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IR investigations of CO_2 adsorption on chromia surfaces: Cr_2O_3 (0001)/Cr(110) versus polycrystalline α-Cr_2O_3

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Abstract

The adsorption of carbon dioxide has been studied on a single-crystalline Cr_2O_3(0001) film as well as on samples of polycrystalline α-Cr_2O_3. The Cr_2O_3(0001) film has been grown on the (110) surface of a chromium single crystal. Upon CO_2 dosage, two chemisorbed and two weakly bound adsorption states are identified. We associate the strongly bound carbon dioxide with carboxylates, bent $CO_2^{\delta-}$ species adsorbed on top of the chromium ions of the 'polar' (0001) surface. An assignment to surface carbonate formed upon adsorption on surface oxygen ions is not compatible with the vibrational data. The IR spectra of CO_2 chemisorbed on polycrystalline α-Cr_2O_3 differ substantially from the IRAS spectra of the $CO_2/Cr_2O_3(0001)/Cr(110)$ system. As the faces of the microcrystals show mainly non-(0001) termination, we consider different modes of coordination of the CO_2 chemisorbates. In particular, bidentate carbonate species are discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Carbonates; Carbon dioxide; Carboxylates; Chemisorption; Chromium oxide; Infra-red spectroscopy

1. Introduction

The adsorption of CO_2 on clean and alkali modified surfaces of metal single crystals has been the subject of many surface science studies. Reviews can be found in Refs. [1,2]. However, less work has been performed investigating the CO_2 species formed upon adsorption on well-defined oxide surfaces of given crystallographic orientation [3–19]. In particular, there is still a lack of systematic studies utilizing vibrational spectroscopy. Whereas the infra-red data of CO_2 adsorption on polycrystalline oxide materials are well-documented (e.g. Refs. [20,21]) only few IR spectra of CO_2 adsorbed on single crystalline oxides are published, e.g. in the work of Heidberg and his group. They characterized ordered structures of CO_2 physisorbates on MgO(100) performing LEED and FTIR spectroscopy [5,6].

At low temperatures, the detection of weakly bound, molecularly undistorted CO_2 is typical for all single crystal oxides [3–19]. However, on some oxide substrates, CO_2 chemisorbates are formed as well. Generally, CO_2 chemisorption on oxides is explained by the formation of surface carbonates [8,12–19]. Pacchioni et al. [22] have analyzed CO_2 adsorption on the (100) surfaces of MgO and CaO in a theoretical study. For MgO, a weakly

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bound complex was predicted, whereas a chemically bound carbonate should be formed via coordination to an oxygen ion at the CaO surface. The essential factor for the difference in reactivity was explained in terms of the electrostatic stabilization of the surface anion. The O^{2-} ion at the surface is stabilized by the Madelung potential of the ionic crystal, which is smaller for CaO than for MgO, thus leading to a higher basicity and reactivity of CaO. However, CO_2 chemisorption on metal oxides should not lead to surface carbonates exclusively. In fact, the formation of CO_2^-, i.e. carboxylate structures, has been reported for ZnO-single-crystal surfaces [12,14,15].

A specific issue concerning CO_2 adsorbates on oxides is the investigation of polar surfaces. Polar surfaces are hardly accessible via cleavage of bulk single crystals. However, in recent years, some experience has been acquired in the preparation and characterization of thin oxide films exposing polar surfaces [23]. An important structural aspect of these systems is the compensation of the divergence of the electrostatic surface potential. In the case of corundum surfaces, it has been suggested that the reduction of charge in the surface occurs via removal of half of the number of surface ions [24]. Previously, we have studied the Cr_2O_3(0001) surface prepared on a Cr(110) single crystal performing quantitative LEED and molecular dynamic simulations [25]. In addition to the half-occupation of the terminating chromium layer we have detected very pronounced relaxations that occur between several layers near the surface [25]. Recent ab-initio calculations [26] complete the picture of the stabilized Cr_2O_3(0001) system with the identification of covalent interactions at the surface. A charge of +2 (instead of +3) is estimated for the terminating chromium ions and a charge of −1.7 for the oxygen ions in the first oxygen layer.

In this paper, we present the first investigations of the CO_2 adsorption on the Cr_2O_3(0001)/Cr(110) system, applying infra-red reflection absorption spectroscopy (IRAS) and thermal desorption spectroscopy (TDS). The experimental results provide evidence for the formation of $CO_2^{\delta-}$ species. Therefore, the interpretation of a former study using photoelectron spectroscopies (UPS, NEXAFS) and suggesting carbonate formation [3] has to be revised. Carboxylate formation can be understood with regard to the characteristics of the polar Cr_2O_3(0001) surface.

On α-Cr_2O_3 microcrystals, however, faces with (0001) termination are basically absent. This conclusion has been drawn from HRTEM experiments and computer-graphics studies [27]. Further evidence is given in a comparison of the chromyl IR frequencies which are measured after oxygen adsorption on the different chromia systems. The detailed IR investigations of CO_2 adsorption on polycrystalline chromia systems also show pronounced differences to the IRAS spectra of CO_2 chemisorbed on Cr_2O_3(0001). We suggest the formation of bidentate carbonates on the non-(0001) chromia surfaces as proposed in an former study [28].

2. Experimental

The investigation of the CO_2/Cr_2O_3(0001)/Cr(110) system has been performed in an ultra-high-vacuum apparatus. The base pressure of the multiple chamber system is 3×10^{-10} Torr [29,30]. The preparation unit is equipped with an Omicron 4 grid-spectraLEED optics to check the surface order by LEED and its chemical constitution by Auger electron spectroscopy. Furthermore, the preparation chamber contains facilities for TDS measurements: a quadrupole mass spectrometer and a specially designed doser system [29]. The IRAS measurements are performed using a modified Mattson RS-1 FTIR spectrometer. The interferometer is mounted in a home-made steel chamber, which is evacuated to 10^{-3} Torr. The liquid-nitrogen-cooled MCT detector is placed into a separate chamber that is flushed with dry nitrogen. The interferometer chamber and the detector chamber are attached to the UHV system via two viton-O-ring sealed KBr windows. The angle of incidence of the IR light on to the sample placed in the IRAS cell of the UHV system is about 85°. Further details of the experimental set-up are discussed elsewhere [29,30]. All single-beam spectra in this work were recorded with a spectral resolution of 2 cm^{-1}, accumulating 500 scans for each spectrum. The transmittance spectra were calculated from the single-beam spectra of the clean and the adsorbate-covered surface. Afterwards, they were baseline-corrected.

The chromium oxide film with (0001) orientation was grown on a Cr(110) single crystal surface via oxidation and thermal treatment cycles. The recipes have been published in detail previously [3,25,31–34]. The thickness of the oxide film has been estimated to be about 40 Å. Concerning the IRAS measurements in grazing-incidence geometry, the reflectivity of the well-ordered thin oxide film is still very high due to the metal support. Furthermore, the dipole selection rule of IRAS spectroscopy on metal samples [35] still holds for thin films grown on metal single crystals, so-called buried metal layer ('BML') systems [36].

The IR investigations of CO_2 adsorption on polycrystalline chromia were performed using a Bruker IFS 48 spectrometer equipped with a MCT detector. The FTIR spectra were recorded with a resolution of $2\,cm^{-1}$.

The α-Cr_2O_3 used in the experiments (BET specific surface area $40–70\,m^2\,g^{-1}$) was obtained by exothermic decomposition of $(NH_4)_2Cr_2O_7$. The polycrystalline material was compressed in the form of pellets, suitable for IR transmission measurements. Afterwards, the chromia samples were outgassed at 973 K (or 1073 K) for about 2 h in a quartz cell, allowing in-situ high-temperature activation as well as low-temperature CO_2 dosage.

3. Results and discussion

3.1. CO_2 adsorption on $Cr_2O_3(0001)/Cr(110)$

Fig. 1a shows the thermal desorption spectra measured after the $Cr_2O_3(0001)/Cr(110)$ surface has been exposed to carbon dioxide at 90 K. At low coverage, there is a broad desorption feature of mass 44 (CO_2) observed at around 330 K. This can be assigned to strongly bound, chemisorbed species. With increasing coverage, additional signals appear at lower desorption temperatures, at 180 K and finally also at 120 K. These peaks can be associated with weakly bound or 'physisorbed' CO_2. The surface is saturated with CO_2 using a dosage of about 8 L. Multilayer adsorption of CO_2 does not occur on $Cr_2O_3(0001)/Cr(110)$ at 90 K.

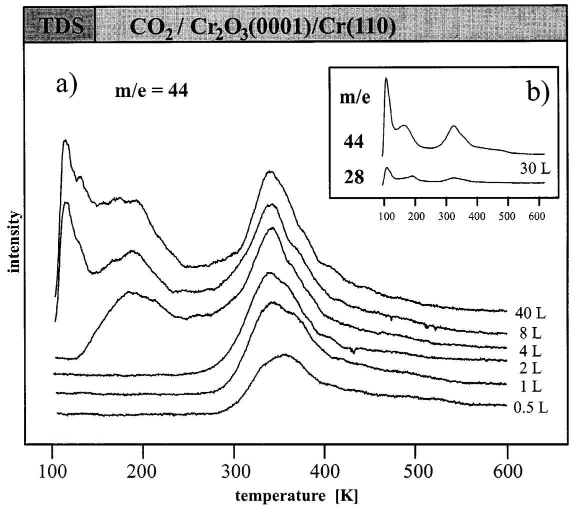


Fig. 1a. (a) Thermal desorption spectra (m/e = 0–44) of CO_2 from $Cr_2O_3(0001)/Cr(110)$ for various dosages. (b) Thermal desorption spectrum (m/e = 28 and 44) of CO_2 from $Cr_2O_3(0001)/Cr(110)$ (saturation coverage).

The IR spectra confirm the presence of different CO_2 species on $Cr_2O_3(0001)$. Fig. 2 shows a series of IRAS spectra as a function of initial CO_2 dosage at 90 K. In the regime of the asymmetric stretching vibration of the linear CO_2 molecule (gas phase value, $\nu_{gas} = 2349.3\,cm^{-1}$ [37]) two partially overlapping signals can be detected. At a low dosage, (0.3 L), a peak appears at $2346\,cm^{-1}$, shifting to $2353\,cm^{-1}$ with increasing coverage. CO_2 exposures above 4 L yield a second signal of the asymmetric stretching vibration at $2375\,cm^{-1}$. If we consider the coverage dependence of the two signals at 2353 and $2375\,cm^{-1}$ (Fig. 2), they are associated with the two desorption maxima of the physisorbed CO_2 (Fig. 1). The species desorbing at 180 K shows its asymmetric stretching vibration at $2353\,cm^{-1}$, and the species with a desorption maximum at 120 K is related to the band at $2375\,cm^{-1}$. This assignment is supported by a heating experiment. The IR spectra shown in Fig. 3 are measured after annealing the CO_2-saturated $Cr_2O_3(0001)$ at higher temperatures. (For technical reasons, the data acquisition itself has to be performed each time after recooling to 90 K.) The spectrum at the bottom again shows the signals of

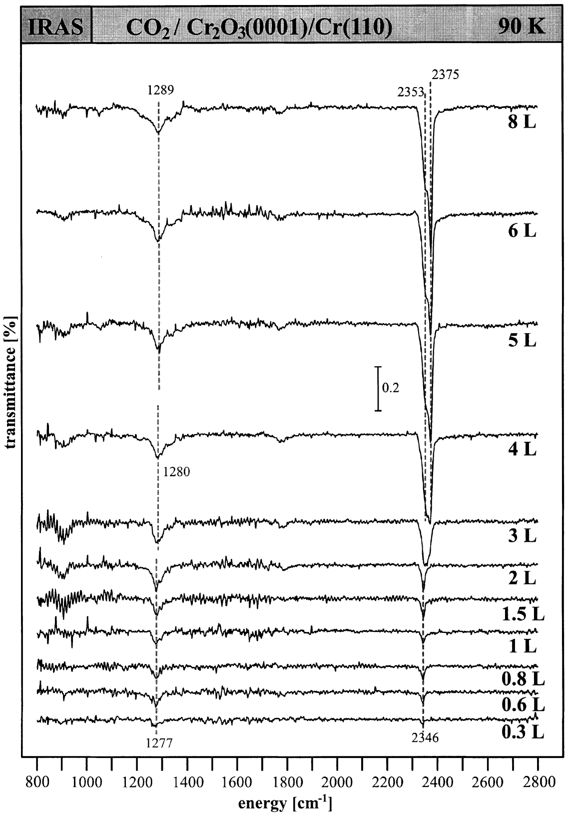


Fig. 2. Infra-red reflection adsorption spectra of CO_2 adsorbed on $Cr_2O_3(0001)/Cr(110)$ as a function of dosage.

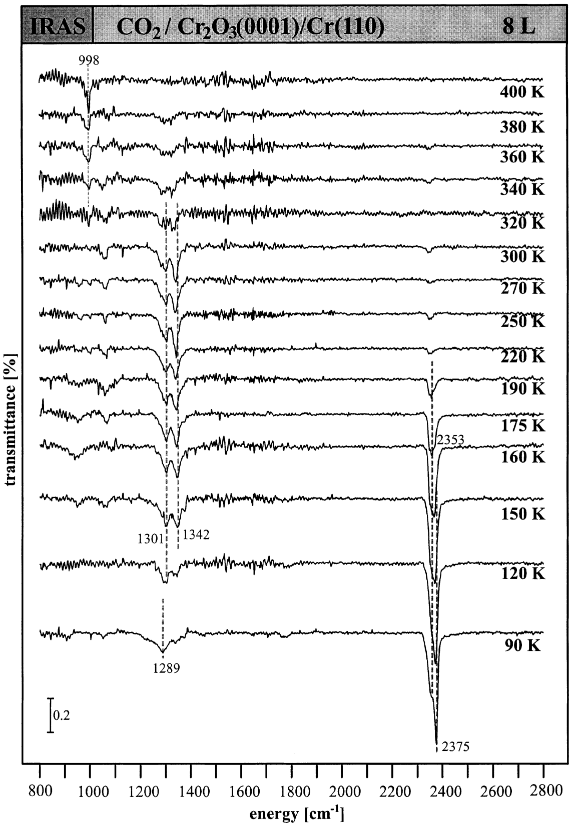


Fig. 3. Infra-red reflection adsorption spectra of CO_2 adsorbed on $Cr_2O_3(0001)/Cr(110)$ as a function of temperature after dosing 8 L at 90 K.

the two different CO_2 physisorbates at 2353 and 2375 cm^{-1}. The vibrational feature at 2375 cm^{-1} disappears upon heating above 120 K, which supports the assignment to the desorption peak at 120 K. The intensity of the peak at 2353 cm^{-1} decreases at about 170 K, accompanying the CO_2 desorption at 180 K in the TD spectra (Fig. 1).

At low CO_2 exposure (0.3 L), a vibrational feature at 1277 cm^{-1} is observed in the IRAS coverage series (Fig. 2). While the dosage is increased, the signal gains intensity and shifts to 1289 cm^{-1}. Its maximum intensity is reached using a CO_2 dosage of 4 L at 90 K. Upon heating (Fig. 3), the signal slightly shifts to 1301 cm^{-1}, and at about 150 K, a second signal of comparable intensity grows in. As both signals disappear at temperatures above 300 K, they should be associated with the desorption signal of the CO_2 chemisorbate. (The signal at 998 cm^{-1} in the spectra of higher temperatures is assigned to chromyl groups formed by oxygen segregation to the surface. This characteristic effect occurs on the adsorbate-free $Cr_2O_3(0001)/Cr(110)$ system when it is annealed above room temperature. The atomically bound oxygen desorbs at about 830 K [30,38].)

Comparing the coverage dependence of the TDS and IR spectra (Figs. 1 and 3), a remarkable effect is observed at low exposures. Whereas the TDS only shows a broad desorption maximum at 330 K, physisorbed and chemisorbed molecules are identified in the IR spectra taken at 90 K. We can draw the conclusion that the physisorbate is partially converted into the chemisorbate upon heating. This transformation probably occurs in the case of higher coverages, too. The assignment of the different IR signals to CO_2 adsorbates is supported by experiments using isotopically labeled $^{13}CO_2$ (Fig. 4). The signals of both physisorbed and chemisorbed CO_2 show significant shifts to lower wavenumbers, as expected for the ^{12}C–^{13}C substitution. It has to be noted that the $Cr_2O_3(0001)/Cr(110)$ systems of Fig. 4 possess less surface defects than the oxide preparations of Figs. 2 and 3. As the inhomogeneous line broadening [35] is reduced, the two signals of the CO_2 physisorbates can be clearly resolved. (Using the same preparations, smaller line widths have been observed for adsorbed oxygen species as well [30].) Furthermore, comparing Figs. 3 and 4, we can state that CO_2 chemisorbates should be bound mainly on regular terrace sites, but not on defect sites. The intensity of their IR signals is only slightly influenced by the number of surface defects.

The IRAS spectra of the CO_2 chemisorbates on $Cr_2O_3(0001)/Cr(110)$ differ significantly from the vibrational spectra of linear CO_2 species, which indicates a different molecular geometry and/or charge. Bent, negatively charged CO_2 chemisorbates have been identified in experiments on several metal single crystals ([39], which are surveyed in [1,2]). Usually, these $CO_2^{\delta-}$ species are stable up to 200 K. Their formation is facilitated by low work functions of the metal substrates, but the presence of appropriate adsorption sites is also very important. The vibrational identification of $CO_2^{\delta-}$ relies on the symmetric and antisymmetric OCO-stretching vibrations, which are observed at about 1200–1300 cm^{-1} and 1600 cm^{-1}, respectively (Table 1). (The bending vibration at about 800 cm^{-1} is at the border of the frequency range accessible to the IRAS set-up used in this work.) Due to the surface selection rule [35], the band of the antisymmetric stretching vibration cannot be observed if the $CO_2^{\delta-}$ species is adsorbed in C_{2v} symmetry [40]. The bent $CO_2^{\delta-}$ molecule 'stands' on the surface via the carbon atom or with both oxygen atoms. The vibrational spectra of the CO_2 chemisorbates on $Cr_2O_3(0001)/Cr(110)$ are in line with the assignment to $CO_2^{\delta-}$ molecules adsorbed in (local) C_{2v} symmetry. The signals at about 1280–1340 cm^{-1} can be associated with the symmetric stretching vibration of (different) $CO_2^{\delta-}$ species. The absence of bands in the range of the antisymmetric stretching vibration points to an adsorption geometry characterized by an alignment of the O–O axis parallel to the surface.

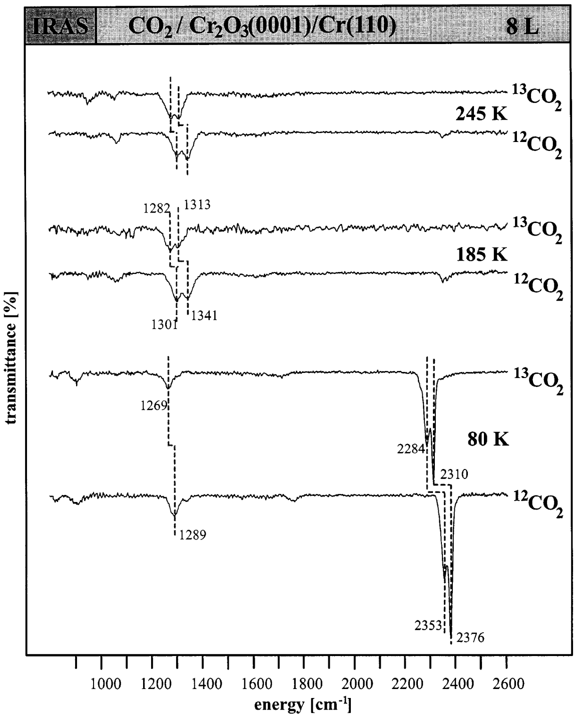


Fig. 4. Comparison of infra-red reflection adsorption spectra of $^{12}CO_2$ and $^{13}CO_2$ adsorbed on $Cr_2O_3(0001)/Cr(110)$ as a function of temperature after dosing 8 L at 90 K.

However, as mentioned above, the chemisorption of CO_2 on metal oxides is mainly related to the formation of carbonate-like species, so-called surface carbonates. A simple model describes a charge transfer from surface oxygen to the approaching CO_2, a simultaneous bending of the molecule and the formation of a $[O–CO_2]^{2-}$ complex [56]. This process shows similarities to the formation of the $(M^{\delta+}$-) $CO_2^{\delta-}$-complex, whereas the corresponding CO_2 adsorption sites (metal ions versus oxygen ions) differ substantially. In the following, we have to prove the assignment of the CO_2 chemisorbate on $Cr_2O_3(0001)$ to $CO_2^{\delta-}$ species. At this point, we can exclude that carbonates are formed on $Cr_2O_3(0001)$ via CO_2 disproportionation. CO molecules, which would be the by-product, are detected neither in the IR spectra (Figs. 2 and 3) nor via TDS (compare mass 28,

Table 1
Vibrational frequencies (cm^{-1}) of CO$_2^{\delta-}$ species [40–55]

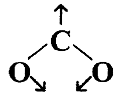
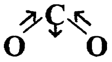
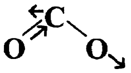
System	 δ	 ν_s	 ν_{as}	
CO_2/Ni(110)	750	1130/1390	1620	[40,41]
CO_2/Re(0001)	(650)	1230	1625	[42–44]
CO_2/Fe(111)	800	1064/1160	1360/1600	[45]
CO_2/Fe(100)		1232	1634	[46]
CO_2/K+Rh(111)	840	1340	1630	[47]
CO_2/Na+Pd(111)	744	1210	1530	[48–50]
CO_2/K+Pt(111)	820	1340	1600	[51–54]
Li–CO_2 (C_{2v})	799	1330	1570	[55]

Fig. 1b). In case of CO adsorption on Cr_2O_3(0001)/Cr(110), we have identified (weakly) chemisorbed CO species that are characterized by their stretching vibration at 2170 cm^{-1} and at a desorption temperature of 180 K [29,57].

One might regard the formation of CO$_2^{\delta-}$ species on the surface cations of oxides as energetically unfavourable if only the requisite charge transfer from the metal ion to the carbon dioxide were considered. However, the characteristics of the Cr_2O_3(0001)/Cr(110) substrate have to be taken into account. As mentioned above, the first layer of the polar Cr_2O_3(0001) surface is occupied by chromium ions [25]. Therefore, the interaction between the adsorbates and substrate should occur via the exposed chromium ions. (A limited accessibility of the oxygen ions is maintained by half occupation of the terminating chromium layer and by relaxation of the topmost layers.) Furthermore, we have to consider the covalent interactions and reduced ion charges (+2/−1.7) on the Cr_2O_3(0001)/Cr(110) surface [26]. We regard the charge transfer from oxygen to chromium on the Cr_2O_3(0001) surface as the prerequisite for the charge transfer from chromium to the adsorbed CO_2. In fact, the formation of CO$_2^{\delta-}$ species has already been discussed in case of CO_2 adsorption on reduced surface cations of metal oxides [12,14,15,58,59]. For example, IR bands with maxima at 1219 and 1635 cm^{-1} have been assigned to CO$_2^{\delta-}$ species on TiO_2 powder [58]. These chemisorbates should be bound via the C atom to Ti^{3+} ions that occur in the vicinity of O^{2-} vacancies. Signals at 1310 and 1660–1670 cm^{-1} are also detected for C-bonded CO$_2^{\delta-}$ species on powder samples of other transition metal oxides which enable charge transfer from reduced surface cations to CO_2 [59]. On single crystals, formation of C-bonded CO$_2^{\delta-}$ has been reported for the (0001)- and $(10\bar{1}0)$-surfaces of ZnO. This effect has also been related to zinc ions next to oxygen vacancies [12,14,15]. Unfortunately, the latter systems have not been characterized by vibrational spectroscopy so far.

Proving the assignment of the CO_2 chemisorbate on Cr_2O_3(0001)/Cr(110) to CO$_2^{\delta-}$ species means precluding carbonate formation, which is thought to be much more typical for the CO_2 adsorption on metal oxides. As vibrational data are not available for surface carbonates on oxide single crystals, we have to refer to the literature dealing with CO_2 adsorption on polycrystalline or amorphous samples (surveys in Refs. [20,21]). A detailed comparison with the CO_2 adsorption experiments on polycrystalline α-Cr_2O_3 will follow in Section 3.2.

Surface carbonates are systematized, according to the number of bonds to the substrate. Single-bonded ('monodentate') and double-bonded ('bidentate') species are distinguished (Fig. 5b). A discrimination by means of vibrational spectroscopy concentrates on the modes that are measured between 1200 and 1700 cm^{-1}. The intense stretching vibration of the free carbonate at 1415 cm^{-1}

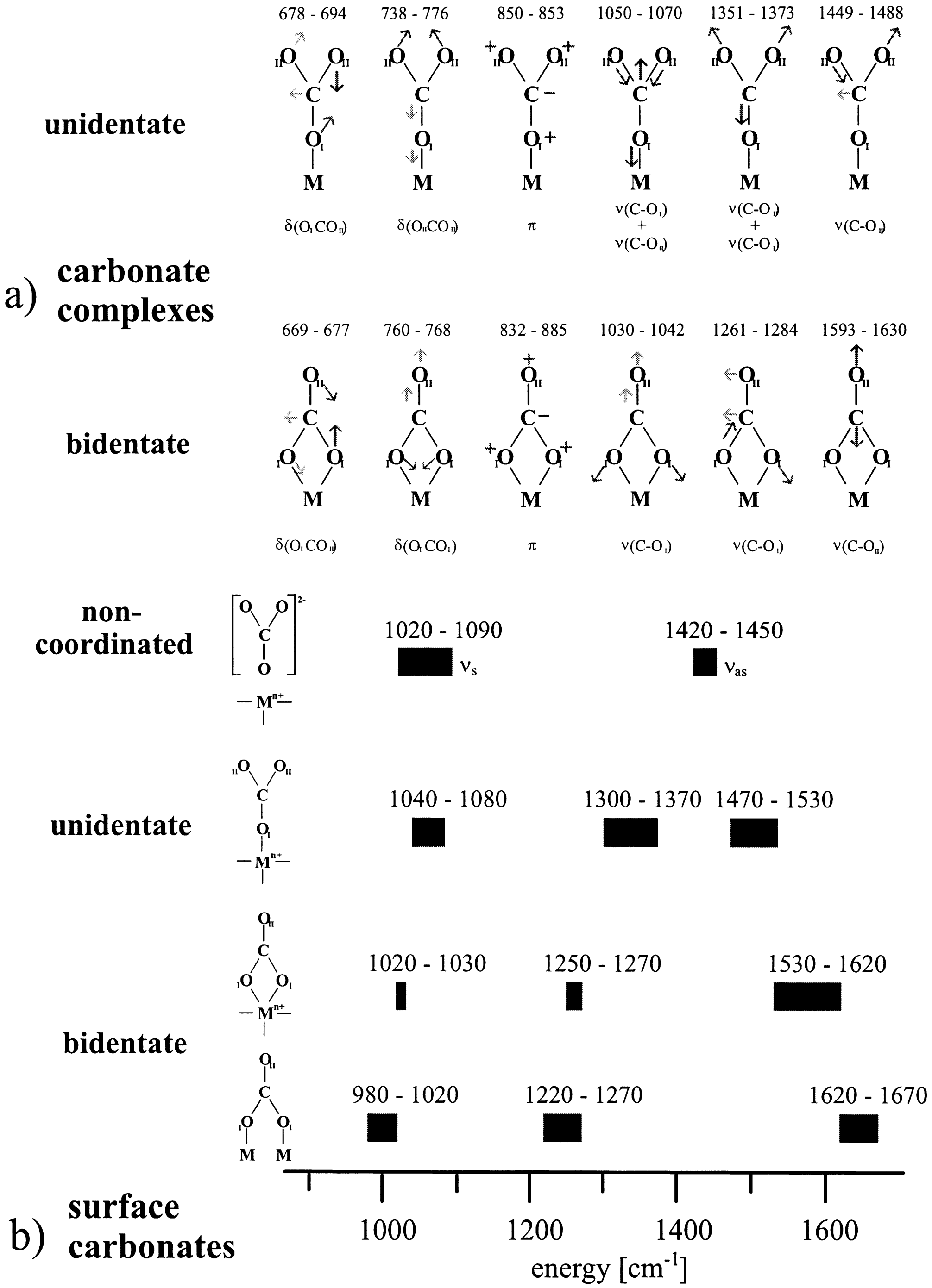


Fig. 5. (a) Vibrational modes of unidentate and bidentate carbonate complexes. The frequencies are taken from the spectra of $Co(NH_3)_5CO_3^+X^-$ (unidentate) and $Co(NH_3)_4CO_3^+X^-$ (bidentate) with ($X^-=Br^-$, Cl^-, I^-, NO_3^-) [61,62]. The assignment and nomenclature follow the normal mode analysis of Fujita [61]. (b) Correlation diagram of characteristic CO_3 vibration frequencies of surface carbonates after Davydov [20].

[60] splits, in the case of surface carbonates, into two signals. The magnitude of the splitting can be related to the bonding geometry of the carbonate complex. The assignment is associated with the IR spectra of cobalt(III)–carbonate complexes in which the carbonate ions are bonded via one or two oxygen atoms to the metal centre. In contrast to the four vibrations of free CO_3^{2-} (D_{3h} symmetry), the metal-bound carbonate shows six vibrational modes due to the symmetry reduction. Normal mode analyses have been performed by Fujita [61] and Goldsmith [62]. Fig. 5a shows the vibrational modes of unidentate and bidentate cobalt (III) carbonate complexes according to the nomenclature of Fujita and Nakamoto [61,63]. However, Goldsmith [62] uses opposite symmetries for the two high-energy modes. This controversial assignment is continued in the literature for surface carbonates.

The IR signals of the CO_2 chemisorbates on $Cr_2O_3(0001)/Cr(110)$ are measured between 1280 and 1340 cm^{-1}. They are in the characteristic range of one vibrational mode of surface carbonates—right between the frequencies typical for unidentate and bidentate species [20]. However, the high-frequency mode of the carbonate stretching vibrations is missing in the spectra. With regard to typical IR spectra of carbonates on oxide surfaces [20], we would expect the signal to be found at about 1600 cm^{-1}. Its intensity should exceed the signal of the counterpart at about 1300 cm^{-1}.

Considering the possibility of carbonate formation on $Cr_2O_3(0001)/Cr(110)$, we have to look for an explanation for the absence of the high-frequency mode. With regard to the surface selection rule [35], we might assume that the dynamic dipole moment of the missing mode would be orientated parallel to the surface plane. This condition cannot be fulfilled in the case of bidentate carbonates. Their high-frequency mode would have the character of a $C–O_{\text{non-bonded}}$ stretching vibration (Fig. 5a), and its (high) dynamic dipole moment would be aligned to the surface normal. Merely the adsorption geometry of single-bonded carbonates could fulfil the requirement, but only if the mode assignment follows the normal mode analysis of Fujita [61] (Fig. 5a). A flat-lying carbonate species can be excluded with respect to the NEXAFS spectra of the CO_2 chemisorbate. Previously [3,64], these spectra were assigned to a surface carbonate oriented with its plane perpendicular to the substrate. However, an assignment of the NEXAFS signals to the π-resonance $CO_2^{\delta-}$ adsorbed in C_{2v} symmetry would be possible as well.

A distinction between surface carbonate and $CO_2^{\delta-}$ might be based on the frequency range at about 1050 cm^{-1}. In this regime, characteristic modes are found for unidentate or bidentate carbonates (Fig. 5) but not for $CO_2^{\delta-}$ species (Table 1). However, these distinctive features cannot often be used in practice—especially on samples of supported metal oxides, which are opaque below 1100 cm^{-1}. Furthermore, the IR studies of the cobalt (III) carbonate complexes [62,63,65] show much smaller intensities for the signal at 1050 cm^{-1} than for the bands measured between 1250–1370 and 1450–1650 cm^{-1}, respectively. In the case of CO_2 chemisorption, on $Cr_2O_3(0001)/Cr(110)$, even the peaks about 1300 cm^{-1} are relatively small (ca. 0.1% in transmittance). Therefore, we cannot expect to detect the band at 1050 cm^{-1} for a hypothetical surface carbonate. (The features at about 1070 cm^{-1} that occur in only some of the IRAS spectra are not reproducible and have to be assigned to artifacts.)

Carbonate formation should occur via reaction of CO_2 with surface oxygen, whereas $CO_2^{\delta-}$ species should be adsorbed on surface cations. Therefore, an insight into the chemisorbate–substrate interaction is expected in experiments in which isotopically labeled $^{18}O_2$ is used for the preparation of the $Cr_2O_3(0001)$ oxide. Fig. 6 shows IRAS spectra of CO_2 adsorption on $Cr_2{}^{18}O_3(0001)$ as a function of heating temperature. The comparison with the data taken on $Cr_2{}^{16}O_3(0001)$ does not reveal any significant differences in band positions—either for the physisorbates or for the chemisorbed species. We can draw the conclusion that the ^{18}O atoms of the substrates do not take part in the vibrational mode detected for the CO_2 chemisorbate. This condition is fulfilled by the assignment to the symmetric stretching vibration of $CO_2^{\delta-}$ species bound on surface cations. Conversely, we would expect an isotope effect for

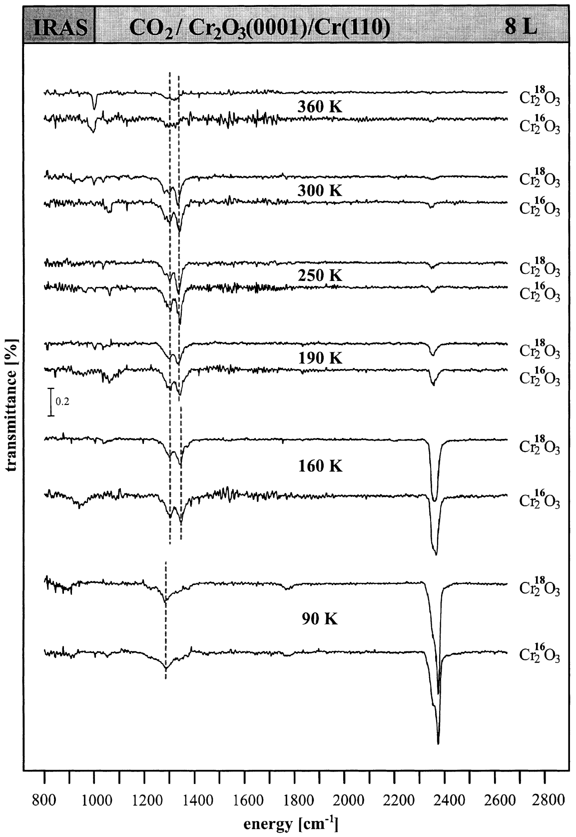


Fig. 6. Comparison of infra-red reflection adsorption spectra of CO_2 on $Cr_2{}^{16}O_3(0001)/Cr(110)$ and $Cr_2{}^{18}O_3(0001)/Cr(110)$ as a function of temperature after dosing 8 L at 90 K.

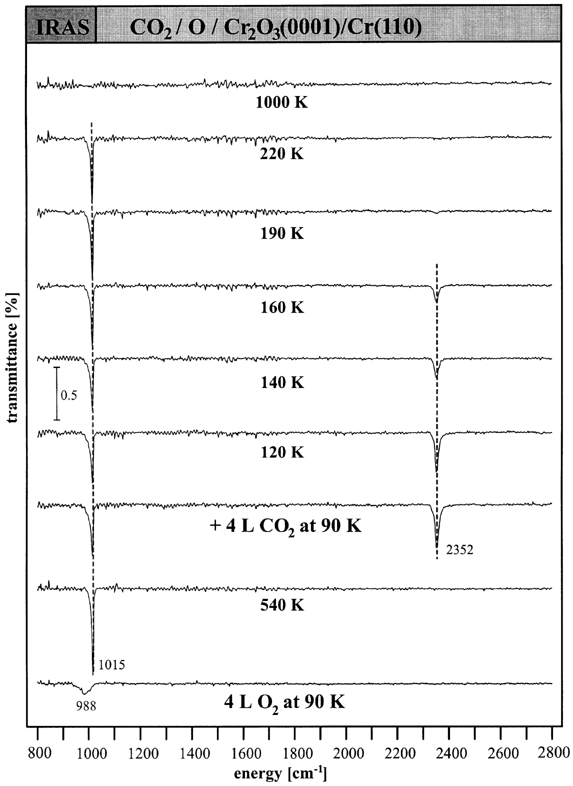


Fig. 7. Infra-red reflection adsorption spectra of CO_2 on oxygen-predosed $Cr_2O_3(0001)/Cr(110)$. The surface was exposed to 4 L O_2 at 90 K and subsequently flashed to 540 K. After recooling to 90 K, the surface was saturated with CO_2 (here 4 L dosage). In the following, the system was heated to the specified temperatures.

the vibrations of surface carbonates. Even the symmetric stretching vibration of unidentate carbonate involves the bond between C atom and surface oxygen (Fig. 5a).

Finally, the interaction of CO_2 with the metal ions of $Cr_2O_3(0001)/Cr(110)$ can be checked via oxygen precoverage. We know from a detailed IRAS study that oxygen interacts strongly with the metal ions on the $Cr_2O_3(0001)$ surface [30,38]. Fig. 7 shows the IR spectra of CO_2 adsorption on $Cr_2O_3(0001)/Cr(110)$ precovered with atomic oxygen. At first, the $Cr_2O_3(0001)$ surface was exposed to O_2 at 90 K. The broad vibrational feature at about 990 cm^{-1} (lowest trace) can be assigned to the O–O stretching vibration of several molecular oxygen adsorbates [30,38]. Subsequent annealing at 540 K leads to partial dissociation of adsorbed O_2, and the other fraction is desorbed. The atomically bound oxygen on $Cr_2O_3(0001)/Cr(110)$ is characterized by the very intense chromyl (Cr=O) vibration at 1015 cm^{-1} [30,38]. Upon CO_2 exposure, the chromyl band slightly loses intensity. This attenuation can be explained by shielding effects [66] because after CO_2 desorption, the signal regains its previous intensity. CO_2 coadsorption has no influence on the atomically bound oxygen, which is expected, with regard to the high thermal stability of the chromyl groups. The chromyl oxygen desorbs upon heating to temperatures above 830 K [30,38]. The CO_2 species adsorbed on $O/Cr_2O_3(0001)/Cr(110)$ are characterized by the signal at 2352 cm^{-1}. Upon heating, it disappears at about 190 K. The

ν_{as}(OCO) frequency is comparable to one of the CO_2 physisorbates, which are detected without oxygen precoverage. Consequently, the corresponding CO_2 species should be adsorbed on the oxygen ions of the substrate ('C' in Fig. 8). We do not have any indications for CO_2 chemisorption on the oxygen-precovered surface. Signals in the region at about 1300 cm^{-1} do not appear in the spectra of the coadsorbate system. Therefore, the accessibility of the surface chromium ions should be necessary for the formation of CO_2 chemisorbates on Cr_2O_3(0001). CO_2 chemisorption cannot occur if the chromium ions are selectively blocked by oxygen. We can exclude the formation of an unidentate surface carbonate on the exposed O atoms bonded on Cr_2O_3(0001)/Cr(110), as shown in Fig. 8 ('F'). This is another indication that the CO_2 chemisorbates on Cr_2O_3(0001)/Cr(110) are not surface carbonates bound to oxygen in unidentate coordination, but $CO_2^{\delta-}$ species adsorbed on chromium ions.

To summarize, the IR investigations show the formation of $CO_2^{\delta-}$ species upon CO_2 chemisorption on Cr_2O_3(0001)/Cr(110). The bent molecules are adsorbed on the Cr ions in a geometry with the C_2 axis perpendicular to the surface. Evidence is given by the absence of a vibrational feature at about 1500–1600 cm^{-1}, the lack of an isotope effect upon adsorption on the ^{18}O oxide and by the attenuation of chemisorption via selective blocking of chromium ion sites by oxygen. All these effects can hardly be correlated with the model of unidentate surface carbonate species. The formation of bidentate carbonate on Cr_2O_3(0001) is strictly ruled out because the intense C=O stretching band is missing.

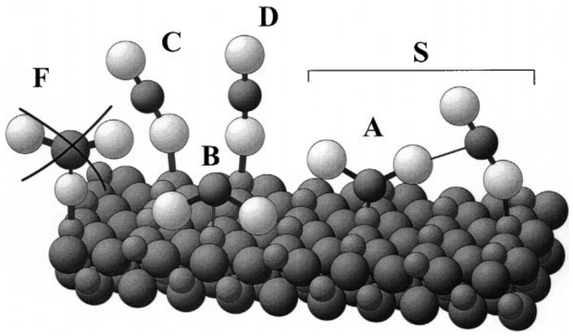


Fig. 8. Schematic representation of CO_2 adsorbates on Cr_2O_3(0001)/Cr(110). Chemisorbed $CO_2^{\delta-}$ ('A', 'B'), physisorbed CO_2 ('C', 'D'), bent $CO_2^{\delta-}$ solvated by linear CO_2 ('S') (see text). The formation of a possible unidentate surface carbonate ('F') can be excluded. The figure was produced with the help of BALSAC (Version 2.11, © Copyright K. Herrmann 1991–1998). The BALSAC software was developed by K. Herrmann, Ftitz-Haber-Institut, Berlin, Germany.

Concerning the different positions of the symmetric stretch of the $CO_2^{\delta-}$ chemisorbate, we have to consider interactions with the physisorbates as well as different adsorption sites and geometries. Thus, upon heating from 90 to 150 K, the signal shifts from 1289 to 1301 cm^{-1}, and the second signal at 1341 cm^{-1} increases, while the 2375 cm^{-1} signal of the physisorbate disappears. Simultaneously, a CO_2 desorption peak is measured at 120 K in the TDS. The weakly bound physisorbate probably occupies the same surface sites as the $CO_2^{\delta-}$ species. The coadsorption experiments with oxygen support the idea of a Cr adsorption site for the physisorbed CO_2 with ν_{as}(OCO) at 2375 cm^{-1} ('D' in Fig. 8). After blocking the surface chromium, we have only measured asymmetric stretching vibrations at 2352 cm^{-1}. Additionally, we have to consider the solvation of the bent $CO_2^{\delta-}$ species by the weakly adsorbed linear CO_2 molecules ('S' in Fig. 8). Stable $(CO_2)_n^{\delta-}$ ions ($2 \leq n \leq 6$) are well known [1,67]. Furthermore, the CO_2 solvation of alkali–CO_2 complexes has been identified in matrix isolation experiments [68,69]. For the $(CO_2)_2^{\delta-}$ dimer, a T-shaped geometry is calculated. The linear 'solvating' CO_2 molecule is bound via the carbon to an O atom of the $CO_2^{\delta-}$ species [1,69]. Finally, different adsorption sites of $CO_2^{\delta-}$ may result from different sites of the terminating chromium ions on the first oxygen layer of the Cr_2O_3(0001) lattice. However, two different adsorption geometries of $CO_2^{\delta-}$ give a reasonable explanation for the two IR bands of the chemisorbed species as well. The bent CO_2 may be bonded via the central carbon atom or via both oxygens to the surface cations ('A' and 'B' in Fig. 8).

3.2. *CO_2 adsorption on polycrystalline Cr_2O_3*

Fig. 9 shows IR data from CO_2 adsorbed on a α-Cr_2O_3 sample outgassed at 973 K. The spectrum

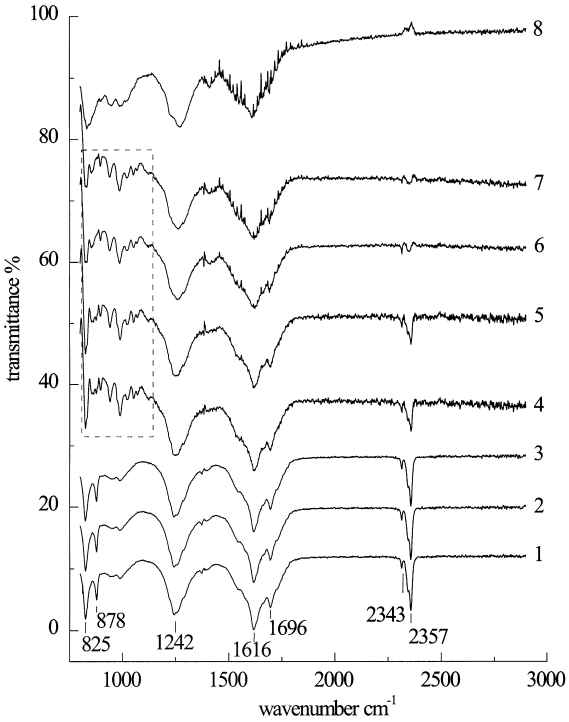


Fig. 9. Infra-red spectra of CO_2 (0.1 Torr) adsorbed on polycrystalline α-Cr_2O_3 (outgassed at 973 K) as a function of temperature. From the bottom, spectrum 1 corresponds to 100 K, and spectra 2–8 are taken at increasing temperatures up to 300 K (spectrum 8).

at the bottom corresponds to CO_2 adsorption ($p \cong 0.01$ Torr) at ~ 100 K. The spectra above are taken at increasing temperatures up to 300 K. All the IR spectra in Fig. 9 are background-subtracted.

The IR spectra of the CO_2/α–Cr_2O_3 system are characterized by the presence of two broad features in the 1200–1300 and 1600–1700 cm^{-1} region. At a sample temperature of 100 K (spectrum no. 1), we detect peak maxima at 1242 and 1616/1696 cm^{-1}, respectively. Smaller signals are measured at 825 and 878 cm^{-1}, and a very small feature is detected at 990 cm^{-1}. Upon heating to 300 K (spectrum no. 8), the bands at about 1240, 1650 and 850 cm^{-1} become broader but do not lose intensity. Therefore, we can assign these features to chemisorbed CO_2 species. Their molecular geometry significantly differs from the linear gaseous molecule or weakly bound CO_2 which give rise to small signals at 2357 and 2343 cm^{-1}, observed for low temperatures. (The spectral features in the dashed window are artifacts. As multiphonon modes of the oxide occur in the frequency regime below 1100 cm^{-1}, background subtraction of the spectra is very sensitive to temperature changes during the measurements.)

Comparing the vibrational data of the CO_2 chemisorbate on the polycrystalline α-Cr_2O_3 sample (Fig. 9) with the IRAS spectra of CO_2 chemisorbed on Cr_2O_3(0001)/Cr(110) (Figs. 2–4), we observe several striking differences. The intense signal at about 1650 cm^{-1} and the weaker signals in the 850 cm^{-1} region are detected in the case of the microcrystals. If we assume that the species formed on polycrystalline chromia and on Cr_2O_3(0001)/Cr(110) are both carboxylates, the broad band at about 1650 cm^{-1} can be attributed to the asymmetric stretching mode. This feature should be visible because the surface selection rule of IRAS spectroscopy is not valid for the IR transmission measurements performed with the polycrystalline material. The signals in the 800–900 cm^{-1} regime may belong to the bending mode of the carboxylate species (Table 1), which are not detected in the IRAS measurements because of a lower signal-to-noise ratio. However, the shift of the signal in the 1200–1300 cm^{-1} region indicates differences in the surface coordination of the chemisorbates. Thus, the vibrational data, especially the intense band at ≈ 1650 cm^{-1}, are compatible with surface carbonates. In this model, the signals at ≈ 850 cm^{-1} can be assigned to the π mode of carbonate (Fig. 5).

To obtain further information on the interaction of CO_2 with polycrystalline chromia, we have studied the effect of oxygen precoverage—as for the Cr_2O_3(0001)/Cr(110) system. The results of these coadsorption experiments are shown in Figs. 10 and 11 for the α-Cr_2O_3 samples outgassed at 973 and 1073 K, respectively. Figs. 10 and 11b represent exploded views of the 950–1020 cm^{-1} interval. The figures show the spectra of O_2 (0.1 Torr) dosed at 100 K (no. 1, at the bottom) followed by those taken at increasing temperatures up to 300 K (no. 2 and no. 3). After recooling the sample to 100 K, we carried out adsorbtion of CO_2 (0.1 Torr) (no. 4), and finally, spectra were taken at increasing temperatures up to 300 K (no.

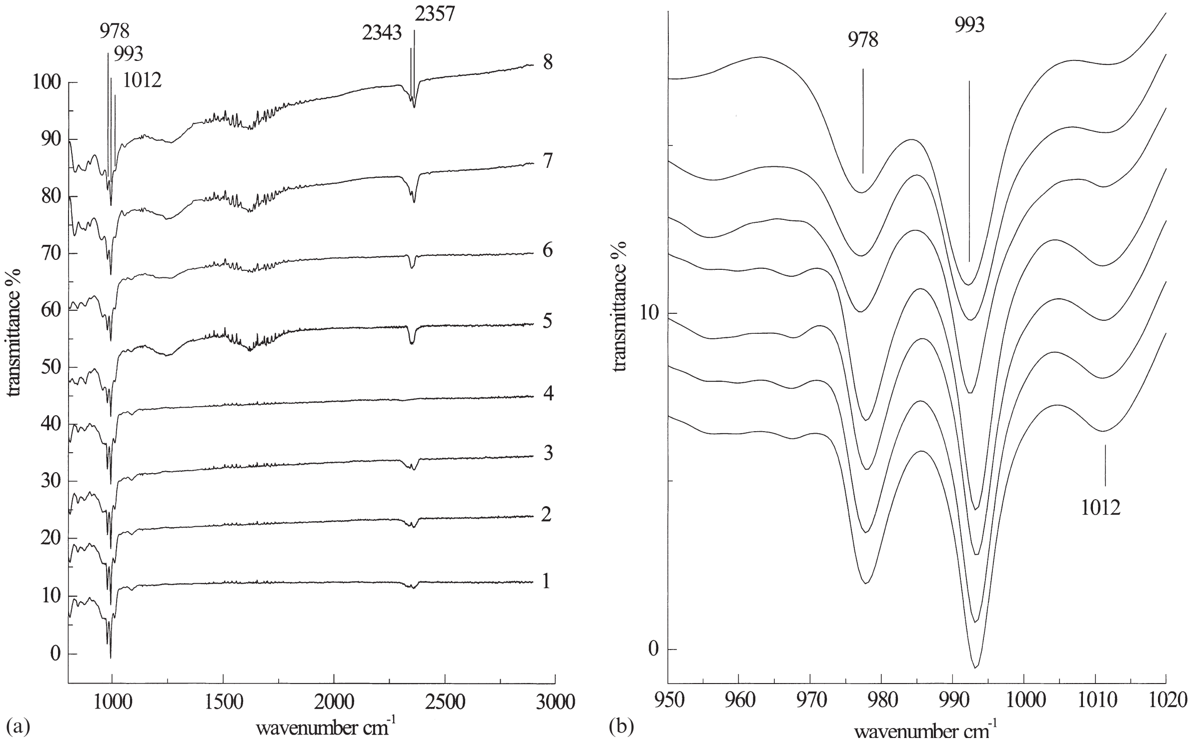


Fig. 10. (a) Infra-red spectra of CO_2 on oxygen-predosed on polycrystalline α-Cr_2O_3 (outgassed at 973 K). The surface was exposed to 0.1 Torr O_2 at 100 K (spectrum 1) and subsequently heated to 300 K (spectrum 3). After recooling to 100 K CO_2 (0.1 Torr) was dosed (spectrum 4). In the following, the system was heated stepwise to 300 K again (spectrum 8). (b) Exploded view of the 950–1020 cm^{-1} interval of (a).

5 to no. 8). For both samples (Figs. 10 and 11a), the frequency region 970–1020 cm^{-1} becomes rather intense upon preadsorption of oxygen. However, the bands in the regions 1240–1250 and 1620–1700 cm^{-1} are strongly attenuated. The latter observation indicates that—as for the $Cr_2O_3(0001)/Cr(110)$ system—the more strongly bound CO_2 species needs access to the surface chromium ions of α-chromia crystals. These surface chromium ions are blocked by the preadsorbed oxygen.

For the adsorbed oxygen, three predominant components at 978, 993 and 1012 cm^{-1} are observed in the experiment performed with α-chromia outgassed at 973 K (Fig. 10b). However, only two components at 978 and 993 cm^{-1} are present in the case of α-chromia outgassed at 1073 K (Fig. 11b). With regard to earlier experiments on oxygen adsorption on polycrystalline α-chromia [70], we assign the different components to chromyl species on different faces. In this model, the absence of the 1012 cm^{-1} band on the samples activated at higher temperatures could be explained by effects of surface relaxation or reconstruction caused by the progressive sintering. Additionally, if we compare the region of the chromyl groups with the IR data of the $O/Cr_2O_3(0001)$ system, we can speculate about the surface termination of the microcrystals. Thus, the 1012 cm^{-1} signal in Fig. 10b may be assigned to the same species as the 1015 cm^{-1} band in Fig. 7, namely to chromyl groups on the (0001) face. The attenuation of the 1012 cm^{-1} signal after outgassing the polycrystalline chromia at 1073 K means that for the best sintered materials, the (0001) plane is basically absent. However, the intensity of the 1012 cm^{-1} signal measured for α-chromia outgassed at 973 K (Fig. 10b) is considerably

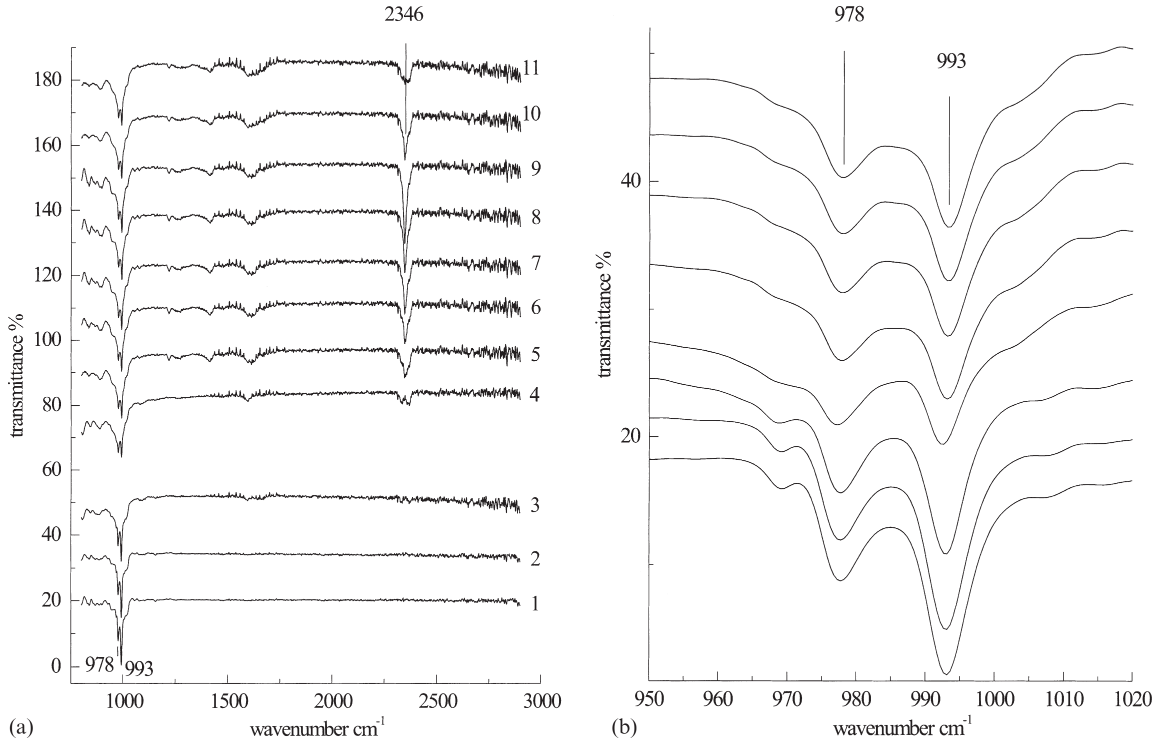


Fig. 11. (a) Infra-red spectra of CO_2 on oxygen-predosed on polycrystalline α-Cr_2O_3 (outgassed at 1073 K). The surface was exposed to 0.1 Torr O_2 at 100 K (spectrum 1) and subsequently heated up to 300 K (spectrum 3). After recooling to 100 K, CO_2 (0.1 Torr) was dosed (spectrum 4). In the following, the system was heated stepwise to 300 K again (spectrum 11). (b) Exploded view of the 950–1020 cm^{-1} interval of (a).

smaller than the intensity of the components at 978 and 993 cm^{-1}. Consequently, also, these chromia samples show only a very small number of (0001) facets, which is understandable in terms of the peculiarities of this polar surface, as discussed above. A detailed analysis of the predominant facets of the chromia microcrystals using HRTEM experiments and computer graphics studies is given in Ref. [27].

As the microcrystals expose mainly non-(0001) faces, the different termination may lead to a different surface coordination of the CO_2 chemisorbates. This conclusion would be compatible with the differences in the spectra of CO_2 adsorbed on $Cr_2O_3(0001)$ and on the microcrystals respectively. The formation of monodentate carbonate on the polycrystalline α-Cr_2O_3 samples can be ruled out because the attenuation of CO_2 chemisorption upon oxygen precoverage proves the interaction between CO_2 and chromium ion sites. However, we may think of bidentate surface carbonates formed via CO_2 adsorption on Cr^{3+}–O^2-ion pairs of the surface. This model explaining the suppression of CO_2 chemisorption upon oxygen precoverage has already been used in an early investigation of the CO_2/chromia system [28]. Nevertheless, the possibility of the formation of carboxylates on the chromia microcrystals still remains because the different surface termination may give rise to the observed band shifts in the 1200–1300 cm^{-1} region (Fig. 9). To summarize, we can argue that on the (0001) surface, the carboxylate species is present and on the other surfaces either different carboxylates or—more likely—metal–oxygen coordinated carbonates are present.

4. Summary

The adsorption of carbon dioxide on the Cr_2O_3(0001) surface as well as on samples of polycrystalline chromia has been studied with infra-red spectroscopy. At 90 K, CO_2 forms chemisorbed as well as physisorbed species on Cr_2O_3(0001)/Cr(110). Whereas the physisorbates desorb at 120 and at 180 K, respectively, the chemisorbed species are stable up to room temperature. Their IRAS spectra are compatible with bent $CO_2^{\delta-}$ species that are bound on the metal ions of the surface. The formation of $CO_2^{\delta-}$ instead of surface carbonates can be explained with regard to the characteristics of the polar Cr_2O_3(0001)/Cr(110) surface, which is terminated by chromium ions with a reduced charge. Predosing the surface with oxygen leads to an attenuation of CO_2 chemisorption because the chromium ions are blocked by strongly bound oxygen (chromyl species: Cr=O). Chromia microcrystals mainly expose non-(0001) surfaces. The IR spectra of the CO_2 chemisorbates on the polycrystalline samples differ substantially from the IRAS spectra of the bent $CO_2^{\delta-}$ species on Cr_2O_3(0001). The data are compatible with a different kind of carboxylate or—more likely—with bidentate surface carbonates formed via CO_2 adsorption on Cr^{3+}–O^2-ion pairs.

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