

XPS Study of Gold Oxidation with Nitrogen Dioxide in Model Au/C Samples

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Abstract—The interaction of NO₂ with model samples obtained by the gold sputter deposition onto the surface of highly oriented pyrolytic graphite (HOPG) has been studied by X-ray photoelectron spectroscopy (XPS). It has been shown that 3D metal particles characterized by an Au4f_{7/2} binding energy (BE) of 84.0 eV form on the initial smooth graphite surface. During the sputter deposition onto the surface of HOPG preliminarily activated by means of ion etching, gold atoms chemically bound to the carbon atoms form in the area of surface defects. Such atoms are characterized by a positive shift of BE(Au4f_{7/2}). It has been established that the 3D particles are resistant to the action of NO₂ under the pressure $P_{\text{NO}_2} = 5 \times 10^{-5}$ mbar at room temperature. On the contrary, atomic gold oxidizes under these conditions into Au(III) complexes bound to the graphite surface. It is assumed that gold atoms on the support surface play the role of active sites of gold catalysts in oxidation reactions.

Keywords: gold catalysts, pyrolytic graphite, carbon dioxide, oxidation, XPS

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INTRODUCTION

Gold catalysts demonstrate high activity in a number of oxidation processes, first of all, in CO oxidation [1]. The mechanism of action of these catalysts is being widely discussed because there is no evidence of the interaction of oxygen with gold under the reaction conditions. Generally, energetic gas phase activation, e.g., as a result of an electric discharge [2, 3], or oxygen atomization on a hot metal wire [4, 5] is required for the formation of an adsorbed oxygen layer or oxide film on gold. In certain cases, particularly strong oxidizers, such as oxygen plasma [6] or ozone [7], are used for these purposes. In order to form oxidized gold nanoparticles on an inert support, the sputtering of a gold wire under the action of a radio frequency discharge in an oxygen atmosphere was used [8]. However, these conditions are far from real catalysis and do not answer the question about the nature of the active sites of gold catalysts.

We discovered earlier that nitrogen dioxide obtained by lead nitrate thermal decomposition directly in the vacuum chamber of an X-ray photoelectron spectrometer possessed the ability to selectively oxidize platinum particles smaller than 3 nm in model Pt/C samples, while larger platinum particles (more than 5.5 nm) retained their metallic nature under these conditions [9]. This result explains the occurrence of the size effect in NO oxidation with atmospheric oxygen for automotive catalysts operating

under lean fuel conditions [10]. In the present work, this approach is used in investigating the possibility of gold oxidation with nitrogen dioxide in model samples obtained by metallic gold sputter deposition onto highly oriented pyrolytic graphite (HOPG).

EXPERIMENTAL

All the works on the preparation of Au/C samples and study of the action of NO₂ on them were conducted on an X-ray photoelectron spectrometer (SPECS, Germany). The instrument is equipped with several independent vacuum chambers providing different specimen treatment and XPS spectra recording sequences without any contact with air. Spectra were obtained using different X-ray sources, namely, non-monochromated and monochromated AlK_α radiation ($h\nu = 1486.6$ eV) and monochromated AgL_α radiation ($h\nu = 2983.4$ eV) irradiation. The high sensitivity and narrow width of the spectral lines was ensured by using a PHOIBOS-150-MCD-9 hemispherical analyzer with a nine-channel detector coupled with the instrument. Before conducting the studies, HOPG SPI-3 (Structure Probe Inc., United States) was annealed for 1 h in an ultrahigh vacuum at 500°C. The survey XPS spectra of such samples contained only photoelectron and Auger lines of carbon.

The sputter deposition of gold onto graphite was conducted using an EFM3 vacuum metal sputtering source (Omicron, Germany) at a support temperature

close to room temperature. Two series of samples were prepared for the study. In the first series, initial HOPG was used as the support (these samples were designated Au/HOPG after gold deposition). In the second series, initial HOPG was treated with argon ions for a short time using an ion gun (argon pressure of $P_{\text{Ar}} = 5 \times 10^{-7}$ mbar, accelerating voltage of 0.5 kV, treatment time of 5 s) before the sputter deposition in order to generate defects on the support surface. The samples obtained in this way were designated Au/HOPG-A.

At low concentrations of deposited gold, its coverage is proportional to the sputtering source operating time. The particle size and gold coverage were estimated from XPS data according to the procedure proposed by Davis [11] as the intensity of two gold lines, Au4f and Au3d_{3/2}, determined from the spectra of Au/C samples and gold foil. The spectra were recorded using AgL_α radiation. Figure 1 shows the survey spectrum of the foil, in which the positions of the Au4f (Au4f_{7/2}-Au4f_{5/2} doublet) and Au3d_{3/2} lines are indicated. The great difference between the kinetic energies of photoelectrons corresponding to these lines—~2900 eV for Au4f_{7/2} and ~690 eV for Au3d_{3/2}—ensures a substantial difference between the electron mean free paths— $\lambda_{4f} = 2.763$ nm and $\lambda_{3d} = 0.948$ nm [12]—and thus creates favorable conditions for using the Davis procedure. The particle size (d) and coverage (Θ) in the Au/C samples were estimated under the assumption that the particles are arranged on a perfectly flat support surface and have a hemispherical shape. The coverage—Au4f_{7/2}/C1s intensity ratio relationship, with the lines recorded using AlK_α radiation, was derived from the coverage values determined for Au/C samples with different amounts of deposited gold. Within the coverage range used in the work, this relationship was linear and served as the calibration plot in Θ determination. Θ was calculated in Au monolayers (ML) under the assumption that the thickness of 1 ML was 0.288 nm (metallic Au atom diameter).

In order to verify the correctness of the Davis method for our system, one of the Au/HOPG-A samples was studied by scanning tunneling microscopy (STM). The values of $\Theta = 0.02$ ML and $d = 1.6$ nm were preliminarily calculated for it from XPS data. The STM images were obtained on a UHV 7000 VT high-vacuum scanning tunneling microscope (RHK Technology) in the constant current mode. Processing procedures included in the control software package for an XPMPPro 2.0 microscope were used for processing and analyzing the STM images. In order to plot the particle size distribution histogram, more than 300 particles were examined. According to the STM data, the distribution diagram maximum for this sample was at 1.5 nm.

The samples were treated with nitrogen dioxide in the preparation chamber of the spectrometer using an NO₂ vacuum source, whose operating principle is

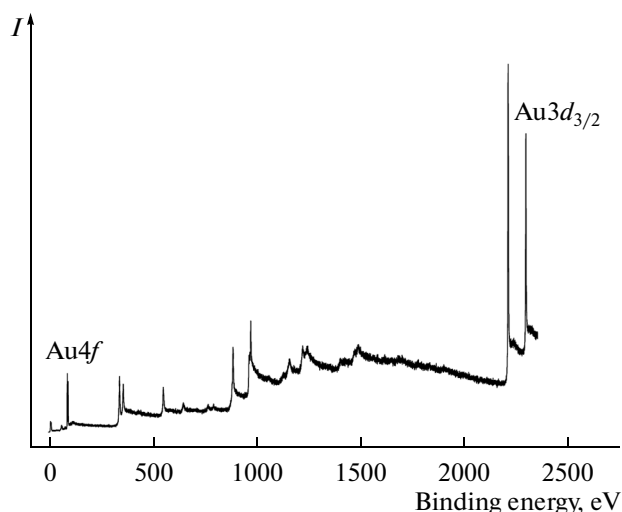


Fig. 1. Survey XPS spectrum of gold foil obtained using AgL_α radiation.

based on the thermal lead nitrate decomposition. In all experiments, the sample temperature during such a treatment was near room temperature, while the NO₂ pressure was 3×10^{-5} mbar. The treatment procedure is described in detail in earlier reports [9, 13, 14].

RESULTS

Gold deposition onto graphite gave rise to XPS lines characteristic of gold. Figure 2 shows a series of Au4f spectra obtained at an increasing metal deposition time for the samples based on HOPG and HOPG-A. As can be seen from Fig. 2, for initial graphite the BE values and the energy half-width $\Delta E_{1/2}$ of the Au4f_{7/2} line remain constant over the range of gold sample coverages and are the same as the values characteristic of the gold foil. For the samples based on HOPG-A, the doublet of Au4f lines is notably broadened at small coverages ($\Theta \approx 0.004$ ML), while the Au4f_{7/2} line maximum is shifted towards higher energies by 1.1 eV relative to the line of the massive metal. In this case, the increase in Θ is accompanied by an decrease in $\Delta E_{1/2}$, while the Au4f_{7/2} peak maximum gradually shifts towards lower binding energies. At $\Theta > 0.02$ ML for the Au/HOPG-A samples the values of $\Delta E_{1/2}$ and BE of the Au4f_{7/2} level approach the values characteristic of massive gold. Figure 3 plots the changes in the binding energy and energy half-width of the Au4f_{7/2} level versus surface coverage for the series of samples based on the initial and activated graphite.

The model samples prepared in this way were treated with nitrogen dioxide. The samples based on the initial graphite demonstrated high resistance to this treatment. No changes were observed in the Au4f region for the Au/HOPG sample series at gold coverages of $\Theta = 0.003$ – 0.05 ML and a treatment duration

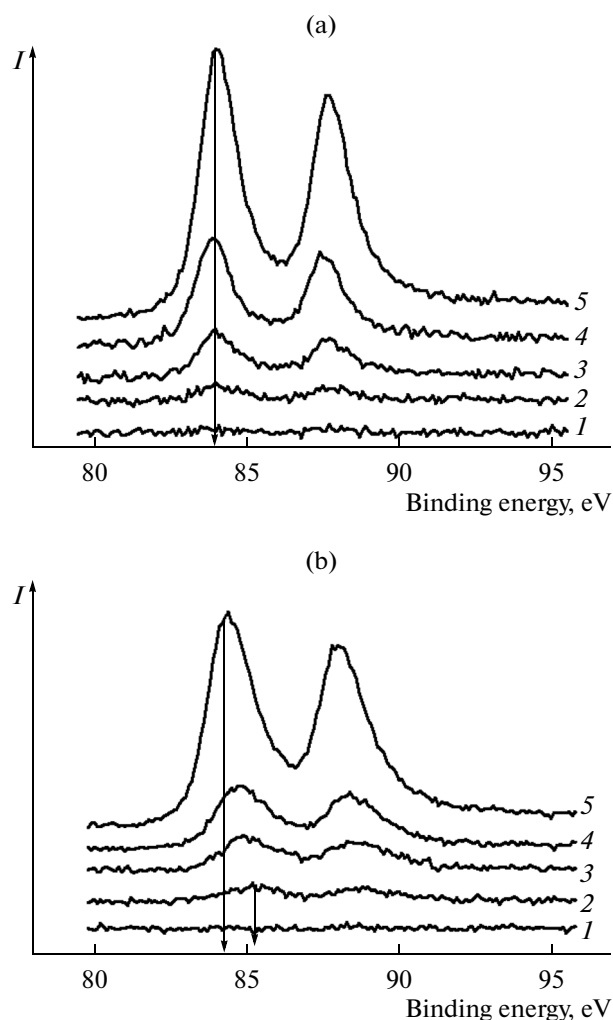


Fig. 2. Au4f XPS spectra of the samples obtained by gold sputter deposition onto (a) HOPG and (b) HOPG-A. Gold coverages: (a) (1) 0, (2) 0.003, (3) 0.008, (4) 0.017, and (5) 0.046 ML; (b) (1) 0, (2) 0.004, (3) 0.009, (4) 0.017, and (5) 0.059 ML.

of 150 min. The occurrence of a low-intensity peak at BE = 532.5 eV in the O1s region is apparently due to the partial oxidation of graphite itself [9].

On the contrary, the action of NO₂ on the Au/HOPG-A samples was accompanied by substantial changes in the state of gold. Figure 4 shows the Au4f spectra of these samples treated with nitrogen dioxide for 150 min. This treatment time turned out to be sufficient for completing the changes in the spectra. As can be seen from Fig. 4, an additional peak at BE = 85.6 ± 0.2 eV occurs after such a treatment in the Au4f_{7/2} region in the case of coverages below ~0.1 ML. This peak position does not depend on the gold content of the sample; however, the proportion of this state increases substantially with decreasing Θ. In case of a gold coverage of 0.0035 ML, this state dominates in the spectrum.

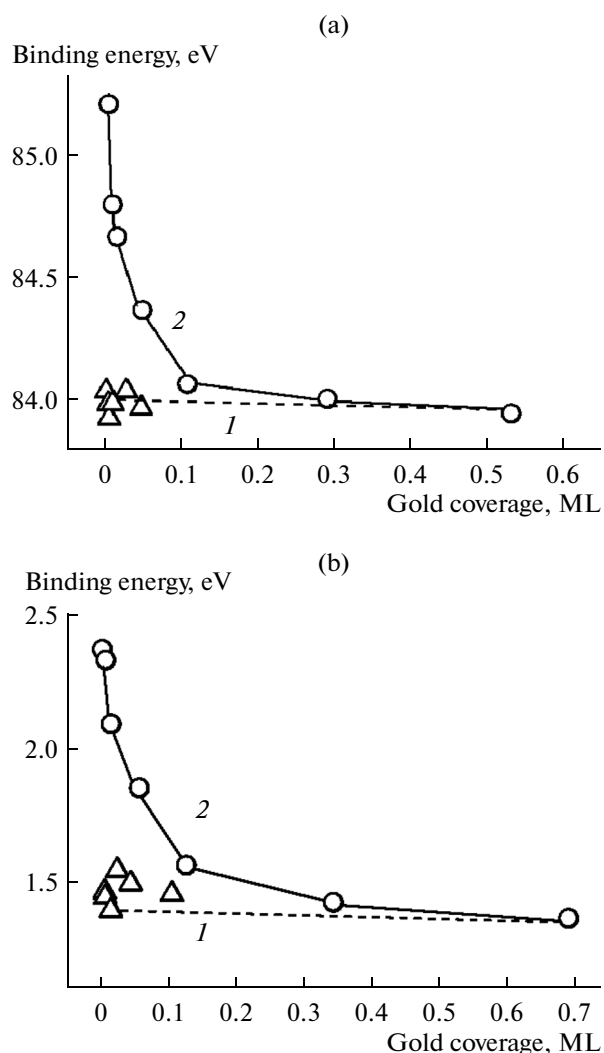


Fig. 3. (a) Binding energy and (b) energy half-width of the Au4f_{7/2} line as a function of the gold coverage of the graphite surface for the (1) Au/HOPG and (2) Au/HOPG-A samples.

The changes in the state of gold under the action of NO₂ are most pronounced for the Au/HOPG-A sample at Θ = 0.016 ML. Figure 5 shows its Au4f spectra recorded before and after treatment with nitrogen dioxide. In this case, the initially broad Au4f_{7/2} peak is split after the treatment into two peaks at BE = 84.0 and 85.6 eV.

DISCUSSION

Gold sputter deposition onto the smooth HOPG surface was studied by XPS and STM [15–18], and it was shown that, for this system, the BE value of the Au4f_{7/2} level does not depend on the amount of deposited metal and is 84.0 eV even in the case of extremely low coverages. According to STM data, gold particles with an average size of 2 nm are formed on the surface in this case [15]. As can be seen from Fig. 2, the results

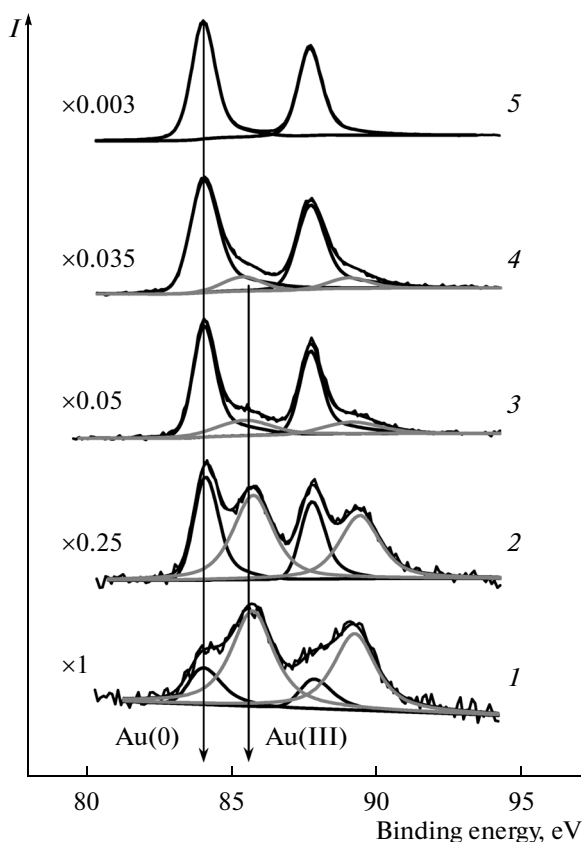


Fig. 4. Au4f XPS spectra of the Au/HOPG-A samples treated with NO₂ at gold coverages of (1) 0.0035, (2) 0.016, (3) 0.039, (4) 0.056, and (5) 0.490 ML. Treatment conditions: 150 min, $P = 3 \times 10^{-5}$ mbar, room temperature.

of our studies are completely the same as the literature data: for the Au/HOPG system with a surface coverage of 0.003 ML and above, the BE(Au4f_{7/2}) value is the same as the corresponding value for massive gold. This result differs substantially from the data for the Pt/HOPG system, in which the Pt4f_{7/2} line for 5.5-nm particles is shifted towards larger BE values by 0.3 eV relative to the same line for massive metal. This effect is stronger for smaller particles, and the shift is 0.9 eV for $d = 2.5$ nm [9]. This result is generally explained by the occurrence of the so called final state effect during photoemission with the participation of few-nanometer sized metal particles in porous catalysts and model samples prepared by sputter deposition of certain metals onto oxide supports and graphite. Apparently, this effect is not typical of the Au/C system, and, as a result, the BE(Au4f_{7/2}) value remains constant for 3D particles of any size and is 84.0 eV, which is characteristic of the atoms of massive gold.

As distinct from what was observed for the initial HOPG surface, substantial changes were observed in the Au4f spectrum after the gold deposition onto the activated graphite surface at Θ coverage values below 0.2 ML. In this case, the Au4f_{7/2} peak shifted towards larger BE values relative to the same peak for massive gold and the doublet lines themselves broadened

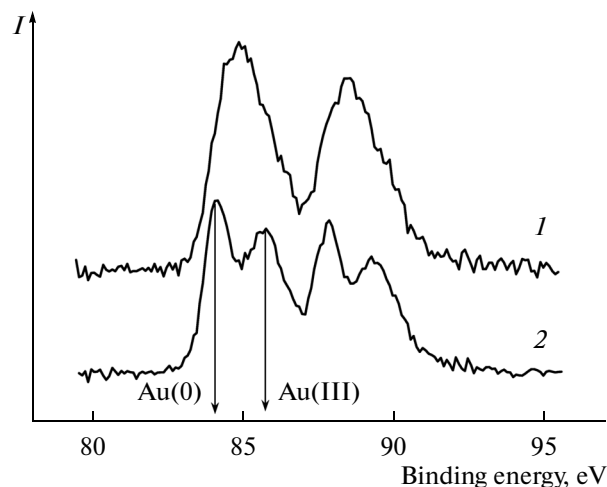


Fig. 5. Au4f XPS spectra of the (1) initial and (2) NO₂-treated Au/HOPG-A samples ($\Theta = 0.016$ ML). Treatment conditions: 150 min, $P = 3 \times 10^{-5}$ mbar, room temperature.

(Fig. 3). The effect manifested itself to the maximum extent at the minimum Θ value, which was 0.0035 ML in this study. A similar result was obtained when studying gold sputter deposition onto graphite activated with argon plasma and amorphous carbon [15, 17]. The broadening of the Au4f line was explained by the formation of ultrafine gold particles stabilized on surface defects of these surfaces in addition to relatively large, >2 nm particles. It is assumed that the BE value for such particles is 1–1.5 eV larger than for the large particles, which leads to the increase in the energy width of the Au4f doublet lines. In order to explain the cause of the increase in BE for ultrafine gold particles, it was hypothesized that gold transforms into a “non-metal state” as the number of atoms in the particles decreases below 70 [15]. According to the opinion of Kitsudo et al. [15], this transition radically changes “hole” relaxation parameters during photoemission and thereby leads to a positive shift of the Au4f lines. In this case, gold occupies a special position among the catalytically active metals, and this situation seems very unlikely. Moreover, the issue of why there is no positive shift for the smooth HOPG surface (even in the case of extremely low coverages implying the formation of extremely small gold particles) remains obscure within the suggested hypothesis. We suppose that the abnormal behavior of gold in its sputter deposition onto the activated HOPG surface is primarily determined by the features of this surface. The exposure to argon ions leads to the destruction of the upper layer of the graphite basal face with the appearance of a large number of carbon atoms containing unsaturated bonds. The gold atoms being deposited fix themselves to the graphite surface by forming a chemical bond with one or several carbon atoms, thus yielding surface Au–C_n compounds. Here, electron density transfer from the gold atom to carbon occurs, which results in a positive shift of the Au4f lines. It is reasonable to assume that the shift value for these compounds

increases with an increasing degree of gold coordination on the surface (n). As a result, the presence of these compounds along with 3D particles forms the broadened Au4f peak. Therefore, the chemical interaction of gold with carbon is the cause of the increase in BE upon gold deposition onto the activated HOPG surface. The possibility of Au–C chemical bond formation was demonstrated when studying the behavior of ionized gold carbide clusters in the gas phase [19]. Gold binding to the surface of a porous carbon support as a result of ion or ligand exchange with the functional groups on the carbon surface is considered as an efficient way of preparing Au/C catalysts active in CO oxidation [20]. It is assumed that, in this case, molecular (or near-molecular) dispersion of the precursor takes place, and also a strong chemical bond between the active component and the support is ensured.

The assumption concerning the chemical interaction of gold atoms with the activated graphite surface with the formation of Au–C_{*n*} complexes explains the changes in the Au4f spectra of the Au/HOPG-A samples caused by the action of NO₂. As can be seen in Fig. 5, two gold states characterized by Au4f_{7/2} binding energies of (a) 84.0 and (b) 85.6 eV result from this treatment. Apparently, state (a) is 3D metallic gold particles, while state (b) is possibly the oxidation product of the initial Au–C_{*n*} complexes. We suppose that, in this case, a single oxidized gold complex that is bound to the graphite surface by a single-center bond, C–Au=O, forms at any n . Formally, the gold oxidation state in this compound is 3+. Similar BE(Au4f_{7/2}) values were obtained for Au₂O₃ formed as a result of gold foil oxidation under the action of an electric discharge in an oxygen atmosphere or metallic gold sputter deposition onto an inert support using a microwave discharge in an oxygen atmosphere [3, 8].

The possibility of the selective oxidation of graphite-supported gold atoms with NO₂, a common reagent, under mild conditions suggests that they are active sites of gold catalysts in oxidation processes. Apparently, the nature of the support does not play any significant role in this case. It can be assumed that the binding of atomic gold to the surface of any support is a necessary condition for the appearance of catalytic activity. Apparently, its occurrence is based on the lowering of the activation barrier to Au–O bond formation under the action of oxidizers upon the origination of a positive $\delta+$ charge on gold in the case of the formation of a chemical bond with the support. The presence of positively charged gold, presumably in the Au(I) state, is considered as the crucial factor in the high activity of the Au/MgO catalyst in CO oxidation [21].

The active site structure proposed by us accounts for the increased proneness to deactivation shown by most gold-based catalysts [1]. Apparently, the loss of activity by these catalysts under the action of a number of factors is due to the irreversible transition of gold atoms chemically bound to the support into 3D particles that are inert in the reaction.

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