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Hydroxyl groups on oxide surfaces: NiO(100), NiO(111) and $Cr_2O_3(111)$

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Hydroxyl groups at the surfaces of NiO(100), NiO(111), and $Cr_2O_3(111)$ have been studied using different surface sensitive spectroscopies The OH groups are readily formed by the interaction of the oxide surfaces with the residual gas atmosphere or by dosing of water They can be removed by annealing at temperatures $T \ge 600$ K (NiO) or $T \ge 540$ K (Cr_2O_3) OH does not bond to regular NiO(100) sites so that for a cleaved NiO(100) single crystal surface no OH adsorption could be observed. For the more defect containing NiO(100)/Ni(100) film the existence of OH could be verified by isotope exchange with OD As indicated by TDS (thermal desorption spectroscopy) of an NO adsorbate, OH groups fully block the (111) oriented surface of NiO for NO adsorption which indicates that OH groups bond to regular NiO(111) surface sites. For $Cr_2O_3(111)$ thermal decomposition of water at defect sites and photochemical dissociation is observed. The latter path seems to involve water molecules in the second layer and leads most likely to an occupation of regular surface sites.

1. Introduction

From oxide powders it is known that they are often fully or partly covered with OH groups [1,2] The OH groups may be formed by the interaction of hydrogen with surface oxygen ions or by the interaction of water with metal ions at the surface Hydroxyl groups are known to influence the catalytic properties of oxide surfaces since they may take part in reactions where they act as proton donors or they may be exchanged for other anions In industrial catalysis OH groups are supposed to play an important role in the catalytic cracking of hydrocarbons [2] Since technically important catalysts often consist to a large part of oxide powder it is important to study the microscopic aspects of the interaction of OH with oxide surfaces in more detail

As will be shown in this paper, defect sites play an important role for the formation of hydroxyl groups at oxide surfaces Under UHV conditions no OH formation is observed at regular surface sites of $N_1O(100)$ und $Cr_2O_3(111)$, only hydroxylation of defect sites takes place On the other hand, on

NiO(111) also regular surface sites seem to bond hydroxyl groups

In a previous paper we have studied the adsorption of NO on a NiO(100) film which was grown by oxidation of Ni(100) [3] We found that the NO adsorbate is not significantly influenced by the defects which exist in appreciable amounts on epitaxially grown NiO(100) films As will be shown in this paper this is likely due to a blocking of the defect sites by OH

Adsorption of OH at defect sites has been observed previously for NiO(100) [4–8] Also for NiO [9] and Cr_2O_3 [1,10,11] powder samples a hydroxyl contamination was found

In this paper we present data for epitaxially grown NiO(100), NiO(111), and $Cr_2O_3(111)$ surfaces which reveal the existence of strongly bound OH species up to temperatures of above $T \approx 500$ K For comparison also data for a cleaved NiO(100) single crystal surface are presented

 $Cr_2O_3(111)$ is a very reactive oxide surface Previously we have studied the adsorption of CO, CO₂, NO, NO₂, and O₂ [12,13] on this surface The high reactivity of this oxide surface seems to be due to Cr^{2+} ions which exist on the clean, flash-heated oxide surface. Hydroxyl groups on $Cr_2O_3(111)$ may be formed by the interaction with water. Two reaction paths are observed, a thermal and a photochemical one. The thermal path leads to a hydroxylation of defect sites, similar to the case of the NiO surfaces. The photochemical path on the other hand leads to a higher OH coverage so that it is near at hand to assume that in this case also regular surface sites are occupied by OH. The latter reaction path is observed only for a thick layer of water indicating that the second or higher water layers play a crucial role for the photochemical decomposition of water on $Cr_2O_3(111)$. More general information on adsorption on oxide surfaces may be found in ref. [14].

2. Experimental

For this study three different UHV systems have been used. Two systems contain hemispherical electron energy analysers rotable in two orthogonal planes for angle resolved electron detection. One of these systems is additionally equipped with a hemispherical electron monochromator for angle resolved EELS (electron energy loss spectroscopy). The third system contains an EELS setup consisting of a double pass cylindrical electron analyser and monochromator. Additionally, all systems are equipped with LEED (low energy electron diffraction) systems, quadrupole mass spectrometers for residual gas analysis and TDS, and ion guns for sample preparation. The ARUPS (angle resolved ultraviolet photoelectron spectroscopy) data were taken partly with light from the TGM 2 beamline at the BESSY electron storage ring in Berlin and partly with light from a He discharge lamp.

The metallic samples which were used for the preparation of the thin film oxides were spot welded to two tungsten rods which were connected to a liquid nitrogen reservoir. With this arrangement temperatures below T=100 K could be reached. A tungsten filament was mounted behind the samples which could be used for sample heating by electron impact or radiative heating. The samples were cleaned by repeated cycles of etching with Ne ions and annealing.

Studies on the oxidation of Ni have been performed rather early by Conrad et al. [15]. The NiO(100) and NiO(111) films have been prepared by oxidation of Ni(100) and Ni(111) single crystal surfaces in an oxygen atmosphere. NiO(100) was grown by cycles of oxidation with 1000 L ($1L=10^{-6}$ Torr s) of O₂ at elevated temperature (T=570 K) followed by annealing at T=650 K. These cycles were repeated until the LEED pattern indicated the formation of an ordered oxide film. The NiO(111) layers were prepared in a similar way. Both types of oxide films exhibit an appreciable amount of defects as indicated by the rather high background intensity and by the large half widths of the spots in the LEED patterns (fig. 1).

Immediately after preparation the NiO(100) and NiO(111) films were found to be covered with OH groups, compatible with the H₂O and H₂ background pressure. These could be removed by annealing at $T \ge 600$ K. After cooling down, the formation of OH species could be observed again, indicating that the hydroxyl species were formed by a reaction of the oxide surfaces with the residual gas atmosphere. For the isotope exchange experiments the hydroxylated oxide films were briefly flashed to T=660 K in an atmosphere of 10^{-6} mbar of D₂O.

Some experiments have also been performed with a NiO(100) single crystal surface. The single crystal rod was cleaved in vacuo. This procedure resulted in a well ordered (100) surface with a very small concentration of defects which gave rise to a sharp (1×1) LEED pattern with low background intensity. On the cleaved surface no OH formation in detectable amounts was observed. Since the thermal contact of the single crystal rod to the sample holder was not as good as for the spot welded metal samples we used a helium cryostate for cooling purposes.

The Cr₂O₃(111) films were prepared by oxidation of a Cr(110) single crystal surface. For this purpose the Cr(110) sample was annealed at T = 500 K in an atmosphere of 10^{-6} mbar of O₂ for 3 min. After this treatment the sample was annealed at T = 1000 K in order to remove excess oxygen from the surface. The LEED pattern of the oxide film exhibits a hexagonal symmetry as expected for Cr₂O₃(111) (fig. 2).



Fig. 1. LEED patterns of epitaxially grown NiO(100) and NiO(111) (top), and Ni(100) and Ni(111) (bottom) and schematic representations of the oxide structures.





 $Cr_2O_3(111)/Cr(110)$



Fig. 2. LEED patterns of epitaxially grown $Cr_2O_3(111)$ (top) and Cr(110) (bottom) and a schematic representation of the oxide structure.

3. OH and NO/OH coadsorption on NiO(100) and NiO(111): results and discussion

Most of the data presented for nickel oxide in this paper are EELS spectra which have been taken in the energy range of the NiO optical gap. A EELS spectrum of a cleaved NiO(100) single crystal surface is shown in fig. 3 for a more extended energy range. The spectrum has been recorded in specular detection geometry with an electron energy of 60 eV. The optical gap of NiO extends down to an energy of about 3.8 eV [16]. At higher loss energy the optically allowed excitations of NiO are found. In the gap region transitions to different excited configurations of the 3d electrons of the nickel ions are found. These states are labelled in fig. 3 according to references [16–19] and the results of ab initio calculations which we have presented in a previous paper [20].

In fig. 4 a set of EELS data is shown for NiO(111)/ Ni(111), NiO(100)/Ni(100), and a NiO(100) single crystal surface. For each thin film oxide two spectra are shown: one spectrum taken before and another one taken after a flash to T=680 K and T=700K, respectively. The spectra differ in that prior to the flash a narrow loss peak is observed at an energy of 460 meV which is missing after the flash. For the cleaved NiO(100) surface this loss is only observed after the surface has been shortly sputtered (1 min, 500 eV Ne⁺). This loss is not an intrinsic part of the oxide EEL spectrum which consists of the phonon losses near to the elastic peak and of the remaining broad losses which are due to transitions within the



Fig. 3. EEL spectrum of a NiO(100) single crystal surface. $E_p = 60$ eV.



Fig. 4. Comparison of EEL spectra for NiO(111)/Ni(111) and NiO(100)/Ni(100) recorded before and after annealing at T=680 K and T=700 K, respectively. ($E_p=13$ eV). For comparison also two spectra of a cleaved NiO(100) single crystal are shown, taken before and after sputtering the surface for 1 min with Ne⁺ ions (500 eV). $E_p=100$ eV.

3d manifold of the nickel ions. Most of the latter losses may be assigned on the basis of optical absorption spectroscopy [16,17] and earlier EELS data [18,19]. The losses at 570 meV and 1620 meV are, however, not to be found in the cited spectra. As revealed by a comparison of experimental data with ab initio cluster calculations these losses are due to surface states of nickel oxide which are located at the nickel surface ions [20]. This result is in agreement with conclusions Gorschlüter et al. have drawn recently from their EELS data which also showed the loss at 570 meV [21].

As may be seen from the data shown in fig. 4, sputtering of a NiO(100) single crystal surface results in a strong attenuation of the bulk loss at 1.1 eV whereas the surface loss at 570 meV is only slightly affected. The attenuation of the bulk loss at 1.1 eV indicates that the sputtering process destroyed the structure of several layers of NiO. The reason that the loss at 570 meV is less attenuated is possibly that not only Ni ions at the surface but also nickel ions near to an oxygen vacancy give rise to a loss at this energy. This type of defects will be introduced by the sputtering process. According to ab initio cluster calculations, the excitation energy of nickel atoms at the surface differs only slightly from the excitation energy of nickel ions near to oxygen vacancies [20].

The narrow loss peak at 460 meV in the spectra shown in fig. 4 has been observed previously by Andersson et al. [22]. They argued that this loss should be due to OH. In order to prove this we performed isotope exchange experiments. For this purpose the OH covered NiO(100)/Ni(100) surface was shortly flashed to T=660 K in an ambient pressure of 10^{-6} mbar of D₂O. The corresponding EEL spectra are shown in fig. 5. Prior to the flash the surface was covered with OH groups as indicated by the narrow loss at 460 meV. The tiny loss at 532 meV, near to the OH



Fig. 5. EEL spectra of NiO(100)/Ni(100) and NiO(111)/ Ni(111) taken after annealing in a D₂O atmosphere in comparison with the OH covered surfaces before annealing. $E_p = 13$ eV.

loss, is most likely due to electrons which have excited an OH vibration and a NiO phonon. Upon treatment with D_2O the intensity of the OH loss decreases and a new narrow loss peak grows at a loss energy of 335 meV. Since the ratio of the loss energies is about $\sqrt{17/9}$ the latter loss is to be attributed to OD. From this result it is rather obvious that the loss at 460 meV is due to adsorbed OH.

OH does not bond to regular NiO(100) surface sites as indicated by the EELS data for the cleaved NiO(100) surface (fig. 4) which contains only a very small number of defects. Only after sputtering OH adsorption is observed. An additional hint corroborating this conclusion is provided by a comparison of EEL spectra of clean, OH covered, and NO covered NiO surfaces. As may be seen from the spectra shown in fig. 6 the surface states of NiO at 570 and 1620 meV shift in energy when NO is adsorbed onto the surface, but no shift is observed for the hydroxylated surface with respect to the dehydroxylated surface.



Fig. 6. EEL spectra of dehydroxylated, hydroxylated, and NO covered hydroxylated NiO(100)/Ni(100) surfaces. $E_p=13 \text{ eV}$. For comparison also spectra of a clean and a NO covered NiO(100) single crystal surface are shown ($E_p=100 \text{ eV}$).

Since the surface states are located at regular NiO(100) surface sites it follows that the NO molecules interact with regular surface sites whereas the OH groups do not.

For the cleaved NiO(100) single crystal surface the loss at 570 meV still remains visible after NO adsorption. Only its intensity is reduced. A possible reason for this result is that we could not reach full NO coverage since the temperature was possibly too high.

As oxidic crystals cannot be spot welded, the thermal contact to the sample holder was not as good as it was for the thin film oxides. For the same reason the determination of the temperature of the single crystal was a problem. Another reason for the remaining intensity of the loss at 570 meV may be the high electron energy that we had to use in these experiments due to charging of the oxide surface at low temperature. This might result in an enhanced cross section for stimulated desorption of the NO molecules.

The formation of surface OH groups is also visible in the ARUPS data. In fig. 7 UP spectra of hydroxylated and dehydroxylated NiO(111)/Ni(111) and NiO(100)/Ni(100) films are compared. The difference spectra show two emissions at 7 and 11 eV which are to be attributed to the 3σ and 1π emissions of OH as revealed by a comparison with a spectrum of KOH/K/Pt(111) (top) [23]. Interestingly the 1π emission is situated in a region where also the $3d^7$ final state of the substrate is located [3,24,25], so that care must be taken not to attribute the 1π emission to the $3d^7$ state.

In XPS the hydroxyl groups lead to a small peak near to the O1s peak of the oxide substrate (fig. 8) [8]. Similar spectra have been observed earlier by Roberts et al. for NiO powder samples [9]. In the cited publication the small peak near to the O1s peaks was also assigned to O1s level of hydroxyl groups. This assignment is corroborated by O1s XPS spectra of Ni(OH)₂ [26]. In this work the O1s peak was found at a binding energy of 531.4 eV which is quite near to the binding energy of the shoulder of the O1s peaks of the NiO films (fig. 8). As expected for an adsorbate peak the intensity increases at grazing exit angles. From the data shown in fig. 8 and other XPS data the OH coverage has been estimated. Using a mean free electron path in NiO as calculated from the data of Seah and Dench [27] one finds that the



Fig. 7. ARUP spectra of hydroxylated and dehydroxylated NiO(111)/Ni(111) and NiO(100)/Ni(100) surface ($\hbar\omega$ = 40.82 eV). At the top a spectrum of KOH/K/Pt(111) is shown for comparison [23].

OH coverage on NiO(111) is typically about 0.4. For NiO(100)/Ni(100) the coverage is about half of this value, i.e. about 0.2. For NiO(100) the coverage is given relative to the number of Ni surface ions whereas for NiO(111) it is given relative to the number of surface atoms. This has been done because the density of the Ni surface ions of NiO(100) is not much different from the density of surface atoms on NiO(111), i.e. the densities differ by about 13%. It should be mentioned that the coverage depends somewhat on the actual preparation of the oxide film. But in all cases an appreciable amount of OH was found on the epitaxially grown NiO surfaces.

OH formation on defect containing NiO(100) surfaces has been observed previously. For a NiO single crystal surface reduced in a hydrogen atmosphere, UP spectra which point towards the formation of OH species have been observed [4]. Also, sputtering leads to a reduction of NiO. Henrich et al. observed OH species in appreciable amounts on a sputtered NiO(100) single crystal surface [5], simi-



Fig. 8. O1s XP spectra of hydroxylated NiO(100)/Ni(100) and NiO(111)/Ni(111) surfaces (Al K α) taken at two different electron exit angles.

lar to our results. They found that pretreatment of the sputtered surface with oxygen considerably increases the OH yield. Also, after exposing a cleaved NiO(100) single crystal surface to air at atmospheric pressure the O1s XPS peak of OH has been observed with considerable intensity [6].

In order to study the influence of surface hydroxyl groups on coadsorbed molecules we performed thermal desorption experiments for a NO adsorbate. In fig. 9 a set of TD spectra for NO on NiO(100)/Ni(100) (panel a) and NiO(111)/Ni(111) (panel b) is shown as a function of the NO dose. The OH groups have not been removed from the surfaces prior to NO adsorption. For both substrates the spectra consist of a dominant desorption peak at $T \approx 220$ K with a small shoulder at $T \approx 280$ K, and a shoulder at $T \approx 160$ K which is only visible as an asymmetry in the spectra of the surfaces which are densely covered with NO.

By a comparison of the TD spectrum of NO on a cleaved NiO(100) surface with the spectrum of NO



on a NiO(100) film [3] the NO desorption peak at T=220 K could previously be assigned to NO molecules desorbing from regular (100) surface sites. The shoulder at $T\approx 280$ K may be associated with desorption from defect sites or sites near to OH groups. The other shoulder ($T\approx 160$ K) is only visible in the spectra of the surfaces which are densely covered with OH. Therefore it is possibly due to repulsive interactions between adsorbed NO molecules.

The NO desorption spectra of the hydroxylated NiO(100) and NiO(111) films are rather similar (fig. 9). One way to interpret this observation is to assume that on the hydroxylated NiO(111) film NO adsorbs only on (100) oriented patches. Such NiO(100) patches should exist on the NiO(111) film since the EELS data (fig. 4) show that the surface states of NiO(100) at 570 and 1620 meV are also visible in the data of the NiO(111) film. This provides preliminary evidence for the existence of (100) oriented patches on the NiO(111) film.

When the surfaces are dehydroxylated prior to NO adsorption, in the TD spectra of NO/NiO(100)/ Ni(100) only small changes are observed whereas the spectra of NO on the NiO(111) film change considerably (fig. 10). For NO/NiO(111)/Ni(111) the spectra are rather complicated with maxima at about $T \approx 180$ K, $T \approx 200$ K, $T \approx 220$ K, $T \approx 280$ K, and $T \approx 470$ K. Similar desorption spectra have been observed previously by Yoshinobu et al. [28]. The high temperature desorption peak may be due to desorption from oxygen deficient sites formed during the annealing procedures since NO desorption from Ni(100) precovered with chemisorbed oxygen is also observed in this temperature range [29]. It is, however, also possible that this state is due to a reaction of NO with the NiO surface. A NO desorption peak at this temperature has been observed previously on a NiO powder sample where it was attributed to reacted NO, i.e. nitrate or nitrite [30].

The peak area of the spectrum of the dehydroxylated NiO(111) taken at saturation coverage of NO (spectrum at the top in fig. 10) is larger by a factor

Fig. 9. Series of TD spectra (mass 30, NO) of NO/NiO(100)/ Ni(100) (panel a) and NO/NiO(111)/Ni(111) (panel b) as a function of the NO dose. The OH groups have not been removed prior to adsorption. Exposure is given relative to the exposure needed for saturation coverage.



Fig. 10. Similar to fig. 9, but in this case the surfaces have been dehydroxylated prior to NO adsorption.

2.5 than the corresponding value for the hydroxylated surface. This indicates that about 2/3 of the surface area of the NiO(111) film are blocked by OH. Since for the hydroxylated surface only adsorption at (100) oriented patches is proposed, it is reasonable to assume that the increase of the NO saturation coverage by a factor of 2.5 upon dehydroxylation is due to adsorption on the (111) oriented parts of the surface, which are no longer blocked when the OH species are removed. This indicates that OH bonds to regular NiO(111) surface sites, in contrast to the adsorption behaviour of NiO(100). There are also indications that the NiO(111) surface is stabilized by OH groups. Some of our data show that the similarity of the NiO(111) EEL spectrum to the NiO(100) EEL spectrum increases when the surface is dehydroxylated. This points towards a conversion of (111) oriented surface parts into (100) oriented patches. However, it is not clear at the moment whether the conversion is triggered by the removal of OH or just by the annealing process. From an energetic point of view is is not unreasonable to assume that the (111) surface is stabilized by OH. The ideal unreconstructed NiO(111) surface is a polar surface. This means that the (111) film consists of consecutive layers of oxygen ions and nickel ions, respectively. For such an arrangement of charges the Madelung potential energy converges only if the electric charge density of the first and the last layer of the film is reduced to 50% of that of the bulk layers. If this is not the case the Madelung energy increases with increasing film thickness. To solve this problem it has been argued that the surface is restructured [31]. The proposed reconstruction would lead to a (2×2) superstructure in the LEED pattern. We could observe weak indications of such a structure in some of our LEED photographs, but we do not think that these observations are sufficient evidence to propose that larger parts of the surface are restructured. Further LEED studies will be performed. The requirement that the surface charge has to be reduced to stabilize the surface may also be fulfilled by covering the surface densely with OH groups. The formal charge of the OH groups is -1 which is 50% of the formal charge of the oxygen ions in the NiO bulk. This would lead to a stabilization of the unreconstructed (111) surface. However, the OH coverage of 0.4 is too small to stabilize the whole (111) surface. Therefore also

other stabilization mechanisms must exist. The surface will be additionally stabilized if it is not purely terminated by nickel or oxygen layers but by small patches of oxygen and nickel layers. As indicated by ISS (ion scattering spectroscopy) the surface consists to 70% of nickel ions and to 30% of oxygen ions. Considering the high OH coverage this could of course also mean that the surface is terminated by a nickel layer which is hydroxylated, since a Ni terminated (111) surface with an OH coverage of about 30% would also give rise to the observed IS spectrum.

For NO/NiO(100)/Ni(100) the NO desorption spectra seem to be more or less identical for the hydroxylated (fig. 9a) and the dehydroxylated (fig. 10a) surface. There are two possible explanations for this result. The first explanation is that NO does not bond to the defect sites which become unoccupied when the OH groups are removed. The second explanation is that under the conditions present in our experiment it is not possible to prepare a NO adsorbate without hydroxylating the surface at the same time, which is probably due to the interaction of the surface with the residual gas atmosphere. This explanation is corroborated by EEL spectra of NiO(100) (see for instance fig. 6) in which the OH loss at 460 meV was always observed after dosing of NO even when the oxide was dehydroxylated prior to NO adsorption. Thus one is led to the conclusion OH groups form with a high rate at the defects on a NiO(100)film. However, in contrast to NiO(100)/Ni(100), clear differences are observed between the TD spectra of NO on hydroxylated NiO(111)/Ni(111) and dehydroxylated NiO(111)/Ni(111). This might indicate that for regular NiO(111) sites the reaction rate for OH group formation is not as large as the corresponding reaction rate for the defects.

After the TDS experiments on the dehydroxylated films the surfaces were allowed to saturate again with OH. The NO desorption spectra from these surfaces were similar to the spectra shown in fig. 9 so that possible changes of the surface structures and compositions of the NiO(100) and NiO(111) films are most likely not the reason for the differences between the spectra shown in figs. 9 and 10.

4. OH groups and water adsorption on $Cr_2O_3(111)$: results and discussion

The interaction of water with $Cr_2O_3(111)$ also



Fig. 11. ARUP spectra of H_2O on $Cr_2O_3(111)$ taken after annealing to different temperatures.

leads to the formation of OH groups at the surface. In fig. 11 a set of UP spectra is shown for H_2O on chromium oxide. The spectra have been taken after annealing an ice film (spectrum at the bottom) at different temperatures. At T=160 K most of the water is desorbed and only a comparably small signal of the adsorbate remains. Annealing at T=270 K leads to a further reduction of the photoemission intensity of the adsorbate, so that in spectrum g only the small peak at 11 eV binding energy reminds of the water adsorbate. The species which is responsible for this peak remains at the surface up to temperatures of about $T \approx 500$ K (spectrum k). The peak is found at approximately the same binding energy as the peak of OH on NiO (see fig. 7) so that it is suggestive to identify this species also with OH. Like for NiO(100) the OH groups on Cr_2O_3 seem to be bound to defect sites since it was not possible to vary the coverage significantly by variation of the amount of dosed water, the dosing temperature, or the annealing procedure. It was, however, possible to increase the amount of adsorbed OH by irradiating the primary ice layer with UV light as shown in fig. 12. This figure shows the influence of the preparation



Fig. 12. ARUP spectrum of flashed $Cr_2O_3(111)$ (a) in comparison with spectra of chromium oxide treated with H_2O under different experimental conditions (spectra b to d).

conditions on the amount of produced OH. It is obvious that irradiation with UV light significantly increases the OH coverage. There are small differences between spectra (b) and (c) which have been taken at different dosing temperatures. Whether these differences are significant or whether they are just due to different defect densities at the oxide surfaces is, however, not clear at present.

The only way to increase the OH coverage significantly by photon irradiation was to irradiate an ice layer at low temperatures. Irradiation of a (sub)monolayer of water did not increase the OH coverage significantly. Since it is unlikely that OH groups, which are photochemically produced far away from the surface in the ice layer, diffuse to the surface at T=90 K it has to be assumed that the second layer of water takes part in the photochemical dissociation process. A possible explanation for this observation is that the O-H bond of the first layer is weakened by the hydrogen bridge bonds to the water molecules of the second layer. We observed photon induced OH formation at all photon energies used in our study of H₂O/Cr₂O₃(111) (20, 36 and 40 eV). Therefore we conclude that the photochemical dissociation of water is not a resonant process.

For doped iron oxide suspended in a dilute solution of NaOH the photocatalytic decomposition of water has been investigated by Somorjai and coworkers [32,33]. According to their interpretation the first step in the dissociation process is the production of an electron hole pair in the oxide. To answer the question whether this is also the case for the photochemical OH production on $Cr_2O_3(111)$ one would have to measure the OH production rate as a function of the photon energy in order to find out whether the onset for OH production is connected with the energy of the band gap of chromium oxide.

When the chromium oxide surface is covered with oxygen prior to H_2O adsorption then the oxygen at the surface is consumed during the photochemical dissociation process when the layer is irradiated. This is shown in fig. 13. At a photon energy of 40 eV, ox-



Fig. 13. ARUP spectra of flashed (a), oxygen covered (b), and water on an oxygen precovered $Cr_2O_3(111)$ surface (c, d). Before spectra c and d have been recorded the water covered oxide surface has been heated to T=475 K with (d) and without (c) irradiation with UV light.

ygen at the chromium oxide surface leads to a characteristic emission at a binding energy of about 7 eV. This emission survives when a water layer on the oxygen precovered surface is not irradiated whereas it strongly decreases in intensity when the water layer is irradiated with "white light" from the synchrotron. This indicates that the oxygen at the surface takes place in the photochemical reaction. It is most likely reacted towards OH.

The small peak in the ARUP spectra, which is indicative of OH (see for instance fig. 11) is due to the OH 3σ level. The wavefunction of this electronic state has cylindrical symmetry and can therefore be used to determine the adsorption geometry of OH by recording ARUP spectra in the so called allowed and forbidden geometries [34]. In both geometries the light is incident along the surface normal ($\alpha = 0^\circ$, see inset in fig. 14). Due to the cylindrical symmetry of the 3σ wavefunction, for an OH molecule adsorbed in an upright geometry no emission intensity of the



Fig. 14. Set of ARUP spectra of OH adsorbates on $Cr_2O_3(111)$ taken in allowed ($\alpha = 0^\circ$, $\varphi = 0^\circ$, $\vartheta = 60^\circ$) and forbidden ($\alpha = 0^\circ$, $\varphi = 90^\circ$, $\vartheta = 60^\circ$) geometry, respectively. For comparison also data for a freshly flashed surface are shown.

 3σ level is expected in a plane which is perpendicular to both the surface plane and the electric field vector of the incident light ($\varphi = 90^\circ$, forbidden geometry) whereas no restriction for the emission intensity exists in the light incidence plane. The latter plane is defined by the electric field vector and the surface normal ($\varphi = 0^\circ$, allowed geometry). A set of data for OH on $Cr_2O_3(111)$ is shown in fig. 14. The angle ϑ was chosen to be 60° in all cases. The spectra in fig. 14 show that the 3σ emission at 11 eV is appreciably stronger in the allowed geometry than in the forbidden geometry. This holds for the OH species formed by dosing of H_2O at room temperature (spectra (c)) and (d)) as well as for the OH species formed by heating an ice layer prepared on an oxygen precovered $Cr_2O_3(111)$ surface to room temperature under photon irradiation (spectra (e) and (g)). From these data it must be concluded that the molecular axes of the adsorbed hydroxyl species are more or less oriented parallel to the surface normal.

The other species observed in the spectra shown in fig. 11 is only stable up to $T \approx 250$ K. Its main emission is found at a binding energy of about 13.5 eV. This emission is likely due to water as revealed by the spectra shown in fig. 15. Spectrum (a) is a UP spectrum of a flashed $Cr_2O_3(111)$ surface and (b) shows a spectrum of a water adsorbate which has been annealed at T=220 K. At the top the difference spectrum (c) is compared to a spectrum of a multilayer of water. This comparison reveals that the species remaining at T=220 K at the surface are OH ($E_B=11$ eV) and H₂O. Since at T=220 K the water multilayer is desorbed the H₂O which remains at T=220K must be bound directly to the chromium oxide surface.

5. Summary

In this paper we have shown that strongly bound OH groups exist at NiO and $Cr_2O_3(111)$ surfaces. They may be removed by annealing at $T \ge 600$ K (NiO) or $T \ge 540$ K (Cr_2O_3). On NiO(100) and $Cr_2O_3(111)$ the formation of OH occurs exclusively at defect sites. On $Cr_2O_3(111)$ also regular surface sites may be hydroxylated by promoting the dissociation of adsorbed water by irradiation with UV light. In contrast to regular NiO(100) sites, the regular sites



Fig. 15. Comparison of the ARUP spectrum of a multilayer of water taken at T=90 K to the spectrum of the same layer after annealing at T=220 K.

of NiO(111) seem to interact strongly with OH groups. In view of the inherent instability of polar surfaces the high coverage of OH on NiO(111) may be rationalized as to be due to a stabilization of the (111) surface by hydroxyl groups. NO adsorbates behave quite similar on hydroxylated NiO(100)/Ni(100) and NiO(111)/Ni(111) films which indicates that on hydroxylated NiO(111) films the NO molecules only adsorb on (100) oriented patches of the films. When the NiO(111) film is dehydroxylated the thermal desorption pattern gets more complicated and the NO coverage increases by a factor of 2.5 indicating that on the dehydroxylated surface NO also adsorbs on the (111) oriented parts of the NiO(111) film.

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References

- A.A. Davydov, Infrared spectroscopy of adsorbed species on the surfaces of transition metal oxides (Wiley, New York, 1990).
- [2] G.C. Bond, Heterogeneous catalysis (Oxford Univ. Oxford, 1990).
- [3] H. Kuhlenbeck, G. Odörfer, R. Jaeger, G. Illing, M. Menges, Th. Mull, H.-J. Freund, M. Pöhlchen, V. Staemmler, S. Witzel, C. Scharfschwerdt, K. Wennemann, T. Liedtke and M. Neumann, Phys. Rev. B 43 (1991) 1969.
- [4] K.W. Wulser, B.P. Hearty and M.A. Langell, Phys. Rev. B 46 (1992) 9724.
- [5] J.M. McKay and V.E. Henrich, Phys. Rev. B 32 (1985) 6764.
- [6] St. Uhlenbrock, Chr. Scharfschwerdt, M. Neumann, G. Illing and H.-J. Freund, J. Phys. C 4 (1992) 7973.
- [7] M. Bäumer, D. Cappus, G. Illing, H. Kuhlenbeck and H.-J. Freund, J. Vacuum Sci. Technol. A 10 (1992) 2407.
- [8] M. Bäumer, D. Cappus, H. Kuhlenbeck, H.-J. Freund, G. Wilhelmi, A. Brodde and H. Neddermeyer, Surface Sci. 253 (1991) 116.
- [9] M.W. Roberts and R.St.C. Smart, J. Chem. Soc. Faraday Trans. I 80 (1984) 2957.
- [10] R.L. Burwel, G.L. Haller, K.C. Taylor and J.F. Read, Advan. Catal. 29 (1969) 1.
- [11] K. Morishigo, S. Kittaka, S. Twasaki and T. Morimoto, J. Phys. Chem. 85 (1981) 570.
- [12] C. Xu, B. Dillmann, H. Kuhlenbeck and H.J. Freund, Phys. Rev. Letters 67 (1991) 3551.
- [13] H. Kuhlenbeck, C. Xu, B. Dillmann, M. Hassel, B. Adam, D. Ehrlich, S. Wohlrab, H.-J. Freund, U.A. Ditzinger, H. Neddermeyer, M. Neuber and M. Neumann, Ber. Bunsenges. Physik. Chem. 96 (1992) 15.
- [14] H.-J. Freund and E. Umbach, eds., Adsorption on ordered surfaces of ionic solids and thin films, Springer Series in Surface Sciences, in press.
- [15] H. Conrad, G. Ertl, J. Küppers and E.E. Latta, Solid State Commun. 17 (1975) 497.
- [16] D. Adler and J. Feinleib, Phys. Rev. B 2 (1970) 3112.
- [17] R. Newman and R.M. Chrenko, Phys. Rev. 114 (1959) 1507.
- [18] P.A. Cox and A.A. Williams, Surface Sci. 152 (1985) 791.
- [19] J.P. Kemp, S.T.P. Davies and P.A. Cox, J. Phys. Condens. Matter 1, (1989) 5313.
- [20] A. Freitag, V. Staemmler, D. Cappus, C.A. Ventrice Jr., K.Al Shamery, H. Kuhlenbeck and H.-J. Freund, Chem. Phys. Letters 210 (1993) 10.

- [21] A. Gorschlüter and H. Merz, J. Phys. Cond. Matter (1993), in press.
- [22] S. Andersson and J.W. Davenport, Solid State Commun. 28 (1978) 677.
- [23] H.P. Bonzel, G. Pirug and A. Winkler, Surface Sci. 175 (1986) 287.
- [24] A. Fujimori and F. Minami, Phys. Rev. B 30 (1984) 957.
- [25] G.J.M. Janssen and W.C. Nieuwpoort, Phys. Rev. B 38 (1988) 3449.
- [26] N.S. McIntyre and M.G. Cook, Anal. Chem. 47 (1975) 2209.
- [27] M.P. Seah and W.A. Dench, Surf. Interface Anal. 1 (1979) 2.

- [28] J. Yoshinobu, X. Guo and J.T. Yates Jr., J. Vacuum Sci. Technol. A 9 (1991) 1726.
- [29] G. Odörfer, R. Jaeger, G. Illing, H. Kuhlenbeck and H.-J. Freund, Surface Sci. 233 (1990) 44.
- [30] B. Egersdörfer and H. Papp, private communication.
- [31] D. Wolf, Phys. Rev. Letters 68 (1992) 3315.
- [32] J.E. Turner, M. Hendewerk and G.A. Somorjai, Chem. Phys. Letters 105 (1984) 581.
- [33] M.M. Khader, G.H. Vurens, I.-K. Kim, M. Salmeron and G.A. Somorjai, J. Am. Chem. Soc. 109 (1987) 3581.
- [34] H.-J. Freund and M. Neumann, Appl. Phys. A 47 (1988) 3.