Formation of a liquid film of $AgNO_3$ on a silver surface

D. Zemlyanov [a,*], G. Weinberg [b], U. Wild [b] and R. Schlögl [b]

[a] *Boreskov Institute of Catalysis, Pr. Ak. Lavrentieva 5, 630090 Novosibirsk, Russia*
E-mail: dzem@wpi.edu
[b] *Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, D-14195, Berlin, Germany*

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The behavior of a $AgNO_3/Ag_2O/Ag$ "sandwich" upon heating in vacuum was studied by *in situ* X-ray photoelectron spectroscopy (XPS) and *ex situ* scanning electron microscopy (SEM). The $AgNO_3/Ag_2O/Ag$ "sandwich" was prepared by exposure of a silver foil to a $NO:O_2$ mixture. The upper layer of the "sandwich" consists of $AgNO_3$ crystals of a mean size between 0.1 and 0.4 μm. Heating at 550 K in vacuum results in melting of the $AgNO_3$ crystals. A liquid film of $AgNO_3$, readily wetting the silver, covers the surface. Cooling below the melting point of $AgNO_3$ leads to the agglomeration of silver nitrate to long islands with a size reaching a few tens of micrometers (μm). The possible effects of $AgNO_3$ liquid-phase formation on surface processes are discussed.

Keywords: X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), silver, oxidation, surface chemical reaction, NO, NO_x

1. Introduction

The removal of NO_x from industrial and automotive emissions is a question of crucial importance [1]. SCR (selective catalytic reduction) of NO with NH_3 can be offered as one of the solutions of this problem [2]. In order to avoid the well-known transport and storage problems connected with NH_3, the last decade, the research efforts concentrated on the search of an alternative reducing agent such as hydrocarbons [3]. Recently, interesting results on the reduction of NO_x in the presence of excess O_2 on zeolite-based catalysts by non-methane hydrocarbons, e.g., propane, propene, and ethylene were reported [4,5]. One of the serious factors which hinder the use of zeolite-based catalysts, is their low hydrothermal and thermal stability. While Co-ZSM-5 seems to offer some hydrothermal stability, it still suffers from a reduction in activity at the 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.

Recently, it was reported about the activity of alumina-supported silver catalysts towards the SCR of nitric oxide with hydrocarbons or oxygen-containing organic compounds in the presence of oxygen [6,7]. The formation of a surface isocyanate (–NCO) species was found after an exposure of alumina-supported silver catalysts to a mixture of NO, O_2 and ethanol at 150 °C and subsequent heating at >300 °C in vacuum [6]. Alumina-supported silver catalysts showed high activities in the presence of water and excess oxygen at ~450 °C [7]. To understand the catalytic activity of silver, the interaction of silver with oxygen, NO and a mixture of NO and O_2 should be studied in detail.

Attempts of the model studies of the interaction between silver and a $NO:O_2$ mixture were undertaken by us [8,9]. The treatment of a polycrystalline silver foil with a 1 : 100 $NO:O_2$ mixture at atmospheric pressure and room temperature led to the formation of a $AgNO_3/Ag_2O/Ag$ "sandwich" in which no sharp boundary between the superimposed layers could be detected. The upper layer consisted of $AgNO_3$ crystals with an average size of ca. 0.1–0.4 μm. The thickness of the underlying Ag_2O film was estimated to be 20–30 ML. It is suggested that silver(I) oxide was the product of the oxidation of metallic silver, whereas $AgNO_3$ resulted from the subsequent reaction of Ag_2O with NO_2 in the presence of O_2. Since the melting point of $AgNO_3$ is equal to 485 K [10], under SCR conditions described in [6,7] one could not exclude the formation of a liquid film of $AgNO_3$ on the surface of a catalyst. The present work is aimed to illustrate the formation of the liquid phase on a silver surface, which takes place at temperatures much below the melting point of Ag and which results from the reaction between silver and a NO/O_2 mixture, producing easily melted $AgNO_3$.

2. Experimental

The XPS measurements were carried out in the stainless-steel chamber of a modified Leybold LHS 12 MCD system (base pressure 10^{-10} mbar) described in detail elsewhere [8,9]. A commercial polycrystalline silver foil (Heraeus, 99.995%) was used for the study. The cleaning procedure included the circles of Ar^+ and He^+ etching and annealing in oxygen and vacuum. Oxygen with a purity of 99.9999% and nitric oxide with a purity of 99.5% were

* To whom correspondence should be addressed. Present address: Worcester Polytechnic Institute, Department of Chemical Engineering, 100 Institute Road, Worcester, MA 01609, USA.

supplied by Linde. The treatment of the silver foil at atmospheric pressure of oxygen and NO previous to the XPS and SEM experiments was performed in the attached preparation chamber of the Leybold LHS 12 MCD system (base pressure $\sim 10^{-9}$ mbar). After XPS characterization, the treated silver foil was transferred through atmosphere to the SEM within ca. 10 min.

The XPS data were obtained using the Mg Kα radiation ($h\nu = 1253.6$ eV) and a fixed analyzer pass energy of 48 eV corresponding to a resolution of 0.9 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 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.

3. Results and discussion

3.1. Scanning electron microscopy

Figure 1 shows the SEM micrographs obtained from the silver foil treated in a 1 : 100 $NO : O_2$ mixture at atmospheric pressure and 300 K. The particles with size varying between 0.1 and 0.4 μm are observed on the surface of the treated silver (figure 1). The particles have a regular shape and are statistically distributed on the surface, with a mean distance comparable to their size. As established by the combined XPS/SEM study [9] these particles are the crystals of $AgNO_3$ and the thick layer of Ag_2O underlies the $AgNO_3$ particles. The surface between the particles is rough, as shown in the bottom SEM micrographs of figure 1. The absence of the peak characterizing Ag_2O in the O 1s core spectra taken from the treated silver allows us to suggest that the area between the $AgNO_3$ crystals is covered by a thin $AgNO_3$ film; the thickness is estimated to be a few monolayers [9]. It is quite surprising to observe the formation of big $AgNO_3$ crystals at a temperature below the melting point of $AgNO_3$, which is 485 K [10]. The agglomeration might be evidence of a low energy of the interaction of $AgNO_3$ with the support. We exclude that the $AgNO_3$ particles form due to an artifact effect such as an electron beam of the electron microscope because no changes were observed in the SEM pattern during the experiments.

The chemical compounds, belonging to the $AgNO_3$/Ag_2O/Ag "sandwich" structure, exhibit an interesting thermal stability. $AgNO_3$ melts at 485 K and decomposes at 717 K [10]. The temperature of Ag_2O decomposition is equal to $\sim$513 K [10]. One can expect that the heating

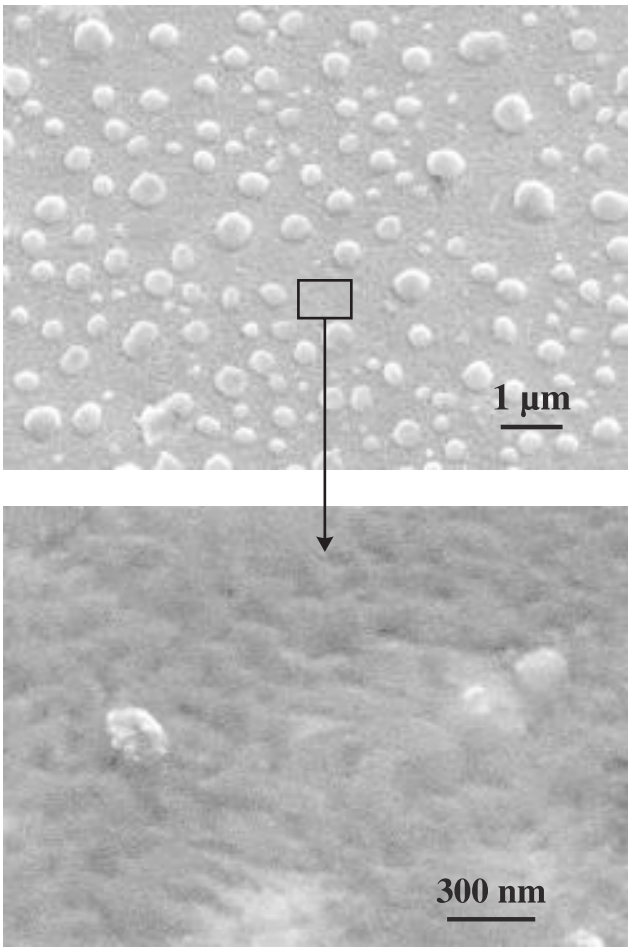

Figure 1. SEM micrographs of the silver foil treated in a mixture of NO/O_2 (1 : 100) under atmospheric pressure for 15 min at 300 K.

of the $AgNO_3/Ag_2O$/Ag structure above the decomposition temperature of Ag_2O could result in the decomposition of the oxide film and melting of silver nitrate. It should be reflected in the morphology of the surface. Indeed, the heating of the treated silver foil at 550 K in vacuum changes drastically the surface morphology, as shown in figure 2 (compare with figure 1). Instead of the "small" $AgNO_3$ crystals with a size of 0.1–0.4 μm, long stretched $AgNO_3$ islands are observed. The islands of $AgNO_3$ extend along surface defects (likely the grain boundaries) and reach a length of several tens of μm. The surface between the $AgNO_3$ crystals is quite smooth and looks like being fused (the bottom SEM micrographs of figure 2). Such fused structure was not observed after the cleaning procedures and has appeared after the melting of $AgNO_3$ by heating at 550 K.

3.2. X-ray photoelectron spectroscopy

Figures 3 and 4 show the X-ray excited Ag $M_{4,5}VV$, Ag $3d_{5/2}$, O 1s and N 1 s spectra taken from the silver foil after the treatment with a NO_2/O_2 reaction mixture at 300 K for 15 min and upon the subsequent heating and cooling in vacuum. The XPS data unambiguously prove that $AgNO_3$

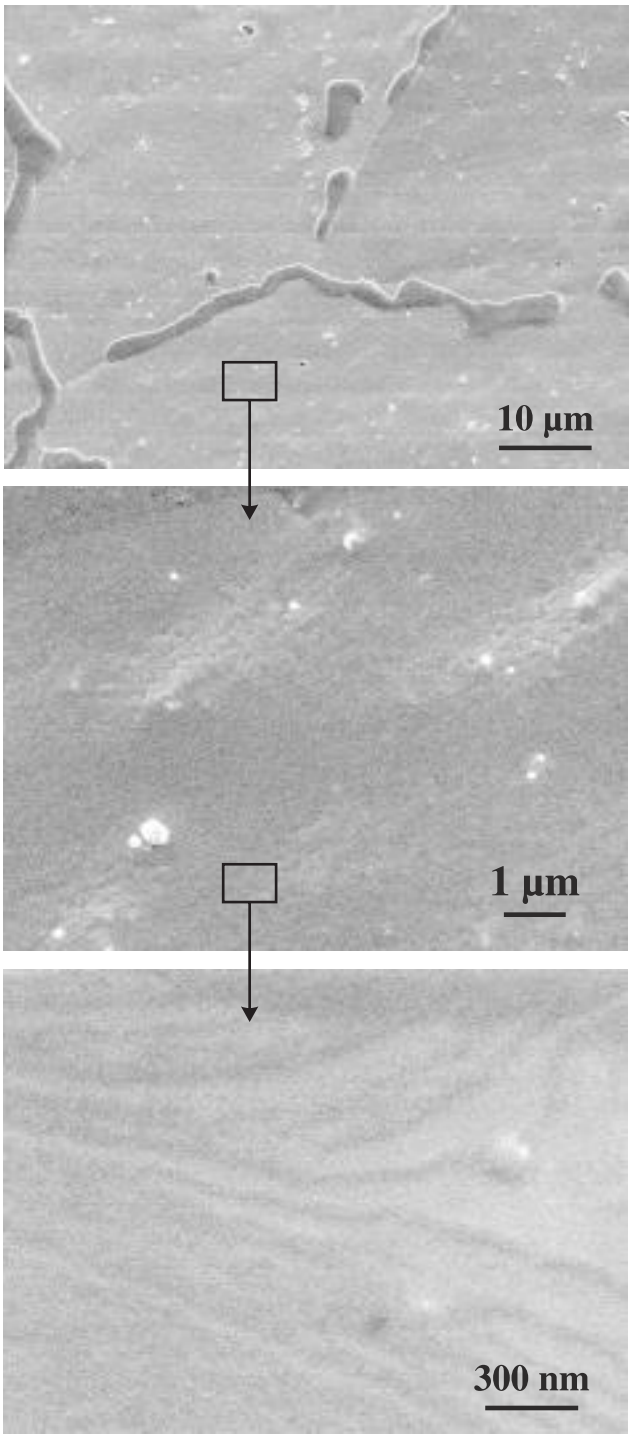

Figure 2. SEM micrographs of the silver foil treated in a mixture of NO/O_2 (1 : 100) under atmospheric pressure for 15 min at 300 K and subsequently flashed up to 550 K in UHV.

is the main compound in the near-surface region of the treated silver foil. Thus, the XP parameters of the treated silver such as the position and shape of the Ag $M_{4,5}VV$ features, BE of the Ag $3d_{5/2}$ peak, the modified Auger parameter [11] (spectra (a) in figure 3) are identical to those observed from $AgNO_3$ [8]. The O 1s and N 1s spectra taken from the treated silver exhibit the intense peaks at 532.2 and 406.1 eV, respectively (spectra (a) in figure 4), which are characteristic of $AgNO_3$ as well [8]. The XPS data on the different oxygen-containing species, which are discussed in the present work, are presented in table 1.

The $M_{4,5}VV$ Ag, O 1s and N 1s peaks do not change upon heating at 550 K in UHV (spectra (b) in figures 3 and 4). The Ag $3d_{5/2}$ peak gets broader and slightly shifts towards higher BE (spectra (b) in figure 3). The curve fit of the Ag $3d_{5/2}$ peak, assuming a Doniac–Sunijc peak shape [18], allows the increasing contribution of metallic silver to be distinguished. This reflects the decrease of the thickness of the surface compounds, screening metallic silver, by means of the decomposition of the Ag_2O layer. On the other hand, the absence of the metallic features in the Auger spectra can be explained by a shorter mean free path for Auger electrons than the mean free path for photoelectrons emitted from the core level.

The pronounced changes in XP spectra are detectable after cooling the sample down to 470 K (spectra (d) in figures 3 and 4). Two new peaks characterizing metallic silver appear in the X-ray excited Ag $M_{4,5}VV$ spectrum. The intensity of the Ag $3d_{5/2}$ peak slightly increases, the peak becomes narrower and is centered at 368.3 eV BE. According to the results of the curve fit analysis, the metallic feature at 368.3 eV dominates the peak at 367.9 eV. The latter likely consists of the joined contribution of the peaks at 367.7 (Ag_2O) and 368.1 eV ($AgNO_3$) [8]. The intensity of the O 1s and N 1s peaks decreases approximately by a factor of two. A new weak broad feature at ca. 528.7 eV appears in the O 1s spectrum. The curve fit analysis shows two peaks at 529.3 and 528.3 eV. The peak at 528.3 eV is assigned to atomically adsorbed oxygen (O_a) [16]. The peak at 529.3 eV is very close to the value reported by Tjeng et al. [14] and Weaver et al. [15] for the BE of the O 1s signal from Ag_2O.

The N 1s, Ag $3d_{5/2}$ and $M_{4,5}VV$ spectra do not change practically after the further cooling down to 450 K (spectra (e) in figures 3 and 4), whereas the feature at 528.7 eV increases mainly due to the rising contribution at 529.3 eV, indicating the formation of the Ag_2O phase. The Ag_2O and O_a species occur as products from the oxidation of silver by $AgNO_3$. Cooling down to room temperature does not affect the XP spectra. It should be stressed that the changes in the XP spectra were observed only after the cooling of the silver down to 470 K; the XP spectra taken at higher temperatures are identical with the ones taken at 570 K. Since the temperature of 470 K is close to the melting point of silver nitrate, the changes in the XP spectra discussed above reflect the freezing and agglomeration of $AgNO_3$ into the long islands shown in figure 2.

The repeated heating at 490 K (higher than the $AgNO_3$ melting point) reverts the changes in the XP spectra as shown in figures 3 and 4 (spectrum (f)). The spectra become identical to the ones taken in the course of the first heating at 490 K (compare with spectra (c) in figures 3 and 4). Re-cooling the sample below the melting point of $AgNO_3$ results again in the decrease of the effective $AgNO_3$

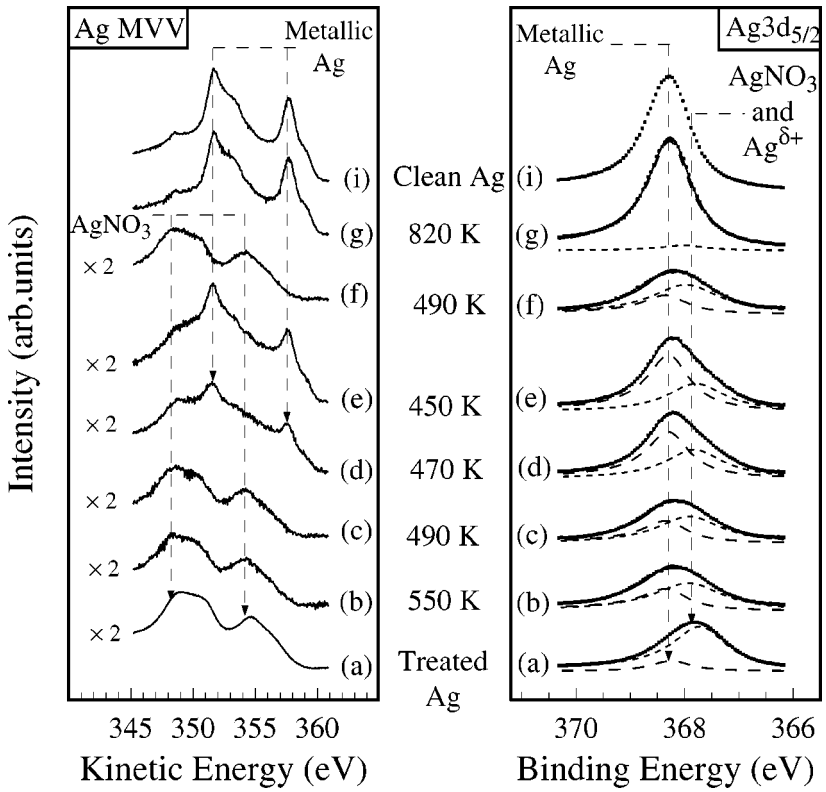

Figure 3. X-ray excited Ag MVV (left panel) and Ag $3d_{5/2}$ XP (right panel) spectra taken from (a) silver foil treated in a mixture of O_2 (1000 mbar) and NO (10 mbar) at 300 K for 15 min, (b) heated at 550 K and (c)–(e) cooled down a specified temperature, (f) repeatedly heated at 490 K and (g) flash up to 820 K, and (i) from the clean silver foil. The spectra were recorded at the temperature specified.

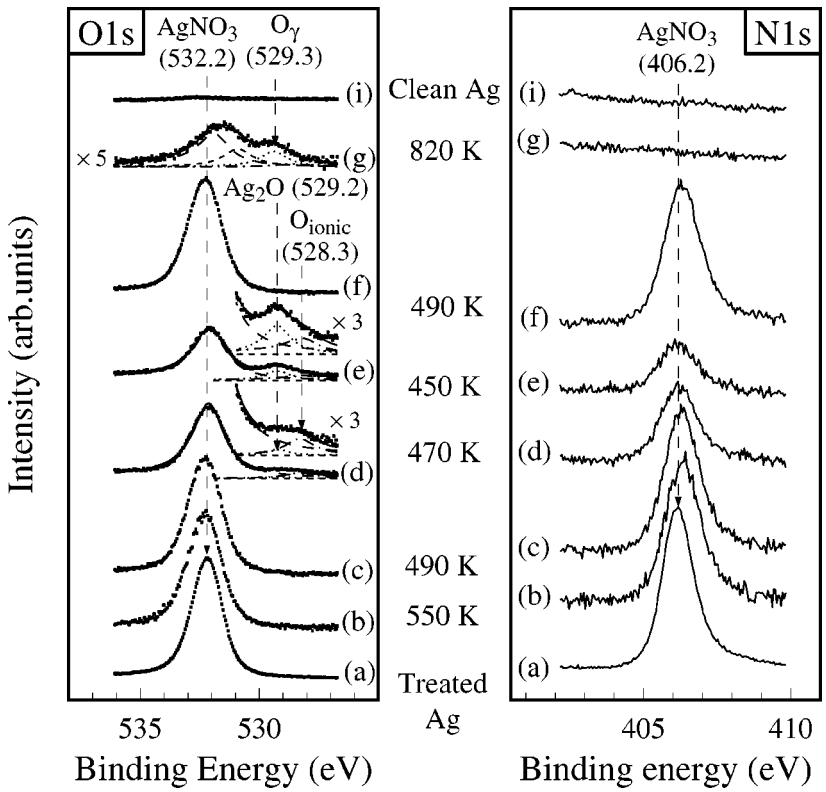

Figure 4. O 1s (left panel) and N 1s (right panel) core level XP spectra taken from (a) silver foil treated in a mixture of O_2 (1000 mbar) and NO (10 mbar) at 300 K for 15 min, (b) heated at 550 K and (c)–(e) cooled down a specified temperature, (f) repeatedly heated at 490 K and (g) flash up to 820 K, and (i) from the clean silver foil. The spectra were recorded at the temperature specified.

Table 1
XPS characteristic lines and the modified Auger parameter for silver compounds and oxygen incorporated in several species adsorbed on silver.

	Ag $3d_{5/2}$ BE (eV)	Ag M_5VV KE (eV)	α'[a] (eV)	O 1s (eV)	N 1s (eV)	Ref.
Silver	368.3	357.9	726.2	~530.5[b]	–	[8] and refs. therein
Ag_2O	367.8	356.7	724.5	~529.1	–	[8,12,14]
$AgNO_3$	368.1	354.5	722.6	532.1	406.1	[8]
NO/O_2-treated silver foil	368.0	355.2	723.2	532.1	406.1	[8], this work
O_a	367.7	–	–	528.1–528.4	–	[16,17]
O_γ/Ag(111)	367.3	–	–	529.0		[13]

[a] The modified Auger parameter was calculated as BE(Ag $3d_{5/2}$) + KE(Ag M_5VV) [11].
[b] A weak broad feature at 530.5 eV is characterized as residual oxygen sometime hardly removed from the surface.

coverage due to the agglomeration into the islands; the oxidized states of silver re-appear. Such cycles of heating and cooling can be repeated several times until the complete consumption of the $AgNO_3$. It is reasonably to suppose that $AgNO_3$ is consumed in the course of the silver oxidation,

$$Ag + AgNO_3 \rightarrow Ag_2O + NO_2 \quad (1)$$

The formed Ag_2O is decomposed under subsequent heating.

Heating at 820 K results in the complete decomposition of $AgNO_3$. Thus, the Auger spectrum is identical to the one taken from the clean silver foil; the Ag $3d_{5/2}$ spectrum exhibits a narrow peak at 368.3 eV; the O 1s and N 1s spectra do not show the characteristic peaks of silver nitrate. A residual amount of oxygen demonstrates a broad double peak centered at ca. 529.2 and 531.5 eV. The spectrum was taken at 820 K, and, therefore, the peak at 529.2 eV is attributed to a high thermal stabile species O_γ [13]. It is quite surprising to find the formation of O_γ after the decomposition of the $AgNO_3/Ag_2O/Ag$ "sandwich" in vacuum because usually this subsurface species forms after a severe treatment of silver in oxygen atmosphere at high temperatures [13]. The formation of O_γ is accompanied by the surface reconstruction [19]. During $AgNO_3$ decomposition, in fact in a liquid film, O_γ can be easily formed because oxygen should be in excess on the surface and high-mobile silver atoms can build up Ag(111) facets, which are favorable for O_γ formation. The two peaks at 530.5 and 531.7 eV, contributing to the broad feature at 531.5 eV, are assigned to oxygen species dissolved in the near-surface region such as atomic oxygen and hydroxyl groups [15]. The appearance of the dissolved oxygen species also proves that the processes, which take place upon the decomposition of the "sandwich" structure in vacuum, really affect the near-surface region of silver.

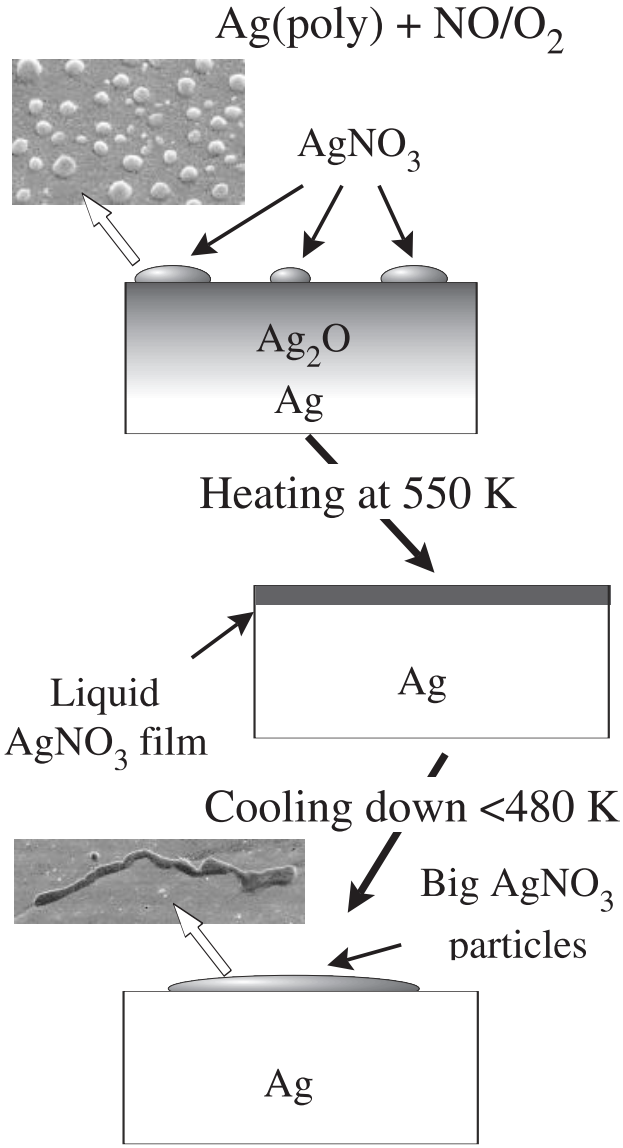

Figure 5. Schematic interpretation of the experiments.

4. Concluding remarks

Figure 5 schematically illustrates the behavior of an $AgNO_3/Ag_2O/Ag$ "sandwich" upon heating in vacuum. An exposure of a polycrystalline silver foil to a mixture of NO (10 mbar) and O_2 (1000 mbar) at 300 K leads to the formation of a $AgNO_3/Ag_2O/Ag$ "sandwich" structure. Silver nitrate forms particles with a regular shape and size varying between 0.1 and 0.4 μm. An Ag_2O film underlies the particles of $AgNO_3$.

Heating of the $AgNO_3/Ag_2O/Ag$ "sandwich" at 550 K results in the decomposition of the Ag_2O layer, whereas

$AgNO_3$ melts and covers the surface as a liquid film. In [6] the formation of a surface isocyanate (–NCO) species was observed after exposure of an alumina-supported silver catalyst to a mixture of NO, O_2 and ethanol at 150 °C and following heating at >300 °C in vacuum. Except for a reducing agent (ethanol), the conditions of the $AgNO_3$ formation reported in the present paper are quite similar to the conditions in [6]. Moreover, we exposed an Ag foil to a mixture of NO (1–3 mbar), O_2 (10 mbar) and reducing agent (3–10 mbar); H_2, CO and ethylene were used as reducing agents. Even under these conditions $AgNO_3$ was the main surface compound up to a temperature of 720 K. This means that for a correct description of SCR on supported silver catalysts one should bear in mind the possibility of the formation of a liquid film, therefore, the processes on the interface between solid state and liquid should be considered. The real role of the liquid film of $AgNO_3$ under SCR conditions is not clear and needs to be clarified by special experiments; one could not exclude both passivating and activating roles of the $AgNO_3$ liquid.

At temperatures below the melting point of $AgNO_3$ (485 K) liquid silver nitrate is frozen, forming extended islands of silver nitrate along surface defects such as grain boundaries. Silver(I) oxide and O_a formed at <470 K, reflecting the oxidation of silver by $AgNO_3$. The silver oxidation is supposed to be a complex multistep process and Ag_2O formation proceeds through O_a.

In this paper we demonstrated how a liquid phase can form on a silver surface at temperatures below the melting point of Ag. Thus, the treatment of silver in a NO/O_2 mixture leads to the formation of easy-melted silver nitrate. The formation of liquid phase should affect the dynamics of chemical processes on the surface. Liquid phase may facilitate the surface reconstruction as well. For instance, the formation of the O_γ species, which is accompanied by the surface reconstruction, was found after decomposition of the $AgNO_3/Ag_2O/Ag$ "sandwich". Since O_γ species show a catalytic activity towards the selective oxidation of methanol, the addition of NO in a reaction stream could facilitate the reaction.

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