Adsorption and Reaction on Oxide Surfaces: CO and CO₂ on Cr₂O₃(111)

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Adsorption / Spectroscopy, Photoelectron / Surfaces

We have investigated the adsorption of CO and CO₂ on epitaxially grown $Cr_2O_3(111)$ by means of EELS, LEED, ARUPS, NEXAFS and XPS. CO is found to adsorb on the oxide surface in an ordered $(|\sqrt{3} \times |\sqrt{3})R30^\circ$ structure with the molecular axis oriented approximately parallel to the surface. CO₂ on the other hand reacts with the chromium oxide to form a surface carbonate. Adsorption of CO, respectively reaction of CO₂ only takes place on a clean, freshly flashed oxide surface. Preadsorption of oxygen leads to a surface which is rather inert to adsorption, likely due to electronic or steric reasons.

1. Introduction

Oxides are commonly used as supports for many technically important catalysts. For this reason the first studies of adsorption on oxides have already been performed in the fifties [1,2]. In the literature kinetic data like reaction orders and reaction rates may be found for many reactions on model catalysts [3]. These data provide empirical information but often a model for the microscopic electronic and geometric properties of these systems is missing. However, in order to derive a systematic understanding of the elementary processes of catalysis microscopic models are strongly needed.

One first approach to this goal is the study of adsorption on well defined oxide single crystal surfaces under UHV conditions applying surface science methodology. Such studies should allow to get information on the geometric and electronic structure of the adsorbate and on the adsorbate/substrate interaction. One problen 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 crystalline 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 [4] and Heiland and Lüth [5]. The best characterized systems are probably ZnO [6-14] and TiO₂ [15-20] where data are even available for adsorbates on cleaved surfaces of these oxides. For benzene on ZnO(10I0) an ordered structure could be observed [14]. Less data are available for adsorbates on NiO(100) [21-25].

Concerning Cr_2O_3 much is known about adsorption on powder samples [26, 27]. The catalytic activity of this oxide for various reactions, like for instance polymerization of olefines [28], hydrogenation of alkenes [29], reduction of NO and decomposition of N_2O_4 [26] is rather high. A single crystalline film of this oxide with (111) orientation can be grown by oxydation of Cr(110). For clean films some electron spectroscopic data are available [30-33]. Also, data are published for the adsorption of O_2 on such a film [34].

In this paper we will deal with the adsorption of CO and CO_2 on an epitaxially grown $Cr_2O_3(111)$ film. We have employed several surface sensitive electron spectroscopic methods like EELS (Electron Energy Loss Spectroscopy), LEED (Low Energy Electron Diffraction), ARUPS (Angle Resolved Ultraviolet Photoelectron Spectroscopy), NEXAFS (Near Edge X-ray Absorption Fine Structure) and XPS (X-ray Photoelectron Spectroscopy). The discussion is divided into three parts. First, some structural and electronic properties of the clean and oxygen covered $Cr_2O_3(111)$ surface are discussed. These informations are needed for the interpretation of the CO and CO_2 data which are presented next.

As will be shown in the following adsorption, respectively reaction of CO and CO₂ only takes place on a clean, freshly flashed $Cr_2O_3(111)$ surface. Such a surface exhibits chromium ions that are at least partly in a 2+ oxidation state whereas the chromium bulk ions are in a 3+ oxidation state. The adsorption of oxygen leads to a surface where a part of the surface chromium ions is hidden by oxygen atoms and no Cr^{2+} signal can be observed. On this surface adsorption, respectively reaction is strongly hindered. It appears that the presence of Cr^{2+} ions together with the free accessibility of the surface chromium ions is responsible for the high reactivity of the clean, flashed $Cr_2O_3(111)$ surface.

2. Experimental

The experiments have been performed in four different UHV systems. All systems contain facilities for LEED, AES and residual gas analysis with a quadrupole mass spectrometer. For the vibronic HREELS investigations we have used a system of the type ELS 22 (Leybold AG) equipped with a double cyclinder electron mono-

Ber. Bunsenges. Phys. Chem. 96 (1992) No. 1 © VCH Verlagsgesellschaft mbH, W-6940 Weinheim, 1991 0005-9021/92/0101-0015 \$ 3.50 + .25/0

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chromator and analyser. The resolution was typically set to 8 meV. The other three UHV systems contain a hemispherical electron analyser mounted on a double axis goniometer for angular resolved electron detection. For the NEXAFS and ARUPS experiments the electrons were excited with light from the HETGM2 and TGM2 beamlines at the BESSY synchrotron radiation center in Berlin with resolutions of about 300 meV and 100 meV, respectively. The chamber used for electronic EELS experiments additionally contains a hemispherical electron monochromator with medium to high resolution. In this case the experimental resolution was about 150 meV.

The samples were spotwelded to two tungsten wires which were connected to two tungsten rods mounted on a liquid nitrogen reservoir which allowed cooling down to about 100 K. Heating was possible either via electron bombardment from a filament mounted



Fig. la LEED pattern of clean Cr2O3(111)

behind the crystal or by passing a current through the tungsten wires.

The Cr(110) samples were cleaned by prolonged sputtering with Ne ions at elevated temperatures (900 K). When AES indicated that the contaminations, consisting mostly of oxygen, carbon and nitrogen, were strongly reduced the crystal was oxidized. This was achieved by annealing the sample to T = 500 K in an atmosphere of 10⁻⁶ mbar oxygen for a time of 3 minutes. After this treatment the sample was annealed to T = 1000 K to remove excess oxygen from the surface. On this oxide no nitrogen or carbon impurities could be detected by AES and the LEED pattern exhibited a well defined hexagonal pattern of Cr₂O₃(111) with missing substrate spots.

CO and CO_2 were adsorbed at a temperature of about 100 K. CO is easily desorbed upon irradition with electrons or UV-light. Due to this sensitivity the ARUP spectra of the CO adsorbate could only be taken with a background pressure of CO of about 5 · 10⁻⁵ mbar. The oxygen covered surface was prepared by adsorption of about 50 L O₂ at about 100 K with subsequent annealing to T =400 K.

3. Results and Discussion

3.1. The $Cr_2O_3(111)$ surface

In Fig. 1a a LEED pattern of a clean Cr₂O₃(111) oxide film expitaxially grown on Cr(110) is shown. The spots are arranged in a hexagonal manner as expected for this oxide surface [30, 31]. They are somewhat broader than the spots usually observed for clean and well ordered single crystal surfaces indicating the presence of an appreciable amount 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(100) substrate are visible in the LEED pattern of the oxide film.

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



Fig. 1b

Structural models for two differently terminated Cr₂O₃(111) surfaces. For these models it has been assumed that the arrangement of atoms at the surface is equal to the arrangement of atoms in the bulk. The left panel shows an oxygen terminated surface and on the right panel a chromium terminated surface is shown

and a chromium terminated surface. The atomic arrangement of these surfaces in shown in Fig. 1b. It should however be noted that these plots show ideal terminations; the real surface terminations may be somewhat different from the ones shown here.

In Fig. 2 a set of EEL spectra, taken with a primary electron energy of $E_p = 100$ eV is shown. The spectrum at the bottom is that of a clean, freshly flashed oxide surface. Upon adsorption of O₂ a strong loss peak develops at about 9 eV. Similar losses are observed upon CO₂ and NO₂ adsorption. Losses in this energetic range are attributed to oxygen-chromium charge-transfer excitations [35]. Since CO₂, NO₂, and O₂ react with the surface we interpret this loss to be characteristic for surface chromium-oxygen bonds. For CO₂ adsorption the situation is somewhat different as compared to O₂ and NO₂ in that CO₂ reacts to form carbonate. This difference is also documented in the different peak shape of the loss at about 9 eV.



Fig. 2 EELS spectra for different adsorbates on $Cr_2O_3(111)$ taken with a primary energy of $E_p = 100 \text{ eV}$

CO and NO on the other hand adsorb without any signs of dissociation or reaction. Accordingly in these cases the strong loss at 9 eV is not observed. Another interesting feature in these spectra is the 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 one 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 an 2+ oxidation state because for compounds containing Cr^{2+} ions the energy needed for the d-d excitation [36] is near to the 1.2 eV observed in our ELS spectra.

This interpretation is corroborated by Cr2p-XP spectra [37] where a peak at the lower binding side of the $Cr2p_{3,2}$ main line is observed, which is attenuated by oxygen adsorption. The difference in binding energy between these two lines is consistent with differences in binding energies reported for compounds containing Cr^{2+} and Cr^{3+} ions [37].

In Fig. 3 ISS spectra for freshly flashed $Cr_2O_3(111)$ and for oxygen covered $Cr_2O_3(111)$ are compared. ISS spectra are very surface sensitive and so it can be expected that the signal intensity reflects the atomic surface composition. Obviously the chromium signal is attenuated by a factor of about two upon oxygen adsorption indicating that only a part of the surface chromium ion is covered by oxygen on the oxygen dosed surface.



Fig. 3

ISS spectrum of a clean, freshly flashed Cr₂O₃(111) surface in comparison with a spectrum of an oxygen dosed surface

To get informations on the interaction of the Cr ions with oxygen we have investigated the adsorption of oxygen using HREELS, ARUPS and TDS. In Fig. 4 ARUP spectra are shown for O₂ and NO₂ adsorbed on Cr₂O₃(111) in comparison with a spectrum of a flashed surface. Upon adsorption of oxygen at 100 K additional intensity is observed at 7.5 eV and 8.8 eV binding energy. Thirty minutes later the intensity of the 8.8 eV feature has decreased whereas the state at 7.5 eV has gained intensity. Now the spectrum looks quite similar to the one of the NO2 dosed surface. NO2 is known to dissociate upon adsorption on Cr₂O₃(111) into NO and atomic oxygen [37]. The NO molecules are easily desorbed upon irradiation with UV light [37] and so only the atomic oxygen species remains on the surface. Therefore the spectrum of the NO₂ dosed surface is characteristic for a Cr₂O₃(111) surface covered with atomic oxygen. The similarity of this spectrum to the one of the oxygen covered oxide taken thirty minutes after preparation indicates that the oxygen molecules are dissociated, forming a layer of atomic oxygen. This similarity is also found in the ELS spectra presented in Fig. 2 which is an additional hint concerning the dissociation of molecular oxygen on Cr2O3(111).



ARUP spectra for O_2 and NO_2 dosed $Cr_2O_3(111)$ surfaces in comparison with a spectrum of the clean oxide surface

The differences between the oxygen spectrum taken immediately after preparation and the one taken thirty minutes later are probably connected with the desorption of O_2^- and/ or the conversion of O_2^- to atomic oxygen. As has been shown by Davydov [27] the adsorption of oxygen on Cr₂O₃ powder at room temperature leads to the presence of atomic O^{2-} ions and molecular $O_{\overline{2}}$ on the surface where the amount of the latter species should depend on the sample pretreatment. Emissions of $O_{\overline{2}}$ are to be found at about 8 eV binding energy [38] which is near to the peak at 8.75 eV found in our ARUPS data for oxygen on Cr₂O₃(111) (see Fig. 4) so that this peak is probably an indication of the presence of $O_{\overline{2}}$ on the oxygen dosed chromium oxide. Additional information is supplied by the HREEL spectra shown in Fig. 5. The spectrum at the bottom is that of a clean, freshly flashed Cr₂O₃(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 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 [27] so that this loss could in principle be attributed to molecularly adsorbed oxygen. However, it seems to be 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 splitted off from the neighboring oxide phonon loss by the interaction of the chromium oxide with the adsorbed oxygen.



Fig. 5

HREEL spectra of oxygen dosed $Cr_2O_3(111)$ taken at different temperatures in comparison with a spectrum of a clean $Cr_2O_3(111)$ surface

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 [27, 39, 40] or to the O-Ovibration of molecular O_2^- [27]. The shift of the loss at 967 cm⁻¹ (T = 100 K) to 1003^{-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 (see Fig. 6) we observe around T = 200 K desorption signals of molecular oxygen, mass 32 so that the shift in the HREEL spectra is most likely connected with these signals. According to Davydov [27] oxygen adsorbs at low temperatures on some oxides, including Cr₂O₃, also in a molecular uncharged form. These oxygen molecules should desorb at about T = 170 K to $\dot{T} = 200$ K so that the desorption signals around T = 200 K are most likely due to such uncharged oxygen molecules. In this context the shift of the loss at 967 cm⁻¹ to 1003 cm⁻¹ at about T = 200 K is most likely to be attributed to the interaction of the surface O^{2-} ions with the uncharged oxygen molecules. Due to the dipole selection rules molecular oxygen should only lead to a small HREELS signal (1460 cm⁻¹ for Cr₂O₃ [27]) which might by invisible in the spectra.





TD spectrum (mass 32, O_2) obtained from an oxygen dosed $Cr_2O_3(111)$ surface. Oxygen was admitted at T = 100 K

Another possible explanation for the shift of the peak at 967 cm⁻¹ would be the dissociation of the O_2^- molecules at this temperature but this process must be considered to be rather unlikely because the latter species should be stable up to 100° or 200° above room temperature [27]. The molecular uncharged oxygen species could no be observed in the ARUPS spectra of the oxygen adsorbate taken at low temperature. This is not a contradiction to the conclusion drawn above since CO as well as NO [37] are easily desorbed upon irradiation with UV light and so it is not unreasonable to assume that this is also the case for molecular oxygen. The TD spectrum shown in Fig. 6 is somewhat different to a TD spectrum of oxygen adsorbed on epitaxially grown Cr₂O₃(111) published by Foord et al. [34]. The authors adsorbed oxygen at room temperature and observed desorption signals at about 400 K and 950 K. We did not observe desorption signals at about 400 K even in TD spectra from an oxygen adsorbate prepared at room temperature. Whether this difference is due to differences in the preparation of the oxide film, to differences in the preparation of the oxygen adsorbate, or to differences in the technical equipment can, however, not be decided from present data.

Putting together the results of the ISS, HREELS, ARUPS, and TDS investigations we arrive at a model for the oxide surface covered with atomic oxygen where approximately every second surface chromium ion is hidden by an oxygen ion in ISS. As indicated by ELS (see Fig. 2) such a surface does not exhibit Cr^{2+} ions. This means that either on the flashed surface only part of the Cr ions is in a 2+ state, i.e. those which interact with the oxygen molecules, or that all surface chromium ions are influenced by the presence of the oxygen ions. Considering this the inertness of the oxygen covered surface may be attributed to the missing of Cr^{2+} ions and to the somewhat hindered access to the remaining chromium surface atoms.

3.2. Adsorption of CO

3.2.1. LEED and TDS

Upon adsorption of CO on $Cr_2O_3(111)$ a $(\sqrt{3} \times \sqrt{3})$ R 30° superstructure is observed in LEED. This superstructure is very sensitive to electron and photon irradiation; the LEED pattern faints after several seconds of observation. Due to this sensitivity it was not possible to obtain a good photograph of this pattern.

CO desorbs from $Cr_2O_3(111)$ at T = 160 K as revealed by the TD spectrum shown in the top of Fig. 7. The adsorption enthalpy as calculated by the Redhead formula [41] is about 43 kJ/mol which classifies the CO molecules to be weakly chemisorbed. In the bottom of Fig. 7 a TD spectrum for CO adsorbed on a $Cr_2O_3(111)$ surface precovered with oxygen is shown. In agreement with the discussion in the previous chapter the pressure signal is strongly attenuated clearly indicating that the adsorption of CO is strongly hindered on an oxygen precovered surface.



Fig. 7

Comparison of TD spectra for CO adsorbed on a clean, freshly flashed $Cr_2O_3(111)$ surface and CO adsorbed on an oxygen predosed $Cr_2O_3(111)$ surface

3.2.2. ARUPS

Some information on the molecular orientation of the CO molecules is supplied by the ARUP spectra shown in Fig. 8. The spectra have been recorded with a fixed angle, i.e. 90°, between the incident light beam and the direction of electron detection. It is well known that the σ valence states of CO, i.e. 4σ and 5σ , emit strongest along the molecular axis if the electric field vector of the exciting light points along this axis [42]. Thus from the intensity of the σ ionizations as a function of the experimental geometry the orientation of the molecules may be deduced. Two CO induced features are visible in Fig. 8 which are most intense at near perpendicular light incidence and accordingly near grazing electron exit angles. These peaks are located at binding energies of 11.8 eV and 14.3 eV with respect to the Fermi level which are rather high binding energies for CO valence states. To identify these features we consider the photon energy dependence of the cross sections of the CO valence states. It is well known that the σ valence states of the CO molecules emit strongly at the photon energy the spectra have been taken with, i.e. 36 eV, due to the presence of the σ shape resonance whereas the π states are rather weak at this photon energy [42-44]. For this reason we identify the ionizations at 14.3 eV and 11.8 eV binding energy to be due to the σ valence states of the CO molecules. The observation that these states emit strongest at near perpendicular light incidence and near grazing electron excidence then means that the CO molecules must by lying more or less flat on the surface. In agreement with this finding we observe the σ shape resonance of the σ ion states at grazing electron exit angles whereas no intensity resonance is observed at normal electron emission as shown in Fig. 9. The 1π inten-



Fig. 8 Series of ARUP spectra for CO adsorbed on $Cr_2O_3(111)$. The spectra have been taken such that the electron exit angle was always equivalent to the direction of the electric field vector of the incident light. For comparison also in each case a spectrum of a flashed $Cr_2O_3(111)$ surface is shown

sity has been obtained by a fitting procedure assuming the 1π ionization to be situated near to the 4σ ionization as explained below.





Intensities of the CO valence ionizations as a function of photon energy plotted for two different experimental geometries. Upper panel: near perpendicular light incidence and grazing electron detection ($\Theta = 70^{\circ}$). Lower panel: grazing light incidence and normal electron detection ($\Theta = 0^{\circ}$).

This result is consistent with ARUP spectra taken in the so called allowed and forbidden geometries as shown in Fig. 10. The experimental geometries may be read off from the inset in this figure. For CO molecules standing upright on the surface the σ valence states should only be observable in the allowed geometry whereas in the forbidden geometry only the 1π levels should show up. But obviously there is nearly no difference between the two experimental geometries concerning the intensities of the CO induced features. This means that the CO molecules can not be standing upright on the surface. They must be strongly tilted. An open question at the moment is: where are the 1π orbitals. For CO molecules lying flat on the surface the 1π orbitals are expected to be split into two components for symmetry reasons. One component should be oriented parallel to the surface $(1\pi_{xy})$ whereas the other one should stick out of the surface plane $(1\pi_z)$. The $1\pi_{xy}$ level should be intense at angles where the σ levels are also intense because the latter levels are also oriented parallel to the surface plane. This means that the $1\pi_{xy}$ emission might be hidden below the strong σ emissions. The situation is different for the $1\pi_z$ orbital. Its emission should be intense when the σ emission is weak, i.e. at normal electron emission. The $1\pi_z$ level will interact strongly with the substrate. This interaction will shift this level to higher binding energy because the substrate levels are located at lower binding energy than the 1π orbitals. Thus the $1\pi_r$ level is most likely not energetically situated in the region of the substrate levels but below the substrate levels. As can be seen from the spectra shown in Fig. 8 the 5 σ emission at 11.8 eV binding energy is totally suppressed at near normal electron emission. If the $1\pi_z$ level were located near to the 5σ level there should be some remaining intensity since the $1\pi_z$ level would show up in this geometry. This means that for CO adsorbed on $Cr_2O_3(111)$ the $1\pi_2$ valence ionization is not energetically close to the 5σ ionization as is the case for CO on most metals.



Fig. 10

Comparison of ARUP spectra of CO adsorbed on $Cr_2O_3(111)$ taken in the so called allowed and forbidden geometries

Inspection of Fig. 8 shows that whereas the 5σ emission is nearly totally supressed at near normal electron exit angles a broad feature remains in the region of the 4σ emission between 13 eV and 16 eV. Since the 4σ and 5σ intensities should behave similar to some extent it is tempting to attribute the remaining intensity between 13 eV and 16 eV to the CO $1\pi_{z}$ level. If this is true then the energetic position of this level indicates that its interaction with the substrate must be really strong and that it is different from all the cases observed so far. In Fig. 11a comparison of CO binding energies for different substrates is shown [45-50]. The binding energies are referenced to the vacuum levels of the respective adsorbate system. For CO adsorbed on Cr₂O₃(111) the binding energies of all valence levels are larger than the binding energies observed so far for metallic substrates. This is especially true for the $1\pi_z$ level. Assuming the Cr₂O₃(111) surface to be bulk terminated we propose a model of the adsorbate geometry as shown in Fig. 12. The CO 4σ and 5σ lone pairs interact with two different chromium atoms building up σ bonds towards these ions. These bonds shift the σ levels to higher binding energies. The 1π levels on the other hand additionally interact with the oxygen atoms below the molecule. Since the O^{2-} ions are in a closed shell configuration this interaction will be basically repulsive. The O²⁻ levels of the oxide are situated at lower binding energies than the CO 1π levels so that O^{2-} levels will be shifted to lower binding energies whereas the 1π levels are energetically stabilized. Although there are some changes visible in the spectra in the region of the oxide O^{2-} levels the effect on these levels is hard to judge. The effect on the $1\pi_2$ level on the other hand, i.e. the pronounced downward shift, is obvious from Fig. 11. Since the interaction of the 1π levels with the oxygen atoms will be repulsive the interaction of the σ orbitals with the chromium atoms must be bonding because otherwise the CO molecules would not adsorb on the surface. It is evident from this discussion that the bonding of CO to $Cr_2O_3(111)$ is different from the bonding of CO to all metallic surfaces investigated so far.



Fig. 11

Comparison of electronic valence binding energies for CO adsorbed on different substrates. The binding energies are referenced to the vacuum level of the respective adsorption system. Since we do not know the work function for CO/Cr(110) we have hatched the regions in which we expect to ionization to occur. Data have been taken from refs [45-50]



Fig. 12 Structural model for CO $(\sqrt{3} \times \sqrt{3})$ R 30°/Cr₂O₃(111). The adsorbate unit cell is indicated

As can be seen from Fig. 8 the intensities of the valence ionizations of CO on $Cr_2O_3(111)$ are similar to intensities observed for CO on metallic surfaces. In order to bring the CO coverage near to the coverage of CO on Ag(111) or N₂ on graphite where the molecules are also lying flat on the surface we had to put three CO molecules into the $(1/3 \times 1/3)$ R 30° unit cell of CO on $Cr_2O_3(111)$ as shown in Fig. 12. The adsorbate unit cell is indicated in this figure. In case the unit cell contains only one molecule only the CO molecules at the edges of the indicated unit cell have to be considered.

3.2.3. NEXAFS

To deduce additional informations concerning the adsorption geometry of CO on $Cr_2O_3(111)$ we have performed NEXAFS investigations at the BESSY synchrotron radiation center. In Fig. 13 a series of NEXAF spectra taken at the C1s absorption edge are shown. The spectra have been recorded with different angles of light incidence with respect to the sample normal. At the botton a spectrum of the clean $Cr_2O_3(111)$ surface is shown. The features in this spectrum are all normal photoemission peaks of the oxide with the largest one being due to the O2s ionization. Upon adsorption of CO two additional features get visible. The sharp one at 286.0 eV is due to the C1s $\rightarrow 2\pi$ excitation, the so



Fig. 13

C1s NEXAF spectra of CO adsorbed on $Cr_2O_3(111)$ for different angles of light incidence

called π -resonance, and the broad feature at about 305 eV corresponds to an excitation of a C1s electron into the 60 continuum state, i.e. the σ -resonance. Since the intensities of these excitations are governed by dipole selection rules they can be used to get informations concerning the adsorption geometry of the adsorbate molecules. The C1s \rightarrow 2π excitation is only possible if the component of the electric field of the light perpendicular to the molecular axis is different from zero whereas for the σ-resonance light polarized parallel to the molecular axis is needed. It has been shown that from the ratio of the intensity of the C1s $\rightarrow \sigma$ excitation versus the intensity of the the C1s $\rightarrow \pi$ excitation as a function of the light incidence angle the molecular orientation can be deduced [51, 52]. Since it is difficult to obtain the intensity of the C1s $\rightarrow \sigma$ excitation sufficiently exact from these spectra only the behaviour the the π -resonance shall be discussed. If all CO molecules were standing upright on the surface the intensity of the C1s $\rightarrow \pi$ excitation should be largest at normal incidence of the light whereas at grazing incidence the intensity should go towards zero. For molecules lying flat on the surface with random azimuthal oriention the intensity of the C1s $\rightarrow \pi$ resonance will only weakly depend on the light incidence angle. In a $(1/3 \times$ $\sqrt{3}$ R 30° structure of CO on Cr₂O₃(111) with flat lying molecules the molecular axes are more or less randomly oriented due to the three possible overlayer domains. Obviously the spectra shown in Fig. 13 are more consistent with a flat orientation of the molecules.

3.2.4. HREELS

In Fig. 14 a HREEL spectrum for CO on $Cr_2O_3(111)$ is shown in comparison with a spectrum of the clean, flashed surface. For the clean surface several intense features are observed due to electrons that are singly and multiply scattered by the optical phonons of the chromium oxide. Upon CO adsorption an additional loss develops at 320 cm⁻¹ which is possibly due to the vibration of the CO molecules versus the oxide substrate. The C-O vibrational loss itself





HREEL spectrum of CO on $Cr_2O_3(111)$ in comparison with a spectrum of the clean, freshly flashed oxide surface. In the inset the full spectra are shown. Two parts of these spectra are reproduced on an extended scale

is very weak. It is found at $2167 \pm 12 \text{ cm}^{-1}$, near to the third overtone of the strongest oxide phonon. This frequency is similar to the CO gas phase value (2143 cm⁻¹ [53]) which indicates that the structure of the molecules is not too much perturbed by the presence of the oxide surface.

Knözinger and coworkers [53] have investigated the adsorption of CO on Cr₂O₃ powder samples with IR spectroscopy. The microcrystals of such a sample preferentially expose basal hexagonal faces which correspond to the (111) surface and prismatic faces to the vacuum so that in the IR spectra a superposition of vibrational losses of CO molecules adsorbed on these surfaces is observed. At 77 K and 100 K the most prominent feature in the spectra of Knözinger et al. is found at 2164 cm^{-1} which is quite near to the loss energy of the C-O stretching vibrations of CO adsorbed on the exitaxially grown Cr₂O₃(111) layer. They attribute this loss to CO adsorbed on Cr3+ ions on the prismatic oxide surfaces. If this loss corresponds to the loss at 2167 cm^{-1} for CO on the expitaxially grown surface then the assignment of Knözinger et al. must be doubted since the oxide film does not expose prismatic faces to the vacuum. It can also be ruled out that the CO molecules mainly adsorb on Cr_{5c}^{3+} defects existing somewhere on the surface since in this case we would not have observed a CO induced superstructure in the LEED pattern.

The C-O vibrational loss at 2164 cm^{-1} as observed by Knözinger et al. on the powder sample has an intensity which is quite normal whereas the loss observed with HREELS on the expitaxially grown oxide is comparably weak. It is rather probable that in the case of the the epitaxially grown oxide the C-O vibrational loss is weakened by the existence of the chromium metal below the oxide film. The charge of the slow incident electron and its image charge in the metal build up a dipole with a vanishing component of the electric field parallel to the surface (E_{\parallel}) at the oxide-metal interface so that in first order in this plane no interaction with dipole moments oriented parallel to the surface is possible. At the oxide surface, however, E_{\parallel} is different from zero, with the actual field intensity depending on the distance of the electron to the surface and on the thickness of the oxide film. The typical electron molecule spacing for the electron-dipole interaction is about 60 Å [54] which is larger than the thickness of the oxide film (about 50 Å) so that E_{\parallel} at the oxide surface will be rather weak. This in turn means that the C-O vibrational loss must be weak too since the CO molecular axis is oriented more or less parallel to the surface.

3.2.5. XPS

We have studied the ionization of the CO C1s and O1s core levels with XPS to get informations on the shake up structure of these levels and thus on the interaction of the adsorbate with the substrate. Although we used monochromatized $Al_{k\alpha}$ radiation we could not separate the CO O1s ionization from the oxide O1s level. The C1s level (see Fig. 15) on the other hand was clearly visible, but it turned out to be very broad (about 3 eV). We could not resolve a clear fine structure in the C1s peak but its broadness points

towards the existence of shake up states respectively different molecular species on the surface. In view of our TDS, HREELS and ARUPS results which did not yield any eyidence for the existence of different CO species on the surface we infer that the broadness of the C1s level is most likely due to shake up states concerned with the adsorbate-substrate interaction. Shake up's have often been observed for weakly chemisorbed CO and N₂ molecules on metals, like CO on Cu, Ag, Au and N₂ on Ni [55-61]. Concerning the adsorption of small molecules on oxide surfaces not so much is known about shake up structures in the adsorbate core level spectra. Recently we have reported on the adsorption of NO on NiO(100) [21] where the NO N1s core level exhibits a pronounced splitting due to the interaction of the NO molecules with the NiO surface. This is to our knowledge the first observation of such a splitting. The adsorption enthalpy of NO on NiO(110) is similar to the adsorption enthalpy of CO on $Cr_2O_3(111)$, i.e. both adsorbates are weakly chemisorbed. Since for weakly chemisorbed adsorbates pronounced shake up structures in the core level ionization are quite usual as has been shown for adsorption on metals [55-61] the existence of shake up structures in the C1s core level for CO on $Cr_2O_3(111)$ seems to be a proper explanation for the broadness of this level in the XP spectrum. The binding energy of the center of the C1s ionization peak is 290.8 eV with respect to the Fermi level and 296.6 eV with respect to the vacuum level. The latter value is near to the gas phase value of CO (295.9 eV [62]) which means that the electronic structure of the CO molecules is not too much distorted by adsorption on chromium oxide. It is, however, remarkable the the C1s ionization energy is slightly larger than the gas phase value. This observation is in line with the observed shift of the valence ionizations to higher binding energies as compared to the gas phase values and might be connected with the strong electric field existing at the oxide surface.



Fig. 15

C1s XP spectrum for CO adsorbed on $Cr_2O_3(111)$ taken with monochromatized Al_{K_2} radiation

3.3. Adsorption of CO₂

As has already been mentioned in chapter 3 CO_2 reacts with the surface even at low temperatures to form a carbonate species. In the electrohid EELS spectra shown in Fig. 2 the $CO_2 - Cr_2O_3(111)$ interaction is manisfested in the disappearence of the surface loss at 1.2 eV and in the appearance of a strong loss at about 9 eV. The similarity with the spectra of the NO₂ and O₂ adsorbates points towards the forming of Cr - O bonds at the surface. In contrast to CO adsorption we did not observe a CO₂ induced superstructure in the LEED pattern. This is probably due to the formation of carbonate even at 100 K.

3.3.1. ARUPS

In Fig. 16 a set of ARUP spectra for CO₂ adsorbed on $Cr_2O_3(111)$ is shown. The adsorption of CO_2 at about 100 K (spectrum b) leads to the development of three peaks in the region between 10 eV and 15 eV binding energy and some additional emission in the region of the $Cr_2O_3(111)$ oxygen bands, i.e. between 5 eV and 9 eV binding energy. Annealing the adsorbate to about T = 170 K leads to spectrum e. The most obvious difference to spectrum b is that the peak at about 12.5 eV binding energy is missing now. The difference of the spectra b and e is shown in spectrum c. This spectrum is quite similar to the spectrum of physisorbed CO₂ on Ni(110) (d) [63] so that we attribute the difference in the spectra of $CO_2/Cr_2O_3(111)$ taken at 100 K and 170 K to the desorption of physisorbed CO_2 . To identify the emissions remaining at 170 K (spectrum e) we substracted the spectrum of the clean surface from this spectrum. The result of this procedure (spectrum f) looks like the spectrum of a carbonate film on Pd(111) [64]. Thus we conclude that the adsorption of CO₂ on Cr₂O₃(111) leads to a mixture of car-



Fig. 16

Set of ARUP spectra of CO₂ adsorbed on $Cr_2O_3(111)$ taken at different temperatures. Difference spectra are compared to the spectra of CO₂ adsorbed on Ni(110) and carbonate on Pd(111)

bonate and physisorbed CO_2 at 100 K. Upon warming the surface up to 170 K the physisorbed CO_2 desorbs and only carbonate remains on the surface. This carbonate layer is stable up to room temperature.

3.3.2. HREELS

Fig. 17 shows a set of HREEL spectra for ${}^{12}CO_2$ and ${}^{13}CO_2$ on Cr₂O₃(111) taken at two different temperatures. The strongest losses in these spectra, i.e. those at 410 cm⁻¹, 700 cm⁻¹, 1420 cm⁻¹ and 2100 cm⁻¹ are due to the optical phonons of the oxide film. The adsorption of CO₂ and thus the formation of carbonate shifts these losses by some cm⁻¹, indicating the strong interaction of the carbonate with the oxide surface. At T = 100 K the asymmetric stretching vibrations of linear, undistorted CO₂ at 2360 cm⁻¹, respectively 2290 cm⁻¹ are clearly visible. Upon annealing to 220 K these losses strongly decrease in intensity. Some residual intensity is due to readsorption of CO₂ from the residual gas since the sample was only shortly annealed to T = 220 K. The measurements were performed when the crystal was cooled down to 100 K.





HREEL spectra of ${}^{13}CO_2$ and ${}^{12}CO_2$ adsorbed on $Cr_2O_3(111)$ taken at two different temperatures

In the spectra of the cold layer some weak structure is visible to the left and the right of the phonon loss at 1420 cm⁻¹. Upon annealing these losses get stronger so that they are most likey due to carbonate. We identify losses at 1630 \pm 20 cm⁻¹ (1600 \pm 20 cm⁻¹), 1285 \pm 20 cm⁻¹



Fig. 18

Left panel: vibrational energies for differently coordinated carbonate species on oxides in comparison with the loss energies observed for carbonate on $Cr_2O_3(111)$. Data have been taken from Ref. [27]. Right panel: schematic representation of differently coordinated carbonate complexes

 $(1260 \pm 20 \text{ cm}^{-1}), 1035 \pm 20 \text{ cm}^{-1} (1015 \pm 20 \text{ cm}^{-1})$ and 920 $\pm 20 \text{ cm}^{-1} (900 \pm 20 \text{ cm}^{-1})$. The numbers in brackets are the loss energies for ${}^{13}\text{CO}_3^{2-}$. These loss energies are graphically represented in Fig. 18a in comparison with data from the literature for differently coordinated carbonate species [27]. The different surface coordinations of carbonate are schematically shown in Fig. 18b. From the data shown in Fig. 18a it is clear that the carbonate species on $\text{Cr}_2\text{O}_3(111)$ is most likely twofold coordinated to the oxide, i.e. it is a bidentate.

3.3.3. NEXAFS

The reaction of CO₂ with $Cr_2O_3(111)$ is also documented in the C1s NEXAF spectra shown in Fig. 19. This figure shows a set of NEXAF spectra for CO₂ adsorbed on $Cr_2O_3(111)$ in comparison with a NEXAF spectrum of CO. In this set two spectra for the clean surface have been included since we have chosen different analyser energies for the CO and the CO₂ NEXAF spectra. Als already mentioned the features in the spectra of the clean surface are due to photoemission from the Cr_2O_3 valence bands and the O2s level of the oxide.

After adsorption of CO_2 at T = 100 K two additional sharp peaks at 286.9 eV and 290.2 eV and a broad feature at about 308 eV develop. Upon annealing the sample the strong feature at 290.2 eV gets weaker whereas the peaks at 286.9 eV gains intensity. The peak at 286.9 eV vanishes at about 170 K whereas the other features exists up to some K above room temperature. These data have to be interpreted in view of the results of our ARUPS study which showed that at low temperature physisorbed CO₂ and carbonate coexist on the surface whereas at higher temperatures, up to about room temperature only carbonate remains on the surface. This means that the resonance at 290.2 eV must be due to physisorbed CO₂ and carbonate. The other feature which vanishes at about 170 K is most likely the π resonance of CO which is known to desorb at 170 K. CO was not observed in the ARUPS spectra of the CO₂ adsorbate which is understandable in view of the sensitivity of CO towards irradiation with UV light. Whether the CO signal in the NEXAF spectra is due to a contamination from the residual gas or whether it is due to CO formed by the reaction $2 \text{ CO}_2 + 2e^- \rightarrow \text{CO} + \text{CO}_3^{2-}$ can not conclusively answered from the NEXAFS data.



Fig. 19

C1s NEXAF spectra of CO₂ adsorbed on $Cr_2O_3(111)$ as a function of temperature. For comparison also a NEXAF spectrum for CO/ $Cr_2O_3(111)$ is shown

To get informations on the bonding geometry of the carbonate species we recorded NEXAF spectra for two different angles of light incidence, i.e. 0° and 70° with respect to the surface normal which are shown in Fig. 20. The spectra have been taken at T = 170 K so that there should be no physisorbed CO₂ at the surface. As can be seen the carbonate π resonance at a photon energy of 290.2 eV is much stronger for perpendicular light incidence than for grazing incidence. This result is characteristic for a carbonate species standing more or less upright on the surface. In line with the results derived from our HREELS investigation we thus conclude from the NEXAFS data that the carbonate molecules are bound to the oxide surface via two oxygen molecules with the molecular plane oriented approximately perpendicular to the surface.



Fig. 20

Comparison of C1s NEXAF spectra of CO2 adsorbed on Cr₂O₃(111) for two different angles of light incidence. The spectra have been taken at T = 165 K. At this temperature only carbonate remains on the surface

3.3.4. XPS

The formation of a surface carbonate is also documented in the XP spectra of the CO₂ adsorbate. In Fig. 21 a set of C1s and O1s XP spectra of CO₂ on Cr₂O₃(111) taken at different temperatures is shown. Two peaks are visible in the C1s spectra, one at $E_{\rm B} = 291.8$ eV and another one at $E_{\rm B} = 290.2 \text{ eV}$ with respect to the Fermi level. Upon annealing the peak at higher binding energy vanishes so that it must be due to physisorbed CO2 which desorbs at low temperatures. So the other one must be the C1s level of the surface carbonate. Obviously even at T = 90 K the carbonate signal is larger than the CO₂ signal. In agreement with our other spectroscopic data at room temperature all physisorbed CO₂ is desorbed and only carbonate remains at the surface.





Ols and Cls XP spectra of clean Cr₂O₃(111) and CO₂/Cr₂O₃(111) for two different temperatures. The spectra have been taken with monochromatized Alka radiation

In the O1s spectra the carbonate peak is visible as a weak shoulder at $E_{\rm B} = 532.5$ eV near to the O1s substrate emission. From literature data it is known that the O1s level of physisorbed CO₂ is usually located near to $E_B = 534.5 \text{ eV}$ [65]. At this energy only a weak indication of a structure is visible in the O1s taken at lowest temperature.

Summary

We have investigated the adsorption of CO and CO_2 on epitaxially grown Cr₂O₃(111). CO weakly chemisorbs on a clean, flashed Cr₂O₃(111) surface in an ordered ($\sqrt{3}$ × V(3) R 30° structure with the molecular axis oriented approximately parallel to the surface plane. The electronic properties of the adsorbed CO molecules differ strongly from those adsorbed on metal surfaces. The valence state binding energies are found to be larger than even the gas phase values and the ordering of the valence states is also different from the ordering usually observed on metallic surfaces in that the 1π ionization seems to be near to the 4σ ionization. These observations are explained by a bonding model where the CO valence states interact with both the chromium an the oxygen ions of the oxide surface. CO adsorption is strongly hindered by preadsorption of oxygen, indicating that surface Cr2+ ions, which only exist on a clean, flashed surface, play an important role in the $CO - Cr_2O_3(111)$ bonding.

CO₂ not only adsorbs on the Cr₂O₃(111) surface in a molecular uncharged form at low temperatures but also reacts to form a surface carbonate. As indicated by HREELS and NEXAFS this carbonate species is most likely coordinated to the surface by two oxygen atoms with the molecular plane oriented approximately perpendicular to the surface. The species is stable up to above room temperature.

We are grateful to the Deutsche Forschungsgemeinschaft (DFG), the Bundesministerium für Forschung und Technologie (BMFT) and the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen for funding our research. HJF thanks the Fonds der Chemischen Industrie for financial support.

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(Received on September 6th, 1991; E 7763 final version on October 24th, 1991)