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Interaction of Silver with a NO/O₂ Mixture: A Combined X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy Study

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The treatment of a silver polycrystalline foil with a 1:100 NO/O₂ mixture at atmospheric pressure and room temperature led to the formation of a AgNO₃/Ag₂O/Ag "sandwich" in which no sharp boundary between the superimposed layers could be detected. The morphology of the as obtained structure was studied by means of X-ray photoelectron spectroscopy and scanning electron microscopy. The upper layer consisted of AgNO₃ crystals of average size between 0.1 and 0.4 μm. It is suggested that silver(I) oxide was the product of the oxidation of metallic silver, whereas AgNO₃ resulted from the subsequent reaction of Ag₂O with NO₂ in the gas phase. The underlying Ag₂O layer, which was characterized by a rough surface and a high porosity, could be characterized after uncovering it by selective dissolution of the AgNO₃ in water at room temperature.

1. Introduction

An effective solution for the removal of NO_x from industrial and automotive emissions is a question of crucial importance.¹ Among other solutions, such as the catalytic decomposition of NO into N₂ and O₂² and the thermal De-NO_x process,³ SCR (selective catalytic reduction) of NO with NH₃ has established itself.⁴ In the past decade, research efforts concentrated on the search for an alternative reducing agent such as hydrocarbons,⁵ in order to avoid the well-known transport and storage problems connected with NH₃. Recently, interesting results on the reduction of NO_x in the presence of excess O₂ on zeolite-based catalysts by nonmethane hydrocarbons, e.g., propane, propene, and ethylene, were reported.^{6,7} One of the serious factors, that hinders the use of zeolite-based catalysts is the low hydrothermal and thermal stability. While Co-ZSM-5 seems to offer some hydrothermal stability, it still suffers from a reduction in activity at high water vapor concentration in exhaust streams. For this reason, the search for an optimal catalyst for the reduction of nitric oxide is still in progress.

Silver is well-known as a catalyst for the selective oxidation of ethylene and methanol.^{8–10} Recently, the activity of alumina-supported silver catalysts toward the selective catalytic reduction (SCR) of nitric oxide with

hydrocarbons or oxygen-containing organic compounds in the presence of oxygen was reported.^{11,12}

Since the end of the 1960s, several studies have been carried out on Ag/O₂,^{13–27} Ag/NO,^{28–31} and Ag/NO₂.^{32–35}

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systems. However, despite the atomic-molecular level of the numerous observations, the "pressure gap" problem has not allowed researchers to make unambiguous conclusions about the structure of the active sites in real catalysts. The study of the oxygen/silver system is complicated by the fact that oxygen is usually present in many forms, depending upon the history of the system. The confused state of the oxygen/silver literature is readily apparent, illustrating the complexity of this system.

In the present work an attempt was made to bridge the pressure "gap" between "real-life" catalytic conditions and the ultrahigh vacuum (UHV) required by the spectroscopic and microscopic investigation techniques by treating the samples at atmospheric pressure. Since the selective catalytic reduction process takes place in excess of oxygen in the gas phase, our attention was devoted to the study of the interaction of a 1:100 NO/O₂ mixture with the silver surface at atmospheric pressure. This enabled the discrimination of several oxygen species, which may be responsible for the proceeding of the key catalytic steps. The present work is concerned with (i) a preliminary study of the interaction of the Ag/NO–O₂ mixture at atmospheric pressure, and (ii) an investigation of the way in which the surface chemistry of oxygen on the silver surface is modified by the presence of NO.

The exposure of a silver foil to the above-mentioned mixture at 300 K and at atmospheric pressure resulted in the formation of a sandwich-like structure, consisting of two superimposed layers of AgNO₃ and Ag₂O.³⁵ Gradual sputtering by He⁺ ions allowed ion scattering (IS) spectra and X-ray photoelectron (XP) spectra to be obtained at different depths, which gave insight into the depth distribution of the chemical compounds. According to these measurements, a silver nitrate layer, having a thickness of approximately 5–15 ML (monolayers), covered the surface. Silver(I) oxide with a thickness of 20–30 ML underlaid the AgNO₃ layer. No sharp boundary was detected between the two layers.

The information about the element distribution in the "sandwich" supplied by XP and IS spectroscopy (XPS and ISS) in a previous study³⁵ was alone not sufficient to give a complete picture of the morphology of the layers. The XPS and ISS data showed some evidence of a nonhomogeneous lateral disposition of the various compounds, which had to be clarified. First, according to XPS data, the concentration of AgNO₃ decreased strongly after the first sputtering, whereas about 20 ML had to be sputtered off in order to remove the silver nitrate completely from the surface. Second, parallel to the decrease in the nitrate concentration, Ag₂O appeared already after sputtering off approximately one monolayer. The present paper is concerned with the extension of the previous study³⁵ to the surface structures by means of scanning electron microscopy (SEM) and XPS. To overcome the problem of possible conversion of AgNO₃ into Ag₂O by the He⁺ ion beam during ISS measurements, which would introduce a systematic error in the determination of the layer thickness, AgNO₃ was here removed by selective dissolution in distilled water at room temperature. This allowed the characterization of the morphology of the uncovered Ag₂O layer.

2. Experimental Section

The XPS measurements were carried out in the stainless steel chamber of a modified Leybold LHS 12 MCD system equipped with facilities for UV photoelectron spectroscopy (UPS), XPS, and ISS (base pressure approximately 10^{–10} mbar). The object of the study was a commercial polycrystalline silver foil (Heraeus, 99.995%). The foil was mounted on a stainless steel transfer rod

with an internal heater allowing heating of the sample to 1000 K. The cleaning procedure included Ar⁺ and He⁺ etching and annealing in oxygen and vacuum. Exposure to atmospheric pressure of a mixture of oxygen and NO was performed in the preparation chamber (base pressure 2 × 10^{–9} mbar). The sample was then transferred to the UHV analyzer chamber within ca. 5 min. Oxygen with a purity of 99.999% and nitric oxide with a purity of 99.5% were supplied by Linde.

The selective dissolution of AgNO₃ was performed by simply immersing the treated foil up to the middle into freshly distilled water at room temperature for a few seconds. Since the immersion in water was carried out in air, a certain extent of carbonization of the water cannot be ruled out.

The XPS data were obtained using the Mg Kα radiation (*hν* = 1253.6 eV) and a fixed analyzer pass energy of 108 eV corresponding to a resolution of 1.2 eV measured as the full width at half-maximum (fwhm) of the Ag 3d_{5/2} peak. The binding energy (BE) values referred to the Fermi level were calibrated using the Au 4f_{7/2} = 84.0 eV and Cu 2p_{3/2} = 932.7 eV peaks. (The Ag 3d_{5/2} peak was set at 368.3 eV BE.) The atomic concentrations of the chemical elements in the near-surface region were estimated after a Shirley type background subtraction taking into account the corresponding atomic sensitivity factors.³⁶

The SEM experiments were performed in a Hitachi S-400 instrument equipped by an EDAX DX4 system for electron energy disperse X-ray (EEDX) analysis. Low acceleration voltages of 3 and 5 kV were used in order to enhance the surface contribution to the image contrast. It is estimated that the primary electrons penetrate down to 50 nm. The spot sizes of the element analysis were 3 and 4.2 nm for 5 and 3 kV, respectively. The treatment of the silver foil at atmospheric pressure of oxygen and NO previous to the SEM experiments was also performed in the preparation chamber of the Leybold LHS 12 MCD system. After XPS analysis, the treated silver foil was transferred through the atmosphere to the SEM within ca. 10 min.

3. Results

3.1. Scanning Electron Microscopy. The exposure of the sample to a mixture of O₂ (1000 mbar) and NO (10 mbar) at 300 K for 15 min resulted in variation of the color of the silver foil. The originally shiny surface became opaque and looked like being covered by a thin layer of snow. The drastic change of color on the surface points out to the significant thickness of the layer(s) produced. As discussed above, the treatment of the silver foil in a NO/O₂ mixture led to the formation of AgNO₃ and Ag₂O layers of a significant thickness. It is well-known that silver nitrate and silver (I) oxide are characterized by a different solubility in water at room temperature,³⁷ offering an additional tool for the investigation of the "sandwich" structure.

Figure 1-0 shows a photograph of the silver foil after treatment in a (1:100) NO/O₂ mixture and subsequent dissolution of the AgNO₃ by distilled water up to the middle of the sample. A striking difference in color is observed between the right side of the foil, which was rinsed with distilled H₂O, and the left one, which did not come into contact with water. This can be explained by the different solubility of silver nitrate and silver(I) oxide in water at room temperature. Silver nitrate is much more soluble than silver(I) oxide; therefore it can be expected that only Ag₂O covers the area, which came in contact with water, whereas AgNO₃ still coats the unwashed part of the foil. Hence, the different composition of the surface results in different optical property: the AgNO₃ layer is opaque whereas the uncovered Ag₂O reflects light. The apparent red color of the "washed" area of the sample is due to the reflection of light by the shiny surface.

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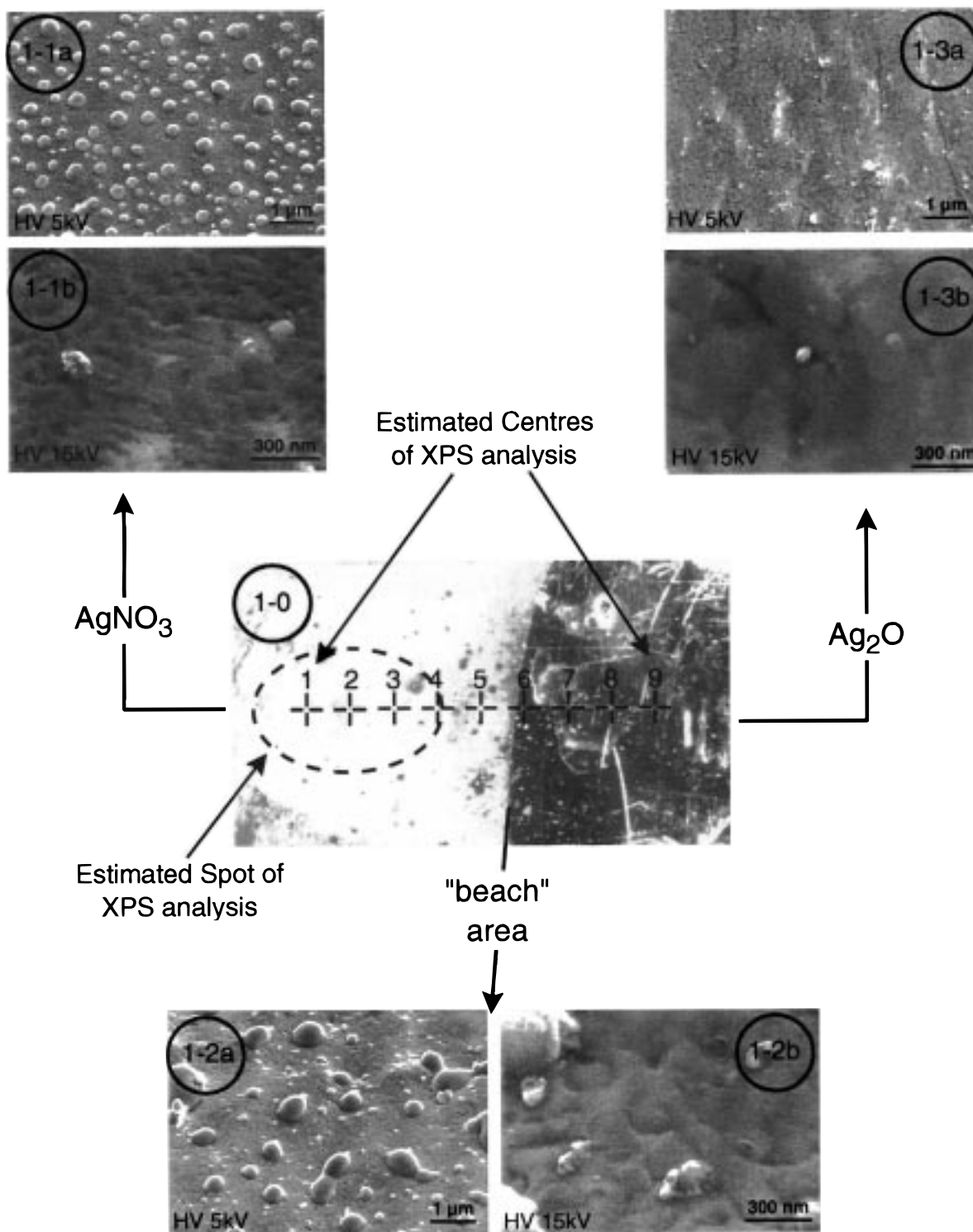


Figure 1. Photograph of the silver foil treated in a mixture of NO/O_2 (1:100) under atmospheric pressure for 15 min at 300 K and washed by distilled water on the right side (1-0). SEM micrographs of (1-1) the left "nitrate" part, (1-2) the "beach" area, which is located in the middle between the washed part of the treated foil and the unwashed one, and (1-3) the right "oxide" side.

To characterize the morphology of the layer on the "oxide" area and on the "nitrate" one, the silver foil shown in Figure 1-0 was studied by means of SEM. Parts 1-1 through 1-3 of Figure 1 show the SEM micrographs obtained from the "nitrate" side of the sample, from the boundary one and from the "oxide" area, respectively. Figure 1-1 clearly demonstrates that the exposure of the silver foil to the NO/O_2 mixture drastically changes the morphology of the surface. Figure 1-1a shows the formation of particles with size varying between 0.1 and 0.4 μm .

The particles have a regular shape and are statistically distributed on the surface, with a mean distance comparable to their size. A local EEDX analysis unambiguously revealed the presence of nitrogen in the particles, supporting the XPS data, which clearly pointed out to AgNO_3 being the main surface compound. The surface morphology of the boundary area is shown in Figure 1-1b. The originally smooth surface of the silver foil is now uneven. Attempts to obtain quantitative EEDX data from the areas between the AgNO_3 crystals were unsuccessful,

due to the overlap of the C_K, N_K, and O_K X-ray emission lines. The local EEDX analysis performed in the area between the AgNO₃ crystals revealed a nitrogen concentration significantly lower than the stoichiometric value for AgNO₃. This may be explained by assuming the presence of a thin AgNO₃ film: if the thickness of the nitrate layer was smaller than the depth of analysis of our EEDX, also the underlying Ag₂O would be detected, resulting in an apparent overall nitrogen deficiency. The thickness of the film may be therefore estimated to be a few monolayers. The detection of AgNO₃ as the only species in the uppermost layers by EEDX well correlates with the XPS data, which have shown the absence of silver oxide and the presence of only AgNO₃ in the upper surface layers of the treated silver foil.

The morphology of the underlying Ag₂O layer is shown in Figure 1-3, the SEM micrographs were obtained after washing off AgNO₃ with distilled H₂O. The surface appears to be considerably rough (Figure 1-3a). The EEDX analysis revealed the presence of only silver, carbon, and oxygen on the surface. No nitrogen could be detected on this part of the sample.

Figure 1-2 shows the central area ("beach") of the sample at low and high magnification, at the boundary with the edge which was soaked in water where the silver nitrate layer came only shortly into contact with H₂O and could not be completely dissolved. The "beach" area is characterized by the development of large AgNO₃ crystals. The crystals exhibit a wide size distribution, ranging from less than 0.1 to 1.3 μm, and are characterized by an irregular shape in contrast to the AgNO₃ crystals formed after treatment with the NO/O₂ mixture (Figure 1-1). As may be expected, a considerable recrystallization of the AgNO₃ crystals seems to have been caused by contact with water. As can be seen from the micrograph at high magnification in Figure 1-2b, this boundary region exhibits a different morphology than the "nitrate" area. The large AgNO₃ crystals of the "beach" area are discrete and dispersed onto a substrate, which shows strong morphological similarities to the uncovered Ag₂O (see Figure 1-3b). The EEDX analysis of the regions between the AgNO₃ crystal in this area revealed exclusively the presence of silver, carbon, and oxygen.

Summarizing the result of the SEM analysis, the following key features should be noted.

The exposure of silver to a NO/O₂ gas mixture at 300 K leads to the formation of a AgNO₃ layer onto the surface. This compound can be efficiently washed off by H₂O to uncover a rough, porous Ag₂O layer, as shown in parts 1-1 through 1-3a of Figure 1.

The as formed silver nitrate layer consists of small AgNO₃ particles, embedded probably in a continuous AgNO₃ film. The short contact of this layer with water, as in the "beach" area, results in the collapse of the structure and the formation of a discrete, big (up to 1.3 μm) AgNO₃ crystal, partially uncovering the substrate. The agglomeration of the AgNO₃ particles in the "beach" area points to a weak interaction of AgNO₃ with the underlying compound (supposedly Ag₂O).

The formation of AgNO₃ crystals was observed at a temperature, which is significantly lower than the melting point of AgNO₃ ($T_m(\text{AgNO}_3) = 485 \text{ K}$).³⁷ The probable mechanism of the AgNO₃ crystal formation will be analyzed in the discussion.

3.2. X-ray Photoelectron Spectroscopy. XPS was employed as analytical tool in order to determine the nature of the chemical compounds on the surface of the treated silver foil shown in Figure 1-0. The vacuum conditions in the XPS analyzer chamber (base pressure

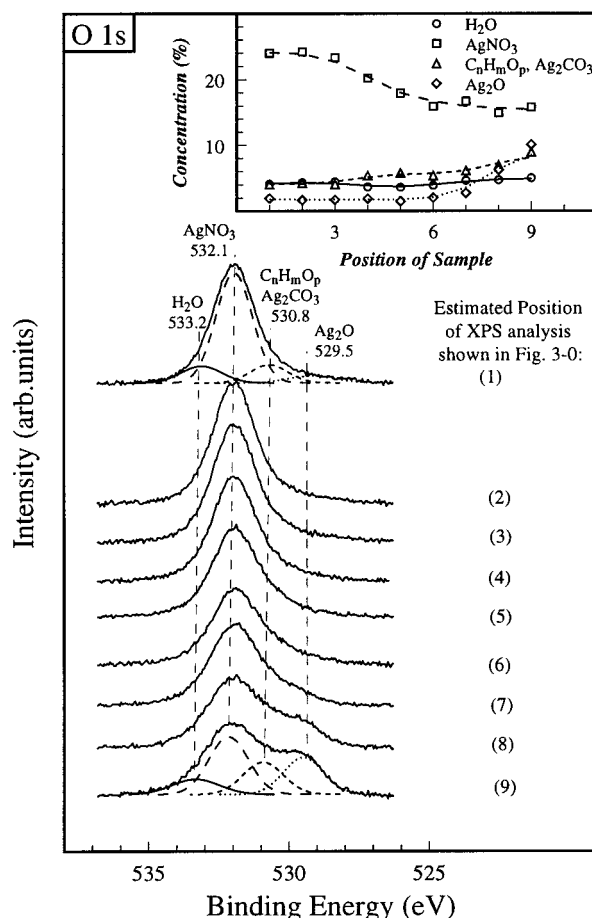


Figure 2. Core level XPS spectra of O 1s obtained from the silver foil treated with a mixture of NO/O₂ and partially soaked in distilled water. The spectra were recorded at the positions shown in Figure 1-0. The result of the curve fit analysis for O 1s spectra 1 and 9 is presented.

~10⁻¹⁰ mbar) are better than in the SEM (base pressure ~10⁻⁶ mbar). The better vacuum partly suppresses carbon deposition, which is indeed a major problem of electron microscopes, because the adsorbed hydrocarbons are converted into graphite by the high-energy electron beam. Such a carbon contamination is practically absent under XPS working conditions.

The XPS spot of analysis of our instrument is approximately 4 × 7 mm, viz., significantly larger than the area analyzed by SEM and EEDX. The "nitrate" area measured about 8 × 8 mm and the "oxide" area was approximately 6 × 8 mm. Several XP spectra were recorded at different positions on the center of the spot of analysis in order to obtain information about the spatial distribution of the elements. The core level XP spectra of the O 1s, N 1s, and C 1s lines recorded at different positions are shown in Figures 2 through 4, respectively. The estimated positions of the center of the spot of analysis during each measurement are marked in Figure 1-0. The O 1s spectrum obtained at the right edge of the sample (where we assumed Ag₂O) shows a strongly asymmetric feature (see Figure 2-9), whereas the O 1s spectrum measured at the left edge displays a broad, nearly symmetric, peak at ~532.0 eV (Figure 2-1). A curve fit analysis showed that both spectra can be described as a linear combinations of four Gaussian peaks, having approximately the same fwhm of ~1.7 eV and located at 533.2, 532.1, 530.8, and 529.5 eV. Comparison of these data with literature (Table 1) allows the peaks to be assigned as follows. The O 1s peak at 532.1 eV arises

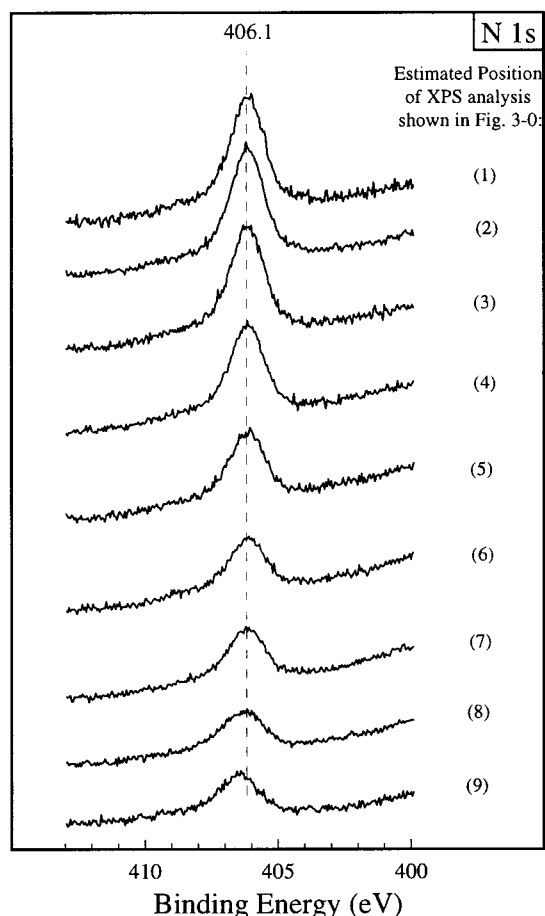


Figure 3. Core level XPS spectra of N 1s obtained from the silver foil treated with a mixture of NO/O₂ and partially soaked in distilled water. The spectra were recorded at the positions shown in Figure 1-0.

from oxygen incorporated into AgNO₃. This assignment is supported by the simultaneous appearance of a N 1s peak at 406.1 eV (Figure 4), which is characteristic of silver nitrate.³⁵ The right area ("nitrate") of the sample exhibits a main O 1s peak at 532.0 eV and a N 1s signal at 406.1 eV (Figures 2 and 3). This supports the assumption that the main species covering the surface of the treated silver is AgNO₃.

The peak at 529.5 eV presented in Figure 2 is very close to the value of 529.2 eV reported by Tjeng et al.²⁶ and Weaver et al.²⁷ for the BE of the O 1s signal of oxygen in Ag₂O. For these reasons, the peak at 529.5 eV might be assigned to the oxygen of silver(I) oxide. The O 1s peak at 530.8 eV may be due to oxygen dissolved in the bulk silver^{10,14,21,25,27,38} or to carbonates.^{16,20–22} Eventually, a weak peak at 533.2 eV could be distinguished by means of curve fit analysis assuming a Gaussian peak shape. A study of the interaction of water and oxygen with Ag(110) by Au et al.¹⁴ report an O 1s BE of ca. 533.5 eV for molecular water. However, it is known that H₂O molecules on silver oxide partially dissociate and partially desorb at 150 K.¹⁴ The SEM micrograph of the area that was soaked in water revealed a very rough and porous structure. Such an oxide surface might show an enhanced activity toward the adsorption of H₂O at room temperature, and it seems reasonable to assign the O 1s peak at 533.2 eV to H₂O or to OH-groups. The possibility of the presence of adsorbed

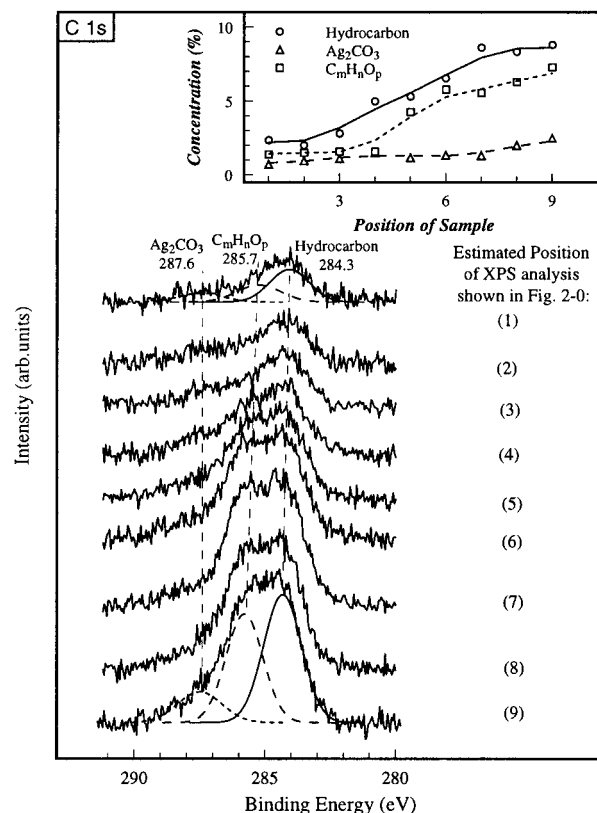


Figure 4. Core level XPS spectra of C 1s obtained from the silver foil treated with a mixture of NO/O₂ and partially soaked in distilled water. The spectra were recorded at the positions shown in Figure 1-0. The result of the curve fit analysis for spectra 1 and 9 is presented.

water at 300 K on a Ag₂O sample was discussed by Weaver and Hoflund.²⁷

The C 1s feature consists of two unresolved peaks at 284.4 and 285.5 eV and an extended tail toward high BE values (Figure 4). The curve fit analysis of this feature reveals the presence of three peaks with maxima at 284.3, 285.7, and 287.6 eV that could be tentatively assigned to hydrocarbons, to O-containing hydrocarbons such as alcohol, and to carbonates, respectively. Rehren et al. reported²¹ about the C 1s peak at 287.6 eV being a peculiarity of carbonates on the silver surface. The ratio between the area of the oxygen peak at 530.8 eV and the area of the carbon signal at 287.6 eV is equal to 3.60. This ratio is higher than the stoichiometric O:C atomic ratio in carbonates: this is probably due to the contribution of other oxygen- and carbon-containing species. Thus, the appearance of a C 1s peak at 285.7 eV may be assigned to oxygen-containing hydrocarbons, which can form by contact of the treated silver foil with water and air. The ratio between the area of the O 1s peak at 530.8 eV and the sum of the areas of the C 1s peaks at 285.7 and 287.6 eV measured at position 1 (right edge of the silver foil) is approximately 0.92.

The O 1s, N 1s, C 1s XP spectra, obtained subsequently after shifting the sample by steps of approximately 1–1.5 mm from the unwashed "nitrate" to the "oxide" area of the foil, are shown in Figure 2 through Figure 4. The curve fit analysis of the O 1s signal, examples of which are shown in spectra (1) and (9) in Figure 4, allowed an estimation of the atomic ratio between the different O-containing species at each point of the sample. The result is presented in the inset of Figure 2. The same procedure for the C-containing species gives the result shown in the inset

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Table 1. BE of the O 1s Peak and Properties of Oxygen Species on Silver

sample	species	BE O 1s, eV	localization	ref
Ag(110), Ag(111), silver foil	nucleophilic or ionic atomic oxygen	528.1–528.4	incorporated between two upper substrate layers	16, 22
Ag(111), silver foil	O _α or electrophilic (covalent) oxygen	530.4–530.5	adsorbed on the surface	10, 22, 25
Ag(111), Ag ₂ O, Ag(110)	O _β	530.0–531.0	incorporated in the bulk	10, 14, 21, 25, 27
Ag(111)	O _γ	529.0	two-dimensional oxide of Ag ₂ O-type, embedded in the silver layers	10, 25
Ag(110)	OH _{ads}	531.7	adsorbed on the surface	14
Ag(110)	H ₂ O	533.5	adsorbed on the surface	14
Ag(110), Ag(111), silver foil	CO _{3,ads} (carbonate)	529.9–530.5	adsorbed on the surface	16, 20–22
Ag(111)	NO _{3,ads}	531.8		32
Ag ₂ O		528.6–529.6		17, 26, 27
AgNO ₃		532.1		35

of Figure 4. The relative shift of the spot of XPS analysis from the “oxide” toward the “nitrate” area results in the decrease of the O 1s peak at 529.4 eV, which drops significantly down to 1.5% at position 6 (Figure 1-0). The concentration of AgNO₃-oxygen grows and reaches a plateau after position 3: this S-shaped concentration profile along the sample clearly reflects the motion of the spot of analysis from the oxide area through the “beach” to the nitrate area. The intensity of the O 1s peak at 532.0 eV well correlates with the N 1s at 406.1 eV (Figure 3) and points unambiguously to AgNO₃ as the main surface species in this area of the sample. The ratio between the areas of the above-mentioned oxygen and nitrogen signals is about 2.5 and remains approximately constant with an accuracy of ca. 15% in all measured points. Also, the kind of carbon-containing compounds on the surface varies from the oxide to the nitrate area (Figure 4), which may be explained to adsorption of CO₂ (H₂CO₃) on Ag₂O from the distilled water used to wash AgNO₃ off in addition to adsorption of C-containing compounds from the atmosphere. The concentration of these species drastically increases from the silver nitrate part to the oxide area. Thus, the total carbon concentration is 18.6% at position 9 (oxide area), whereas it drops down to 4.4% at position 1 (nitrate area) as shown in the inset of Figure 4.

4. Discussion

The SEM analysis helped to clarify some apparently incongruous ISS data presented in a previous work³⁵ on the nature of the compounds formed on the surface of the Ag foil after treatment with a mixture of NO and O₂ at room temperature and atmospheric pressure. Figure 1-1 clearly shows that the silver nitrate layer is built up of discrete AgNO₃ crystals with a size of 0.1–0.4 μm probably embedded in a thin AgNO₃ film. The presence of deep cavities was detected on in the Ag₂O surface (Figure 1-3).

The XPS analysis of the surface after the SEM observations was compelling in order to support the EEDX data and delivered some additional piece of information about the reactivity of the surface toward carbon-containing compounds. Thus, according to the XPS data, the “oxide” part (Figure 1-0) reveals a significantly higher activity toward adsorption of hydrocarbon than the “nitrate” one. The transfer of the silver foil from one instrument to the other required the exposure of the sample to air for ca. 10 min. This resulted in a detectable carbon contamination of the Ag₂O area, whereas the nitrate-covered area was practically inert toward the adsorption of organic compounds. The following explanation can be suggested: silver nitrate readily dissolves in H₂O whereas silver(I)

oxide reacts to the hydroxide by contact with water³⁹ according to the reaction

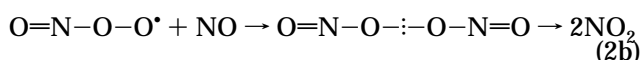
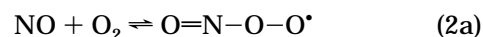


This would increase the basicity of the uncovered oxide surface, leading to the preferential adsorption of CO₂³⁹ and, probably, of hydrocarbons from the atmosphere and/or from the water. Also, some dissolution of Ag₂O in water as a consequence of reaction 1 cannot be ruled out.

As already reported, the curve fit analysis of the C 1s feature from the oxide-covered area of the sample revealed the presence of three signals. The peak at 287.6 eV was assigned to Ag₂CO₃, whereas the peak at 284.3 eV is attributed to adsorbed hydrocarbons. It is assumed that the peak at 285.7 eV originates from aldehydes, alcohols, or ketones adsorbed on the oxidized surface. The position of the C 1s signal, between hydrocarbon and carbonate, indicates a certain extent of positive charge on the C atom, due to a double bond between carbon and oxygen. The second argument for oxygen-containing hydrocarbon is the ratio of the intensity between the O 1s peak at 530.8 eV and the carbon peaks at 285.7 and 287.6 eV. The ratio between the O 1s peak and the C 1s peak at 287.6 eV exceeds 3, whereas the ratio between the O 1s peak and the sum of the C 1s peaks at 285.7 and 287.6 eV is about 1. The presence of approximately the same amount of oxygen and carbon atoms suggests the formation of other oxygen-containing species in addition to carboxylates. Moreover, the basic surface produced through reaction (1) may as well favor the formation of aldehydes and ketones.

The self-organization of AgNO₃ molecules into crystals on the surface at a temperature of 180 K, below the melting point of AgNO₃ and in the absence of any solvents, points out the fact that the intermolecular interaction is stronger than the interaction with the support. Indeed, according to XPS data on the different depths,³⁵ AgNO₃ was concentrated on the surface region. This suggests that the AgNO₃ particles are deposited on the Ag₂O layer. The thickness of the Ag₂O layer is thicker than that for AgNO₃.

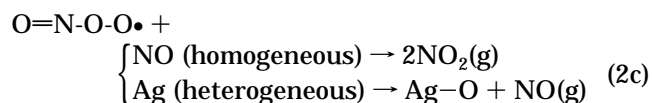
The practically full conversion of NO into NO₂ should proceed in the excess of oxygen at atmospheric pressure and 300 K. The conversion includes the following steps³⁹:



Step 2a can be rewritten taking in to account the possibility

(39) Holleman, A. F.; Wiberg, N. *Lehrbuch der Anorganischen Chemie*; Holleman-Wiberg, de Gruyter: Berlin and New York, 1985.

of interaction with silver:



The probability of the deactivation of the $\text{NO}_3\cdot$ radical on the silver foil should be significant. The adsorption of a $\text{NO}_3\cdot$ radical will result in its dissociation, leading to the formation of atomic oxygen adsorbed on the surface. In such a manner, the conversion of nitric oxide into NO_2 would be a source of active oxygen atoms on the surface, and the reaction of oxidation of silver by this oxygen should be the primary reaction. The interaction of silver with the products of the homogeneous reaction (NO_2) cannot be ruled out as well. The formation of AgNO_3 is a subsequent reaction and most probably proceeds via the interaction of silver oxide with NO_2 . The formation of AgNO_3 was observed in the reaction of Ag metal powder with a mixture of $\text{NO}_2/\text{N}_2\text{O}_4$ in the temperature range of 290–350 K by means of surface-enhanced Raman scattering and ellipsometric measurements.³³

The reaction of Ag_2O with NO_2 is supposed to be responsible for the formation of AgNO_3 crystals. Thus, Oza et al.⁴⁰ report the following mechanism



The forming AgNO_2 should be in equilibrium with AgNO_3 ⁴¹



Under the condition of practically full conversion of NO to NO_2 , as in our case, the equilibrium of reaction 4 is shifted to the right. To check the possibility of interaction of the silver(I) oxide with a NO/O_2 mixture, the special experiment was performed. The treatment of Ag_2O powder (Aldrich, 99%) under the same experimental conditions as for the Ag foil with a 1:100 $\text{NO}:\text{O}_2$ mixture led to its conversion into AgNO_3 , as shown by XPS analysis (XP spectra are not shown here). This fact confirms the supposed mechanism.

(40) Oza, T. M.; Oza, V. T.; Thaker R. T. *J. Chem. Soc.* **1955**, 65, 2457.

(41) Oza, T. M. *J. Indian Chem. Soc.* **1955**, 32, 617.

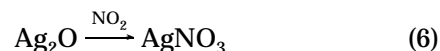
5. Conclusion

The exposure of a silver foil to a NO/O_2 (1:100) mixture at 300 K results in the formation of a “sandwich” structure consisting of superimposed layers of AgNO_3 and Ag_2O . The topmost layer consists of silver nitrate and is made up of discrete AgNO_3 crystals, which are statistically distributed on the surface and have a size of 0.1–0.4 μm . A thin AgNO_3 film, with a thickness of a few monolayers, covers the surface between the AgNO_3 crystals. The structure of the underlying Ag_2O layer was studied after dissolving the AgNO_3 in distilled H_2O . The oxide layer has a rough surface, characterized by a high porosity. The silver nitrate surface exhibits a low activity toward the adsorption of hydrocarbons from the surrounding atmosphere, whereas the oxide area is readily coated with different carbon-containing compounds after a short exposure to air.

Two key stages of the interaction of silver with a mixture of NO and O_2 could be distinguished. The first stage is the oxidation of silver:



Ag_2O is characterized by a porous structure; therefore the oxidation is not diffusion-limited and can proceed to considerable depth. The second stage is the formation of silver nitrate by subsequent reaction of silver(I) oxide with NO_2 :



The continuous AgNO_3 film connecting the silver nitrate crystals may form a closed surface and in this way inhibit the further reaction of Ag_2O with NO_2 from the gas phase. The nitrate passivation of the surface may play an important role in catalytic process, acting as a source of active oxygen atoms and at the same time preserving the surface from poisoning via adsorption of hydrocarbons.

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