4f_{7/2}$ peak normalized to the area of the C 1*s* peak (internal standard) and has no effect on the binding energy of the Au $4f_{7/2}$ electrons within the measurement error. The weakening of the Au $4f_{7/2}$ peak indicates a decrease in the surface concentration of gold atoms (Table 1). At the same time, a TEM examination of ground Au/C samples did not reveal any difference in Au particle size between the ground and nonground specimens of the same sample. Therefore, the observed decrease in the concentration of Au atoms in the surface layer cannot be explained by sintering of metal particles (e.g., as a result of local overheatings during grinding). It is most likely due to the low depth of penetration of Au into the support granule. Grinding Sibunit granules exposes their interior, so the decrease in the integrated intensity of the Au $4f_{7/2}$ peak suggests that the gold of the catalysts examined is concentrated on the outer surface of the support. In other words, we have an egg shell type distribution of the supported component over the support granule.

Activity of the Catalysts

The catalytic activities of Au/C samples prepared by different methods were compared under conditions imitating the removal of CO (1 vol %) from flowing humid air at a temperature (40°C) slightly above ambient temperature. The results of these tests are presented in Table 2 and Fig. 4. Under these conditions, the Au(DP)/C catalyst, which contained only large Au crystallites with $d_i \geq 10$ nm, did not show any significant CO oxidation activity. The other reference catalyst, Au(Imp)/C, with a bimodal Au particle size distribution in the 2–45 nm range, showed only low activity and was completely deactivated 2 h after the beginning of the test. By contrast, the catalyst that was prepared by cationic adsorption and mainly contained small Au particles ($d_i < 3$ nm) was very active. In the initial minutes of the test, the CO conversion over this catalyst was near 100%. Later, it gradually decreased to 32% over 6 h and then remained practically invariable until the end of the test.

It was interesting to compare the CO oxidation activity of the Au(CA)/C catalyst and that of Au/Al_2O_3 catalysts prepared by the conventional DP method, which are considered to be a potential substitute for the palladium and platinum catalysts currently used in CO removal from air, industrial gas emissions, and automotive exhaust [1]. For comparison, we took a catalyst obtained by loading δ-Al_2O_3 with 1.8 wt % Au via the procedure described in our earlier article [6]. A TEM examination of this sample demonstrated that it had the same volume/surface area Au particle diameter as the Au(CA)/C catalyst (d_{vs} = 4.3 nm). Therefore, the degree of dispersion of the supported metal ($D_{Au} \sim (d_{vs})^{-1}$ [22]) in these catalysts can be

Table 2. CO oxidation with excess humid air at 40°C on gold catalysts in a flow reactor

Catalyst	X, %			$A \times 10^3$, mol (g Au)$^{-1}$ s^{-1}		
	time on stream, min			time on stream, min		
	10	60	420	10	60	420
Au(CA)/C	96.4	57.0	30.3	—**	79	42
Au(Imp)/C	13.4	7.0	1.1	3	2	<0.5
Au(DP)/C	<1	<1	<1	<0.5	<0.5	<0.5
Au/δ-Al_2O_3*	19.4	25.4	23.7	69	93	86

Note: The characteristics of the Au/C catalysts are presented in Table 1. The average Au particle diameters for the 1.8% Au/δ-Al_2O_3 catalyst calculated from the TEM histogram are $d_l \pm \sigma = 3.9 \pm 1.0$ nm, $d_{vs} = 4.3$ nm, and $d_m = 4.5$ nm.
* The catalyst was tested at GHSV = 240000 h^{-1}.
** Catalytic activity could not be determined because of the very high conversion.

taken to be the same. As is clear from Fig. 4, the Au(CA)/C catalyst displays a much higher initial CO oxidation activity than the Au/δ-Al_2O_3 catalyst, but the latter shows a more stable performance ($X = 20$–25%). One hour after the beginning of the test, the activities of the Au(CA)/C and Au/δ-Al_2O_3 catalysts were nearly equal. (Note that the CO conversion in the presence of Au(CA)/C at this point in time was still fairly high, $X \approx 60\%$, so the A value given for this catalyst in Table 2 is likely underestimated.) In the steady state (6–8 h after the beginning of the test), the activity of the Au(CA)/C catalyst was approximately 2 times lower than the activity of Au/δ-Al_2O_3. Note that the steady-state activity of Au(CA)/C in CO oxidation can be enhanced by increasing the steam content of the reaction mixture fed to the catalyst. Raising the H_2O concentration in the feed from 2.4 to 5.6 vol % leads to a rapid increase in X from 32 to 41%; however, after the H_2O concentration is returned to its initial level, X falls rapidly down to its initial value (Fig. 4, curve *3a*). In this respect, our Au/C catalyst is similar to oxide-supported gold catalysts, Au/EO_x, for which it is known that they need the presence of steam in the feed for stable CO oxidation performance and that their activity increases reversibly as the steam content is raised to a certain limit [23, 24].

Thus, this study proved the usability of cationic gold complexes as precursors in the preparation of Au/C catalysts with a uniform Au particle size of <5 nm. We examined tetraamminegold(III) nitrate, a readily water-soluble compound, as a gold precursor. This compound can be obtained from $HAuCl_4$ and purified from chloride ions. The $[Au(NH_3)_4]^{3+}$ complex is fairly strongly adsorbed by Sibunit, a mesoporous carbon support, and can be reduced with H_2 at 400°C to obtain Au^0 with a dominant particle size of <5 nm. Most of the gold particles are located on the outer surface of the support granules. The Au/C catalyst prepared in this way is highly active in CO oxidation with excess humid air. Its activity is comparable with the activity of the Au/Al_2O_3 catalyst with the same Au particle size obtained by the long-accepted DP method. The reference Au/C catalysts prepared with the use of conventional precursors, specifically, $[AuCl_{4-x}(OH)_x]^-$ complexes, which were dominated by Au particles tens of nanometers in size, were catalytically inactive or showed only a low activity. The almost entire absence of coarse particles in the catalyst derived from $[Au(NH_3)_4]^{3+}$ is most likely due to the fact that this complex is not reduced by the carbon matrix or is reduced much less readily than the Au^{III} complexes containing only Cl- and/or OH-ligands (compare the standard redox potentials of the following redox pairs: $[Au(NH_3)_4]^{3+}/Au^0$, 0.325 V [25]; $[Au(OH)_4]^-/Au^0$, 0.485 V [26]; $[AuC_4]^-/Au^0$, 1.000 V [27]). It is likely that the exchange of the protons of surface groups of carbon for gold cations takes place

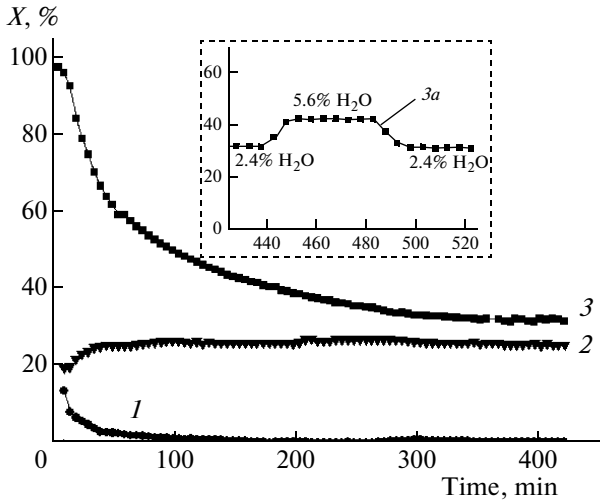

Fig. 4. (*1*–*3*) CO conversion into CO_2 (X) at 40°C as a function of the reaction time for the (*1*) 1.9% Au(Imp)/C, (*2*) 1.8% Au/δ-Al_2O_3, and (*3*) 1.3% Au(CA)/C catalysts. (*3a*) Effect of the steam content of the feed on X for the 1.3% Au(CA)/C catalyst. GHSV = (*1*, *3*, *3a*) 60000 and (*2*) 240000 h^{-1}.

instead of $[Au(NH_3)_4]^{3+}$ reduction by electrons of the carbon matrix. The exchange reaction is favored by the fact that, because the pH of the solution of $[Au(NH_3)_4](NO_3)_3$ (pH 5–6) is above the point of zero charge of carbon (pH 2–3), the support surface is negatively charged and attracts gold cations as the complex is supported. Upon treatment with H_2, the surface groups reacting with the cationic gold complex can serve as gold nanoparticle binding sites, thereby preventing their aggregation. Note that the nanostructured Au/C composites obtained by supporting $[Au(NH_3)_4](NO_3)_3$ on the Sibunit surface, which are advanced carbon materials with improved properties, can be of interest as catalysts for CO oxidation in air cleaners, gas masks, fuel cells, gas sensors, etc. These catalysts are also promising for liquid-phase oxidation of organic compounds.

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