

Molecules on oxide surfaces

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Abstract

Metal oxides may be prepared as thin (5–50 Å) films on top of metallic substrates. By such means oxide substrates with properties identical to bulk oxides may be formed which can be studied via electron spectroscopies without being hindered by charging, as well as cooling problems. We report here on results on NiO and on Cr₂O₃ surfaces.

We discuss some structural aspects of oxide surfaces such as surface reconstruction of polar rock salt-type surfaces, and structural phase transitions on corundum type structures. The nature of the phase transition will be discussed with respect to the magnetic properties of the oxide.

Furthermore we report on the interaction of those surfaces with molecules from the gas phase. In particular we study the interaction with small molecules such as CO, NO, O₂, CO₂, H₂O and C₂H₄. We observe via various surface sensitive techniques such as thermal desorption spectroscopy (TDS), X-ray photoelectron spectroscopy (XPS), angle resolved photoemission (ARUPS), electron energy loss spectroscopy (HREELS), infrared-reflection-absorption-spectroscopy (IRAS), and near-edge-X-ray-absorption-fine-structure spectroscopy (NEXAFS), associative as well as dissociative adsorption and in the case of ethylene also polymerization reactions. Via isotopic labelling techniques combined with IRAS we study in detail the interaction of oxygen with the oxide surfaces, a process of general interest in connection with oxidation reactions.

Keywords: Oxide surfaces; Oxidation reactions; Isotopic labelling; Dissociative adsorption

1. Introduction

Molecular adsorption on oxide surfaces has been studied for a long time [1–18]. One reason of course has been the eminent importance of oxide substrates as support for disperse metal catalysts as well as active catalysts themselves [19]. For mechanistic surface studies three strategies have been applied:

1. adsorption and reaction studies on microcrystalline materials, e.g. by the Torino [15] and Munich groups [16],
2. adsorption studies on surfaces of single crystal oxides by a number of groups including

the Yale [1], Kopenhagen [7,8], Manchester [9,10] and Tübingen [11,12] groups,

3. adsorption and reaction studies on thin oxide single crystal films grown on metallic substrates, e.g. by the Texas A and M [13,14], Berkeley [17,18] and Bochum groups [5,6].

The third strategy has proven to be particularly useful if electron spectroscopic techniques were applied for surface characterization, and if surface crystallographic orientations which do not exist as cleavage planes are of interest.

In this paper we review some of our results which may be of relevance in catalysis on the polar surfaces of NiO [20,21] and Cr₂O₃ [22,23]

which are grown as films on metallic substrates. We investigate the interaction of water, CO and NO with NiO(111) [24] in comparison with NiO(100) [25,26]. On Cr₂O₃(0001) we investigate the dynamics of transition metal ions on the surface where phase transitions are observed at low temperatures. These transitions are connected with adsorption properties of various molecules such as CO, NO, water, oxygen [27] and ethylene. In particular we dwell on the adsorptive and reactive properties of oxygen, and its influence on the adsorptive and polymerization properties of ethylene. The latter may be important for an understanding of the Philips catalyst for ethylene polymerization [28].

2. Experimental

The oxide surfaces have been prepared according to well known recipes described in detail elsewhere [1–26]. The metal substrates were spotwelded to tungsten rods which were connected to temperature variable sample manipulators. Gases were admitted via a dosing system from the gas phase. Experiments have been performed in several ultrahigh vacuum systems which are equipped with the various electron spectroscopic methods, among them are photoelectron spectroscopy, electron energy loss spectroscopy, thermal desorption spectroscopy, and low energy electron diffraction. Some experiments (photoelectron spectroscopy and near edge X-ray absorption fine structure) have been performed at BESSY in Berlin.

3. Results and discussion

Non-polar and polar surfaces of ionic oxides exhibit fundamentally different behaviour with respect to their chemical reactivity. We have discussed the differences in depth elsewhere [6]. Briefly, the situation may be summarized on the basis of Fig. 1. In the top panel a non-polar (100) surface of NiO is shown. On the right

hand side the ideal surface is viewed from above. On the left the crystal is viewed perpendicular to the surface normal. This reveals the stacking of planes, each of which is electrically neutral such that the resulting dipole moment disappears as indicated in the figure. The energy of this surface is rather low, i.e. 1.74 J m^{-2} [29]. Such an ideal non-polar surface is chemically rather inert, although weak molecular chemisorption may be observed for particular molecules such as NO on the surface [25]. Only if defects are introduced in the surface does the chemical reactivity of the system increase [30]. For example, if a NiO film with global (100) orientation is grown on a Ni(100) surface, the large lattice misfit leads to a morphology where ideal terraces are separated by areas with high defect density [31]. Such a film dissociates molecular water to form hydroxyl groups on the surface in contrast to the ideal surface which is inactive in water dissociation. In the bottom panel a polar (111) surface of NiO is shown. The important point is not the hexagonal arrangement of the oxygen ions in a ideally oxygen (as opposed to nickel) terminated surface as plotted in the left corner of the top view, but rather the stacking of planes of ions as schematically shown on the top left. Different from the vanishing dipole moment in the case of the non-polar surface the polar stacking leads to a dipole moment parallel to the surface normal between two layers which in turn yields a diverging surface potential V for increasing numbers of layers N . If layers are separated by a distance b , and the surface unit cell covers an area S , then the surface potential V depends on the charge σ which resides on the top and bottom planes of the stacked layers [32]. σ is given in this case in units of the charge per unit cell in the nominally fully ionic system. Consequently, the surface potential is infinite for the ideally terminated layer. It may be reduced via various routes, two of which we would like to mention in this review. One is a possible surface reconstruction, the other one is the adsorption of charge reducing species from the gas

phase such as hydrogen, which via the formation of single negative hydroxyl groups on the surface reduce the charge with respect to the double negative oxygen ions. Let us consider first the case of surface reconstruction. Lacman [33] and later Wolf [34] have shown that the so-called octopolar reconstruction, which is shown for the oxygen terminated as well as for the nickel terminated surface in the structural model on the right hand side indeed stabilizes the surface at a finite surface energy. The octopolar unit sticking out of the surface is shown enlarged in the inset. For such a reconstructed surface the surface energy is finite, i.e. 4.28 J m^{-2}

m^{-2} [34], but still considerably higher than for the non-polar surface. The surface energy may be used to drive chemical reactions. Fig. 2 illustrates this for the $\text{NiO}(111)$ surface. On the left hand side at the top an electron energy loss spectrum is shown for a $\text{NiO}(111)$ prepared in the presence of water in the background gas [20]. The surface exhibits a hexagonal LEED pattern (as shown in the middle of Fig. 2) and carries considerable amounts of hydroxyls on the surface as revealed by the sharp features in the EEL spectrum. It is very likely that the surface may be represented by an ideally arranged $\text{NiO}(111)$ surface whose first layer how-

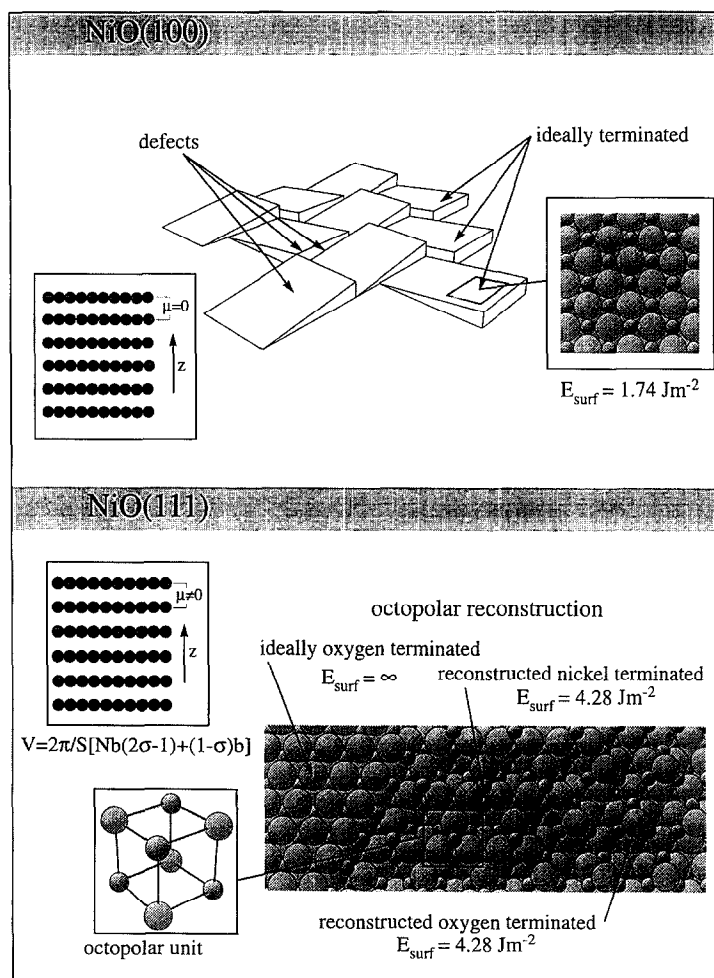


Fig. 1. Schematic representations of surface structures observed for $\text{NiO}(100)$ and $\text{NiO}(111)$ films. Surface energies are given, and the insets show the stacking of planes.

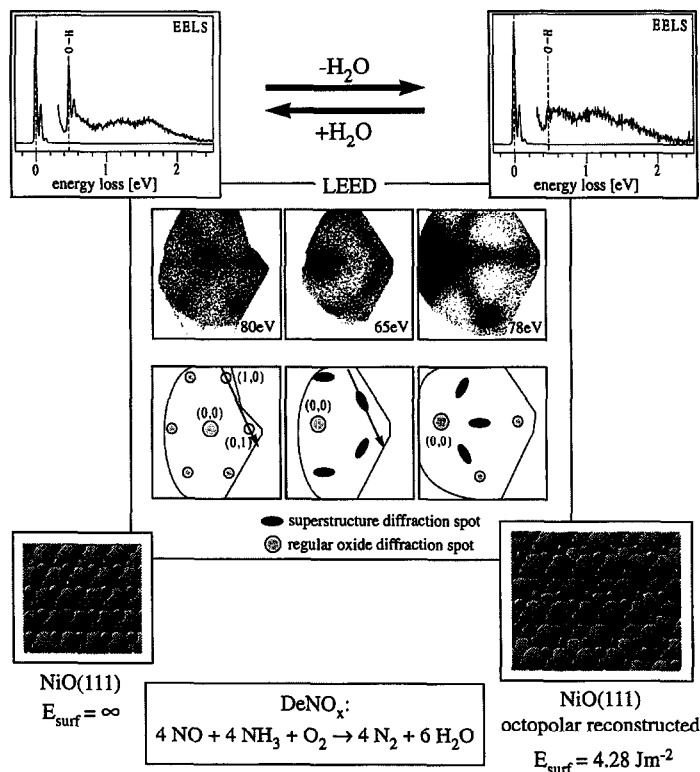


Fig. 2. Electron energy loss spectra and low energy electron diffraction data for the hydroxyl covered NiO(111) surface and the dehydroxylated, reconstructed (octopolar) NiO(111) surface.

ever does not consist of oxygen ions but rather hydroxyl ions thus stabilizing the polar surface. Upon heating the surface to 500 K it loses water such that the hydroxyls are removed from the surface. Consequently, the surface undergoes a reconstruction of the octopolar type which is indicated in the LEED pattern (see middle panel) by the occurrence of superstructure spots as expected for the $c(2 \times 2)$ unit cell of the reconstructed surface (see panel at the bottom right). The removal of the hydroxyls may be followed by the EELS measurements shown at top right. It is interesting to realize that the system may be cycled between the hydroxylated and the reconstructed situation by heating the hydroxylated surface to 200°C, and exposing the dehydroxylated NiO(111) surface consecutively to water again. We note that the hydroxylated surface is chemically rather inert again. Also, its surface energy is low. On the other

hand, the reconstructed, dehydroxylated surface is chemically active. When such a surface is exposed to NO for example, thermal desorption spectra indicate considerable difference with respect to the non-polar surfaces. Fig. 3 shows TPD spectra of the hydroxylated and dehydroxylated NiO(111) surface after exposure to NO [20]. Two observations are important: Firstly, the amount of adsorbed NO increases by about a factor of three for the dehydroxylated surface, and in addition there are high temperature desorption channels observed, which are probably due to the formation of NO₂ on the surface. In the future it will be interesting to investigate the activity of the model system in a chemical reaction such as the DeNO_x reaction. There are some interesting observations on real catalytic samples reported by Papp and his group [35]. Via so-called topotactic decomposition of Ni(OH)₂, which exhibits a layered structure, it

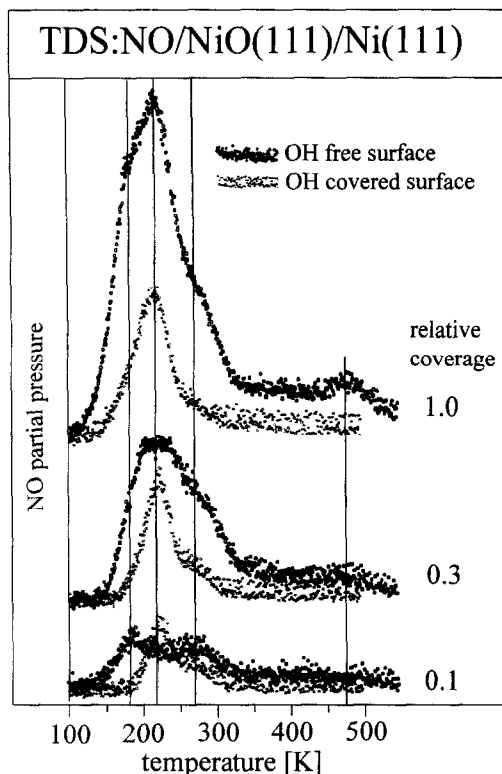


Fig. 3. Thermal desorption spectra of NO adsorbed on the hydroxylated and dehydroxylated NiO(111) surface.

is possible to prepare NiO samples composed of crystallites exposing mainly surfaces of hexagonal symmetry as revealed via electron microscopy [36]. Immediately after preparation these samples are not active in DeNO_x catalysis. However, after heating the samples to 350°C , where they lose a small amount of water they become DeNO_x active. It is not at all hard to map this behaviour onto the behaviour of our model samples. In fact, we feel, that the comparison indicates that the elementary steps discussed for the activation and deactivation of the model system may well apply to the real system.

The second example we want to address in the present paper is the reactivity of a more complex polar surface, namely the $\text{Cr}_2\text{O}_3(0001)$ surface. We have recently demonstrated that such a surface undergoes phase transitions in the temperature regime of $100 < 180 \text{ K}$ [22].

LEED measurements indicate an ideal hexagonal structure at low (i.e. 100 K) temperature [22,37]. EELS spectra may be analysed to assign the local sites of the chromium ions in the surface. Only half of the number of chromium ions as compared with a Cr layer in the bulk are present on the surface. This is a necessary condition to stabilize the polar surface via charge reduction [1]. All the Cr^{3+} ions reside in the quasi-threefold sites where another Cr ion is situated right below the oxygen layer [22]. Upon increase of the temperature it is believed that the ions change site in a concerted manner, possibly driven by magnetic interactions in the anti-ferromagnetic system [38], such that half of the chromium ions now reside in another quasi-threefold site. The observed LEED pattern is no longer simply hexagonal, but exhibits a typical $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ pattern [22]. Upon further increase the ordered structure decays into a disordered structure [22]. Interestingly enough, these phase transitions can either be quenched by the presence of adsorbates [22] or even stabilized by adsorption [23]. Oxygen adsorption, for example, quenches the phase transition. We have therefore investigated in more detail the interaction of the oxide surface with molecular oxygen from the gas phase. Earlier studies employing HREELS spectroscopy [39] indicated the formation of various species on the surface, but the resolution of the EELS experiment was not sufficient to identify the various species [27]. We have therefore setup an FTIR experiment to use the much higher resolution achievable in such an experiment to identify the various species. The experiment will be described in detail elsewhere [27]. We note here, that the thin oxide film samples grown on top of metallic substrates are well suited substrates for reflection measurements. Fig. 4 shows a series of FTIR spectra recorded after the chromium oxide surface has been dosed with oxygen at 80 K until saturation is reached, and heated consecutively in steps to 800 K. Three features are observed, appearing and disappearing in various temperature regimes as indicated in the figure.

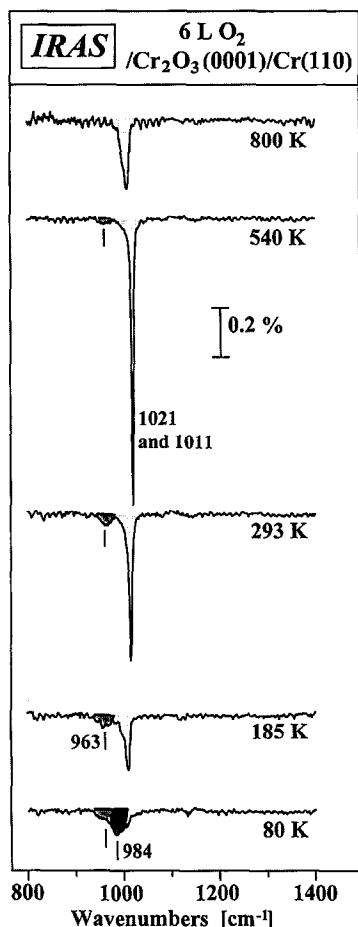


Fig. 4. FTIR spectra of a $\text{Cr}_2\text{O}_3(0001)$ surface exposed to 6L (saturation coverage) of $^{16}\text{O}_2$ at 80 K. The system has been heated to various temperatures (as given).

We find absorptions between 963 cm^{-1} and 984 cm^{-1} , as well as at 1011 to 1021 cm^{-1} , indicating that the O_2 unit has been considerably distorted. As pointed out in Ref. [39], where EELS showed losses within semi energy range, the frequencies would be compatible with both, the formation of partly negatively charged oxygen molecules, and with the formation of chromium–oxygen chromylbonds as it is known in CrCl_2O_2 [40]. For this compound, a doublet at 990 cm^{-1} and 1000 cm^{-1} , which is characteristic for the in-phase and out of phase combination of the Cr–O vibrations known from the molecular compound [40], is observed. Of course, isotopic labelling can be extremely help-

ful to disentangle the assignment. Fig. 5 compares the spectra after the surface has been exposed to $^{16}\text{O}_2$ and $^{18}\text{O}_2$. At the lowest temperature clear isotopic shifts to lower frequencies as expected for a molecularly adsorbed species, which leads us to believe that at lowest temperature a strongly bound O_2 species, corresponding to the absorption between 963 cm^{-1} , and 984 cm^{-1} is formed. This molecular species does not seem to exchange with the lattice oxygen. Also, it is not clear whether we deal with a single or several species. The formation of electronically modified oxygen molecules, however, may also be documented via the analysis of electron energy loss spectra in the range of loss energies characteristic for electronic excitations as shown in Fig. 6 [41]. At the bottom a spectrum of the clean surface exhibits several electronic surface excitations as discussed in

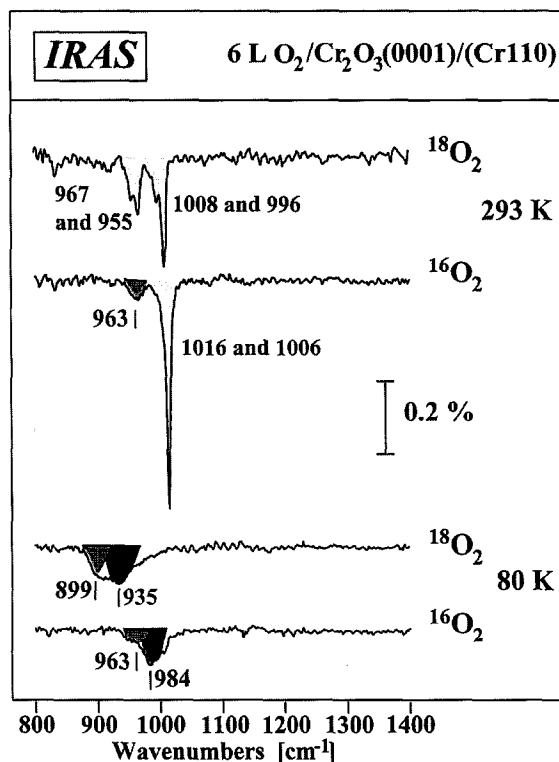


Fig. 5. FTIR spectra of a $\text{Cr}_2\text{O}_3(0001)$ surface exposed to 6L (saturation coverage) of $^{16}\text{O}_2$ and of $^{18}\text{O}_2$ at 80 K, and after heating to 293 K.

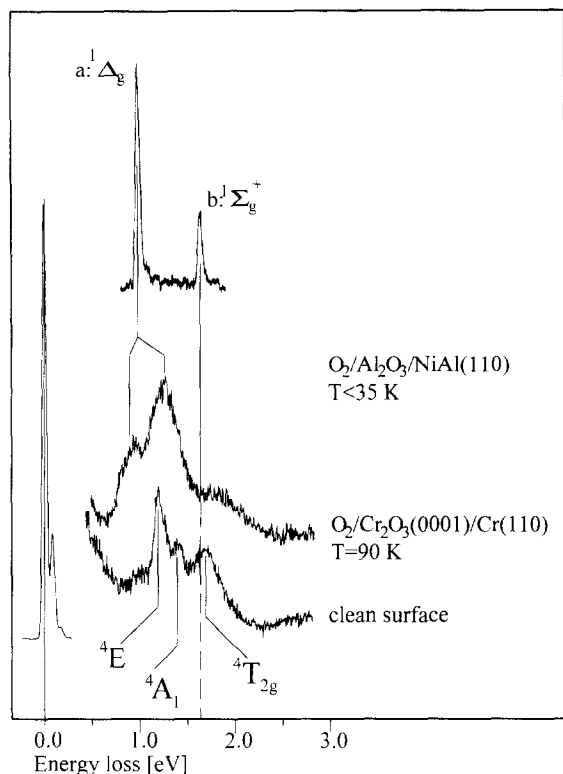


Fig. 6. Electron energy loss spectra of the clean $\text{Cr}_2\text{O}_3(0001)$ surface, the oxygen exposed $\text{Cr}_2\text{O}_3(0001)$ surface at 80 K, and the oxygen exposed $\text{Al}_2\text{O}_3(0001)$ surface at 35 K for comparison.

detail elsewhere [22]. Upon oxygen exposure at lowest temperature the spectrum is modified considerably [41]. New excitations are observed which gradually change in intensity upon increasing the temperature. The oxygen induced excitations may be correlated with the formation of oxygen molecules in an electronically modified state. The low lying excitation around 1 eV may be correlated with excitation into the $a^1\Delta_g$ state of gaseous O_2 . For O_2 only weakly interacting with a corundum type oxide, i.e. Al_2O_3 , the excitation energy into this state is situated close to 1 eV. The excitation into the higher lying $^1\Sigma_g^+$ state is observed but less probable as demonstrated in Fig. 6 for comparison. If O_2 interacts with a surface the degeneracy of the levels is lifted and the energy is shifted depending on the strength of the interaction. Therefore,

the doubly degenerate $^1\Delta_g$ splits into two non degenerate levels. The symmetry of the non degenerate levels, of course, depends on the symmetry at the site which is not known at present. It is therefore conceivable, that the two excitations at 0.85 eV and 1.2 eV observed for $\text{O}_2/\text{Cr}_2\text{O}_3(0001)$ are due to excitations into these levels which have been modified with respect to O_2 in the gasphase, thus corroborating the findings based on the vibrational analysis at low temperature. Once the chromyl bonds are formed, characteristic electronic excitations in the considered energy range are not found but there is still a strong influence onto the electronic excitation spectra as will be discussed in greater detail in another paper [42]. Coming back to the isotopic labelling experiments at this point, the formation of the chromyl bonds is clearly documented when the system is heated to above 150 K. At this temperature the sharp doublet at 1011 cm^{-1} and 1021 cm^{-1} , which shifts with increasing temperature to lower frequencies, occurs for $^{16}\text{O}_2$. For $^{18}\text{O}_2$ the same doublet is found in addition to an isotopically shifted doublet at 955 cm^{-1} and 967 cm^{-1} . Obviously, a species is formed from the isotopically labelled oxygen dosed, but also oxygen present in the lattice is involved. This is in line with dissociately adsorbed atomic oxygen bound within the above mentioned chromyl units. In fact, a chromyl species with both oxygens stemming from the isotopically labelled oxygen dosed from the gas phase is not observed. This indicates that either the dissociation is not achieved via a concerted mechanism, or the exchange is so fast that only partly exchanged species are observed.

Returning to the quenching of the surface phase transition, and considering the results, it is quite clear how, via the formation of the chromyl species, the mobility of the chromium ions is blocked so as not to allow for the necessary site hopping to undergo the phase transition. On the other hand, CO seems to stabilize the phase transition. We know from our earlier studies that CO desorbs near the

temperature range where the phase transitions occur [39]. Once the CO is on the surface, the formed $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern is stable even to lower temperature [23], where on the clean surface, the LEED pattern is simply hexagonal. A possible explanation may be given again on the basis of previous results where we have found that CO adsorbs with its axis parallel or at least strongly inclined with respect to the surface normal [23]. It is conceivable that the parallel bonding needs as a prerequisite chromium ions at a particular distance which is realized in the ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase.

The above described adsorption and reaction of oxygen has considerable consequences for the consecutive adsorption of other molecules such as ethylene [43]. Fig. 7 shows thermal desorption spectra of ethylene from the chromium oxide surface without and with oxygen preexposure. The freshly prepared $\text{Cr}_2\text{O}_3(0001)$ surface exhibits two adsorption states. One at low temperature, i.e. 140 K, and a second one with peak desorption temperature of 240 K. They are due to a physisorbed and a weakly chemisorbed state, respectively. While the chemisorbed state is suppressed on the oxygen preexposed surface, the physisorbed adsorption state is still observed. As in the case of oxygen adsorption, chemisorption of ethylene leads to a full attenuation of the electronic chromium d–d excitations in the surface [43] indicating, that the ethylene molecules are actually coordinated to the chromium ions in the surface. However, as long as the adsorption experiments are done under ultrahigh vacuum conditions, there is no indication of a chemical transformation of the hydrocarbon [43]. If the pressure in the chamber increases, polymerization of ethylene on the oxide surface may be observed [43]. Fig. 8 shows C1s X-ray photoelectron spectra as well as HREELS spectra of the surface for the ethylene adsorbate systems and the polymer covered surface. From the adsorbate, the hydrocarbon may be removed by heating to the desorption temperature according to the TPD spectra shown in Fig. 7. After

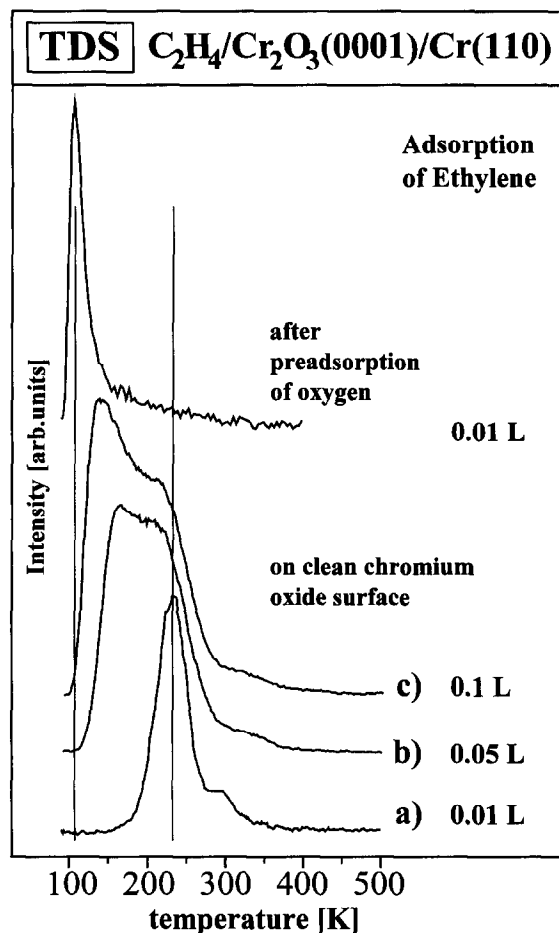


Fig. 7. Thermal desorption spectra of C_2H_4 from $\text{Cr}_2\text{O}_3(0001)$. (a), (b) and (c) represent spectra after exposure to 0.01L, 0.05L and 0.1L. At the top a spectrum after oxygen preadsorption is shown for comparison.

polymerization the surface is irreversibly covered with a hydrocarbon film and the oxide has to be newly prepared. The observed C1s binding energies and binding energy shifts as well as the observed vibrational frequencies and frequency shifts are in line with expectations based on literature data for ethylene adsorbates and polymer films on metal substrates [44–46]. We may therefore conclude at this point that a clean Cr_2O_3 surface exposed to ethylene at moderate pressures does allow polymerization of the hydrocarbon [43]. As far as we can tell at present coordinatively unsaturated chromium ions in the oxidation state 3+ are important in the reac-

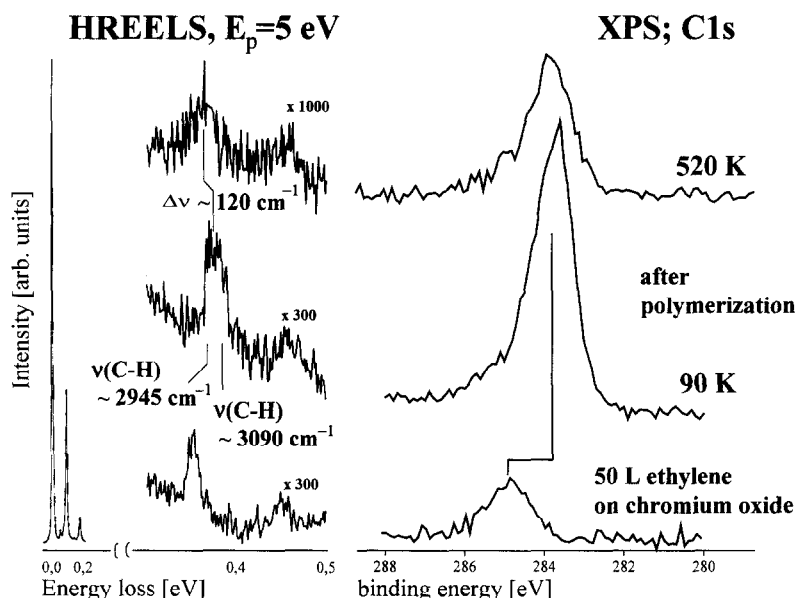


Fig. 8. Electron energy loss spectra in the vibrational regime and C1s X-ray photoelectron spectra of adsorbed ethylene before and after polymerisation.

tion. These findings may be relevant for an understanding of the Philips catalysts [28].

4. Synopsis

It has been demonstrated that polar surfaces of ionic oxides exhibit interesting chemical reactivities. These reactivities are correlated with structural transformation of the oxide surfaces. We have shown via detailed surface science experiments on model systems how molecular adsorption and structural transformations are interrelated. It is speculated that these findings may be relevant for a mechanistic understanding of some processes proceeding on real samples.

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