

# X-ray absorption and photoemission studies of the active oxygen for ethylene epoxidation over silver

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Activation of clean polycrystalline silver by a  $\text{C}_2\text{H}_4 + \text{O}_2$  reaction mixture has been studied by XANES, XPS, and UPS. *In situ* monitoring of the O K-edge XAS spectrum of the pre-treated silver surface revealed a broad signal at 10–20 eV above the threshold. The comparison of the X-ray absorption spectra with O 1s and valence band photoemission data allowed us to attribute this XAS signal to “electrophilic” oxygen ( $E_{\text{b}}(\text{O } 1\text{s}) = 530.4 \text{ eV}$ ) which is known to be active in ethylene epoxidation. The complete absence of XAS features in the photon energy range typical for  $\pi^*$  and  $\sigma^*$  transitions of molecular oxygen (530–535 eV) indicates both the atomic origin of the electrophilic oxygen and the absence of molecular species on the catalyst surface under the present reaction conditions.

**KEY WORDS:** silver; oxygen; ethylene; epoxidation; XPS; XANES

## 1. Introduction

Over many years, the debate over the mechanisms of silver-catalysed ethylene epoxidation has been kept open by the apparent lack of physical methods to characterise the oxygen overlayers at “high-pressure” conditions where ethylene oxide is obtained amongst the reaction products (pressure  $\geq 1$  mbar). A variety of reaction concepts was developed to explain the kinetic data to a better or worse extent. In general, all studies devoted to this reaction can be divided into two main groups depending on their suggestion which type of oxygen, either molecular [1–3] or atomic [4–8], governs the epoxidation route. In the middle of the eighties, the papers of van Santen *et al.* [5,6] and Grant and Lambert [7] seemed to switch over this discussion to a detailed elaboration of the atomic oxygen concepts. The authors have demonstrated that ethylene oxide can be formed as a result of temperature-programmed reaction of ethylene with a silver surface preliminary treated with oxygen [5] or with reaction mixtures [7]. The evacuation to UHV at  $T > 300 \text{ K}$  after the pre-treatments excluded the existence of a weakly bonded molecular oxygen ( $T_{\text{des}} > 220 \text{ K}$ ) before subsequent adsorption of ethylene. However, the absence of direct experimental data proving the atomic nature of epoxidising oxygen retained the possibilities to re-evaluate the molecular oxygen concept. And indeed, the authors of a few recent papers have concluded the existence of molecular oxygen on silver surfaces at the reaction conditions (up to  $350^\circ\text{C}$ ) [9–12] and even proposed its participation in the epoxidation pathway [13]. These conclusions have been based on *in situ* SERS (surface-enhanced Raman spectroscopy) [10] and XPS/UPS (X-ray and ultraviolet photoelectron spectroscopy) [11–13] measurements. At the same time, other groups have assigned identical spec-

troscopic characteristics (XPS/UPS [14–16], SERS [17]) to atomic oxygen. This indicates that the problem of characterisation of the epoxidising oxygen was not yet solved convincingly and requires the use of physical methods that can give more unambiguous information about the nature of this oxygen species.

To tackle this problem we apply X-ray absorption near-edge structure (XANES) spectroscopy. XANES, being an element-specific method, provides direct information about the unoccupied electronic states of the element analysed. Due to the fact that the dipole-selection rule  $\Delta l = \pm 1$  is obeyed, only oxygen p character ( $l = 1$ ) can be reached when an oxygen 1s electron ( $l = 0$ ) is promoted to an excited electronic state by X-ray absorption [18]. The unoccupied  $\pi^*$  and  $\sigma^*$  molecular orbitals of gas phase dioxygen yield features at photon energies of  $\sim 531$  and  $\sim 540 \text{ eV}$  in XANES data [19]. The respective spectra of molecularly chemisorbed oxygen differ significantly from those of gas phase or physisorbed species [19–21] reflecting the significant perturbation of the  $\text{O}_2$  molecule by its chemical bonding with a surface. However, despite significant shifts, the  $\pi^*/\sigma^*$  signature in the range of photon energy 530–535 eV remains a clear indicator of the presence of an oxygen–oxygen bond. The observation (or not observation) of these peaks in oxygen K-edge XAS experiments of adsorbed oxygen will show its molecular (or atomic) origin.

In this paper we present the results of such experiments for the electrophilic oxygen prepared by  $\text{C}_2\text{H}_4 + \text{O}_2$  reaction mixture treatment of clean polycrystalline Ag foil. As shown by us earlier [15,16], namely this oxygen participates in the formation of ethylene oxide. The present experiment was carried out for the first time under gas pressure of several mbar without transfer into UHV, thus allowing the detection of weakly held molecular species, if ever present. A subse-

quent pump-off and annealing experiment relates this study to that of Grant and Lambert [7].

## 2. Experimental

X-ray absorption experiments were carried out in a double-chamber UHV system with a base pressure of  $<5 \times 10^{-9}$  mbar. The main characteristic of the installation is the possibility to record XAS spectra *in situ* at pressures up to 10 mbar [22]. The photon-energy-dependent XAS measurements were performed at the HE-TGM1 beamline of the Berliner Synchrotron Radiation source BESSY-I. The XANES spectra were collected with the 1100 lines/mm grating in the photon energy range of  $250 \text{ eV} \leq h\nu \leq 1000 \text{ eV}$ . C K-edge and O K-edge spectra have been accumulated with total electron yield detection using an accelerating voltage of +4.5 V. O K-edge spectra were calibrated using the XAS signal of gas phase oxygen at 530.8 eV recorded at  $\text{O}_2$  pressure of 0.1 mbar.

X-ray and ultraviolet photoelectron spectra were taken using a VG ESCALAB high-pressure electron spectrometer. The base pressure of the spectrometer was  $\sim 1 \times 10^{-10}$  mbar. XPS spectra were taken using Mg K $\alpha$  irradiation ( $h\nu = 1253.6 \text{ eV}$ ) and calibrated against  $E_b(\text{Ag } 3d_{5/2}) = 368.2 \text{ eV}$ . UPS spectra were measured using He I irradiation ( $h\nu = 21.2 \text{ eV}$ ) and calibrated against the Fermi level.

The same polycrystalline foil of silver (Goodfellow, 99.95%) was used as sample for XAS and XPS/UPS experiments. In both cases, the sample was cleaned by the standard high vacuum cycle:  $\text{Ar}^+$  sputtering, annealing in 10 mbar of  $\text{O}_2$  at 570 K and flashing up to 800 K in UHV. More than ten repetitions of this procedure were necessary to exclude observation of any impurities in the XPS spectra and to obtain reproducible XAS data of the C K- and O K-edges. Further, namely this surface is denoted as clean one.

## 3. Results

Figure 1 shows an O K-edge *in situ* XAS spectrum (1) recorded during treatment of the silver by a  $\text{C}_2\text{H}_4$  (2%) +  $\text{O}_2$  reaction mixture at  $T = 470 \text{ K}$  and  $P = 2 \text{ mbar}$ , with the raw spectrum being divided by the spectrum of a clean silver surface. The pressure value was chosen in accordance with Grant and Lambert's data [7] which stated that 1 mbar is a sufficient pressure to activate the clean silver surface. The strong gas phase absorption contributing to the total (gas phase + sample) signal (1) was recorded independently allowing the separation of the two spectral components. The gas phase XAS spectrum (2) together with the separated surface (= difference) signal (1 – 2) is shown in figure 1. One can see that the *in situ* XAS signal from the sample is characterised by one feature in the photon energy range of 540–545 eV. The range of 530–535 eV (absorption into molecular oxygen orbitals) seems to be free from any features. The

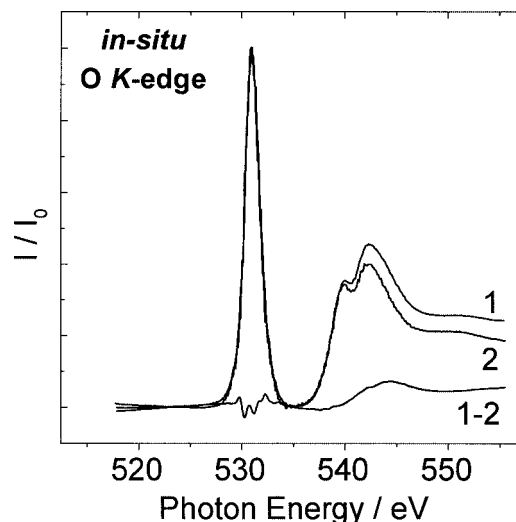


Figure 1. O K-edge X-ray absorption spectrum (1) recorded during treatment of clean polycrystalline silver foil by a  $\text{C}_2\text{H}_4$  (2%) +  $\text{O}_2$  reaction mixture at  $T = 470 \text{ K}$  and  $P = 2 \text{ mbar}$ . XAS spectrum of the gas phase (2) and difference spectrum (1 – 2) are also shown.

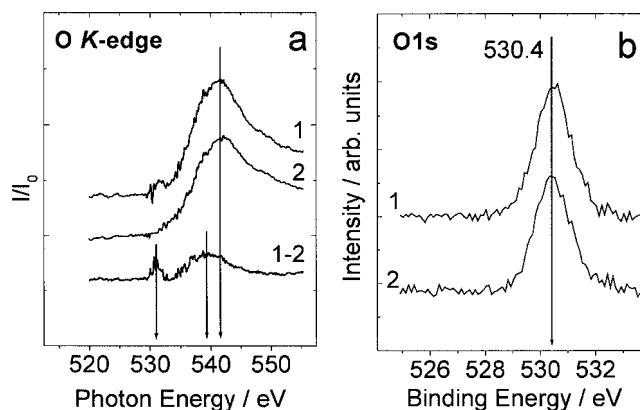


Figure 2. O K-edge X-ray absorption (a) and O 1s core level photoemission (b) spectra from the silver foil pre-treated for 6 h by a  $\text{C}_2\text{H}_4$  (2%) +  $\text{O}_2$  reaction mixture at  $T = 470 \text{ K}$  and  $P = 2 \text{ mbar}$  (1) followed by heating up to  $T = 570 \text{ K}$  in UHV (2). Difference XAS spectrum (1 – 2) is also shown.

difference spectrum obtained by subtraction of two intensive signals exhibits, however, a high level of noise which may mask small signals from adsorbed species. To tackle this problem we have analysed XAS data after evacuation of the reaction mixtures where the signal of gas phase dioxygen does not contribute to the spectra. The results are displayed in figure 2. One can see that the *ex situ* O K-edge XAS spectrum recorded after a reaction treatment for 6 h is very similar to the *in situ* difference spectrum (figure 1, curve (1 – 2)), except for a weak feature near threshold ( $\sim 531 \text{ eV}$ ), which is registered in addition to a broad resonance at  $\sim 542 \text{ eV}$  (figure 2(a), curve (1)). The behaviour of these signals under sample heating is quite different, allowing their assignment to different oxygen species. At 570 K the signal at  $\sim 531 \text{ eV}$  and part of the higher photon energy signal (figure 2(a), difference curve (1 – 2)) disappear, while the XAS signal at  $\sim 542 \text{ eV}$  exhibits stability at this temperature (figure 2(a), curve (2)). O 1s XPS spectra measured at the same con-

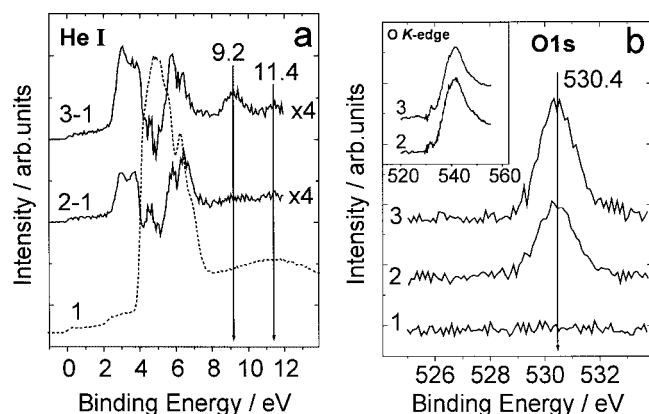


Figure 3. He I valence band (a) and O 1s core level (b) photoemission spectra recorded after interaction of clean polycrystalline silver foil (1) with  $C_2H_4 + O_2$  reaction mixtures at 470 K and various partial pressures: (2)  $P(C_2H_4) = 5 \times 10^{-2}$  mbar/ $P(O_2) = 2$  mbar for 6 h and (3) 0.5 mbar/10.5 mbar for 1.5 h. UPS spectra of the pre-treated surfaces are shown after subtraction of the “clean” spectrum (2 – 1, 3 – 1). The corresponding O K-edge X-ray absorption spectra (inset) are also shown for comparison.

ditions (after reaction treatment followed by annealing the sample at 570 K in UHV) are characterised only by one line at  $530.4 \pm 0.1$  eV (figure 2(b)).

Additional information about the pre-treated silver surface has been obtained using He I-induced valence band spectra which are presented in figure 3 together with O 1s data. This figure shows also XAS spectra taken after similar treatments of the silver foil (figure 3(b), inset). One can see that the UPS spectrum of the clean surface (figure 3(a), curve (1)) is characterised by a strong signal at 4–7 eV below the Fermi level due to Ag 4d emission and a small step near the Fermi level due to 5 s emission. Some intensity in the binding energy range of 2–4 eV is not an indicator of some impurities in the clean sample since it is observed only if He I irradiation is used for measurement of UPS spectra. Earlier, the features in this BE range were assigned to satellites of the Ag 4d lines because of He I $\beta$  ( $h\nu = 23.08$  eV) radiation [23]. The cleanliness of the original silver surface follows also from the absence of any features in the corresponding O 1s spectrum (figure 3(b), curve (1)).

The high intensity of the Ag 4d emission may mask oxygen-induced signals that are typically small for adsorbed layers. Hence we analysed difference spectra (figure 3(a)) which have been obtained by subtraction of the clean surface spectrum from those measured after silver interaction with reaction mixtures at different pressures: 2 mbar (curve (2 – 1)) and 11 mbar (curve (3 – 1)). Since the surface-located adlayer is scaling down the substrate photoemission signal, the spectra from the oxygen-covered surfaces have been multiplied by a factor of 1.15 before subtraction. This value is typical of submonolayer screening and has been chosen to exclude negative values in the difference spectra, which otherwise are easily produced.

The treatment of the clean silver at the same reaction conditions used for monitoring the XAS data presented in figures 1 and 2 ( $P = 2$  mbar and  $T = 470$  K) creates

additional features at  $\sim 3.5$  and  $\sim 6.5$  eV in the UPS spectra. The absence of any peaks below the Ag 4d band is in opposition to the data of recent papers [11–13], where the UPS features with  $E_b > 7.5$  eV, which are not characteristic of atomic oxygen species [24,25], have been used as indirect evidence for the conclusion of the molecular character of epoxidising oxygen. A possible explanation for this disagreement in the results can be the lower pressure used in this work. An experiment with higher pressure ( $P = 11$  mbar and  $T = 470$  K) confirms this suggestion (figure 3(a), curve (3 – 1)). One can see that, in good agreement with the cited papers [11–13], higher pressure treatment gives rise to UPS features below the Ag 4d emission. The appearance of these features is accompanied by a two-fold increase in the intensity of the O 1s feature at 530.4 eV (figure 3(b), curves (2) and (3)). However, no pronounced changes are observed in the XAS spectra (figure 3(b), inset).

#### 4. Discussion

The application of X-ray absorption near-edge structure spectroscopy allowed us for the first time to characterise oxygen adlayers in the course of ethylene epoxidation over silver under gas pressures of a few millibars by a physical method. This is of great significance, since namely this pressure range provides the activation of silver for the production of ethylene oxide [7] and, hence, we could expect accumulation of active oxygen species in measurable amount. The *in situ* XAS signal from the sample is characterised by one broad feature in the photon energy range of 540–545 eV. A similar feature at  $\sim 542$  eV is observed after evacuation of the pretreated silver surface (compare the XAS spectra of the figures 1 and 2(a)) that makes it possible to use *ex situ* XPS data to assign this XAS feature to adsorbed species.

In principle, the corresponding XPS feature at 530.4 eV can belong at least to three surface species: hydroxides, carbonates and adsorbed oxygen [3,6,14–16,26,27], and it is clear that additional arguments are necessary to select these opportunities. Unfortunately, the temperatures of spectra monitoring (470 K) and even sample heating (570 K) can not serve for this purpose. Indeed, although hydroxides ( $T_{\text{dispr}} = 360$  K [27]) and carbonates ( $T_{\text{decomp}} = 420$ – $450$  K [3,6]) are unstable on the clean silver surfaces in this temperature range, they can be stabilised by defect or subsurface location appearing as a result of silver activation at the severe reaction conditions used in the present study. Such facts are well-known for silver [28]. On the other hand, both hydroxides and carbonates should cause the appearance of the features in UPS spectra below the Ag 4d emission (8.2 and 11.0 eV for hydroxide [29], and 8.5 eV for carbonates [29,30]) that is not the case for the silver surface pre-treated at milder conditions. The He I spectrum recorded after silver activation at  $P = 2$  mbar (figure 3(a), curve (2 – 1)) is characterised by two features at  $\sim 3.5$  and  $\sim 6.5$  eV. The complete absence of the features located below the Ag 4d band allows us to assign the O 1s feature at

530.4 eV and, hence, the XAS feature at  $\sim 542$  eV to adsorbed oxygen. According to the literature [30], the UPS features at  $\sim 3.5$  and  $\sim 6.5$  eV can be assigned to oxygen 2p-derived bands which are anti-bonding and bonding with respect to the oxygen–silver bond. This oxygen species that was identified also in our previous papers [14–16] has been denoted as electrophilic oxygen.

A weak additional signal near threshold observed in the *ex situ* XAS spectrum can be assigned to the well-known nucleophilic oxygen ( $T_{\text{des}} = 550\text{--}580$  K [3,6,15,16]). This conclusion is based on the disappearance of this signal as the pre-treated sample is heated at 570 K in UHV. Practically full coincidence of the difference spectrum (curve (1 – 2)) in figure 2(a) with that measured during  $\text{O}_2$  adsorption at  $P = 10^{-4}$  mbar and  $T = 470$  K [31], i.e., at the conditions of effective formation of this oxide-like oxygen with  $\Theta = 0.5$  [3,6,16,31], confirms this assignment. The absence of a corresponding signal with  $E_b(\text{O } 1s) = 528.2$  eV [3,14,15,31] in the XPS data (figure 2(b), curve (1)) can be explained by fast removal of the nucleophilic oxygen *via* reaction with the hydrocarbon background arising from the diffusion pumping of the electron spectrometer. In contrast to the XPS spectrometer the UHV chambers of the XAS set-up equipped by turbomolecular pumps exhibit no reactive background. Unfortunately, the high level of noise in the *in situ* XAS spectrum from the sample arising from the subtraction of gas phase dioxygen signals measured by different detectors does not allow us to conclude whether this oxygen exists under reaction conditions or if it accumulates in the process of pumping-off. However, the similarity of the *in situ* and *ex situ* XAS data revealed in this study indicates that the main surface species in both cases is the electrophilic oxygen which, as shown earlier by isotopic exchange experiments [15], is the active form for ethylene epoxidation. This result is in accordance with the data of Grant and Lambert [7], and van Santen *et al.* [5,6] who have shown that the pre-treated silver surface preserves its activity in ethylene epoxidation even after pumping of reaction mixtures.

O K-edge spectra for the electrophilic oxygen and for molecular oxygen chemisorbed on Ag(110) taken from [21] are compared in figure 4. It is easy to see that in contrast to molecular oxygen the electrophilic oxygen species does not produce any features in the photon energy range of 530–535 eV. This observation can be explained by either complete filling of the empty molecular oxygen orbitals (both  $\pi^*$  and  $\sigma^*$ ) due to electron transfer from silver or their disappearance due to dissociation of the dioxygen molecule. In the case of a molecular oxygen species even its highest charge, (2–) for peroxide ion, would provide filling only of the  $\pi^*$  unoccupied orbital, while the antibonding  $\sigma^*$  orbital would remain vacant (empty). As consequence, the corresponding signals should appear in XANES spectra [32] that are not observed in our case, as shown in figure 4. This fact indicates unambiguously the atomic origin of the electrophilic oxygen. Taking into account the literature data on XANES studies of oxygen interaction with transition and

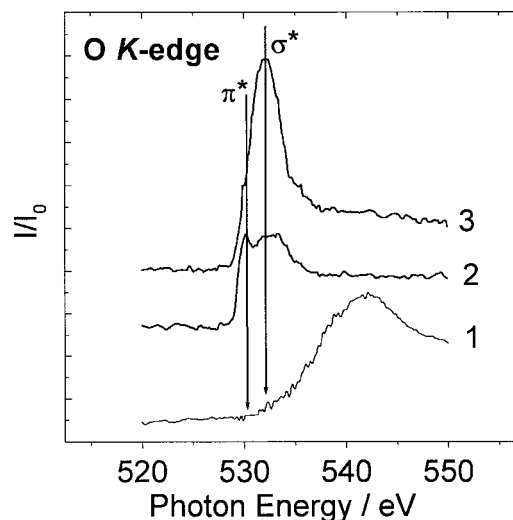


Figure 4. O K-edge X-ray absorption spectra of the electrophilic oxygen (1) and for  $\text{O}_2$  molecularly chemisorbed on Ag(110) single crystal measured at grazing ( $\theta = 20^\circ$ ) and normal ( $\theta = 90^\circ$ ) incidence ((2) and (3), respectively) taken from [21].

noble metals [33–35], the XAS signal located 5–20 eV above the threshold ( $\sim 541$  eV in our case) is attributed to oxygen 2p-character hybridised with silver 5sp states. The XAS feature near threshold observed for the nucleophilic oxygen is indicator of O 2p–Ag 4d hybridisation in the case of this oxide-like oxygen.

In conclusion of this work, it should be noted that more severe reaction conditions causing the appearance of two additional features at  $\sim 9.2$  and  $11.4$  eV in the UPS spectra (figure 3(a), curve (3 – 1)) do not result in any pronounced changes in the XAS spectra (figure 3(b), inset). The range near threshold contains only a weak signal from the nucleophilic oxygen. Therefore, other reasons than the formation of quasi-molecular [11,12] or ozone-like [13] oxygen should be suggested to explain these UPS features at 9.2 and 11.4 eV. The most suitable candidate is a hydroxide species. Indeed, features at  $\sim 3$ , 8.5 and 11.2 eV in UPS spectra [26,28,29] and at 530.5–531 eV in the O 1s spectrum [26,27] have been assigned earlier to  $\text{OH}_{\text{ads}}$ . This suggestion would also fit to the shape of the XAS feature. OH groups on Si(111) exhibit a single broad feature at 538 eV in XANES [36]. In the present data such a feature would be hidden in the broad absorption band at  $\sim 542$  eV.

## 5. Conclusions

Comparison of the XAS spectra *in situ* monitored in the course of ethylene epoxidation over silver with the XAS, XPS and UPS spectra recorded after evacuation of the reaction mixtures allowed us to show that the main surface species in both cases is the electrophilic oxygen, which had been earlier concluded to participate in ethylene epoxidation. This oxygen is characterised by a broad XAS signal at 10–20 eV above the threshold. The complete absence of XAS features near threshold that is typical for  $\pi^*$  and  $\sigma^*$

transitions of molecular oxygen indicates both the atomic origin of the electrophilic oxygen and the absence of molecular species on the catalyst surface under the present reaction conditions.

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## References

- [1] H.H. Voge and C.R. Adams, *Adv. Catal.* 17 (1967) 17.
- [2] W.M.H. Sachtler, *Catal. Rev.* 4 (1970) 27.
- [3] C.T. Campbell and M.T. Paffett, *Surf. Sci.* 143 (1984) 517.
- [4] M.A. Barteu and R.J. Madix, in: *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Vol. 4, eds. D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1982) ch. 4.
- [5] R.A. van Santen and C.P.M. de Groot, *J. Catal.* 98 (1986) 364.
- [6] R.A. van Santen and H.P.C.E. Kuipers, *Adv. Catal.* 35 (1987) 26.
- [7] R.B. Grant and R.M. Lambert, *J. Catal.* 92 (1985) 364.
- [8] A.V. Khasin, *Kinet. Katal.* 34 (1993) 42 (in Russian).
- [9] J. Deng, X. Xu, J. Wang, Y. Liao and B. Hong, *Catal. Lett.* 32 (1995) 159.
- [10] D.I. Kondarides, G.N. Papatheodorou, C.G. Vayenas and X.E. Verykios, *Ber. Bunsenges. Phys. Chem.* 97 (1993) 709.
- [11] A.I. Boronin, S.V. Koscheev, V.F. Malakhov and G.M. Zhidomirov, *Catal. Lett.* 47 (1997) 111.
- [12] A.I. Boronin, S.V. Koscheev and G.M. Zhidomirov, *J. Electron Spectrosc. Relat. Phenom.* 96 (1998) 43.
- [13] A.I. Boronin, V.I. Avdeev, S.V. Koscheev, K.T. Murzakhmetov and G.M. Zhidomirov, *Kinet. Katal.* 40 (1999) 653.
- [14] V.I. Bukhtiyarov, A.I. Boronin, I.P. Prosvirin and V.I. Savchenko, *J. Catal.* 150 (1994) 262.
- [15] V.I. Bukhtiyarov, I.P. Prosvirin and R.I. Kvon, *Surf. Sci.* 320 (1994) L47.
- [16] V.I. Bukhtiyarov, V.V. Kaichev, I.P. Prosvirin and E.A. Podgornov, *Catal. Lett.* 57 (1999) 233.
- [17] C.-B. Wang, G. Deo and I.E. Wachs, *J. Phys. Chem. B* 103 (1999) 5645.
- [18] J. Stöhr, in: *NEXAFS Spectroscopy*, Springer Series in Surface Sciences, Vol. 25, ed. R. Gomer (Springer, Heidelberg, 1992).
- [19] Y. Ma, C.T. Chen, G. Meigs, K. Randal and F. Sette, *Phys. Rev. A* 44 (1991) 1848.
- [20] R.J. Guest, B. Hernäs, P. Bennich, O. Björneholm, A. Nilsson, R.E. Palmer and N. Mårtensson, *Surf. Sci.* 278 (1992) 239.
- [21] J. Pawela-Crew, R.J. Madix and J. Stöhr, *Surf. Sci.* 339 (1995) 23.
- [22] A. Knop-Gericke, M. Hävecker and Th. Schedel-Niedrig, *Nucl. Instrum. Methods Phys. Res. A* 406 (1998) 311.
- [23] D. Sekiba, H. Nakamizo, R. Ozawa, Y. Gunji and H. Fukutani, *Surf. Sci.* 449 (2000) 111.
- [24] N. Rösch and D. Menzel, *Chem. Phys.* 13 (1976) 243.
- [25] R.L. Martin and P.J. Hay, *Surf. Sci.* 130 (1983) L283.
- [26] M.A. Barteau and R.J. Madix, *Surf. Sci.* 140 (1984) 108.
- [27] A.F. Carley, P.R. Davies, M.W. Roberts and K.K. Thomas, *Surf. Sci.* 238 (1990) L467.
- [28] X. Bao, M. Muhler, Th. Schedel-Niedrig and R. Schlögl, *Phys. Rev. B* 54 (1996) 2249.
- [29] I.E. Wachs and S.R. Kelemen, *J. Catal.* 71 (1981) 78.
- [30] K.C. Prince and A.M. Bradshaw, *Surf. Sci.* 126 (1983) 49.
- [31] V.I. Bukhtiyarov, M. Hävecker, V.V. Kaichev, A. Knop-Gericke, R.W. Mayer and R. Schlögl, *Nucl. Instrum. Methods Phys. Res. A*, accepted.
- [32] E. Rühl and A.P. Hitchcock, *Chem. Phys.* 154 (1991) 323.
- [33] Th. Schedel-Niedrig, X. Bao, M. Muhler and R. Schlögl, *Ber. Bunsenges. Phys. Chem.* 101 (1997) 994.
- [34] F.M.F. de Groot, M. Grioni, J.C. Fuggle, J. Ghijsen, G.A. Sawatzky and H. Petersen, *Phys. Rev. B* 40 (1989) 5715.
- [35] J. Purans and A. Kuzmin, Ph. Parent and C. Laffon, *Physica B* 259–261 (1999) 1157.
- [36] R. Lindsay, P.L. Wincott, C.A. Murin, G. Thornton, S.P. Frigo, J.K. Simons and R.A. Rosenberg, *Jpn. J. Appl. Phys.* 32 (1993) 347.