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An XPS and STM study of the size effect in NO adsorption on gold nanoparticles

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The effect of the gold particle size, temperature of the model gold catalyst, and NO pressure on the composition of the adsorption layer was studied by *in situ* XPS and STM methods. Adsorption of nitric oxide was carried out on gold nanoparticles with a mean size of 2—7 nm prepared on the thin film surface of alumina. In high-vacuum conditions ($P_{NO} \approx 10^{-5}$ Pa), only atomically adsorbed nitrogen is formed on the surface of gold nanoparticles. At about 1 Pa pressure of NO and in the temperature range from 325 to 475 K, atomically adsorbed nitrogen coexists with the N_2O adsorption complex. The surface concentration of the adsorbed species changes with a change in both the mean gold particle size and adsorption temperature. The saturation coverage of the surface with the nitrogen-containing complexes is observed for the sample with a mean size of gold particles of 4 nm. The surface of these samples is mainly covered with atomically adsorbed nitrogen, the saturation coverage of adsorbed nitrogen of about ~0.6 monolayer is attained at $T = 473$ K. The change in the composition of the adsorption layer with temperature of the catalysts agrees with the literature data on the corresponding temperature dependence of the selectivity of N_2 formation observed in the catalytic reduction of NO with carbon monoxide on the Au/Al_2O_3 catalyst. The dependences of the composition of the adsorption layer on the mean size of Au nanoparticles (size effect) and temperature of the catalyst are explained by the sensitivity of NO adsorption to specific features of the gold surface.

Key words: nitric oxide, gold, photoelectron spectroscopy, adsorption, size effect.

For a long time gold was considered to be a catalytically inert metal for practically important reactions. However, the works published for the recent two decades showed that gold nanoparticles are very efficient catalysts in the oxidation of CO and unsaturated hydrocarbons, vapor-phase conversion of natural gas, and a series of other reactions.[1—5] At the same time, in spite of intensive studies of the catalytic properties of gold, the reasons for the high catalytic activity of gold nanoparticles is a matter of discussion.

During recent decades, the catalytic reduction of nitrogen oxides on gold was one of the most important directions of research. The catalytic systems containing gold nanoparticles instead of platinum as an active component can efficiently be used in the catalytic reduction of NO in the presence of CO, H_2, and hydrocarbons from incomplete combustion of exhaust gases of automobile engines.[6] The reaction occurs at lower temperatures, which makes it possible to find a solution of the "cold start" problem. In addition, the yield of by-product N_2O decreases. In spite of the practical significance of this reaction, the interaction of NO with gold particles has been little studied by physical or kinetic methods. The adsorption of NO on a stepped Au(533) surface was studied by XPS in the first experiments[7] dealt with adsorption on supported gold. We succeeded to find[7] that atomically adsorbed nitrogen and a surface species with stoichiometry N_2O are formed upon NO adsorption on the surface of supported gold catalysts with a nanometer size of metal particles.

In the present work, we studied the effect of the mean size of supported gold particles, temperature of adsorption, and NO pressure in the gas phase on the adsorption layer composition. The obtained results can be used for the determination of optimum sizes of gold nanoparticles that can provide the efficient catalytic neutralization of nitrogen oxides in exhausts of automobile engines.

Experimental

NO adsorption on model supported gold catalysts was investigated by the XPS method with a VG ESCALAB HP electronic

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spectrometer. The residual pressure in the spectrometer chamber was at least $1 \cdot 10^{-7}$ Pa. The detailed description of the spectrometer, whose characteristic module is a high-pressure cell that allows one to record photoelectronic spectra under gas pressure above the sample up to 10 Pa, was presented earlier.[8] The gas supply to the cell was controlled by a leaking valve and the pressure of the reaction medium above the sample was monitored with an absolute pressure meter (Baratron). Prior to experiments, the spectra were calibrated relative to the Au4f$_{7/2}$ (binding energy –84.0 eV), Ag3d$_{5/2}$ (368.3 eV), and Cu2p$_{3/2}$ (932.7 eV) lines.[9]

A foil of the ALFA-IV aluminum-containing steel FeCrAl alloy (Allegheny Ludlum Corp.) with the composition (wt.%): Cr, 20; Al, 5; Mn, 0.35; P, 0.025; Si, 0.45; C, 0.02; Ce, 0.02; La, 0.01; and the rest is Fe was chosen as a substrate for the preparation of the support.[10] This choice is motivated by the fact that alumina is the most abundant support for commercial neutralizers of exhausts.

To prepare and study the model supported gold catalysts, foil samples of the FeCrAl alloy (~7 mm×7 mm×0.6 mm) were fixed on a holder with tungsten wire "stems" (0.19 mm) spot-welded to the back side of the sample. The construction of the sample holder makes it possible to heat the sample and measure its temperature in any chamber of the spectrometer. The sample was heated by passing current through tungsten stems. To prevent a possible change in the position of the sample due to thermal deformations of assembling, the tungsten stems were mounted on tantalum springs. The temperature of the sample was measured with a K-type thermocouple fixed by point welding to the back side of the foil.

An alumina film 2—3 nm thick was formed on the support surface by oxidation. The procedure of preparation of the film has been described earlier.[11] Thus obtained film close in composition to Al_2O_3 is resistant to both the action of atmosphere and treatment with nitric oxide at pressures below 100 Pa. This makes it possible to study the catalysts by photoelectron spectroscopy at elevated pressures and to remove them from the photoelectron spectrometer chamber into atmosphere and then to place into a scanning tunneling microscope.

The model Au/AlO$_x$/FeCrAl gold catalysts were prepared by thermal vacuum deposition of gold particles in the chamber of a VG ESCALAB HP XPS spectrometer using an EFM3 deposition system (Omicron NanoTechnology GmbH), in which the gold source was heated by an electron impact. The amount of supported gold and the gold particle size were varied by changing the sputtering time. The prepared samples of the model catalysts were studied by scanning tunneling microscopy on a UHV 7000 VT high-vacuum scanning tunneling microscope (RHK Technology). The histograms of particle size distribution were obtained by the results of processing of at least 200 particles for each sample.

In this work, the fraction of surface gold atoms was calculated assuming that all particles in the samples correspond to the mean size of supported particles and lie on the surface as hemispheres. The volume of a gold atom and its surface area were calculated from the kinetic equations $V_{at} = 4/3\pi R^3$ and $S_{at} = 4\pi R^2$, respectively, and the gold atom radius (R) was accepted to be 1.44 Å (see Ref. 12). The volume and surface area of the particles were determined using the equations $V_{particle} = 2/3\pi(<d>/2)^3$ and $S_{particle} = 2\pi(<d>/2)^2$, respectively, where $<d>$ is the mean diameter of supported gold particles for the corresponding sample. The coverage of the gold surface with adsorbed forms was estimated by the equation

$$\Theta = (I_{N1s}/ASF_{N1s})/([i \cdot I_{Au4f}]/ASF_{Au4f}),$$

where I_i are the intensities of the corresponding XPS lines and ASF$_i$ are the atomic sensitivity factors. The fraction of surface gold atoms (i) was determined using the expression $i = n/N$, where $n = S_{particle}/S_{at}$ is the number of atoms on the particle surface and $N = V_{particle}/V_{at}$ is the total number of atoms in the particle.

Results and Discussion

The images of the surface and histograms of size distribution of gold particles for three prepared Au/AlO$_x$/FeCrAl samples are shown in Fig. 1. It is seen that the procedure described above allows one to obtain particles in the range from 2 to 7 nm with a rather narrow particle size distribution. It is these three samples with $<d> = 2$, 4, and 7 nm that were used for the further study of NO adsorption. In this region (2—7 nm), the effect of the gold particle size on the activity is rather pronounced. For example, the study of the size effect in the oxidation of CO on the Au/TiO$_2$ catalysts[13] showed that the gold particles 3—4 nm in size are more catalytically active than the particles of 2 nm, whereas the particles with the size 6 nm and more are inactive in the low-temperature oxidation of CO.

According to the STM data, the number of gold particles per support surface unit is almost independent of the amount of introduced gold, being ~300 per scanning field 500×500 nm^2. It is most likely that the density of the surface particle distribution is primarily determined by the number of specific sites of fixation of particles of the active component on the planar support surface. Assuming that the gold particles supported on the surface of a conventional support ($S_{sp} = 100$ m^2 g^{-1}) take a hemispherical shape, then, according to the calculation, the surface density of the Au particles with a mean size of 2, 4, and 7 nm remains unchanged in the catalysts containing 0.5, 3.8, and 20.8 wt.% gold, respectively.

The interaction of nitric oxide with the supported gold catalysts was studied *in situ*; *i.e.*, the XPS spectra were acquired in an NO flow, and the temperature of the samples was varied from 300 to 525 K. At $P_{NO} = 5 \cdot 10^{-5}$ Pa, a line with the bond energy value about 399.4 eV appeared in the N1s spectra (are not shown) already at 300 K. This line disappeared on heating the sample to 525 K.

Nitric oxide adsorption at elevated pressures was studied using a gas cell, and the NO pressure in these experiments was 1 Pa. The N1s spectra recorded during these experiments for two samples with mean gold particle sizes of 2 and 7 nm are presented in Fig. 2. The treatment of the samples with supported gold particles with nitric oxide at the temperature of the samples 325—475 K results in the appearance of two lines with bond energies

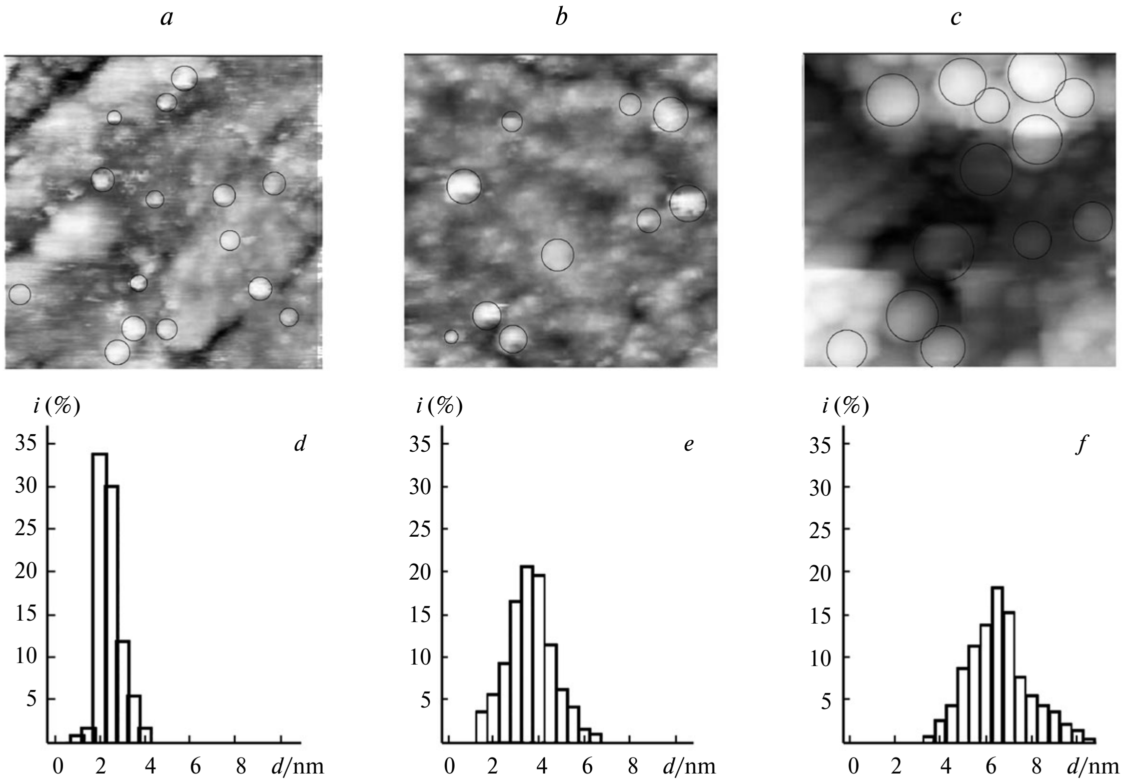

Fig. 1. STM images of the gold particles (*a—c*) (scanning parameters: scan size 40.0×40.0 nm, $U_t = -1.5$ V, $I_t = 0.6$ nA) and histograms of particle-size distribution for the gold particles (*d—f*) in the Au/AlO$_x$/FeCrAl samples. Some particles in the images are contoured with circles; *d* is the particle size, and *i* is the fraction of particles.

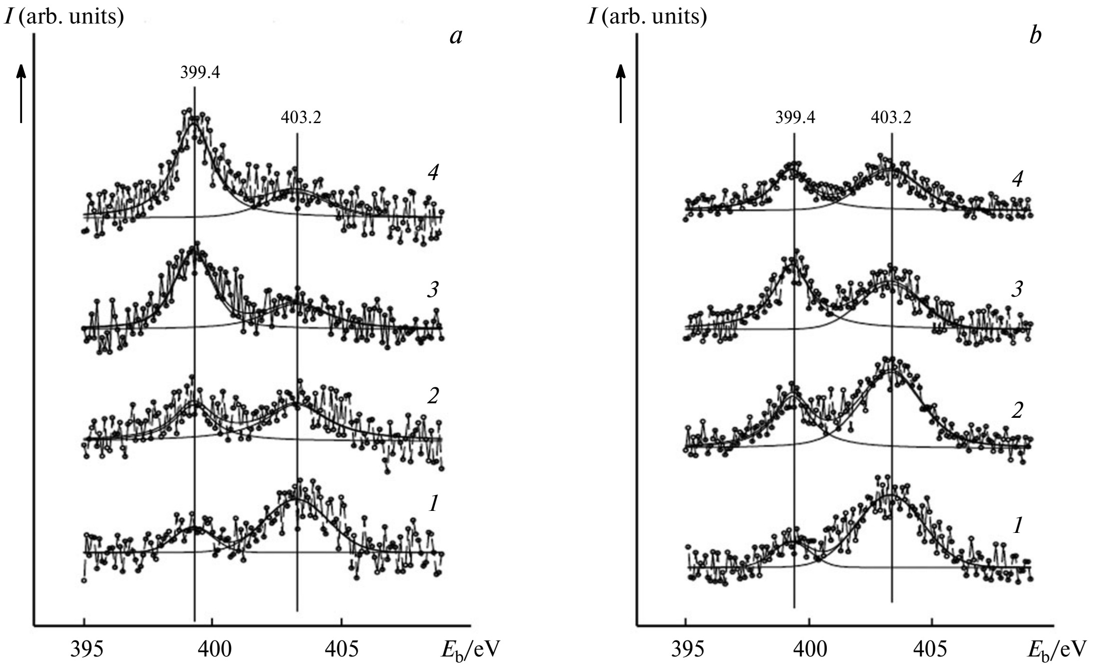

Fig. 2. N1s XPS spectra measured during NO adsorption on the Au/AlO$_x$/FeCrAl samples with <*d*> equal to 2 (*a*) and 7 nm (*b*) at 325 (*1*), 375 (*2*), 425 (*3*), and 475 K (*4*); P_{NO} = 1 Pa.

(E_b) of 399.4 and 403.2 eV in the N1s spectra. The intensity ratios of these lines are different for various samples and they vary with temperature. For instance, when the sample with a mean size of the gold particles of ~2 nm is heated to 425 K, the line with E_b = 403.2 eV that predominated in the spectrum measured at T = 325 K nearly disappears (see Fig. 2, *a*). This behavior is consistent with existence of two states for nitrogen atoms in the adsorption layer. Since the signals of the O1s line from the adsorbed particles (for example, N_2O_{ads}) are disguised by a considerably more intense signal from the oxide support (AlO_x), we do not consider the O1s spectra in this work. Nevertheless, based on our earlier experiments with a stepped single crystal of Au(533), in which we analyzed both the N1s and O1s spectra, the N1s signals with E_b = 399.4 and 403.2 eV can be ascribed to atomic nitrogen and a species with stoichiometry N_2O adsorbed on the gold particle surface,[7] respectively (hereinafter N_{ads} and N_2O_{ads}, respectively). Unlike single crystals, the Au nanoparticles are covered with atomically adsorbed nitrogen already in high-vacuum conditions ($P_{NO} > 10^{-5}$ Pa). At NO pressures about 1 Pa and in the temperature range from 325 to 475 K, atomically adsorbed nitrogen and the N_2O adsorption species coexist on the surface of the gold nanoparticles.

According to the XPS data, the metallic state of gold in the Au/Al_2O_3 catalysts is violated neither under the effect of the reaction medium nor with the change in the particle size. This conclusion follows from the results shown in Fig. 3 in which the spectrum of the Au4f line obtained for the freshly prepared $Au/AlO_x/FeCrAl$ sample with mean sizes of gold particles of 2 nm is compared with the spectrum of the same sample but measured after the NO treatment in the gas phase and with the spectrum of the freshly prepared sample with $\langle d \rangle$ = 7 nm. Indeed, the spectra of the Au4f line for the fresh and treated samples coincide in such a way that the corresponding differential spectrum is a background line with zero intensity (see Fig. 3, *a*). An increase in the mean size of the gold particles from 2 to 7 nm results in an increase in the cumulative intensity of the Au4f line in the spectrum and the shift towards lower values of the bond energy (down to 84.2 eV). The bond energy nearly attains the value typical of bulk metallic gold (84.0 eV (see Ref. 9)). For metallic nanoparticles, the values of E_b are usually higher than those for the bulky samples[13,14] (in our case, 84.7 and 84.6 eV for the samples with $\langle d \rangle$ = 2 and 4 nm, respectively). This difference is explained by both the change in the relaxation effect and the change in the initial state of gold (metal—dielectric transition). The shapes of the spectra presented in Fig. 3, *b* coincide completely, and after equalizing the intensities and shift of one of the spectra by 0.5 eV the differential spectrum represents a background line analogous to that presented in Fig. 3, *a*.

For the quantitative estimation of covarage of the gold nanoparticle surface with various nitrogen-containing adsorbed species, it is necessary to normalize the intensity of the corresponding lines in the N1s spectra to some value characterizing the amount of the active component, in our case, gold. The atomic ratio N : Au is used for this purpose in homogeneous systems. This ratio is calculated from the ratios of the total intensity of the N1s line spectra to the intensity of the Au4f line spectra normalized to the atomic sensitivity factors.[9] However, in the case where an increase in the amount of introduced gold increases the mean size of the supported gold particles, this estimate is

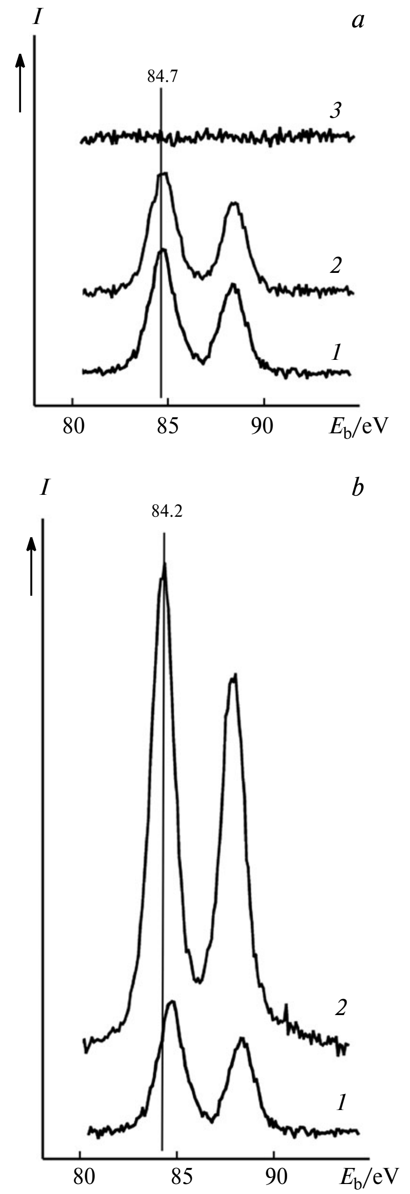

Fig. 3. XPS spectra detected *in vacuo* for the following $Au/AlO_x/FeCrAl$ samples: (*a*) the sample with $\langle d \rangle$ = 2.0 nm before (*1*) and after (*2*) the treatment in NO at P_{NO} = 1 Pa and T = 325 K and their differential spectra (*3*) and (*b*) freshly prepared samples with $\langle d \rangle$ equal to 2 (*1*) and 7 nm (*2*).

poorly informative. The reason is that a fraction of Au atoms within the bulk does not participate in adsorption but contributes to the signal of the Au4f line. This does not allow one to compare the samples with various sizes of gold particles with the coverage of the gold particle surface by adsorbed species.

Similar comparison becomes, however, possible, when the ratio of the N1s line intensity is related not to the total intensity of the Au4f spectrum but to the part of the spectrum belonging to the surface gold atoms. In this case, we can consider the coverage of the surface expressed in fractions of the monolayer $\Theta = N_{ads}/n$, where N_{ads} is the number of adsorbed species and n is the total number of surface gold atoms. The first value can easily be estimated directly from the XPS spectra under the conditions that the adsorbate occupies the catalyst surface. However, to estimate the number of surface gols atoms, only the part of the spectral intensity related to the presence of Au atoms on the surface should be taken into account rather than the cumulative intensity of the Au4f spectra.

Figure 4 shows the influence of the mean particle size (see Fig. 4, *a*) and adsorption temperature (see Fig. 4, *b*) on the total coverage of the gold particle surface $\Theta(N_{tot})$ with the nitrogen-containing complexes (N_{ads} and N_2O_{ads}) during NO adsorption at $P = 1$ Pa and different temperatures. The mean size of supported gold particles exerts an effect on the coverage of the surface with the nitrogen-containing complexes, and the gold particles with a mean size of 4 nm have the highest activity in NO adsorption (see Fig. 4, *a*). The character of changing the surface coverage with temperature depends on the Au particle size (see Fig. 4, *b*). In the case of the sample with a mean particle size of 4 nm, the surface coverage progressively increases with temperature. For the sample with $\langle d \rangle = 7$ nm the decrease in coverage with raising temperature is observed, whereas for the sample with the particle size 2 nm the value of $\Theta(N_{tot})$ remains nearly unchanged with temperature. As a result, the maximum coverage of the gold surface with the nitrogen-containing complexes for the catalysts with $\langle d \rangle = 2$ and 7 nm at $T_{ads} = 325$ K is 0.22 and 0.26, respectively. For the sample with the mean size of the Au particles $\langle d \rangle = 4$ nm, the surface coverage at this temperature is already 0.4, increasing to 0.7 at $T = 475$ K. Note that the gold particles about 5 nm in size exhibit a significant catalytic activity in various reactions.[2,12,15—19]

Let us consider the influence of the adsorption temperature and size of gold crystals on the ratio of two forms of nitrogen adsorption: N_{ads} and N_2O_{ads}. The temperature dependences of the atomic ratios to $N_{ads}(n)$ and $N_2O_{ads}(n)$ for each Au/AlO$_x$/FeCrAl sample studied are presented in Fig. 5. For the samples with the mean sizes of gold particles 2 and 4 nm, the temperature dependences of the coverage are similar: when the surface is occupied by atomically adsorbed nitrogen the coverage increases with temperature T, and when the surface is occupied by species with stoichiometry N_2O the coverage decreases with temperature. In the case of the sample with the smallest mean size of the gold particles, the decrease in $\Theta(N_2O_{ads})$ is almost quantitatively compensated by the increase in

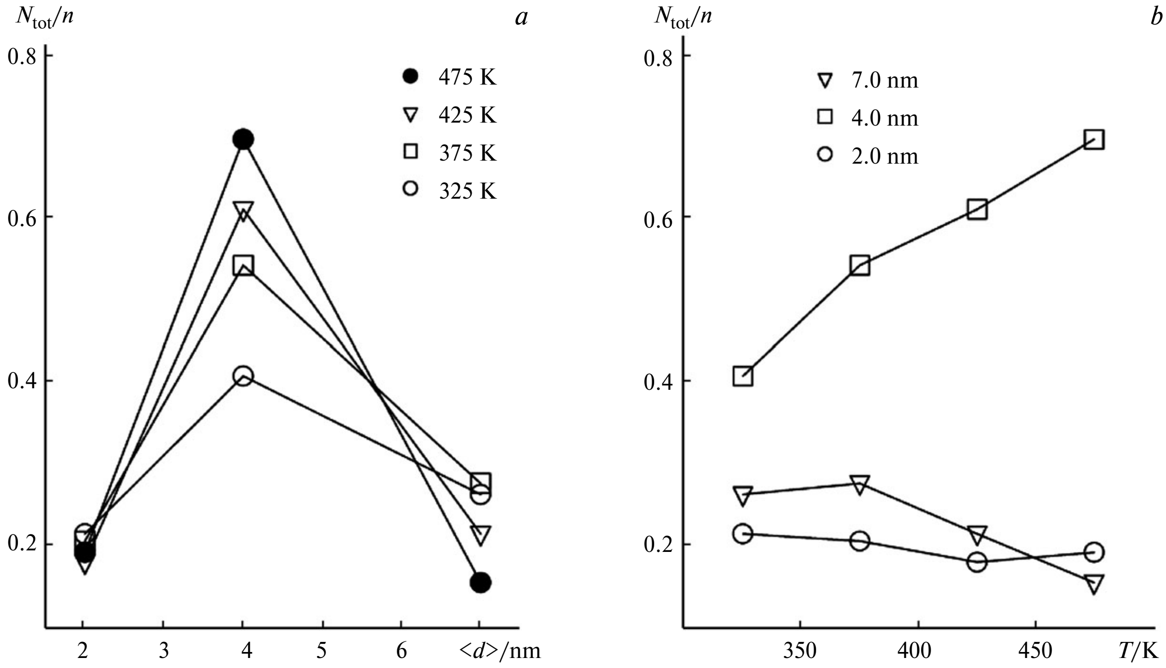

Fig. 4. Atomic ratio N_{tot}/n *vs* mean particle size of gold $\langle d \rangle$ at 325—475 K (*a*) and *vs* temperature (T) of the samples for various particle sizes (*b*) at $P_{NO} = 1$ Pa.

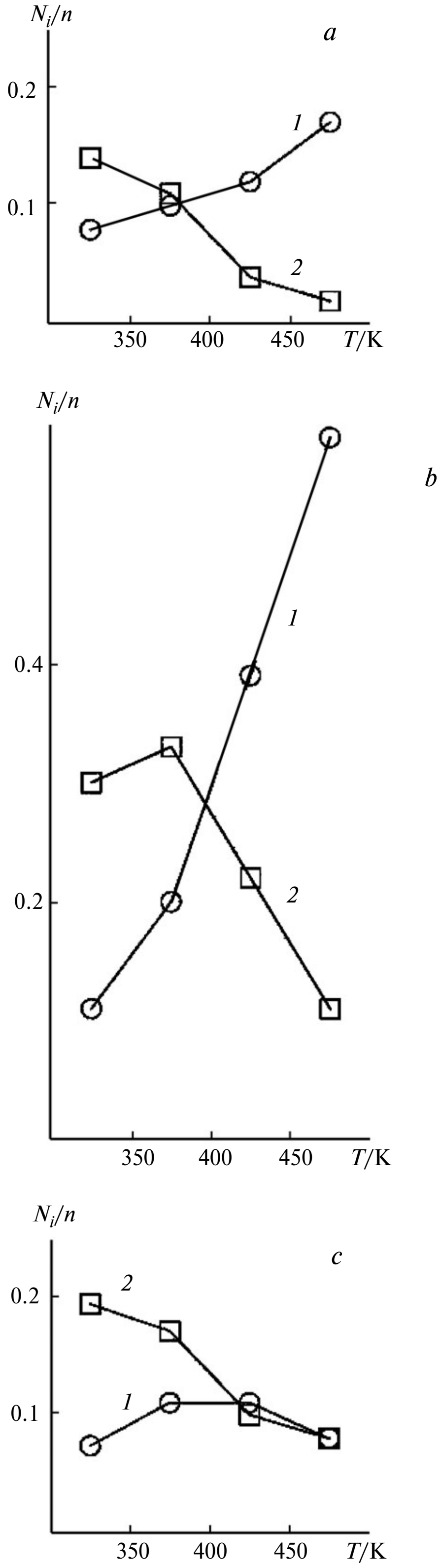

Fig. 5. Temperature plots of the atomic ratios N_i/n for N_{ads} (*1*) and N_2O_{ads} (*2*) for the Au/AlO$_x$/FeCrAl samples with $<d>$ equal to 2 (*a*), 4 (*b*), and 7 nm (*c*) with $P_{NO} = 1$ Pa.

$\Theta(N_{ads})$ (see Fig. 5, *a*), so that the total coverage remains approximately constant (see Fig. 4, *b*). Almost the same temperature dependence of $\Theta(N_2O_{ads})$ is characteristic of the sample with the mean gold particle size 4 nm, although the surface concentration of atomically adsorbed nitrogen increases more noticeably (see Fig. 5, *b*). As a result, the total coverage of the gold surface with the adsorbed species increases with temperature (see Fig. 4, *b*). For the sample with large gold particles (7 nm), the temperature dependence of the coverage with N_{ads} is characterized by the curve with a maximum at $T = 375$ K, although the total coverage decreases with temperature (see Fig. 4, *b*) because of sharper changes in $\Theta(N_2O_{ads})$ observed on heating the sample from 325 to 475 K (see Fig. 5, *c*).

The assumption about the presence of two types of adsorbates (N_{ads} and N_2O_{ads}) in the adsorption layer is well consistent with the earlier obtained catalytic data,[19] according to which the reduction of nitric oxide in the presence of CO on the Au/Al$_2$O$_3$ catalysts affords the same products in the gas phase: molecular nitrogen produced by the main reaction

$$2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2$$

and N_2O due to the side reaction

$$2\,NO + CO \longrightarrow N_2O + CO_2.$$

The major product at 323 K was shown[19] to be N_2O and the selectivity to molecular nitrogen increased with temperature. At $T = 473$ K, N_2 became the only product and the NO conversion attained the maximum value.

These changes in the catalytic properties qualitatively correspond to our data on the change in the composition of the adsorption layer with temperature. An increase in the surface concentration of N_{ads} with temperature is accompanied by a decrease in coverage with N_2O_{ads}, which means that the selectivity of formation of atomically adsorbed nitrogen increases. The recombination of the latter leads to desorption of N_2 to the gas phase. This conclusion is quantitatively confirmed by Fig. 6 showing the temperature dependences of the selectivity of atomic nitrogen formation in the adsorbed layer calculated from the equation

$$S = \frac{\Theta(N_{ads})}{\Theta(N_{ads}) + \Theta(N_2O_{ads})} \cdot 100\%,$$

and of the selectivity of N_2 formation calculated using literature data.[19] It is easily seen that the selectivity both to the concentration of atomically adsorbed nitrogen and to the content of molecular nitrogen in the gas phase increases with rising temperature. The best correspondence is observed for the samples with $<d> = 2$ and 4 nm (see Fig. 6). This suggests that the associative desorption of N_{ads} is the rate-determining step in N_2 formation.

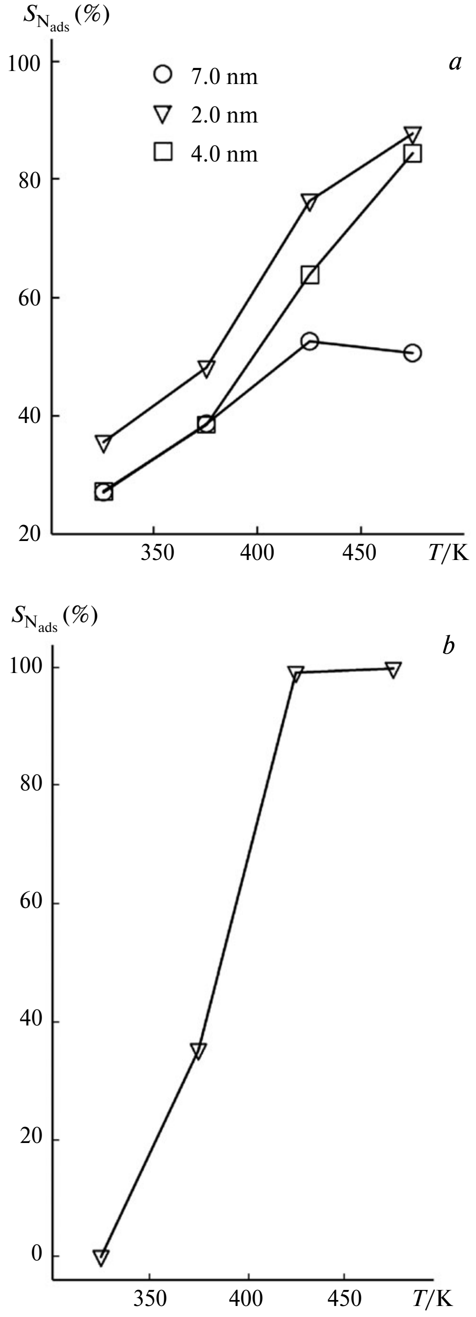

Fig. 6. Temperature plots of the selectivity of formation of N_{ads} in NO adsorption on the Au/AlO$_x$/FeCrAl samples with various <*d*> at P_{NO} = 1 Pa (*a*) and of formation of N_2 in nitric oxide reduction in the presence of CO on the Au/Al$_2$O$_3$ catalysts (*b*) (see Ref. 19).

The obtained temperature dependences of the composition of the adsorption layer suggest the presence of different adsorption sites on the surface of the gold nanoparticles. Therefore, it can be stated that the surface sites on which the N_2O adsorption complex is formed have the same nature in all samples studied. This is indicated by a similar character of the temperature dependence of this adsorption species. The maximum amount of N_2O_{ads} ($\Theta \approx 0.3$—0.35) is observed for the sample with <*d*> = 4 nm, whereas the decrease (to 2 nm) and increase (to 7 nm) in the mean size of the gold nanoparticles decrease the maximum coverage of the surface with these particles to 0.14 and 0.19, respectively). Noniniformity of the particle-size distribution suggests that the corresponding sites are formed on the particles with mean sizes of 3—6 nm, whose contribution is especially high in the sample with <*d*> = 4 nm but is also significant in the samples with smaller and larger crystalline particles (see Fig. 1).

The structure of the surface sites on which N_2O_{ads} is formed has been described previously.[20] It was shown that NO adsorption induces the formation of N_{ads} and N_2O_{ads} species on the face on the gold single crystal Au(533), whereas only atomically adsorbed nitrogen appears at the Au(310) face of the gold single crystal. We explained this effect by the difference in the crystallographic structures of the corresponding faces. The steps of the Au(533) face are formed by the gold atoms separated by a minimally possible distance (2.88 Å). This provides the occurrence of the reaction

$$2\ NO \longrightarrow 2\ NO_{ads} \longrightarrow N_2O_{ads} + O_{ads}.$$

At the Au(310) face, the gold atoms on the steps are located in such positions that the distance (d_{at}) between them is $d_{at} = 1.41a$, where a is the interatomic spacing. In this case, no N_2O_{ads} complexes are formed.

Atomically adsorbed nitrogen presents a more complicated picture. On the one hand, when NO is adsorbed on the Au(310) face consisting of (100) terraces separated by (110) steps, the temperature increase from 300 to 460 K results in a permanent decrease in the coverage of this surface with atomically adsorbed nitrogen. On the other hand, when NO is adsorbed on the (533) face with the surface made of (111) terraces and (100) steps, the maximum value of $\Theta(N_{ads})$ is attained at T = 475 K,* *i.e.*, at the same temperature at which the maximum shown in Fig. 5, *b* occurs.

As for the Au(310) face of the gold single crystal, in the case of the sample with <*d*> = 7 nm, the surface by N_{ads} decreases with temperature (see Fig. 5, *c*). At the same time, for the samples with the mean particles sizes 2 and 4 nm, the surface coverage by atomically adsorbed nitrogen increases with temperature (see Fig. 5, *a* and *b*). For the sample with <*d*> = 4 nm, the temperature increase from 370 to 470 K is accompanied by an increase in $\Theta(N_{ads})$, which is twice as large as the decrease in $\Theta(N_2O_{ads})$. We believe that on heating the sample from 320 to 470 K the coverage of the surface with N_2O_{ads} particles decreases and, correspondingly, additional sites for N_{ads} adsorption become available.

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Although we are unable yet to establish the exact structure sites active for the dissociative adsorption of NO on gold nanoparticles, it can be stated that the structural factor plays the determining role during nitric oxide adsorption. We succeeded to establish that the changes observed in the composition of the adsorption layer depend on the mean size of the gold nanoparticles and adsorption conditions (temperature and NO pressure). It is most likely that the ratio of adsorption species is determined by the difference in the fractions of specific surface atoms composing kinks, steps, and faces of the gold particles of various size.

We found no experimental works in which NO adsorption on supported gold particles was studied and, hence, data on the size effects in this process are lacking. At the same time, the DFT calculations of NO adsorption on the Au(111), (100), (110), and (310) surfaces clearly show that the adsorption energy of the molecules increases strongly with an increase in the number of low-coordinated gold atoms to which the molecules are bound.[20] These results are well consistent with the concepts that the presence of point defects on the surface determines the catalytic activity of gold. It has earlier been proposed that the activation of NO occurs on the stepped faces of the gold crystallites.[21]

According to our data, in the studied catalysts with different sizes of supported particles, gold exists only in the metallic state. Therefore, the described size effect in NO adsorption on the gold nanoparticles is not related, most likely, to the difference of the electronic state of gold (appearance of ionic forms, charge redistribution in the metal—support system). We believe that the structural factor makes a decisive contribution to the appearance of the size effect in NO adsorption on the gold nanoparticles.

Thus, the use of the STM and *in situ* XPS methods for the study of the interaction of NO with the $Au/AlO_x/$ FeCrAl model catalysts made it possible to establish the existence of the size effect in NO adsorption on the gold nanoparticles. The sample with $\langle d \rangle = 4$ nm exhibits the maximum adsorption capacity to the nitrogen-containing adsorption complexes, whereas the decrease (to 2 nm) and increase (to 7 nm) in the mean size of the supported gold particles decreases the coverage of the surface with these complexes.

It was shown that adspecies are formed on the gold nanoparticle surface under the studied conditions: atomically adsorbed nitrogen and the N_2O adsorption complex. The relative occupancy of the surface by these species depends on both the size of the gold nanoparticles and experimental conditions (the temperature of the sample and NO pressure). Under the high-vacuum conditions ($P_{NO} \approx 10^{-5}$ Pa), only atomically adsorbed nitrogen is formed and at NO pressures about 1 Pa N_{ads} coexists with N_2O.

The differences in thermal stability of atomically adsorbed nitrogen found for different samples suggest the existence on the gold surface of adsorption sites of different nature, whose concentration and mechanism of formation depend on the size of the Au nanoparticle. The changes observed in the composition of the adsorption layer indicate that NO adsorption is sensitive to the structure of surface sites.

The correlation between the temperature dependence of the adsorption layer composition and the literature data on the change in the selectivity of N_2 formation was established for the catalytic reduction of NO with carbon oxide on the Au/Al_2O_3 catalysts.

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