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AN XPS STUDY OF THE INTERACTION OF MODEL Ba/TiO₂ AND Ba/ZrO₂ NSR CATALYSTS WITH NO₂

M. Yu. Smirnov,¹ A. V. Kalinkin,¹ D. A. Nazimov,^{1,2}
V. I. Bukhtiyarov,^{1,2} E. I. Vovk,^{1,3} and E. Ozensoy³

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X-ray photoelectron spectroscopy is used to study the interaction of model NO₂ storage-reduction catalysts (NSR catalysts) Ba/TiO₂ and Ba/ZrO₂ with NO₂. The catalysts are prepared on the surface of ultrathin Al₂O₃ film substrates obtained by the FeCrAl alloy oxidation. It is shown that at room temperature the model catalysts react with NO₂ with the successive formation of surface barium nitrite and nitrate. The NO₂ reduction with the formation of barium nitrite at the initial step of the interaction is assumed to be accompanied by the oxidation of residual metallic barium and amorphous carbon impurity. It is found that the formation of barium nitrate proceeds more efficiently on Ba/ZrO₂ rather than on Ba/TiO₂.

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INTRODUCTION

The purification of automobile exhaust gases from harmful impurities is an important practical problem for the solution of which complex catalytic systems are applied. In the composition of these systems the NSR (NO_x storage-reduction) catalysts serve to neutralize nitrogen oxides [1]. They perform the following two functions: 1) oxidation of nitrogen oxides with their fixation in the form of nitrates; 2) reduction of nitrates to molecular nitrogen. Ba-containing compounds (BaO, Ba(OH)₂ or BaCO₃) supported on γ -Al₂O₃ have traditionally been used as the main component absorbing NO_x. In order to provide more efficient oxidation of NO to NO₂ and further to barium nitrate under oxidizing conditions and also the subsequent reduction of nitrate to nitrogen under reducing conditions platinum is introduced into the catalyst composition. A disadvantage of this type of NSR catalysts is their high susceptibility to poisoning by sulfur oxides (SO_x) that form in the exhaust gases as a result of oxidation of S-containing impurities in the fuel composition. It is found that the interaction of the catalyst with sulfur oxides in the oxidizing medium leads to the formation of stable barium sulfates, as a result of which the absorption capacity with respect to nitrogen oxides decreases [2, 3]. It was reported that the stability of the NSR catalyst to poisoning by sulfur compounds could be increased by the replacement of the traditional material of the γ -Al₂O₃ substrate by other oxides, e.g. TiO₂ or ZrO₂, in the presence of which barium sulfate easier decomposes in the reducing medium [4-6].

Using X-ray photoelectron spectroscopy (XPS), we have previously investigated the interaction of NO_x and SO_x

¹Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia; smirnov@catalysis.ru. ²Novosibirsk State University, Russia. ³Bilkent University, Bilkent, Ankara, Turkey. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 55, No. 4, pp. 791-797, July-August, 2014. Original article submitted January 22, 2014.

with the surface of model NSR catalysts of the traditional composition Pt/BaCO₃/Al₂O₃ and Pt/(BaCO₃+CeO₂)/Al₂O₃ and the nature of forming NO_x⁻ and SO_x²⁻ surface compounds was determined [7, 8]. In the present work this approach was applied to study the NO_x absorption process by Ba/TiO₂ and Ba/ZrO₂ model systems.

EXPERIMENTAL

The preparation of model catalysts, their treatment in the gas reaction medium, and the measurement of XPS spectra were performed on the SPECS spectrometer (Germany) with a residual pressure in the analyzer chamber of $< 5 \times 10^{-9}$ Torr. The spectra were measured using non-monochromatic AlK_α radiation ($h\nu = 1486.6$ eV). Before the experiments the binding energy scale of the spectrometer was calibrated by the position of Au4f_{7/2} metallic gold (84.0 eV) and Cu2p_{3/2} copper (932.6 eV) signals. The photoemission spectra were processed after the subtraction of the background approximated by the Shirley function. The spectra were decomposed into separate components using the XPSPeak program [9]. The binding energies (E_{bind}) corresponding to the signals of barium compounds in the XPS spectra of the samples supported on titanium dioxide or zirconium dioxide were determined with respect to $E_{\text{bind}}(\text{Ti}2p_{3/2})$ in TiO₂ or $E_{\text{bind}}(\text{Zr}3d_{5/2})$ in ZrO₂ that were taken to be 458.8 eV and 182.2 eV [10].

The samples of model thin-film catalysts were obtained in the preparation chamber of the spectrometer. Plates of FeCrAl alloy were used as the substrates. The plates were previously annealed in the air at 800°C for 1 h to form a stable aluminum oxide layer on the surface, which prevents the samples of model catalysts from the chemical interaction with the substrate material. Titanium and zirconium dioxides were prepared in the form of thin films by the sputtering of metallic titanium and zirconium on the substrates in vacuum followed by the oxidation of deposited metal in the oxygen atmosphere at a pressure of 10^{-5} Torr and a temperature of 400°C. The thickness of TiO₂ and ZrO₂ films was estimated by a decrease in the intensity of Al2p and Al2s signals during the formation of the substrate, which amounted to ~10 nm.

Barium was deposited on the surface of freshly prepared oxides by sputtering in the vacuum from BaAl₄ alloy. For the obtained Ba/TiO₂ and Ba/ZrO₂ samples the kinetic energy of Ba M₄N₄₅N₄₅ Auger electrons of 597.5-598.3 eV is within the range of values listed in the reference book [10] for BaO, and hence, during the sputtering the oxidation of the main part of metallic barium atoms by residual gases occurs with the formation of Ba²⁺ compounds on the surface of the oxide substrate. The thickness of barium compound films was estimated by a decrease in the Ti2p or Zr3d signal intensity; in all samples studied it was 2.5-3.0 nm, which corresponds to ~10 BaO monolayers [11]. During the sputtering of barium on the TiO₂ film the reduction of a part of Ti⁴⁺ cations to the Ti³⁺ state was noted. During the further short-term interaction with the oxidizing reaction medium the back process of Ti³⁺ oxidation to Ti⁴⁺ occurred.

The NO_x absorption process in the absence of platinum metals in the sample composition was investigated by the interaction of the samples with nitrogen dioxide. Treatment in NO₂ was performed in the preparation chamber of the spectrometer by the procedure described in detail in [12]. NO₂ was directly obtained in the vacuum chamber by the decomposition of lead nitrate by the reaction:



Lead nitrate was placed into a thin-wall tube of stainless steel, which was sealed at one end and nickel-chromium wire was wound on its external surface. The passage of current through the wire provided the heating of the source from room temperature to 400°C. Before the work the source with a Pb(NO₃)₂ portion was degassed by heating in the vacuum for a few hours to remove water traces. During treatment of the samples in NO₂ the source axis was oriented perpendicular to the sample surface and the outlet was placed at a distance of 20 mm from the sample. During the interaction of the sample with NO₂ the pressure in the chamber was regulated by the current passed through the wire and maintained in the range $(3 \pm 0.5) \times 10^{-6}$ Torr. During treatment in NO₂ the sample temperature was maintained as ambient.

After the interaction with the reaction medium (NO₂) the samples without contacting with the atmosphere were transferred to the analytic chamber for the measurement of XPS spectra.

RESULTS AND DISCUSSION

Before the investigation of the model samples containing Ba, the interaction of NO_2 with pure TiO_2 and ZrO_2 substrates was carried out. After long-term treatment in NO_2 for ~ 20 h in the $\text{N}1s$ region a peak with the binding energy of 405.8 eV (TiO_2) and 406.2 eV (ZrO_2) is revealed, which can be assigned to the surface NO_x^- particles. Atomic ratios calculated from the intensities of the corresponding photoemission lines with regard to atomic sensitivity factors show that the number of particles is small: $[\text{N}]/[\text{Ti}] \approx 0.0035$ and $[\text{N}]/[\text{Zr}] \approx 0.011$. Therefore the contribution of NO_x^- particles formed on the substrate surface can be neglected in the further consideration of the interaction of Ba/TiO_2 and Ba/ZrO_2 samples with NO_2 .

After the interaction of NO_2 with freshly prepared Ba/TiO_2 (Fig. 1a) and Ba/ZrO_2 (Fig. 1b) samples two lines are observed in the $\text{N}1s$ region. At the initial step an intense line with the binding energy of ~ 403.5 – 404 eV appears which can be assigned to surface barium nitrite. With an increase in exposition the intensity of this line gradually decreases, and the appearance and growth of the line with the binding energy of 407–407.5 eV is observed, which belongs to surface barium nitrate. In the literature the $\text{N}1s$ lines of barium nitrite and nitrate obtained in the interaction of NO_2 with barium oxide, which was deposited on the Al_2O_3 , $\text{Pt}(111)$, $\text{Cu}(111)$, and Ta surfaces, were measured in the close ranges of the binding energies of 403.8–404.5 eV and 407.5–408.1 eV respectively [11, 13–16].

After treatment in NO_2 the heating of the samples in the vacuum in the temperature range of 300–500°C results in the complete decomposition of surface nitrites and nitrates. Repeated treatment of the heated samples in NO_2 leads again to the formation of the same surface compounds (Fig. 2). However, a comparison of the series of the $\text{N}1s$ spectra shown in Figs. 1 and 2 reveals certain differences in the behavior of freshly prepared and heated samples with respect to the interaction with NO_2 . As seen from the spectra shown in Fig. 2a, on the surface of the Ba/TiO_2 sample nitrate starts to form at the earliest step simultaneously with nitrite. Then with an increase in the exposure of NO_2 a monotonic growth of the intensity of

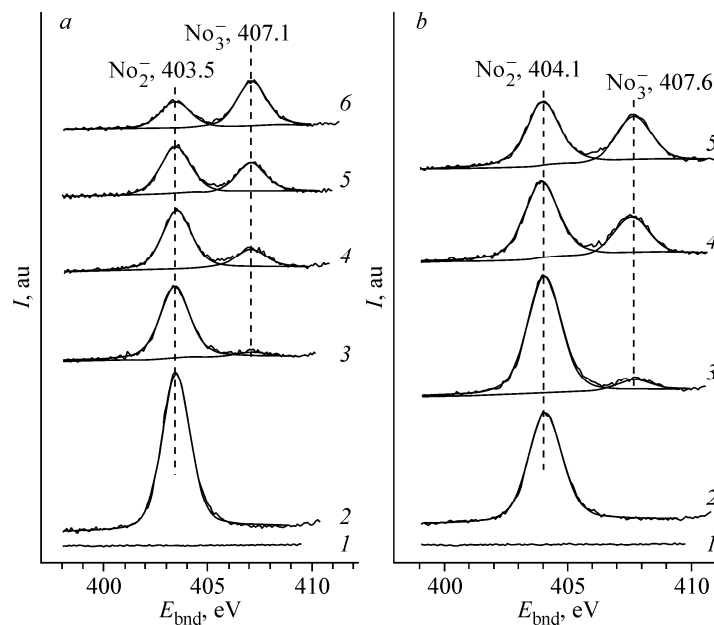


Fig. 1. $\text{N}1s$ spectra measured for the freshly prepared Ba/TiO_2 (a) and Ba/ZrO_2 (b) samples in the initial state (1) and after the interaction with NO_2 for: (a) 5 min (2), 25 min (3), 125 min (4), 275 min (5), 1275 min (6); (b) 5 min (2), 60 min (3), 190 min (4), 310 min (5). The temperature of the samples in the interaction was 30°C.

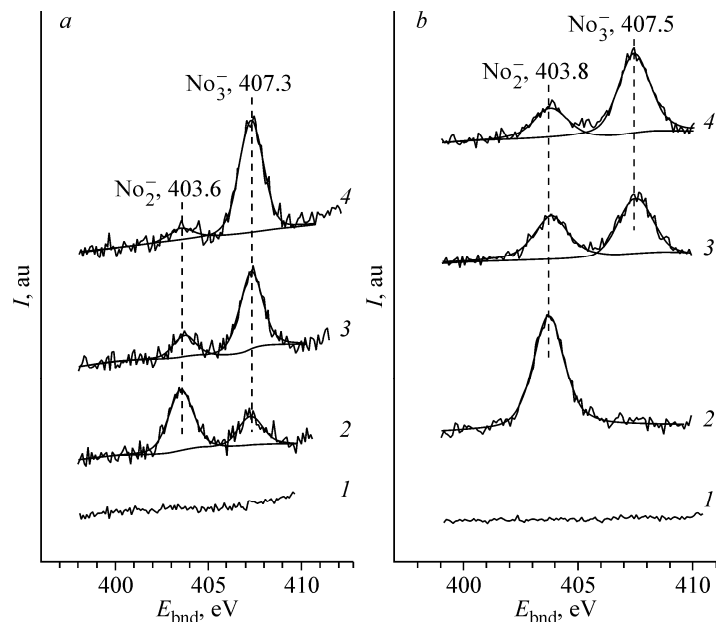


Fig. 2. N1s spectra measured for the annealed in vacuum Ba/TiO₂ (a) and Ba/ZrO₂ (b) samples in the initial state (1) and after the interaction with NO₂ for: (a) 5 min (2), 25 min (3), 60 min (4); (b) 5 min (2), 25 min (3), 120 min (4). The temperature of the samples in the interaction was 30°C.

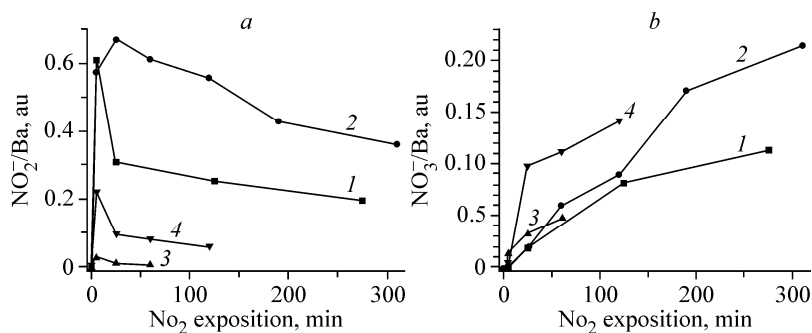


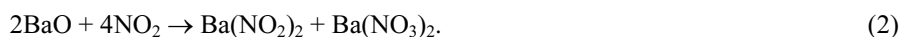
Fig. 3. Change in the [NO₂⁻]/[Ba] (a) and [NO₃⁻]/[Ba] (b) atomic ratios in the interaction of freshly prepared (1, 2) and annealed in vacuum (3, 4) Ba/TiO₂ (1, 3) and Ba/ZrO₂ (2, 4) samples.

the N1s nitrate line is observed whereas the nitrite line intensity monotonically decreases. In repeated treatment in NO₂ of the heated Ba/ZrO₂ sample, as well as for the freshly prepared sample, a successive formation of barium nitrite and nitrate is observed (Fig. 2b). At the same time, it is possible to note that in the case of the heated sample nitrate starts to appear earlier and in a larger amount in comparison with the freshly prepared sample.

Fig. 3 depicts the curves of barium nitrite (Fig. 3a) and nitrate (Fig. 3b) accumulation depending on the exposure in NO₂ for the freshly prepared and heated Ba/TiO₂ и Ba/ZrO₂ samples. In Fig. 3a it is seen that the heating in the vacuum of Ba/TiO₂ and Ba/ZrO₂ samples causes a substantial decrease in the amount of nitrite formed during repeated treatment of the samples in NO₂. On the contrary, after the heating barium nitrate forms in large amounts, which is especially noticeable for the Ba/ZrO₂ sample. Accumulation curves depicted in Fig. 3b show that barium nitrate forms more efficiently when ZrO₂ is used as the substrate, which is consistent with the representation of that the higher the basicity of the substrate the higher the formation rate of barium nitrate is [17]. At the same time, a drop in the efficiency of the interaction of the Ba/TiO₂ sample with NO₂ after the annealing in the vacuum can also be due to the formation of barium titanates. In [18] it is shown that

barium titanates formed in the high-temperature interaction of the TiO₂ film with BaO_x supported on its surface lose the ability to absorb NO₂ in the form of barium nitrite and nitrate. The formation of titanates is manifested, in particular, in a decrease in the Ba/Ti atomic ratio [18]. In our case, the Ba/Ti atomic ratio decreased from 2.5 to 1.1 as a result of sample annealing. For comparison, the Ba/Zr atomic ratio also decreases at the annealing of the Ba/ZrO₂ sample, but to a less extent (from 2.4 to 1.6), which seems to be caused by that barium zirconates are harder to form.

The formation of only barium nitrite at the early step of the interaction with NO₂ of the freshly prepared Ba/TiO₂ (Fig. 1a) and Ba/ZrO₂ (Fig. 1b) samples and also of the Ba/ZrO₂ sample heated in the vacuum (Fig. 2b) in the absence of barium nitrate among the interaction products demands explanation. Indeed, the formation of the nitrite ion from NO₂ means that the degree of oxidation of the nitrogen atom decreases from 4+ to 3+. Therefore the question arises, which of the reagents involved in the reaction is subjected to oxidation. In [13, 19] in the low-temperature (≤ 30°C) interaction of NO₂ with the model BaO catalyst supported on Al₂O₃/NiAl(110), the disproportionation reaction is observed with the formation of equimolar amounts of nitrite (NO₂ reduction) and nitrate ions (NO₂ oxidation)



It was also reported that in the reaction of BaO supported on TiO₂ with NO₂ mainly the formation of barium nitrate occurred, which was accompanied by the release of NO into the gas phase in accordance with the reaction [20]



At the same time, it was also reported that at room temperature the interaction of NO₂ with thin BaO layers supported on the aluminum oxide film grown on the surface of the NiAl(110) single crystal, as in our case, results in the formation of barium nitrite at the early step. Barium nitrate forms only when a certain value of the exposition in NO₂ is reached [15, 21]. It is shown that the NO₂ reduction to nitrite ions is accompanied by the oxidation of the additional amount of aluminum atoms in NiAl alloy [15]. In the work [11] performed on BaO samples supported on the surface of the Cu(111) single crystal, the formation of barium nitrite in the interaction with NO₂ proceeds simultaneously with the oxygen formation by the reaction

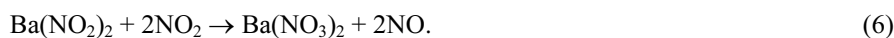


It is also possible that the NO₂ reduction is accompanied by the formation of barium peroxide BaO₂ that is more stable under these conditions than barium oxide BaO [22].

Not excluding the possibility of the formation of oxygen and barium peroxide, in our case it is possible to allow the occurrence of two other oxidizing processes accompanying the nitrogen reduction in the conversion of the NO₂ molecule into the nitrite ion. The first process is the oxidation of residual barium that retained in the metallic state after the sputtering on the oxide substrate

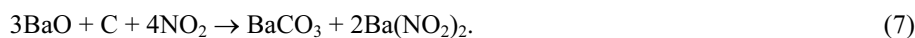


The formation of barium nitrate can occur in the further oxidation of nitrite ions by NO₂ molecules



If metallic barium is present in the freshly prepared sample, then after the reaction with NO₂ the most part of it passes into barium nitrite and nitrate. After the decomposition of Ba(NO₂)₂ and Ba(NO₃)₂ as a result of heating in the vacuum this part of barium does not return into the metallic state. Indeed, as shown in Fig. 3a, repeated treatment of the heated samples in NO₂ yields a much less amount of NO₂⁻, which is consistent with the assumption about the presence of some amount of metallic barium in the freshly prepared samples, which irreversibly passes into the oxidized state after treatment in NO₂.

Another possible process is the reaction of NO₂ with impurity carbon that is contained in the amorphous state on the surface of Ba/TiO₂ and Ba/ZrO₂ samples. The process can be described by the following reaction equation:



In order to confirm the occurrence of reaction (7), Fig. 4 depicts two series of spectra measured in the C1s region in the interaction of NO₂ with the freshly prepared Ba/TiO₂ (Fig. 4a) and Ba/ZrO₂ (Fig. 4b) samples. All spectra contain two lines, one of which that is more intense with the binding energy of ~285-285.5 eV belongs to amorphous carbon impurity.

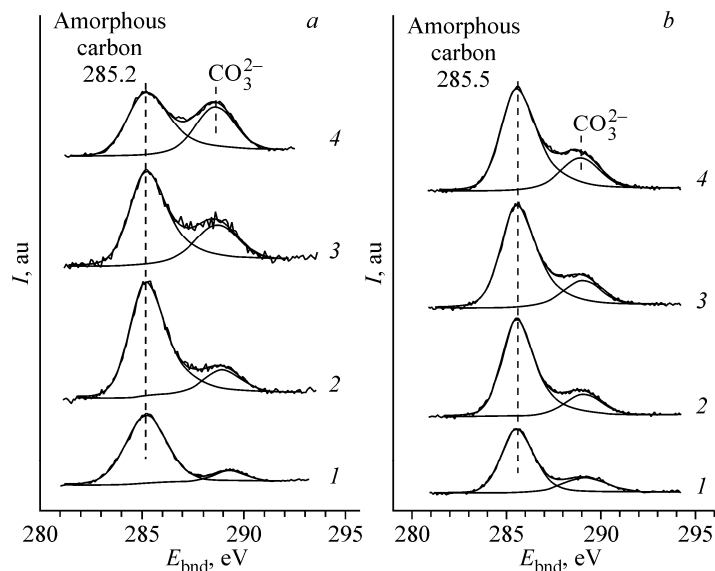


Fig. 4. C 1s spectra measured for the freshly prepared Ba/TiO₂ (a) and Ba/ZrO₂ (b) samples in the initial state (1) and after the interaction with NO₂ for: (a) 5 min (2), 275 min (3), 1275 min (4); (b) 120 min (2), 190 min (3), 310 min (4). The temperature of the samples in the interaction was 30°C.

The less intense line has the C 1s binding energy of ~288.5-289 eV, which is characteristic of carbonates, including barium carbonate BaCO₃ [23]. During the interaction of Ba/TiO₂ and Ba/ZrO₂ samples with NO₂ the intensity of the line belonging to barium carbonate increases monotonically, which may indicate the occurrence of reaction (7).

It should be noted that the study of the oxidation processes of amorphous carbon by nitrogen dioxide can be of independent interest as a model oxidation reaction of diesel soot. The observation of reaction (7) has also great importance because it reveals in NSR catalysts the property not only to neutralize nitrogen oxides, but also additionally participate in the burning process of soot — yet another harmful component in the composition of exhaust gases [24].

CONCLUSIONS

1. The low-temperature interaction of NO₂ with model NO_x storage-reduction Ba/TiO₂ and Ba/ZrO₂ catalysts (NSR catalysts) proceeds with the successive formation of surface barium nitrite and nitrate.

2. At the initial step of the interaction the NO₂ reduction with the formation of barium nitrite is accompanied by the oxidation of residual metallic barium and amorphous carbon impurity.

3. The formation of barium nitrate proceeds more efficiently on Ba/ZrO₂ rather than on Ba/TiO₂.

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