M125

Adsorption and reaction of molecules on surfaces of metal-metal oxide systems

H.-J. Freund*, B. Dillmann, D. Ehrlich, M. Haßel, R.M. Jaeger, H. Kuhlenbeck, C.A. Ventrice Jr., F. Winkelmann, S. Wohlrab and C. Xu

Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, Universitätsstraße 150, 4630 Bochum 1 (Germany); tel. (+49-234)7005529, fax. (+49-234)7094182

Th. Bertrams, A. Brodde and H. Neddermeyer

Institut für Experimentalphysik, Ruhr-Universität Bochum, Universitätsstraße 150, 4630 Bochum 1 (Germany)

Abstract

Molecular adsorption on oxide surfaces is gaining increasing interest both experimentally and theoretically. Adsorption studies on model systems, where well ordered thin oxide films grown on a metal substrate to avoid sample charging in connection with electron spectroscopic measurements, were used, are reported. Two oxide systems are compared: (i) a reactive transition metal oxide surface of $Cr_2O_3(111)$ where it is shown that the surface contains Cr^{2+} ions which trigger its reactivity; (ii) a non-reactive simple metal oxide surface of γ -Al₂O₃(111) which is used as a support model surface. The adsorption of various molecules on both surfaces has been examined, and how the properties of the surface are modified when metals are deposited on the oxide surface have been studied. The results of alkali metal deposits on $Cr_2O_3(111)$ and Pt deposits on γ -Al₂O₃(111) are presented. The applied methods include LEED, STM, TPD, ARUPS, ELS, XPS, HREELS and ISS.

Key words: adsorption; electron spectroscopy: oxide surfaces

Introduction

In catalysis oxides are commonly used either as support materials or often as catalytically active components. In spite of the great technological importance of these systems, systematic surface science studies are rather rare in this field, while adsorption studies on oxide powders are well documented [1]. The adsorption studies have provided empirical information, but often a model for the microscopic processes in these systems is missing. However, in order to derive a systematic understanding of the elementary processes involved in chemical processes at oxide surfaces, microscopic models are strongly needed. A first approach to this goal is the study of adsorption on well defined oxide single crystal surfaces under UHV conditions applying surface science meth-

^{*}Corresponding author.

odology. Such studies should provide information on the geometric and electronic structure of the adsorbate and on the adsorbate/substrate interaction. One problem in applying surface science methods is the limited conductivity of many oxides which hinders the use of electron spectroscopic methods. A way to overcome this problem is the use of thin, single crystal, oxide films which are grown by oxidation on top of metallic substrates. Such films do not tend to charge if they are not too thick.

Reviews of data for clean and adsorbate covered oxide single crystal surfaces have for instance been published by Henrich [2] and Heiland and Lüth [3]. The best characterized systems are probably ZnO [4-12] and TiO₂ [13-18], where data are even available for adsorbates on cleaned surfaces of these oxides. For benzene on ZnO($10\overline{10}$) an ordered structure could be observed [12]. Less data are available for adsorbates on NiO(100) [19-26].

In the present review we discuss the adsorption properties of a reactive oxide surface, namely $Cr_2O_3(111)$ [27–30], and, in comparison, a typical support oxide surface, namely γ -Al₂O₃(111) [31,32]. At the end we show how the adsorption behaviour can be modified by metal deposits on to the oxide surface.

Experimental

The experiments have been performed in various UHV-systems, equipped with facilities for LEED/AES, HREELS, ARUPS, XPS, NEXAFS, TPD, ISS and STM [27-32]. The oxide films have been prepared *via* oxidation of single crystal metal, and single crystal alloy surfaces, respectively.

A Cr(110) single crystal surface was cleaned by prolonged sputtering with Ne ions at elevated temperature. It was oxidized by annealing the sample to T=500 K in an atmosphere of 10^{-6} mbar oxygen for 3 min. After this treatment, the sample was annealed to T=1000 K to remove excess oxygen from the surface. Gases have been adsorbed from the gas phase at a sample temperature of T=100 K.

A well ordered $Al_2O_3(111)$ surface may be prepared by exposing a well ordered, cleaned NiAl(110) surface to an oxygen atmosphere. NiAl(110) was oxidized after sputter-aneal cycles by heating to 1100 K in an oxygen atmosphere of 10^{-7} mbar with subsequent annealing to 1300 K.

Results and discussion

$Cr_2O_3(111)$ surface [27-30]

In Fig. 1a a LEED pattern of a clean $Cr_2O_3(111)$ oxide film expitaxially grown on Cr(110) is shown. The spots are arranged hexagonally as expected for this oxide surface [33-34]. They are somewhat broader than the spots usually observed for clean and well ordered metal single crystal surfaces indicating



Fig. 1. (a) LEED pattern of a $Cr_2O_3(111)$ surface prepared under UHV conditions on a Cr(110) surface. (b) Schematic $Cr_2O_3(111)$ surface exhibiting patches with oxygen termination and Cr termination.

the presence of an appreciable number of defects in the layer. However, the presence of well developed spots of higher order clearly reveals that there must be long range order within the film. As indicated by XPS the thickness of the oxide layer is about 50 Å and so no spots of the Cr(110) substrate are visible in the LEED pattern of the oxide film [28].

Assuming that the arrangement of atoms at the surface is the same as in the bulk, two different surface terminations of the oxide may exist, *i.e.*, an oxygen terminated surface and a chromium terminated surface. The atomic arrangement is shown schematically in Fig. 1b. The small spheres indicate Cr ions, the large spheres O ions. The picture suggests that Cr- and O-termination coexist as adjacent terraces on the surface. Such a model is consistent with ISS spectra [29] taken for the flashed $Cr_2O_3(111)$ surface shown in Fig. 2. Ion scattering spectroscopy (ISS) is very surface sensitive so that the relative in-



Fig. 2. ISS spectrum of a clean, freshly flashed $Cr_2O_3(111)$ surface, compared to an oxygen dosed surface.

tensities reflect the atomic surface composition. Since the oxide film was grown on the clean Cr(110) surface we can use the ISS signal of the clean surface to calibrate the spectra of the oxide surface [35]. From such a procedure we have estimated that about half of the surface is covered with Cr-terminated and the other half with oxygen-terminated patches. Adsorption of oxygen on to the flashed $Cr_2O_3(111)$ surface leads to attenuation of the Cr feature in the ISS spectrum as plotted in Fig. 2 caused most probably by adsorption onto the Crterminated patches. We shall come back to discuss the nature of the $O_2/$ $Cr_2O_3(111)$ interaction below.

A question which now arises is whether the constituent ions in the surface are in the same electronic state as in the bulk. There are several ways to solve this questions. XPS may be used [28] but it was shown that the clearest evidence was revealed by electron energy loss spectra in the regime of electronic excitations [27-29].

In Fig. 3 a set of EEL spectra, taken with a primary electron energy of $E_p = 100 \text{ eV}$ is shown. The spectrum at the bottom is that of a clean, freshly flashed oxide surface. Upon adsorption of O_2 a strong loss peak develops at about 9 eV. Similar losses are observed upon CO_2 and NO_2 adsorption. Losses in this energetic range are attributed to oxygen-chromium charge-transfer excitations [36]. Since CO_2 , NO_2 , and O_2 react with the surface we interpret this loss to be characteristic for surface chromium-oxygen bonds. For CO_2 adsorption the situation is somewhat different compared with O_2 and NO_2 , in that CO_2 reacts to form carbonate. This difference is also documented in the different peak shape of the loss at about 9 eV. CO and NO on the other hand adsorb without any signs of dissociation or reaction. Accordingly, the strong loss at 9 eV is not observed. Another interesting feature in these spectra is the



Fig. 3. Electronic spectra as measured by electron energy loss spectroscopy of clean and adsorbate covered $Cr_2O_3(111)$ surfaces.

behaviour of the sharp loss at about 1.2 eV. It is only visible if the strong loss at 9 eV is not visible. In this energy region the d-d excitations of the chromium ions are situated and the sensitivity of this state towards dissociative adsorption suggests that it might be a chromium surface state. Since only a single surface state is observed, the surface chromium atoms that are responsible for this peak are most likely in a 2+ state. 2+ and 5+ are the only configurations where only one d-d excitation exists, and that the surface chromium ions are in a 5+ oxidation state is rather unlikely because of the reduced number of neighbouring oxygen atoms at the surface as compared to the chromium bulk atoms which are in a 3+ oxidation state. The energetic position of this loss also points towards a 2+ oxidation state because for compounds containing Cr^{2+} ions the energy needed for the d-d excitation [37] is near to the 1.2 eV observed in our ELS spectra. Upon adsorption of oxygen, the peak at 1.2 eV excitation energy disappears. The straightforward explanation is that with oxygen adsorption the Cr^{2+} is oxidized to Cr^{3+} and the oxygen molecule is reduced.

Additional information is supplied by the HREEL spectra shown in Fig. 4. The spectrum at the bottom is that of a clean, freshly flashed $Cr_2O_3(111)$ surface. This spectrum exhibits strong losses due to the optical phonons of the oxide. Adsorption of oxygen at T=100 K leads to an additional loss at 967 cm⁻¹ which shifts to 1003 cm⁻¹ upon annealing to T=550 K. An indication of a loss is found at about 1507 cm⁻¹, independent of temperature. The energy



Fig. 4. Vibronic excitations as measured via electron energy loss spectra of clean and oxygen covered $Cr_2O_3(111)$ surfaces.

of the latter loss is near to the vibrational energy of uncharged molecular O_2 , which is about 1555 cm⁻¹ in the gas phase [1] so that this loss could in principle be attributed to molecularly adsorbed oxygen. However, it seems rather unlikely that molecular oxygen exists on the surface even at 550 K so that at least for the spectrum taken at 550 K this assignment is somewhat doubtful. In this context a more probable explanation is that this loss is split off from the neighbouring oxide phonon loss by the interaction of the chromium oxide with the adsorbed oxygen.

The remaining losses at about 1000 cm^{-1} in the HREELS data could either be attributed to the localized vibration of O^{2-} ions versus a chromium ion [1,38,39] or to the O-O vibration of molecular O_2^- [1]. The shift of the loss at 967 cm⁻¹ (T=100 K) to 1003 cm⁻¹ (T=550 K) indicates that something must happen on the surface between T=100 K and T=550 K. As revealed by a series of HREEL spectra taken at different temperatures between 100 K and 550 K (not shown here) this shift occurs at about T=200 K. With TDS, at around T=200 K, we observe desorption signals of molecular oxygen, mass 32, so that the shift in the HREEL spectra is most likely connected with these signals. It is not unlikely that this band is due to Cr=O double bonds as judged by similar vibrational frequencies (990, 1000 cm^{-1}) in CrO₂Cl [40]. Once these Cr=O bonds are formed on the surface the system is rather unreactive towards further adsorbates.

A more detailed picture of the adsorptive behaviour has been gained for CO adsorption. The ELS spectrum after CO adsorption still shows Cr^{2+} on the surface. Fig. 5 shows photoelectron spectra of the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ CO structure recorded in the so-called forbidden and allowed geometries [41,42] as indicated in the figure in comparison with a normal emission spectrum of a physisorbed monolayer CO on Ag(111) [43].

There are two CO induced features visible in the spectra of the CO adsorbate on $Cr_2O_3(111)$; one at 17.5 eV and a slightly asymmetric one at 20.2 eV. The $CO\sigma$ valence emission should be intense at the photon energy the spectra have been taken with, *i.e.*, 36 eV, whereas the 1π emission should be rather weak. Thus we identify the two CO induced features as the σ -ion states of molecularly adsorbed CO. The electronic binding energies of CO on $Cr_2O_3(111)$ are several eV larger than those of the CO physisorbate on Ag(111). This also holds for CO adsorbates on other metals (see for instance refs. [43-45]), indicating that the substrate-CO interaction on $Cr_2O_3(111)$ is appreciably different from that on metals.

Obviously, there is no significant difference in the spectra of CO/ Cr₂O₃(111) for the two collection geometries in Fig. 5. If the CO molecular axis were oriented perpendicular to the surface, the symmetry selection rules would require the σ -ion states to disappear in the forbidden geometry, and only the ion states of π -symmetry should show up. Since both σ -ion states of CO are observed with comparable intensities in both geometries, we conclude that the CO axis is strongly inclined with respect to the surface normal.

More detailed information on the orientation of the molecular axis can be deduced from Fig. 6, where a set of photoelectron spectra taken with a constant angle, *i.e.* 90°, between the directions of light incidence and electron detection is shown. From Fig. 6 it is obvious that the σ -ion states exhibit the highest intensities for near normal light incidence and near grazing electron emission, whereas at grazing light incidence these features are strongly attenuated, in marked contrast to CO adsorbed standing up on most metal surfaces. Since at a photon energy of 36 eV the σ states emit with highest intensity if the polarization direction and the direction of electron detection both coincide with the CO molecular axis, this behaviour is only compatible with an orientation of the molecular axis approximately parallel to the surface.

In the inset of Fig. 6 we compare the emission intensities of the $CO\sigma$ valence states as a function of photon energy for two different experimental ge-



Fig. 5. Photoelectron spectra of $CO(\sqrt{3} \times \sqrt{3})R30^{\circ}/Cr_2O_3(111)$ taken in the allowed and forbidden geometries, in comparison to the CO/Ag(111) system.

ometries. The data shown in the upper panel were taken at a light incidence angle of 20° with respect to the surface normal, collecting the electrons 70° off normal whereas the data in the lower panel were taken at normal electron emission and near grazing light incidence ($\alpha = 80^\circ$). Obviously a strong σ shape resonance is observed only for grazing electron detection, again clearly indicating that the CO molecules must be strongly tilted.

The same conclusion about the molecular geometry must be drawn from the analysis of our NEXAFS (near edge X-ray absorption fine structure) data [29]. These data show that the intensity of the π -resonance varies only slightly as a function of the light incidence angle as expected for CO molecules lying flat on the surface since one 2π component is oriented parallel to the surface whereas the other one protrudes from the surface. A quantitative estimation of the tilting angle was not possible from our NEXAFS data since the σ resonance was so weak that its intensity only could be evaluated with very large error bars.

From the data discussed so far a quantitative evaluation of the tilting angle was not possible but tentatively we estimate this angle to be greater than



Fig. 6. Photoelectron spectra at various detection geometries. The inset shows the variation of the peak intensities with photon energy.

70°. An obvious question is: where are the 1π orbitals? For flat-lying CO molecules the 1π levels are expected to split into two components, $1\pi_{xy}$ and $1\pi_{z}$, the first one oriented parallel to the surface and the other oriented perpendicular to the surface. Whereas the $1\pi_{xy}$ emission might be obscured by the σ emissions because this level should be intense at grazing emission angles like the σ orbitals, the $1\pi_z$ should be intense at normal emission where the σ emission is weak. As can be seen from Fig. 6 the 5σ emission is nearly totally suppressed at near normal electron emission so that the $1\pi_z$ level is most likely not situated near to the 5σ level as is the case for the 1π levels of CO adsorbed on most metals. One might suppose that the $1\pi_z$ level is located somewhere in the region of the substrate bands but since the $1\pi_z$ orbital will interact strongly with these bands it will most likely be shifted to higher binding energy because the substrate levels are energetically located above the 1π levels. In this light it is rather unlikely that the 1π levels are located somewhere in the region of the substrate bards by the set of the substrate in the region of the substrate bards by shifted to higher binding energy because the substrate levels are energetically located above the 1π levels. In this light it is rather unlikely that the 1π levels are located somewhere in the region of the substrate levels are located somewhere in the region of the substrate levels are located somewhere in the region of the substrate levels are energetically located above the 1π levels. In this light it is rather unlikely that the 1π levels are located somewhere in the region of the oxide emission.

Whereas the 5σ emission is nearly totally suppressed at near normal emission a broad feature remains in the region of the 4σ between 19 and 22 eV (Fig. 6). Since the 4σ and the 5σ emission intensity should behave similarly, it is

tempting to attribute the remaining emission between 19 eV and 22 eV to the $1\pi_z$ level. Another possible assignment would be that this feature is due to a σ shake up state. However, we consider this to be unlikely because such shake up states should be intense at emission angles where the σ main lines are also intense, which is not the case.

Figure 7 compares the binding energies of the present spectra with data reported in the literature [43-48]. All binding energies are larger than the corresponding values known from metal surfaces. They are even larger than the gas phase values. This holds also for the C1s ionization which is found 0.7 eV below its gas phase value [49]. The most interesting finding, however, is the energetic position of the 1π , level which in the present case is most likely situated near to the 4σ level, indicating a fundamentally different interaction of the molecule with the surface as compared with all other cases observed so far. We propose that the CO lone pairs (4σ and 5σ) are bound to two different Cr ions in the sense of two σ -donor bonds which shift the σ binding energies to higher values. If this is true then it is reasonable to assume that the 1π levels interact with both the Cr ions but in addition, and more importantly, with the oxygen layer underneath the terminating Cr layer. This latter interaction between the closed shell O^{2-} ions and CO must be one of repulsion. Since the oxygen levels are situated at lower binding energies than the CO 1π levels, the $1\pi_z$, which is the one that strongly interacts with the O^{2-} ions, is shifted towards higher binding energy and the interacting O^{2-} levels are rearranged as well. The shift of the 1π , level is recognized in the data, while it is more difficult to identify the effect on the oxygen levels. If we judge the observed shifts of CO on $Cr_2O_3(111)$ with respect to gaseous CO we find a shift of all CO levels to



Fig. 7. Comparison of binding energies with respect to the vacuum level for various CO adsorbates and free CO.



Fig. 8. Schematic representation of a $(\sqrt{3} \times \sqrt{3})$ R30° CO/Cr₂O₃(111) structure as deduced from combination of the experimental evidence.

higher binding energies. The shift of the 5σ level is larger than the one of the 4σ level. This is very reasonable because it follows the individual polarizabilities of the levels involved. The interaction may be separated into the two bonding interactions, Cr-CO(5σ) and Cr-OC(4σ), and into a repulsion O²⁻-CO(1π) system, leading to a weakly chemisorptive CO-Cr₂O₃ bond. The bonding of CO towards Cr₂O₃(111) is completely different from the bonding of CO to a metallic Cr surface. It is accidental that CO binds to metallic Cr in a flat bonding geometry as well. The ion state binding energies as well as their sequence are clearly different from the situation on Cr₂O₃(111) as may be seen from the data collection in Fig. 7.

To conclude the discussion of bonding to oxide surfaces as opposed to metal surfaces we note that as the availability of electrons for $d\pi$ -back donation declines, as is the case for metal ions in metal oxides, a primary driving force for linear CO bonding is lost and it is not surprising that the molecule assumes a flat lying bonding geometry.

A structure model of CO on the Cr-terminated patches of $Cr_2O_3(111)$ is presented in Fig. 8 where we show a schematic representation of the CO covered surface. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit mesh is indicated. As suggested by the intensity of the CO valence band emission the surface is most likely rather densely covered with CO molecules as, for instance, is the case for CO on



Fig. 9. HREELS spectra of (a) the clean $Cr_2O_3(111)$ surface, (b) the surface with ≈ 2.2 monolayers (ML) of Na adsorbed on it, and the surface with (c) 4 Langmuirs (L) of D_2O coadsorbed and (d) 20 L of CO_2 coadsorbed with ≈ 2.2 ML of Na. Peaks at wave numbers of 416 and 708 cm⁻¹ correspond to the excitation of the two primary Fuchs-Kliewer surface phonon modes characteristic of the $Cr_2O_3(111)$ surface. The FWHM of the elastic peak of the clean spectrum was $\Delta E_{el} = 7$ meV.

Ag(111) or N₂ on graphite [44], where the molecules are also lying flat on the surface. A structure with one molecule per unit cell would contain only the molecules on the corners of the $(\sqrt{3} \times \sqrt{3})$ R30° unit mesh. In case the unit cell contains more than one molecule the other molecules have to be added.

The ordered structure is a clear indication that the adsorbate site cannot be a defect site. We find that this has been confirmed also for another adsorbate system on an oxide surface, *i.e.*, NO on non-polar oxide surfaces such as the NiO(100) surface [19-26].

In addition to CO adsorption we investigated the interaction of several other molecules, *e.g.*, NO, O_2 , CO_2 , NO_2 , H_2O and C_2H_4 [50] with $Cr_2O_3(111)$.

In order to approach catalytic model systems we have studied metals deposited on oxide surfaces. Because alkali-metal promotors of metal oxide catalysts are well documented [51–52] it was near at hand to study alkali-metal deposition on $Cr_2O_3(111)$ and the interaction of such composite systems with molecules from the gas phase.

Since the catalytic activity of metal oxides is closely related to the charge



Fig. 10. Intensity of the HREELS peak corresponding to the excitation of the 708 cm^{-1} surface mode relative to that of the elastic peak as a function of Na overlayer coverage (line drawn to guide the eye).

state of the surface atom [26–29], as demonstrated above, knowledge of the electronic structure at the surface is fundamental to understanding the catalytic activity of these systems. By measuring the various physical properties of the alkali-metal atoms, both before and after co-adsorption with molecular species, information about charge-transfer mechanisms at oxide surfaces can be learned.

HREELS spectra of (a) the clean $Cr_2O_3(111)$ surface, (b) the surface with ≈ 2.2 monolayers (ML) of Na adsorbed on it, and the surface with (c) 4 Langmuirs (L) of D_2O coadsorbed and (d) 20 L of CO_2 coadsorbed with the Na are shown in Fig. 9. The spectrum for the clean $Cr_2O_3(111)$ surface exhibits losses corresponding to the two primary F-K surface phonon modes characteristic of this surface at wave numbers of 416 cm^{-1} and 708 cm^{-1} . Various losses corresponding to multiple combinations of these losses are also detected at higher energies. These results agree well with previous studies of single crystal $Cr_2O_3(111)$ surfaces [28,29]. The HREELS spectrum for the Na dosed surface shows almost total attenuation of all of the surface phonon modes with only the loss feature at 708 $\rm cm^{-1}$ being visible. A measure of the relative intensity of the 708 $\rm cm^{-1}$ loss feature to that of the elastic peak as a function of Na coverage is shown in Fig. 10. It can be seen that this loss feature attenuates with increasing Na coverage with near total attenuation by a coverage of ≈ 2.2 ML. As seen in Fig. 9, coadsorption with either CO_2 or H_2O returns the relative intensity of the loss features to values approximately equal to those of the clean



Binding Energy [eV]

Fig. 11. ARUPS spectra of (a) the clean $Cr_2O_3(111)$ surface, (b) the surface with ≈ 2.0 ML of Na adsorbed on it, and the surface with (c) 5 L of H₂O coadsorbed and (d) 10 L of CO₂ coadsorbed with ≈ 2.0 ML of Na where α is the angle between the surface normal and the wave vector of the incident light.

 Cr_2O_3 (111) surface. Vibrational losses from the coadsorbed species are also resolved when these spectra are viewed with an expanded scale and will be described in detail in a future publication.

ARUPS spectra of (a) the clean $Cr_2O_3(111)$ surface, (b) the surface with ≈ 2.0 ML of Na adsorbed on it, and the surface with (c) 5 L of H₂O coadsorbed and (d) 10 L of CO₂ coadsorbed with the Na are shown in Fig. 11. For the spectrum from the clean $Cr_2O_3(111)$ surface, peaks centered at binding energies (E_b) of 3 eV and 8 eV are observed which correspond to emission from the Cr 3d and O 2p bands, respectively [27-29]. Some emission from the Fermi level is also observed for this spectra which we attribute to emission from the substrate Cr(110). At a Na coverage of ≈ 2.0 ML, the valence band emission from the Cr_2O_3 is almost fully suppressed with a well developed Na 2p level peak being observed at $E_b=31$ eV. As can be seen in Fig. 11, coadsorption of either CO₂ or H₂O both result in significant broadening of the 2p emission from a FWHM of ≈ 0.75 eV to ≈ 1.5 eV for the CO₂. The LVV Auger transition and

the plasmon loss features are totally or almost totally attenuated. Although the cross-section for emission from the Na 3s level is very low at a photon energy of 50 eV, some Fermi level emission is observed for the Na spectra before coadsorption that is not observed after coadsorption. It is also noted that there is no signature of a return of valence band emission from the Cr_2O_3 substrate, which indicates that the coadsorbed species must form a somewhat uniform overlayer. In other words, significant clustering of the Na upon coadsorption can be ruled out. From comparison of the valence band emission from the Na/CO_2 coadsorbed spectrum with that from a previous coadsorption study on Pd(111) [53], we attribute the valence band features of the coadsorbed system to emission primarily from Na_2CO_3 with traces of emission from physisorbed CO_2 as indicated in Fig. 3. Comparison of the valence band emission for the Na/H_2O coadsorption spectrum with that of NaOH [54] and thick films of ice [54] provides evidence that a mixture of these two species is present at the surface. A shoulder on the low binding energy side of the Na 2p level emission for the Na/H_2O spectrum lies at approximately the same energy as that for the 2p emission from 2 ML Na without coadsorption, probably indicating that there is some unreacted Na remaining in the surface region as well.

The observation of emission from the Fermi level coupled with the existence of an LVV Auger transition, plasmon losses and a Doniach-Sunjic line shape for the 2p emission are considerable evidence that the Na overlayer at ≈ 2.0 ML is in a metallic state on the Cr₂O₃ substrate. The almost complete attenuation of the valence band emission from the Cr_2O_3 substrate at this coverage implies relatively uniform layer by layer growth of the Na. The analysis of the valence band emission after coadsorption which provide evidence for compound formation indicates that the Na reacts strongly with the coadsorbates. The non-metallic nature of the coadsorbed overlayer is confirmed by the lack of emission from the Fermi level and the observation that Auger and plasmon loss features are no longer present. Since the electronic state of adsorbed alkali-metal atoms is not only of great interest for understanding catalytic processes but also for a general understanding of the development of the metallic state of matter, the ability to measure overlayer metallization by observing the degree of attenuation of Fuchs-Kliewer modes with HREELS can provide new insight into the metallization process on oxide substrates.

γ-Al₂O₃(111) surface

As an example for a non-transition metal oxide we have investigated Al_2O_3 . Aluminium oxide is the prototype of a support material and particularly interesting in this respect. An Al_2O_3 layer with a quasihexagonal oxygen layer as the terminating surface can be grown by oxidation on a NiAl(110) alloy surface. The oxide layer is very thin, *i.e.*, it exhibits a thickness of about 5 Å as revealed by XPS and AES. The structure of this film has been studied by various techniques including scanning tunneling microscopy, LEED, EELS and ARUPS [31,32].



Fig. 12. CCT from partly oxidized NiAl(110) obtained with sample bias voltage, U=4 V and tunneling current, I=2 nA. The size of the measured surface area is 50×50 nm². The CCT is a three-dimensional representation, which is illuminated by artificial light sources. The dark band in the upper part of the image corresponds to a monoatomic step of NiAl(110) with a height of 0.2 nm (the right hand terrace is the higher one).

The use of scanning tunneling microscopy (STM) for the measurement of non-conducting surfaces under ultra-high vacuum (UHV) conditions is normally not possible. Atomic force microscopy (AFM) might then be more adequate but the attainment of atomic resolution in AFM is presently restricted to ideal surfaces, *e.g.*, cleaved LiF [56] or to layered systems, such as graphite [57]. Moreover, in the case of studies of the growth mode of an oxide film on a metal surface due to superior resolution of STM more details on the influence of the metallic substrate surface, *e.g.*, on its atomic structure, can be obtained with STM and, in addition, information on the electronic states of



Fig. 13. Measured k_1 dispersions of a γ -Al₂O₃(111) surface. Compared with the experimental data is the result of a tight binding band structure calculation of a two dimensional O²⁻ layer (see text).

the oxide film from I-U characteristics, where the tunneling current I is measured against the sample bias voltage U. We have therefore utilized STM to study the clean surface of NiAl(110) and its oxidation. In Fig. 12 we reproduce an STM image (constant current topography, CCT), which provides an overview of the general growth mode of the Al oxide layer and its orientation on the NiAl(110) substrate. The preparation used in the present case does not yet produce saturation coverage of the oxide layer but already shows the characteristic LEED spots corresponding to an epitaxial Al oxide film. About half of the surface area extending from the left bottom corner of the CCT is covered with a structure showing a distinct pattern of lines with a separation of 1.05 nm. This part of the surface corresponds to the grown Al oxide film. The direction of the lines is inclined by 15° against the [100]-like symmetry directions of the substrate, which are weakly visible on the monitor of the computer workstation by the arrangement of atomic features (mainly the Al atoms) on some parts of the surface not yet covered by the oxide film. Since the highsymmetry directions are hardly visible on the reproduction of the CCT, we have indicated the [100] direction by the solid line in the right upper part of the CCT. The oxide layer is completely flat and obviously exhibits two-dimensional growth mode. An interesting observation is that the step height between the clean (right top corner) and oxide covered part (left bottom corner) of the surface is extremely dependent on the sample bias voltage U. While for small U (some tenths of a volt or lower) the step height is 0 nm, for U=4 V (see Fig. 1) a step height of 0.3 nm is found, which is explained by additional contributions of tunneling electrons from the electronic states of Al oxide. In case of



Fig. 14. EEL spectra of different oxides [19,32,66-68].

small sample bias voltages electronic states in the oxide layer cannot take part in the tunneling process and only the metallic electrons of the substrate determine the tunneling current. It is surprising, on the other hand, that characteristic atomic structures of the oxide film remain visible in addition to the pattern of the substrate when using these smaller values of U (not shown here). The interpretation of the latter type of CCTs is not straightforward, however, since the image essentially reflects the spatial variation of the local tunnel barrier of the oxide film on the metal substrate.

LEED indicates a well ordered structure with a large unit cell in real space [31]. ISS measurements show that the oxide surface is oxygen terminated [58]. The analysis of the intensity distribution of the LEED spots points to a hexagonal or quasihexagonal arrangement of oxygen atoms in the terminating layer. This conclusion is corroborated by ARUPS measurements of the oxide band structure dispersion parallel to the surface. The experimental dispersion curves are shown in Fig. 13 [59] together with a computer simulation for a distorted hexagonal oxygen 2p band structure. The oxygen-oxygen distance in



Fig. 15. EEL spectrum ($E_p = 18 \text{ eV}$, $\theta_{in} = \theta_{out} = 45^{\circ}$) of IL CO on Al₂O₃/NiAl(110) at T = 35 K in comparison with details of the CO gas phase spectrum [66] ($E_p = 48 \text{ eV}$).

the quasihexagonal oxygen layer is about 6% larger compared with the bulk Al_2O_3 [60-65] but this is compatible with the limited thickness of the film. The dispersions have been measured with respect to the two azimuths (110, 100) of the NiAl substrate and these are not high symmetry directions with respect to the oxide brillouin zone. The calculations, which are described in detail elsewhere [59], reproduce the basic features of the band structure except for the two dispersions at the top and the bottom of the oxide band. These we assign to aluminium derived contributions indicating the aluminium-oxygen hybridization. What are the aluminium sites in the oxide? We believe from our HREELS data [19.32,66–68] that this oxide film is related to a $(111)\gamma$ -Al₂O₃ surface as revealed by Fig. 14. In this figure a comparison of HREEL spectra of different substrates is shown. While the spectrum of the thin film does not correlate with NiO or with α -Al₂O₃, it is similar to a thin Al₂O₃ layer grown on an Al single crystal surface. At the bottom a spectrum calculated for γ -Al₂O₃ is shown and compared with the data. The similarity is striking and becomes even stronger if we take into account that the film from which the spectrum was recorded was prepared by using ¹⁸O. Therefore our conclusion so far is that by oxidation we grow a distorted γ -Al₂O₃(111) surface on the NiAl(110) alloy surface.

Most molecules interact with the γ -Al₂O₃(111) surface rather weakly. As an example we show in Fig. 15 the ELS spectra of CO physisorbed on Al₂O₃



Fig. 16. EEL spectra of a ${}^{3}\pi$ state of CO on Al₂O₃/NiAl(110) for different coverages. We have fitted vibrational progressions to the experimental data. The inset shows TPD spectra.

taken at 35 K [59,32]. The ELS spectra of the multilayer system show a rather pronounced vibrational resolution of the electronically excited states. Comparison with gas phase spectra [69] shows a rather close correspondence. It is interesting to note that in the monolayer regime the line widths of the vibrational components increase and the bands shift to higher excitation energy which is demonstrated in Fig. 16 for the $\alpha^3\pi$ excitation of CO [32]. There are various CO states identifiable via their line positions and line widths in ELS and their TDS spectra (see the inset in Fig. 16). On the basis of such results we can estimate the pressure required to create a coverage similar to the low temperature situation at higher temperature. In Fig. 17 the temperature pressure relation for CO species A and B [59], giving rise to the correspondingly marked features in the TPD spectra is shown. Coverages and adsorption enthalphies were chosen as given in the figure. In order to create a coverage of $\theta=0.1$ at 500 K we required for species A a pressure of 1.03 bar and for species B 2.89 bar.

The next steps towards a closer approach of model catalysts is to deposit metals on the Al_2O_3 surface [70,71]. One important point is the structural characterization of such a composite system. Therefore a systematic study of



Fig. 17. Dependence of CO partial pressure on temperature for two CO species (A, B) on $Al_2O_3/NiAl(110)$, adsorption enthalpies have been derived from TPD data (see Fig. 16).



Fig. 18. CCT of an Al_2O_3 surface covered by 1/3 of a monolayer of Ag.



Fig. 19. Thermal desorption spectra of CO from ultra thin Pt films on γ -Al₂O₃(111)/NiAl(110). The Pt coverage (θ_{Pt}) is given in monolayers as calibrated using a quartz balance. The metal was deposited at room temperature. CO was adsorbed at 100 K.

the growth mode of metal deposits on the Al_2O_3 thin film surface has been started. The instrumentation used in the present measurements has been described elsewhere [72]. In Fig. 18 a CCT is displayed, where a 1/3 monolayer of Ag has been deposited by means of an effusion cell on to a completely oxidized NiAl(110) surface which was at room temperature. The Ag atoms condense as three-dimensional clusters with a height of 1–1.5 nm and a typical width of nearly 10 nm. These clusters are easily recognized on the surface. Note that the small protrusions also visible on the terraces are always found on clean and oxidized NiAl surfaces, they correspond to segregated impurities. The Ag



Fig. 20. HREELS spectra of CO on Pt/γ -Al₂O₃(111)/NiAl(110). (a) clean surface, (b) 0.3 monolayers of Pt deposited at 300 K and adsorption of 60 L CO at 90 K. (c) After heating to 800 K.

clusters are not spread uniformly over the sample but are concentrated along step edges, where they grow on both the upper and the lower terraces. We have to mention that the growth mode of Ag on clean NiAl(110) is completely different. In the latter case we observed a layer-by-layer growth mode. For partly oxidized surfaces the Ag deposit is only found on the metallic sites. This means that the interaction between the Ag deposit and the oxide film must be rather weak.

In addition to the study of Ag deposits we have started to investigate Pt deposits on the same substrate as well [70,71]. We have applied a variety of methods, such as ARUPS, HREELS, ELS, XPS and TPD, to study these ultra thin films. Here we briefly mention a series of TPD and corresponding HREELS results for CO adsorption on ultra thin Pt films of varying coverage. Figure 19 shows CO spectra which develop from low Pt coverages to high Pt

coverages into a typical TPD signal exhibited by a stepped Pt surface [73,74]. The CO TPD spectra of low coverage Pt films, which are shown in a separate panel on an expanded intensity scale, reveal in addition to the peak between 350 < T/K < 500 a low temperature feature, which is probably caused by the interaction of CO with the Al₂O₃ film. It is not clear at present whether this is relevant in the observed tendency for CO dissociation.

Figure 20 shows HREELS spectra of a film of intermediate metal coverage (0.3 ML). There are two results we would like to emphasize. Firstly, similar to the situation encountered for the Na/Cr₂O₃(111) system the Al₂O₃ phonons between 350 cm^{-1} and 1000 cm^{-1} are strongly attenuated relative to the elastic peak and the features are washed out. Secondly, in the region of the CO stretch frequencies we only find a single broad feature which is compatible with ontop bonding [73,74]. It is interesting to note that while the phonon features regain structure upon annealing the surface, the CO stretching frequency is not affected. A more detailed study of the concomitant structural changes are in progress [70,71] and may, when extended to even lower Pt coverage, reveal some mechanistic aspects of how CO dissociation takes place on these complex systems.

Conclusions

We have compared the adsorption behaviour of a reactive transition metal oxide, *i.e.*, $Cr_2O_3(111)$, with a non-reactive simple metal oxide, *i.e.*, $Al_2O_3(111)$. The electron spectroscopic measurements indicate that for $Cr_2O_3(111)$ the chromium ions in the surface are in a different oxidation state (Cr^{2+}) as compared with the bulk (Cr^{3+}). The distribution in the surface is not homogenous because the surface consists of oxygen and chromium terminated patches. Only the Cr-terminated patches contain Cr^{2+} ions which are oxidized to Cr^{3+} upon adsorption of various molecules, such as O_2 , NO_2 and CO_2 . Other molecules do not oxidize the surface but assume interesting adsorption geometries. CO lies flat on the Cr-terminated patches of the Cr_2O_3 [14] surface.

The simple metal oxide surface of γ -Al₂O₃(111) in contrast is rather inert with respect to the adsorption of molecules. CO, O₂ and several other molecules physisorb on the basically oxygen terminated Al₂O₃ surface. The energy dissipation into the substrate upon excitation is strongly reduced as compared with metal surfaces. This leads to the possibility of observing vibrationally resolved electronic ELS spectra.

Modification of the oxide surfaces with alkali (Cr_2O_3) or transition metal (Al_2O_3) has a strong influence on the vibrational spectra of the oxide surface. The phonons are strongly attenuated indicating the metallization of the oxide surface. It is interesting to study the structure of such films with STM and observe the clustering of metals on surfaces. Also the chemical reactivity of the oxide surfaces is modified upon metallization and two examples are briefly discussed.

Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft, the Bundesministerium für Forschung und Technologie, Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der Chemischen Industrie.

References

- 1 See for example: A.A. Davydov, Infrared Spectroscopy of Adsorbed Species on the Structure of Transition Metal Oxides, John Wiley & Sons, Chichester, 1990, and references cited therein.
- 2 V.E. Henrich, Rep. Prog. Phys., 48 (1985) 1481.
- 3 G. Heiland and H. Lüth, in D.A. King and D.P. Woodruff (eds.), The Chemical Physics of Solid Surfaces and Heterogenous Catalysis, Vol. 3, Elsevier, New York, 1982, chap. 4.
- 4 W. Hirschwald and D. Hofmann, Surf. Sci., 140 (1984) 415.
- 5 W. Hirsch, D. Hofmann and W. Hirschwald, Proc. 8th Int. Congr. Catal., IV-215, Berlin, 1984.
- 6 C.T. Au, W. Hirsch and W. Hirschwald, Surf. Sci., 199 (1988) 507.
- 7 C.T. Au, W. Hirsch and W. Hirschwald, Surf. Sci., 221 (1989) 113.
- 8 W.T. Petrie and J.M. Vohs, Surf. Sci., 245 (1991) 315.
- 9 J.M. Vohs and M.A. Barteau, Surf. Sci., 201 (1988) 481.
- 10 W. Göpel, R.S. Bauer and G. Hansson, Surf. Sci., 99 (1980) 138.
- 11 G. Zwicker and K. Jacobi, Surf. Sci., 131 (1983) 179.
- 12 D. Pösz, W. Ranke and K. Jacobi, Surf. Sci., 105 (1981) 77.
- 13 K.E. Smith and V.E. Henrich, Surf. Sci., 217 (1989) 445.
- 14 K.E. Smith and V.E. Henrich, J. Vac. Sci. Technol., A7 (1989) 1967.
- 15 K.S. Kim and M.A. Barteau, Surf. Sci., 223 (1989) 13.
- R.L. Kurtz, R. Stockbauer, T.E. Madey, E. Roman and J.L. DeSegovia, Surf. Sci., 218 (1989) 178.
- 17 W. Göpel, G. Rocker and R. Feierabend, Phys. Rev., B28 (1983) 3427.
- 18 W.J. Lo, Y.W. Chung and G.A. Somorjai, Surf. Sci., 71 (1978) 199.
- 19 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. Liedke and M. Neumann, *Phys. Rev.*, B43 (1991) 1969.
- 20 A. Boudriss and L.C. Dufour, in J. Nowotny and W. Weppner (eds.), New Stoichiometric Compound Surfaces, Grain Boundaries and Structural Defects, Kluwer, Amsterdam, 1989, pp. 311-320.
- 21 R.P. Furstenau and H.A. Langell, Surf. Sci., 159 (1985) 108.
- 22 P.M. Ferm, F. Budde, A.V. Hamza, S. Jakubith, G. Ertl, D. Weide, P. Andresen and H.-J. Freund, Surf. Sci., 128 (1989) 467.
- 23 D. Fargues and J.J. Ehrhardt, Surf. Sci., 209 (1989) 401.
- 24 M. Bäumer, D. Cappus, H. Kuhlenbeck, H.-J. Freund, G. Wilhelmi, A. Brodde and H. Neddermeyer, Surf. Sci., 253 (1991) 116.
- 25 M. Bäumer, D. Cappus, G. Illing, H. Kuhlenbeck, H.-J. Freund, K. Marre and H. Neddermeyer, J. Vac. Sci. Technol., A10 (1992) 2407.

- 26 H. Kuhlenbeck and H.-J. Freund, Proceedings of the 1st Australian-German Workshop in Surface Science, Springer Proceedings in Physics, in press.
- 27 C. Xu, B. Dillmann, H. Kuhlenbeck and H.-J. Freund, Phys. Rev. Lett., 67 (1991) 3551.
- 28 C. Xu, M. Hassel, H. Kuhlenbeck and H.-J. Freund, Surf. Sci., 258 (1991) 23.
- 29 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. Phys. Chem.*, 96 (1992) 15.
- 30 C.A. Ventrice, Jr., D. Ehrlich, E.L. Garfunkel, B. Dillmann, D. Heskett and H.-J. Freund, *Phys. Rev. B*, 46 (1992).
- 31 R.M. Jaeger, K. Homann, H. Kuhlenbeck and H.-J. Freund, Chem. Phys. Lett., submitted.
- 32 R.M. Jaeger, H. Kuhlenbeck, H.-J. Freund, M. Wuttig, W. Hoffmann, R. Franchy and H. Ibach, Surf. Sci., 259 (1991) 235.
- 33 P. Michel and C. Jardin, Surf. Sci., 36 (1973) 478.
- 34 S. Ekelund and C. Leygraf, Surf. Sci., 40 (1973) 79.
- 35 M. Haßel, Diplomarbeit, Ruhr-Universität Bochum (1991).
- 36 Y. Sakisaka, H. Kato and M. Onchi, Surf. Sci., 120 (1982) 150.
- 37 C.K. Jorgensen, Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press, Oxford, 1962.
- 38 W.E. Hobbs, J. Chem. Phys., 28 (1958) 1220.
- 39 A. Zecchina, S. Coluccia, L. Cerruti and E. Borello, J. Phys. Chem., 75 (1971) 2783.
- 40 F.A. Miller, G.L. Carlson and W.B. White, Spectrochim. Acta, 15 (1959) 709.; W.E. Hobbs, J. Chem. Phys., 28 (1958) 1220.
- 41 E.W. Plummer and W. Eberhardt, Adv. Chem. Phys., 49 (1982) 533.
- 42 H.-J. Freund and M. Neumann, Appl. Phys., A47 (1988) 3.
- 43 D. Schmeisser, F. Greuter, E.W. Plummer and H.-J. Freund, Phys. Rev. Lett., 54 (1985) 2095.
- 44 C. Jacobi, C. Astaldi, P. Geng and M. Bertolo, Surf. Sci., 223 (1989) 569.
- 45 H.-J. Freund, W. Eberhardt, D. Heskett and E.W. Plummer, Phys. Rev. Lett., 50 (1983) 768.
- 46 C. Schneider, H.-P. Steinrück, P. Heimann, T. Pache, M. Glanz, K. Eberle, E. Umbach and D. Menzel, BESSY Annual Report, 1987 (unpublished).
- 47 D.W. Turner, C. Baker, A.D. Baker and C.R. Brundle, *Molecular Photoelectron Spectros*copy, Wiley-Interscience, New York, 1970.
- 48 N.D. Shinn, J. Vac. Sci. Technol., A41 (1986) 1351.
- 49 K. Siegbahn, C. Nordling, G. Johannson, J. Hedman, P.F. Heden, K. Kamrin, U. Gelius, T. Bergmark, L.O. Werme, R. Manne and Y. Baer, ESCA Applied to Free Molecules, North-Holland, Amsterdam, 1971.
- 50 I. Hemmerich, Thesis, Ruhr-Universität Bochum, in preparation.
- 51 C. Lin, T. Ito, J. Wang and J.H. Lunsford, J. Am. Chem. Soc., 109 (1987) 4808.
- 52 X. Zhang, R.K. Ungar and R.M. Lambert, J. Chem. Soc. Chem. Commun., 8 (1989) 473.
- 53 J. Wambach, G. Odörfer, H.-J. Freund, H. Kuhlenbeck and M. Neumann, Surf. Sci., 209 (1989) 159.
- 54 J.A. Connor, M. Considine and I.H. Hillier, J. Electron. Spectrosc. Relat. Phenom., 12 (1977) 143.
- 55 P.A. Thiel and T.E. Madey, Surf. Sci. Rep., 7 (1987) 211.
- 56 E. Meyer, H. Heinzelmann, D. Brodbeck, G. Overney, L. Howald, H. Hug, T. Jung, H.-R. Hidber and H.-J. Güntherodt, J. Vac. Sci. Technol., B9 (1991) 1329.
- 57 G. Binning, C. Gerber, E. Stoll, T.R. Albrecht and C.F. Quate, *Europhys. Lett.*, 3 (1987) 1281.
- 58 Th. Bertrams and H. Neddermeyer, unpublished data.
- 59 R.M. Jaeger, Thesis, Ruhr-Universität Bochum, (1992).
- 60 K.P. Sinha and A.P.B. Sinha, J. Phys. Chem., 61 (1957) 758.
- 61 H.D. Megaw, Crystal Structures: A Working Approach, Saunders, Philadelphia, PA, 1973, pp. 226ff.

- 62 G. Yamaguchi, I. Yasui and W.-C. Chiu, Bull. Chem. Soc. Jpn., 43 (1970) 2487.
- 63 Struct. Rep., Aust. Aeronaut. Res. Lab., 13 (1950) 223.
- 64 Struct. Rep., Aust. Aeronaut. Res. Lab., 43A (1977) 348.
- 65 Gmelins Handbuch der anorganischen Chemie, 8th edn. Verlag Chemie, Weinheim, 1953, p. 78.
- 66 J.L. Erskine and R.L. Strong, Phys. Rev., B 25 (1982) 5547.
- 67 M. Liehr, P.A. Thiery, J.J. Pireaux and R. Caudano, J. Vac. Sci. Technol., A 2 (1984) 1079.
- 68 A. Rizzi and A. Förster, personal communication.
- 69 E.N. Lassettre, Can. J. Chem., 47 (1969) 1733.
- 70 F. Winkelmann, Thesis, Ruhr-Universität Bochum, in preparation.
- 71 S. Wohlrab, Thesis, Ruhr-Universität Bochum, in preparation.
- 72 Th. Berghaus, A. Brodde, H. Neddermeyer and St. Tosch, Surf. Sci., 184 (1987) 273.
- 73 B.E. Hayden, K. Kretschmar, A.M. Bradshaw and R.G. Grauler, Surf. Sci., 149 (1985) 394.
- 74 H. Steininger, S. Lehwald and H. Ibach, Surf. Sci., 123 (1982) 264.