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Identification of Nitrogen-Containing Species Obtained by Nitric Oxide Adsorption on the surface of Model Gold Catalysts

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Abstract—Nitric oxide adsorption at 300–500 K on gold particles supported on an alumina film has been investigated for the first time by in situ X-ray photoelectron spectroscopy. Two nitrogen-containing adsorption species can form on the surface of gold particles. By test experiments on NO adsorption on the stepped face (533) of a gold single crystal, these species have been identified as adsorbed nitrogen atoms (which are detected throughout the temperature range examined) and a surface complex with N_2O stoichiometry (which is stable in a narrow temperature range of 325–425 K).

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In recent years, investigation of the catalytic properties of gold has become one of the most dynamically developing areas of research in heterogeneous catalysis. According to Haruta [1], over 700 publications devoted to various aspects of catalysis by gold have been appearing annually since 2005. This interest from the catalytic community is likely stirred up by the fact that gold provides an illustrative example of the so-called size effect in catalysis: the activity of dispersed gold is observed only within a narrow particle size range [2, 3], while massive gold does not show significant catalytic activity in any reaction. A number of practically important gold-catalyzed reactions are known at present. These include selective acetylene hydrogenation into ethylene [4], partial oxidations of hydrocarbons [5], selective acrolein and 1,3-butadiene reduction [6], etc. Gold can substitute for platinum in three-way Pt–Pd–Rh catalysts for nitric oxide reduction to dinitrogen in automotive catalytic converters [7]. This makes it possible to conduct the reaction at lower temperatures, providing a solution to the cold start problem, and with a lower yield of N_2O as a by-product.

With the progressively increasing number of publications on the synthesis of supported gold catalysts and on determination of the catalytic activity of gold nanoparticles, there have been only a few fundamental studies aimed at elucidating the nature of the catalytic action of gold by determining the composition and structure of the active sites of gold catalysts by physical and chemical methods. This situation is primarily due to the small size of the objects of investigation (2–5 nm), which makes many physicochemical methods inapplicable because of their insufficient sensitivity or other methodological limitations. In addition, the so-called "pressure gap" problem arises in the investigation of the physicochemical and catalytic properties of gold catalysts. Most instrumental methods are usable only under low-pressure or vacuum conditions. However, the action of the reaction medium can markedly change the composition of the adsorption layer and bring about other reaction pathways.

The above problems cause difficulties in the application of instrumental methods of investigation, including X-ray photoelectron spectroscopy (XPS), to gold catalysts. An interesting attempt to circumvent the methodological limitations was made by Nieuwenhuys et al. [8], who used an Au(310) single crystal to study the catalytic conversion of NO on gold. This eliminated the problem of the low intensity of the photoelectron spectra of gold and nitrogen. Efficient nitric oxide adsorption on massive gold was ensured in that study by cooling the sample to 80–160 K. This technique made it possible to record the N 1*s* spectrum of physically adsorbed nitric oxide and to see how the adsorption layer changes as the sample is heated to room temperature. However, use of cryogenic techniques under high-vacuum conditions leads to additional difficulties in data interpretation, which arise primarily from the uncontrollable effect of the residual gases in the chamber. These gases adsorb readily onto the surface to mask the spectral signal from the adsorbed species resulting from NO adsorption. Nieuwenhuys et al. [8] did not explain in a clear way why, after the total adsorption of NO, they observed a strong O 1*s* peak. Accordingly, they excluded use of nitrogen-to-oxygen atomic ratios in the identification of nitrogen species adsorbed on the gold surface. Furthermore, the adsorption layer composition may change radically on passing from the conditions used in that study to the typical reaction conditions.

We believe that a more promising methodological approach to the investigation of nitric oxide adsorption on gold is to use an elevated NO pressure in the gas phase in combination with in situ XPS measurements. Here, we report an XPS study of the composition of the adsorption layer obtained on alumina-supported model gold catalysts by treating them with NO at pressures of up to 1 Pa. For identification of the resulting adsorption species, we carried out a comparative study of NO adsorption on the (533) face of a gold single crystal under the same conditions.

EXPERIMENTAL

The XPS study of NO adsorption on model gold catalysts was performed on a VG ESCALAB HP electron spectrometer. The residual gas pressure in the chamber of the spectrometer was $\sim 1 \times 10^{-6}$ Pa. A detailed description of this spectrometer, whose distinctive feature is that it is outfitted with a "high-pressure" cell allowing photoelectron spectra to be recorded at gas pressures of up to 10 Pa over the sample, is presented elsewhere [9]. Before measurements, the spectrometer was calibrated against the lines Au $4f_{7/2}$ (binding energy of 84.0 eV), Ag $3d_{5/2}$ (368.3 eV), and Cu $2p_{3/2}$ (932.7 eV) [10].

In the investigation of NO adsorption on the Au(533) face, measurements were carried out on a high-pressure spectrometer at the Advanced Light Source synchrotron radiation center (Berkeley, United States). The spectrometer was equipped with a Scienta hemispherical analyzer with an entrance lens differential pumping system allowing measurements to be taken at gas pressures of up to 100 Pa in the analyzer chamber. The residual pressure in the spectrometer chamber was $\sim 1 \times 10^{-7}$ Pa. For quantitative measurements, the lines of gold, nitrogen, and oxygen were recorded for photoelectrons with a kinetic energy of 200 eV. This ensured the same analytical depth corresponding to the minimum in the photoelectron mean free pass versus photoelectron kinetic energy universal curve [11]. Calculating the N/O atomic ratio, we took into account the photoionization cross sections [12]. In the determination of the binding energy for the N 1*s* line, we used the corresponding Au 4*f* and N 1*s* spectra recorded at the same primary radiation energy $h\nu$. Binding energies were determined using the XPS Peak 4.1 program with an accuracy of 0.2 eV or better.

The Au(533) sample was pretreated by performing several cycles consisting of argon ion sputtering of the gold surface and heat treatment between 600 and 1000 K in the temperature stroll mode in flowing oxygen at a pressure of 3×10^{-5} Pa. After the total disappearance of the spectral lines of impurity elements, the sample was subjected to finishing treatment, which consisted of soft ion sputtering of the surface (20–30 s) alternated with annealing of the sample in vacuo while raising the temperature to 960 K. The quality of the surface was checked by low-energy electron diffraction (LEED). The pretreatment procedure was stopped once a distinct diffraction pattern was obtained at a primary electron beam energy of 8–12 eV. The finishing treatment of the single crystal surface was performed before each series of adsorption experiments.

To study NO adsorption and disproportionation on gold particles, we prepared samples of model catalysts on two types of supports. One of the supports was a thin alumina film obtained by oxidative treatment of the surface of a NiAl(110) single crystal. The preparation of this model support was described by Kulawik et al. [13]. The thickness of the oxide film was 0.4–1 nm, as estimated by comparing the intensities of the Ni 2*p* photoelectron lines before and after its formation. The film was checked for structural order by the LEED method. The second support was a 2- to 3-nm-thick alumina film grown by oxidizing the surface of an aluminum-containing FeCrAl steel alloy. An advantage of these supports is the resistance of their Al_2O_3 film both to the action of the atmosphere and to nitric oxide up to 100 Pa. This makes it possible to study the samples by XPS at elevated pressures and then by scanning tunneling microscopy (STM) after they are transferred, exposed to the air, from the chamber of the photoelectron spectrometer to the microscope.

The model gold catalysts Au/AlO_x/NiAl(110) and Au/AlO_x/FeCrAl were prepared by thermal vacuum evaporation of fine gold particles onto the substrate in the chamber of the VG ESCALAB HP photoelectron spectrometer using an EFM3 evaporating system (Omicron Nano Technology GmbH), in which the source of gold was heated by electron impact. The amount of deposited gold was controlled by varying the evaporation time. STM examinations were carried out on a UHV 7000 VT ultrahigh-vacuum scanning tunneling microscope (RHK Technology).

RESULTS AND DISCUSSION

The STM study of Au/AlO_x/FeCrAl samples demonstrated that the above procedure yields particles 2 nm in size and larger (Fig. 1). The sample with the smallest particle size was used in the investigation of nitric oxide adsorption.

The interaction between nitric oxide and the supported gold catalyst was studied in situ; that is, XPS spectra were recorded while heating the sample (from 300 to 525 K) in flowing NO. At an NO pressure of 5×10^{-5} Pa, the N 1*s* spectrum shows a single line at a binding energy (BE) of about 399.4 eV. As the sample was heated to 525 K, this line disappeared.

Nitric oxide adsorption at elevated pressures was studied in situ using a gas cell. The NO pressure in these experiments was 1 Pa. The N 1*s* spectra recorded in these experiments are presented in Fig. 2.

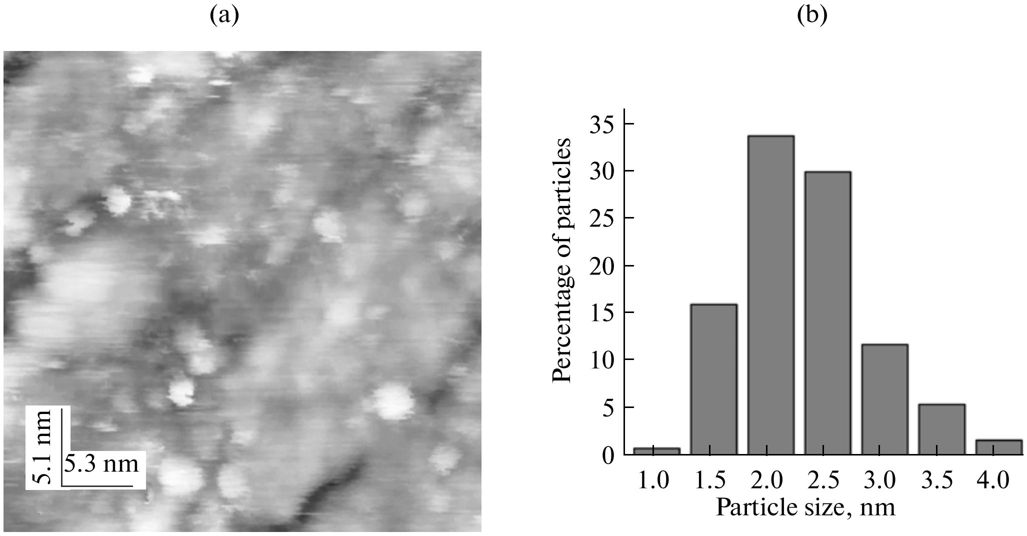

Fig. 1. (a) STM image (scanning parameters: 35.3 nm × 31.9 nm × 7.7 nm, $U_t = -1.5$ V, $I_t = 0.6$ nA) and (b) gold particle size distribution for an Au/AlO$_x$/FeCrAl sample.

Exposure of the sample with supported gold particles to nitric oxide at a sample temperature of 325–425 K causes the formation of two nitrogen states with BE(N 1*s*) = 399.4 and 403.2 eV in the adsorption layer. These N 1*s* lines were assigned to two different adsorption states based on the difference between their thermal stabilities: as the sample was heated to 425 K, only the species characterized by BE = 399.4 eV remains on the surface (Fig. 2).

Investigation of an Au/AlO$_x$/NiAl(110) sample with a similar supported gold concentration demonstrated that, at an NO pressure of 5×10^{-5} Pa, the N 1*s* spectrum again shows a single line at BE = 399.4 eV. At an elevated pressure of 1 Pa and sample temperatures of 325–425 K, the spectrum shows two signals at BE = 399.4 and 403.2 eV (Fig. 3).

Reference experiments on gold-free supports showed that no nitrogen accumulation takes place on these supports as they are treated with NO under the same conditions. Furthermore, the N/Au atomic ratio estimated from the N 1*s* and Au 4*f* peak areas with the atomic sensitivity factors for these XPS lines [9] taken

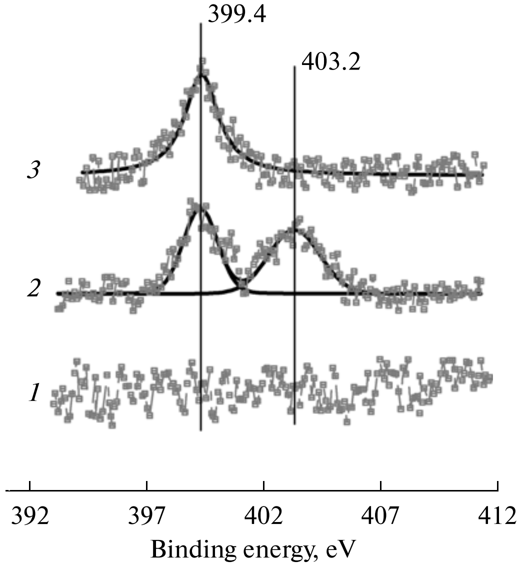

Fig. 2. N 1*s* photoelectron spectra of Au/AlO$_x$/FeCrAl recorded (*1*) before and (*2*, *3*) during its exposure to NO: (*1*) $T = 300$ K; (*2*) $P = 1$ Pa, $T = 375$ K; (*3*) $P = 1$ Pa, $T = 425$ K.

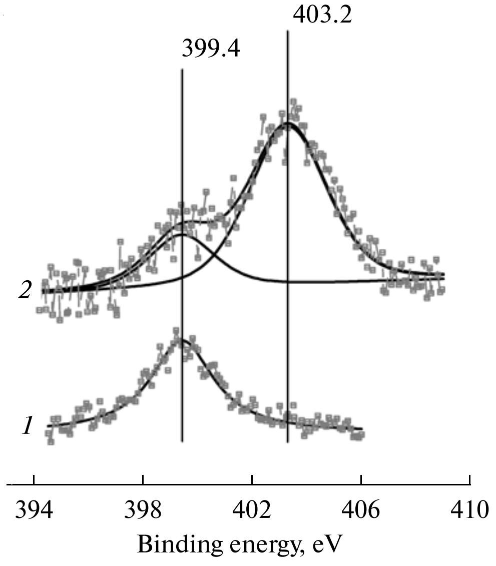

Fig. 3. N 1*s* photoelectron spectra of Au/AlO$_x$/NiAl(110) recorded during its exposure to NO: (*1*) $P = 5 \times 10^{-5}$ Pa, $T = 300$ K; (*2*) $P = 1$ Pa, $T = 375$ K.

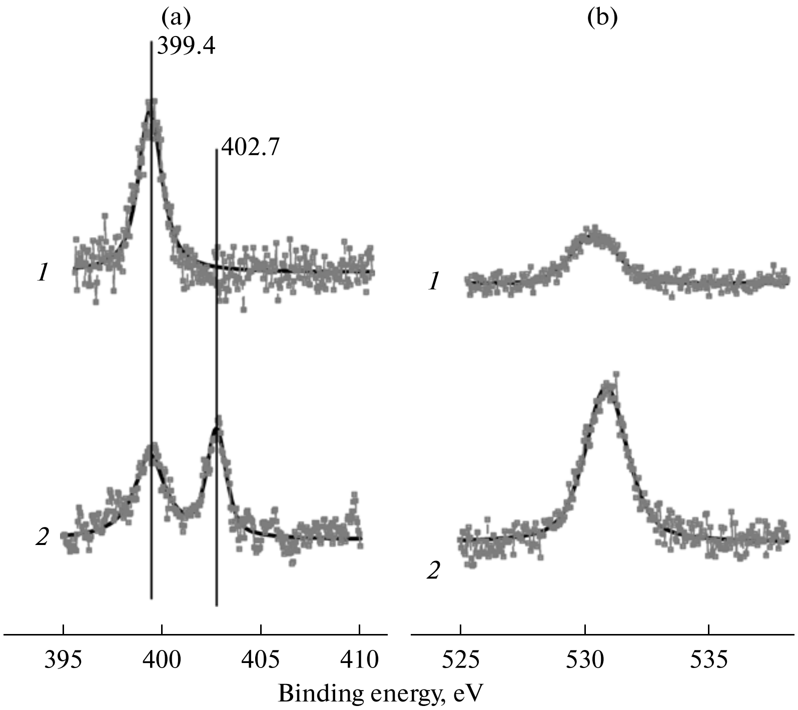

Fig. 4. (a) N 1*s* and (b) O 1*s* photoelectron spectra of an Au(533) single crystal recorded during its exposure to NO at $P = 1$ Pa and $T =$ (*1*) 375 K and (*2*) 425 K.

into account did not exceed 0.7. Therefore, these supports are inactive in nitric oxide decomposition and the nitrogen-containing species are adsorbed by gold particles.

Thus, according to in situ XPS data, two nitrogen-containing adsorption species differing in their electronic properties and thermal stability may result from NO adsorption on nanosized gold particles. However, it is difficult to identify these adsorption species, which may contain both nitrogen and oxygen, on oxide-supported model catalysts by the XPS method, because the oxygen contained in the alumina film makes a large contribution to the O 1*s* signal. As a consequence, it is practically impossible to quantitatively compare the N and O concentrations in the adsorption layer in this case.

For this reason, in order to identify the nitrogen species adsorbed on gold, we carried out additional experiments in which NO was adsorbed on the stepped face (533) of a gold single crystal. In this case, there was no contribution from oxygen of the support to the O 1*s* signal.

Even a prolonged (2-h-long) exposure of the (533) face to NO at pressures of up to 0.1 Pa was insufficient for the formation of an adsorption layer: no measurable signal was observed in the N 1*s* spectrum. As the pressure was increased to 1 Pa, two peaks at BE = 399.4 and 402.7 eV appeared in the N 1*s* spectrum (Fig. 4a). Raising the sample temperature above 375 K caused the disappearance of the peak at the higher binding energy, and only the N 1*s* peak at BE = 399.4 eV remained in the spectrum. The N/O atomic ratio determined from the N 1*s* and O 1*s* peak areas was ~6 in this case, so the N 1*s* peak was assignable to the adsorbed nitrogen atoms resulting from the dissociative adsorption of NO:

$$NO \rightarrow N_{ads} + O_{ads}.$$

The absence of adsorbed oxygen atoms on the surface is explained by the fact that they are highly reactive and are titrated during the experiment by impurities present in the NO flow, such as CO.

The second state of nitrogen, characterized by BE = 402.7 eV, which was observed along with nitrogen atoms, is stable in the same narrow temperature range of 300–375 K as in the case of supported gold catalysts. From the N 1*s* and O 1*s* spectra, we estimated the nitrogen-to-oxygen atomic ratio for this second nitrogen species, which turned out to be ~2. Therefore, this species is adsorbed nitrous oxide, N_2O. This assignment is consistent with conclusions of Vinod et al. [14], who investigated NO adsorption on the (310) face of a gold single crystal at low temperatures of 80–220 K. They deduced from XPS data that the adsorption layer contains not only adsorbed NO molecules (least stable species) and oxygen atoms, but also the adsorbed N_2O complex. This species was assumed to result from the dissociation of an NO molecule followed by the interaction of the resulting nitrogen atom with another NO molecule [14]:

$$2NO \rightarrow N_2O_{ads} + O_{ads}.$$

Note that, in both cases, this complex showed itself as a single N 1*s* peak: BE = 402.7 eV in our experiments (Fig. 4), and BE = 401.5 eV in the above-cited study by Vinod et al. [14]. This is at variance with the well-known nonequivalence of nitrogen atoms in the nitrous oxide molecule. Performing N_2O adsorption at 80 K, Vinod et al. indeed observed two N 1*s* lines at BE = 401.5 and 405.5 eV. However, this state of adsorbed N_2O was extremely unstable. This contradiction is explicable under the assumption that the adsorption complex with N_2O stoichiometry that results from NO adsorption on the stepped faces of a gold single crystal has an unordinary structure. Obviously, additional experiments are necessary for elucidating the nature of this adsorption species.

However, the XPS and thermal stability data alone provide good reason to state that NO adsorption on gold nanoparticles, depending on the adsorption conditions, can yield adsorbed nitrogen atoms with BE(N 1*s*) = 399.4 eV and N_2O_{ads} species with BE(N 1*s*) = 403.2 eV. This assignment is in absolute agreement with the results of catalytic studies by Ueda and Haruta [15], who concluded that nitrogen molecules and nitrous oxide are the only products of the catalytic reduction of NO on supported gold catalysts.

CONCLUSIONS

Thus, this comparative in situ XPS study of NO adsorption on gold particles supported on thin alumina films and on the stepped face (533) of a gold single crystal at elevated NO pressures in the gas phase discovered and identified nitrogen adsorption species—nitrogen atoms and a surface complex with N_2O stoichiometry—on nanosized metal particles. The adsorbed nitrogen atoms form even in a high vacuum ($P_{NO} > 10^{-5}$ Pa). At NO pressures above ~1 Pa in the temperature range from 325 to 425 K, the adsorbed nitrogen atoms coexist with the N_2O complex.

Further investigation of experimental conditions on which the proportions of the nitrogen adsorption species on the model gold catalysts depend (gold particle size, reaction temperature, and reaction mixture composition) is expected to determine the optimum conditions for nitrogen oxide neutralization in automotive exhaust.

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