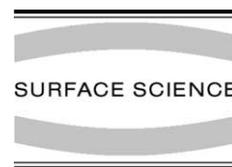




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CO₂ adsorption on Na precovered Cr₂O₃(0001)

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Abstract

CO₂ adsorption and reaction on Cr₂O₃(0001) is considerably modified by the presence of Na on the surface. Depending on Na coverage, different modes of interaction and reaction have been observed. At low coverage Na adsorbs by transferring an electron to the Cr₂O₃(0001) surface. In this case, the formation of bent CO₂⁻ (carboxylate) can be observed similar to what was observed for the clean Cr₂O₃(0001) surface [see Surf. Sci. 421 (1999) 176]. Distinct differences with respect to physisorbed CO₂ are identified. CO₂ desorbs as an intact molecule from the Na-covered surface at temperatures higher than that found for the clean surface. NaCO₂ salts form and also Na₂CO₃ can be observed. Carbonate forms via disproportionation of two CO₂ molecules into carbonate and CO with the latter being released into the gas phase. The intermediate formation of an oxalate species, its geometry on the surface, and CO₂ • CO₂ solvation are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkali metals; Chromium; Carbon dioxide; Electron energy loss spectroscopy (EELS); Thermal desorption spectroscopy; Infrared absorption spectroscopy; Compound formation; Chemisorption

1. Introduction

Studies on CO₂ activation and reaction are often motivated by the desire to find new avenues for the use of CO₂ in chemical reactions [1]. Reasons are that CO₂ emission has turned out to be critical in connection with burning fossil fuels and also with a number of industrial processes. CO₂ represents a C1-building block that is readily available for chemical reactions. However, it is employed in only four industrial processes [2,3]: in urea synthesis from CO₂ and ammonia, in the “Kolbe–

Schmitt”-process to synthesize salicylic acid from Na phenol, in the synthesis of cyclic organic carbonates via reaction of CO₂ with epoxides as well as via the water gas equilibrium partly also in methanol synthesis.

The reason for the limited use of CO₂ in synthesis is, of course, its high latent heat and the rather high kinetic activation the molecule would need to be more useful [4]. In this connection a bent CO₂⁻ intermediate, which can be identified on clean metal surfaces as well as on alkali promoted surfaces is thought to play a key role [5]. There are two comprehensive review articles on CO₂ surface chemistry in the literature [5,6]. While for metal surfaces a considerable literature exists on these processes, a similar data base for oxide surfaces does not exist.

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An early study reported sodium carbonate formation in the system Na/Cr₂O₃(0001)/Cr(110) without discussing the details of adsorption and reaction of the molecules [7,8]. Recently, Moller and his group have studied CO₂ interaction with Na/TiO₂(110) [9] and showed photoemission data consistent with the formation of a bent CO₂⁻ species on the surface that reacts further with oxygen resulting in the formation of carbonates. In the present paper we discuss the results of thermal desorption spectroscopy and vibrational spectroscopy studies on the CO₂ interaction with Na/Cr₂O₃(0001)/Cr(110) in order to reveal some of the issues raised above and compare the reactivity of the Na promoted system with that of the clean surface.

2. Experimental

The experiments have been performed in a double chamber UHV system with a base pressure of 10⁻¹⁰ Torr [10]. The samples are prepared and initially characterized by LEED and Auger electron spectroscopy in a preparation chamber. This chamber also contains a quadrupole mass spectrometer for residual gas analysis and thermal desorption spectroscopy. For the latter, the opening of a Feulner cup is positioned in front of the sample at close distance to prevent desorption from the sample holder from interfering with the measurement. For infrared spectroscopy the sample is moved on a manipulator to a separate chamber with KBr windows where reflection-absorption measurements using a modified Mattson type (RS-1) Fourier transform spectrometer can be performed. The interferometer and the optical path are pumped. The infrared detector is situated in a separate housing. We use a small-band-MCT (Hg(dTc)) system with liquid nitrogen cooling. All single beam spectra 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, recorded before and after adsorption of CO₂. The sample was a Cr(110) single crystal with 2 mm thickness and 10 mm diameter. Via sputter-anneal cycles the nitrogen impurity was vastly reduced and a sharp

(111) LEED pattern of the clean Cr(110) surface was obtained. The oxide film was prepared as reported in the literature [8,11,12] and exhibited a hexagonal (1 × 1) LEED pattern. The film has been shown to be about 30–50 Å thick and the structure of the film surface has been established on the basis of qualitative LEED I–V studies [13,14]. The surface is Cr terminated after flashing at 1000 K. Under oxygen rich conditions the surface is terminated by Cr = O groups instead of Cr ions [8].

3. Results and discussion

Na deposition on Cr₂O₃(0001)/Cr(110) has been discussed before and we refer to the publications for the calibration procedure concerning coverage [8,11,12,15]. It is important to realize that, similar to the case of Na deposition on metals, the work function as a function of coverage undergoes a strong and in the early stage linear decrease, reaches a minimum at about one monolayer and then increases until it reaches the limiting value of the alkali metal work function itself [8,11]. This value is reached almost at about two monolayers. It has been deduced that the Na atoms initially adsorb by transferring an electron to the substrate forming a non-metallic overlayer [8,11,15]. After a transition phase, presumably involving cluster formation they finally form a metallic overlayer. The latter has been confirmed by investigating the electron energy loss spectrum of Cr₂O₃(0001) in ranges of the so-called Fuchs–Kliwer (FK) phonons [7]. The FK phonons are completely attenuated after deposition of two monolayers of Na but their intensity recovers after the metallic Na overlayer is converted into a dielectric one by reacting it with water or CO₂. In the case of reaction with CO₂ a Na₂CO₃ overlayer forms as we shall see in the discussion below [7].

Fig. 1 shows a series of thermal desorption spectra for various Na coverages. At the bottom, the CO₂ TDS spectrum for Na-free Cr₂O₃(0001)/Cr(110) is given for comparison [16].

The features observed on the clean surface have been assigned: the desorption between 280 and 400 K originates from a chemisorbed CO₂⁻ carboxy-

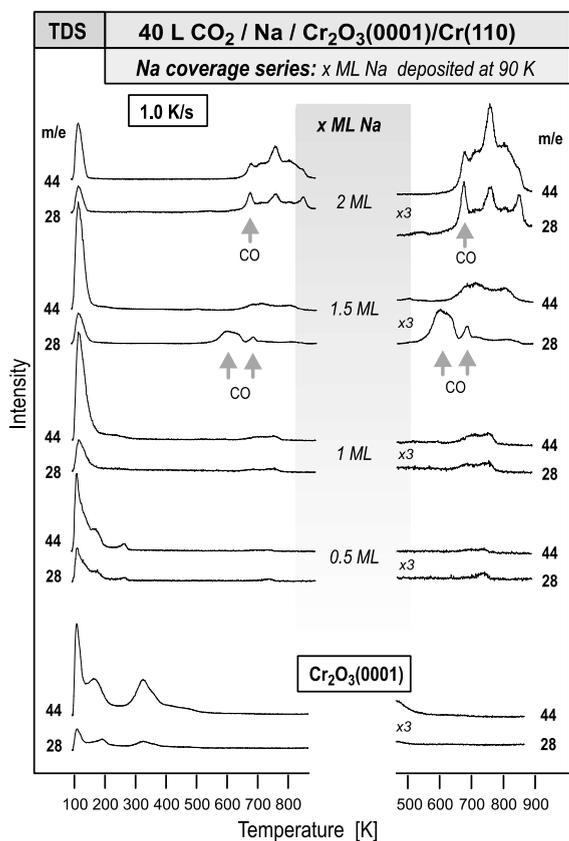


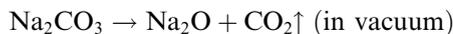
Fig. 1. Series of TDS spectra taken after CO_2 adsorption at 90 K (40 L) on clean and Na precovered $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surfaces with a heating rate of 1 K/s. Na coverage was prepared with the sample at 90 K. Partial pressures of masses 28 and 44 have been recorded simultaneously. On the right hand side the desorption above 450 K is presented on an enlarged intensity scale.

late species bound to the Cr sites on the surface through its carbon atom [16]. The low temperature features at 120 and 180 K are due to linear physisorbed CO_2 in different environments on the surface, i.e. on patches free of CO_2^- or in the multilayer and on patches with co-adsorbed CO_2^- in the monolayer [16].

Upon Na pre-dosage the original CO_2^- feature is strongly attenuated and even before full monolayer Na coverage is reached it is fully suppressed. At monolayer coverage there is only the low temperature feature for physisorbed CO_2 left. Simultaneously, high temperature features between 630

and 750 K develop. This high temperature features prevail for even the highest Na coverages and resolve into several sharp peaks in the spectra at the top. Note that parallel to the trace on mass 44 (CO_2) we show in each case the trace for mass 28 (CO). CO can be formed from CO_2 in the mass spectrometer or it can also be formed on the surface via reaction of CO_2 . Therefore, whenever the trace in mass 44 is tracked by the trace in mass 28, CO is formed in the mass spectrometer indicating that, indeed, CO_2 desorbs from the surface. However, for higher Na coverages there are extra features in the trace of mass 28 indicative of either adsorbed CO or CO being formed on the surface via reaction. The former can be excluded on the basis of the IRAS data discussed below.

It is quite obvious to associate the CO_2 desorption in the range between 630 and 750 K with the decomposition of sodium carbonate although the corresponding temperature for bulk Na_2CO_3 according to



has been determined to be 1250 K (see [17] and literature therein).

A possible explanation for the observation of CO desorption at monolayer Na coverage which will be substantiated on the basis of IRAS data is a disproportionation reaction between CO_2^- moieties or NaCO_2 salts on the surface [18–20]:



The CO released into the gas phase is then observed, of course, before the formed Na_2CO_3 which is a surface species (different from bulk Na_2CO_3) decomposes and releases CO_2 . At high sodium coverages the situation is again different and the combination of the TDS results with spectroscopic measurements is needed to proceed with the analysis (see below).

In order to illustrate the peculiarities of CO_2 adsorption in the various coverage regimes, we compare 0.5, 1.0, 1.5, and 2.0 monolayer sodium coverages: a low coverage before the work function has reached its minimum, an intermediate coverage at the work function minimum, a coverage before the layer reaches full metallicity at the

work function of the alkali metal, and a coverage typical for a fully metallic overlayer.

Fig. 2 shows IRAS spectra of a saturation coverage of CO₂ (30 L at 90 K) on Na precovered Cr₂O₃(0001)/Cr(110) for different Na coverages. For comparison, again, the spectrum of the CO₂ covered oxide surface without sodium pre-coverage is included [16]. The spectra have all been recorded at 90 K without heating the substrate. The spectra are dominated by the intense bands of the CO₂ asymmetric stretch (near 2360 cm⁻¹) characteristic for the linear physisorbed CO₂ molecule [21]. The high-energy signal (peak plus shoulder) for the clean surface is associated with the two desorption features at 120 and 180 K mentioned above as has been discussed in Ref. [16]. In line with the observation of only one low temperature

TDS signal for the Na precovered surfaces only one strong CO₂ asymmetric stretch is observed for these systems. The high intensity of the band is indicative of an adsorption geometry with the molecular axis perpendicular to the surface, as also discussed in Ref. [16].

Between 1000 and 2000 cm⁻¹ for the clean surface there is only one broad signal at 1289 cm⁻¹ which has been assigned to a bent CO₂⁻ species that desorbs at 330 K. The expected second band near 1600 cm⁻¹ is not visible in this case due to surface selection rules as extensively discussed in connection with powder spectra in Ref. [16].

In contrast to this simple spectrum, the spectra taken after CO₂ adsorption on the Na precovered surfaces are much more complex. There are several broader bands detected with a dependence of relative intensities and bandwidths on the Na pre-coverage. The bands are located between 1100 and 1900 cm⁻¹. In view of literature data for CO₂-alkali coadsorption on metal surfaces a series of adsorbate species including CO₂⁻ [22–34], C₂O₄²⁻ [30,32,35,36], and various types of CO₃⁻ [17,37–40], but also CO [24,28,29,32,41–44], must be discussed. We shall attempt an assignment in the following on the basis of temperature dependent IRAS data for the various Na coverages. Fig. 3a–d exhibit spectra recorded after heating the system to the temperatures given and then cooling the surface again down to 90 K. The discussion is primarily based on Fig. 3b, i.e. the monolayer Na coverage but essentially the results can be transferred to the other coverages.

Fig. 3b shows spectra of a system that has been exposed to 1 monolayer of Na at 90 K and then to a saturation coverage of CO₂ at the same temperature. The spectrum at the bottom is identical to the one shown in Fig. 2 exhibiting absorption bands at 1328, 1470, 1655 and 2358 cm⁻¹. After heating above 120 K the asymmetric stretch of the physisorbed species disappears. Note that the weak band observed at higher temperatures is due to re-adsorption of CO₂ after cooling the sample down to the temperature of 90 K at which all spectra have been recorded.

The band at 1470 cm⁻¹ gains intensity upon heating the system and it shifts to higher frequencies. After heating to 660 K it is the only remaining

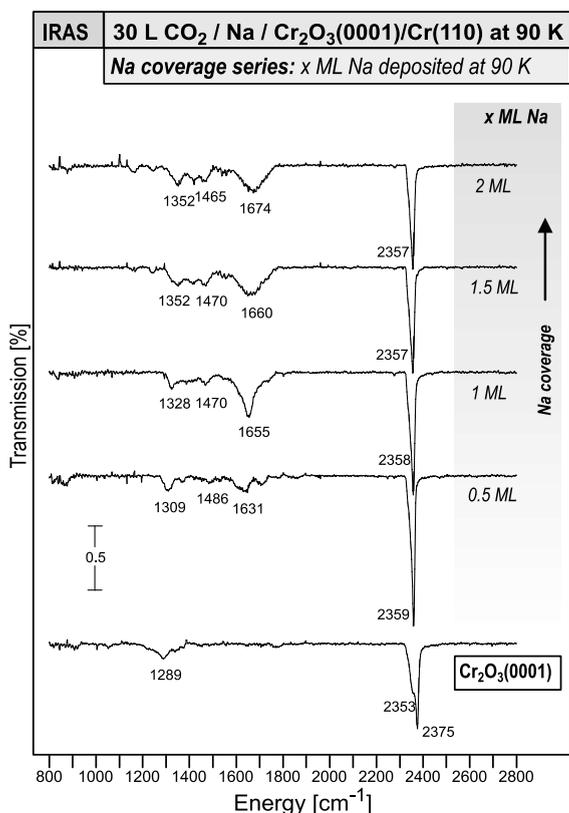


Fig. 2. Series of IRAS spectra of CO₂ (30 L at 90 K) adsorbed on clean and Na precovered Cr₂O₃(0001)/Cr(110) surfaces. Na coverage was prepared with the sample at 90 K.

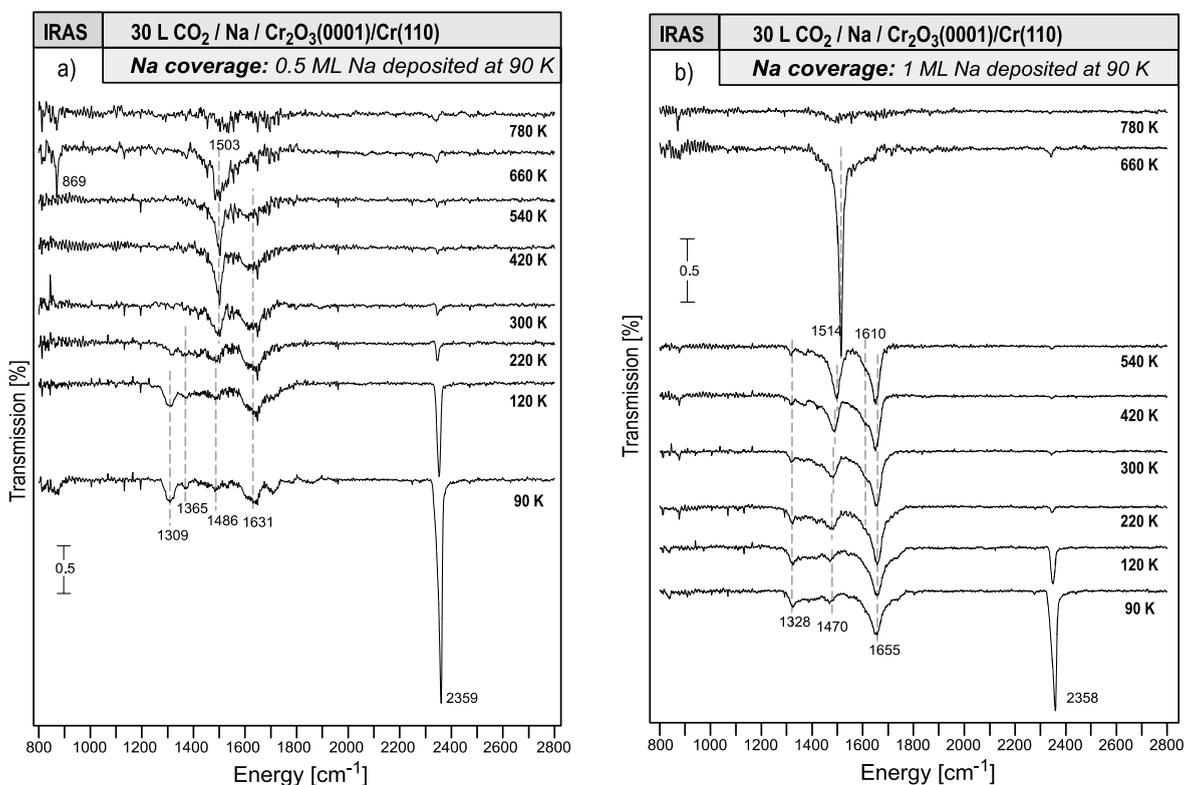


Fig. 3. Series of IRAS spectra taken at various Na coverages exposed to 30 L CO₂ at 90 K, followed by heating the surface to the given temperatures. All spectra were recorded at 90 K. (a) Na coverage: 0.5 monolayers, (b) Na coverage: 1.0 monolayers, (c) Na coverage: 1.5 monolayers, (d) Na coverage: 2.0 monolayers.

signal with a sharp maximum at 1514 cm⁻¹. Heating to higher temperatures leads to a disappearance of this band. This behavior correlates very well with the high temperature desorption feature discussed above. The frequency of the band can be compared with the asymmetric stretch of bulk Na₂CO₃ which has been observed at 1440 cm⁻¹ [17]. The deformation mode is weakly observed at 880 cm⁻¹ [17]. The difference between the vibrational frequencies is very likely due to the interaction of the carbonate with the Cr₂O₃-(0001)/Cr(110) surface as opposed to the interactions within bulk Na₂CO₃. The fact that only one high frequency band is observed with considerable intensity indicates that the CO₃²⁻-plane is preferentially oriented perpendicularly to the oxide surface: the 1140 cm⁻¹ signal of CO₃²⁻ in bulk Na₂CO₃ splits into a high- and a low-energy component for surface-coordinated CO₃²⁻, with the

amount of splitting depending on the coordination to the surface (monodentate or bidentate) [37]. According to Fujita and Nakamoto [38,40] the high-energy band of a twofold coordinated CO₃²⁻ ion would be of A₁ symmetry and thus be observed for a surface-bound species if the CO₃²⁻ plane was oriented parallel to the surface normal. The other A₁ modes have so low intensities that they cannot be observed. The different vibrational spectrum of the surface-coordinated species as compared to bulk Na₂CO₃ is well in agreement with the different chemical stabilities (see above).

We now turn back to the spectrum of the sample prepared at 90 K. Apart from the signal of the physisorbed species, in particular the band at 1655 cm⁻¹ exhibits high intensity. Its intensity, however, only changes little upon increasing the temperature of the sample surfaces. Nevertheless, the signal becomes sharper and a pronounced shoulder at

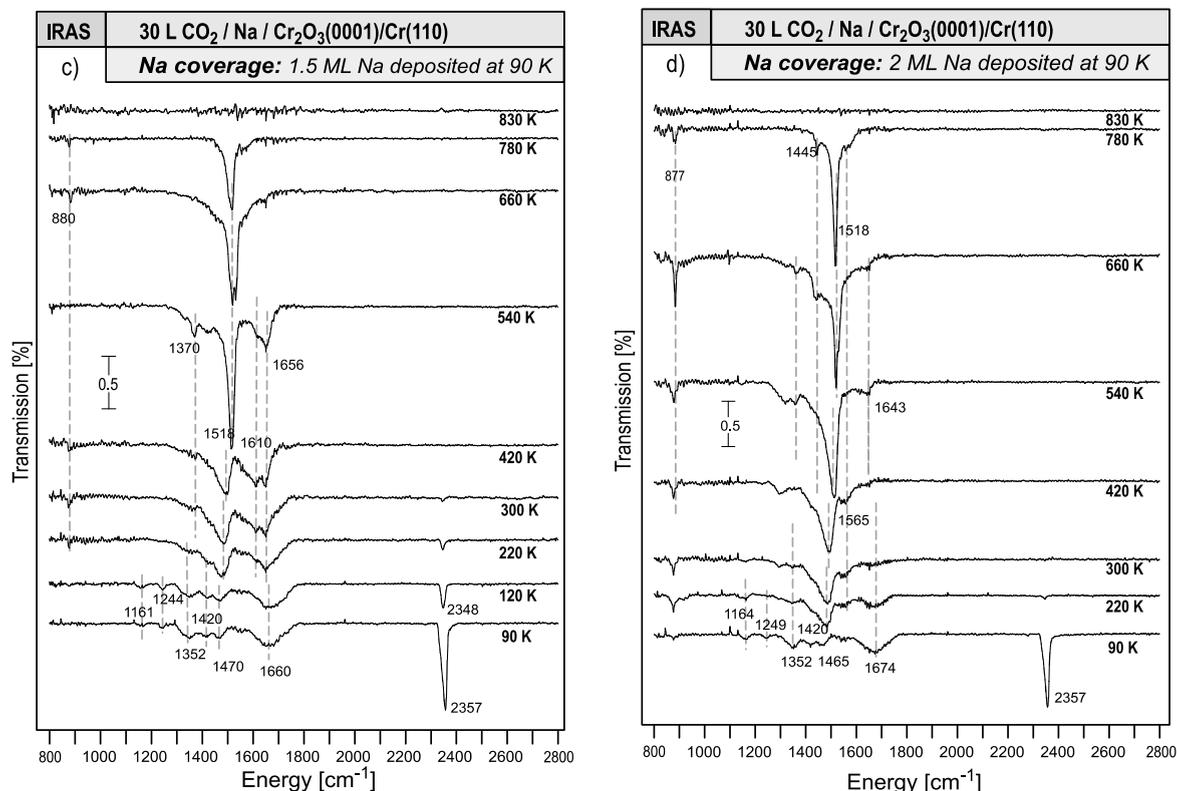


Fig. 3 (continued)

1610 cm⁻¹ appears. Between 540 and 660 K the feature vanishes abruptly. This happens in the range of temperatures where intense CO desorption has been observed in TDS that does not correlate with CO₂ desorption (see above) indicating that the transformations are connected and, considering the concomitant increase in the CO₃²⁻ feature at 1514 cm⁻¹, correlate with a precursor to surface carbonate formation.

The rather weak feature at 1328 cm⁻¹ in the spectra at 90 K show a similar trend in intensity as the band at 1655 cm⁻¹ upon increase of surface temperature. We therefore associate both features with the same chemical species.

To arrive at an assignment of the species we resort to Table 1 which collects literature data [22–36] on vibrational spectra of CO₂-alkali coadsorbates on metals, and on reference compounds such as alkali-CO₂ complexes prepared during matrix isolation and alkali-oxalates. In most studies band

pairs in the ranges 1300–1350 cm⁻¹ and 1600 and 1650 cm⁻¹ have been assigned to symmetric and antisymmetric stretching frequencies of Na⁺CO₂⁻ surfaces complexes. The presence of both bands favors a C_s symmetry of the complex (see also the discussion in Ref. [16] for the CO₂-Cr₂O₃(0001)/Cr(110) complex on the clean surface). It is possible that these complexes are solvated at low temperature by physisorbed linear CO₂ molecules. Such solvation phenomena have been discussed for matrix isolated species [30] and for the first time in connection with surfaces in an early theoretical study [45]. There, also the connection was postulated to the above mentioned disproportionation reaction:

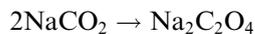


This idea was later adopted in several studies to discuss carbonate formation [6,22–25,46–51]. There

Table 1
Vibrational frequencies (in cm^{-1}) as observed for CO_2^- and oxalate species in a variety of systems

Species	System	$\delta(\text{OCO})$	$\nu_s(\text{OCO})$	$\nu_{as}(\text{OCO})$	Literature
CO_2^-	$\text{CO}_2/\text{K} + \text{Rh}(111)$	840	1340	1630	[22]
	$\text{CO}_2/\text{Na} + \text{Pd}(111)$	744	1210	1530	[23–25]
	$\text{CO}_2/\text{K} + \text{Pt}(111)$	820	1340	1600	[26–29]
	$\text{Li}-\text{CO}_2$	799	1330	1570	[30]
	$\text{Cs}-\text{CO}_2$		1346	1608	[31]
$(\text{C}_2\text{O}_4)^{2-}$	$(\text{C}_2\text{O}_4)^{2-}$ aq. sol.	766	1300	1555	[35]
	$\text{Na}_2\text{C}_2\text{O}_4$ salt	774	1320/1338	1640	[36]
	$\text{K}_2\text{C}_2\text{O}_4$ salt	766	1308	1625/1650	[32]
	$\text{Li}_2^+(\text{C}_2\text{O}_4)^{2-}$ (matrix)	807	1315	1662	[30]
	CO_2/K -monolayer $\text{Ru}(001)$	806	1342	1600–1725	[32]
	CO_2/K -monolayer $\text{Ru}(001)$	765	1345	1625	[32]
	CO_2/K -monolayer $\text{Co}(10\bar{1}0)$		1312	1625	[33]
	CO_2/Na -monolayer $\text{Al}(100)$	920	1350	1650	[34]

are various and conflicting reports on the stability of the species. On clean metal surfaces and also on clean $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ the CO_2^- species leads to CO_2 desorption at temperatures of up to 250 K [21–34]. On alkali promoted surfaces the desorption temperature is about 500 K. In several papers the signal near 1650 cm^{-1} is not assigned to CO_2^- but rather to CO formed [24,28,29] from the disproportionation reaction. Alkali-CO complexes are expected to show frequencies between 1600 – 1650 cm^{-1} on the basis of a review by Bonzel [41] and comparison to alkali-CO compounds [42–44]. It is quite possible that part of the intensity of the band near 1650 cm^{-1} , in particular the shoulder at 1610 cm^{-1} is due to CO bound in such complexes. However, clearly not the entire intensity can be traced back to such species. Note that the bands at 1328 and 1655 cm^{-1} disappear together at temperatures above 540 K together with the before mentioned CO desorption in TDS. It is therefore likely that the precursor for carbonate formation is, indeed, the Na^+CO_2^- complex. Paul and Hoffmann [32,34] proposed the intermediate formation of an oxalate species according to



A clear distinction between CO_2^- and $\text{C}_2\text{O}_4^{2-}$ is rather difficult on the basis of vibrational spectra [32]. Also, the reaction temperature according to:



has been reported to be 700 K [17]. The fact that in the present case we observe temperatures around 600 K is not inconsistent with the decomposition of oxalate to carbonate and CO, but as stated above a clear differentiation with respect to the existence of Na^+CO_2^- monomers is not possible. Note that the CO_2^- on the Na precovered surface shows a considerably higher stability than the corresponding species on the clean $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface [16].

How do these findings relate to the other Na coverages? The general trends are similar in all spectra. However, there are shifts and changes in relative intensities. It seems that with increasing Na coverage the stability of the formed Na_2CO_3 increases as judged by the TDS and IRAS data. Also, for higher coverages there are weak signals near to 1160 and 1240 cm^{-1} . Hoffmann et al. [32] proposed that those should be assigned to CO_2^{2-} on the basis of matrix isolation data on $\text{K}_2\text{CO}_2^{2-}$. The present data cannot be taken to support or disregard this assignment.

Finally, a comment is necessary concerning the behavior of Na deposits themselves upon heat treatment. Early investigations by Bender et al. [10–12] had already shown that Na can migrate into the Cr_2O_3 oxide bulk. In the present case we find that upon heating a layer deposited at 90 K to temperatures between 295 and 420 K, i.e. below the lowest temperature for Na desorption from the surface, that Na_2CO_3 formation is

widely suppressed after offering a saturation coverage of CO_2 to the heated layer. Therefore it is rather important to always prepare a fresh film before TDS and IRAS spectra are taken, and a comparison is made. In fact, a surface that holds implanted Na, possibly and probably in the form of the mixed oxide: $\text{Na}_2\text{O} \bullet \text{Cr}_2\text{O}_3$ behaves completely different from the fresh surface. For example, Na_2CO_3 formation is completely suppressed. This is demonstrated in Fig. 4, where a two monolayer thick Na layer has been heated to 540 (Fig. 4a) and 720 K (Fig. 4b) before exposure to CO_2 . Fig. 4a shows basically two bands, one at 2355 cm^{-1} typical for the physisorbed species, and one at 1292 cm^{-1} . The latter disappears above 160 K. After preheating to 720 K, only the physisorbed species is observed. From a comparison with the data for the clean $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface [16] we believe that after heating to 540 K the surface exposes Cr ions which can bind CO_2 as bent CO_2^- , however with a slightly reduced thermal stability as indicated by the temperature series.

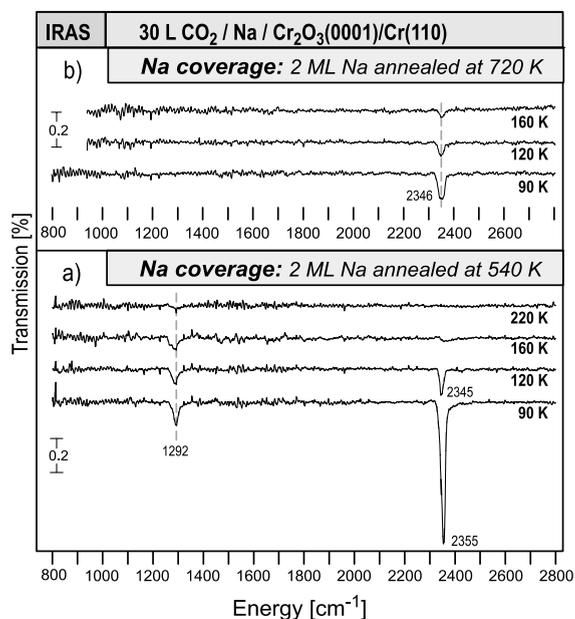


Fig. 4. Series of IRAS spectra taken of a $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface covered with 2 monolayers of Na at 90 K, heated to: (a) 540 K and (b) 720 K and then exposed to 30 L CO_2 at 90 K, followed by annealing at the given temperatures. All spectra were recorded at 90 K.

Remember, that on the clean surface the CO_2^- species has desorbed at about 280 K [16]. Obviously, these sites are no longer available after higher temperature treatment.

4. Summary and conclusion

The absorption and reaction of carbon-dioxide has been investigated for a sodium precovered $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface and compared with results for the clean $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface [16] which has been studied earlier.

It is found via TDS and IRAS measurements that CO_2 exists as physisorbed linear CO_2 on the Na-precovered surface only at temperatures below 200 K. Already at 90 K, however, also chemisorbed species exist on the surface. A detailed analysis of the vibrational spectra identifies these chemisorbed species as Na^+CO_2^- complexes existing on the surface in C_2 symmetry or as $\text{Na}_n^+\text{CO}_2^-$ compounds. Their stability is considerably higher than the CO_2^- species bound to Cr ions on the clean $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface. These latter species form a surface complex with C_2 symmetry, instead. The Na^+CO_2^- complexes on the oxide surface are similar to those observed earlier, first by Solymosi et al. and also by others, on alkali promoted metal surfaces. These Na^+CO_2^- complexes are difficult to differentiate from possibly formed oxalate $\text{C}_2\text{O}_4^{2-}$ species which may also be present on the surface. Both species could be taken as precursors for the observed formation of sodium carbonate at elevated temperatures, starting above 540 K according to



or



The concomitant desorption of CO has been observed in TDS measurements at temperatures considerably below Na_2CO_3 decomposes on the surface, i.e. above 700–800 K. Features around 1610 cm^{-1} could possibly be assigned to sodium–CO complexes on the surface. The carbonate shows considerable interaction with the $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)$ surface, since the spectra are consistent

with a preferred orientation of the carbonate molecular plane, i.e. perpendicular to the Cr_2O_3 -(0001)/Cr(110) surface, suggesting a bidentate configuration on the basis of the observed frequencies.

It is pointed out that Na interacts with the supporting oxide very strongly at elevated temperatures, i.e. at room temperature and above by probably forming mixed $\text{Na}_2\text{O} \bullet \text{Cr}_2\text{O}_3$ oxides. This influences the chemisorption of CO_2 in a very pronounced way. It is therefore crucial for measurements of the kind presented here, that before each experiment the sample is freshly prepared.

Acknowledgements

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