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ORIGINAL PAPER

Carbon Dioxide Adsorption on V_2O_3(0001)

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Abstract The adsorption of carbon dioxide on epitaxially grown V_2O_3 layers on Au(111) has been studied with thermal desorption and infrared absorption spectroscopy. It is shown that the as-grown grown oxide layer does not react with carbon dioxide; the molecule binds weakly to the surface, stays intact and desorbs below 200 K. If the oxide is weakly reduced such that part or all of the oxygen atoms of the surface vanadyl layer is removed, then a surface carboxylate, i.e. CO_2^- bound to surface vanadium is formed. Part of the CO_2 derived species decompose into O+CO upon annealing, with the oxygen atoms re-oxidizing the reduced oxide surface.

Keywords Thermal desorption spectroscopy · Infrared absorption spectroscopy · V_2O_3(0001) · Carbon dioxide · Thin films · Adsorption

1 Introduction

Vanadium oxides are widely used in technological applications, such as electrical and optical switching devices, light detectors, critical temperature sensors and write-erase materials [1, 2]. In addition to that, vanadium oxides are very interesting from a chemical point of view since they are active catalysts for a number of reactions like selective oxidation, selective reduction, and dehydrogenation of hydrocarbons and other organic compounds [1, 2]. Examples are sulfuric acid production and the oxidation of butane to maleic anhydride [3]. The manifold of catalytic applications has triggered numerous fundamental research studies of vanadium oxides aiming to improve the microscopic understanding of the catalytic processes. A complete overview of the present state of the research cannot be given here; the reader is referred to the literature. Some aspects are summed up in recent review papers [2, 4–9]. Catalysts involving vanadium oxides are usually based on V_2O_5, which contains vanadium in its highest oxidation state +5, but under reaction conditions the oxidation state may be lower. Therefore the corundum type oxide V_2O_3 has also been the topic of a number of studies (for an overview, see [2, 9]). These studies benefited from the fact that V_2O_3 layers with (0001) orientation can easily be grown on Au(111), Pd(111), Cu_3Au(100) and W(110) [2, 9–12]. Adsorption studies have been performed for methanol [13, 14], water [15, 16], and O_2 [17]. The surface structure is a critical parameter for the reactivity of a material and therefore the structure of the V_2O_3(0001) surface has been investigated thoroughly. Guided mainly by the presence of an intense vanadyl induced feature in vibrational spectra [10, 11] is was concluded that the surface should be terminated by a layer of vanadyl groups. This was questioned some years ago by studies which reported that the surface should be terminated by a quasi-hexagonal oxygen layer [18–20]. A later I/V–LEED (LEED = low energy electron diffraction; I/V–LEED = LEED intensity analysis) study could show that the initial picture of a vanadyl terminated surface is probably correct [21, 22] and therefore we will use the term 'vanadyl terminated' throughout this text. The vanadyl terminated V_2O_3(0001) surface can be reduced by electron bombardment such that the oxygen atoms of the vanadyl

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groups are removed which leads to a reactive metal terminated surface whose structure has recently been characterized with I/V–LEED and STM [23]. A partially reduced surface can be produced by reduction with a smaller electron dose. For not too high electron doses it was concluded that the electrons remove oxygen atoms of vanadyl groups so that mostly isolated metal sites form [14].

In this publication we report about an investigation of the adsorption of CO_2 on vanadyl terminated, partially reduced and metal terminated $V_2O_3(0001)$. CO_2 is a common component of exhaust gases and its critical role in the global warning process is well known (see for instance [24]). Therefore there are ongoing efforts to find ways to convert CO_2 into useful chemical products. These efforts are documented in a vast number of publications and a comprehensive overview cannot be given at this point. The interested reader is referred to some recent review papers which cover a significant part of this scientific area [25–27]. The conversion of CO_2 to methanol and higher alcohols, to methane and to carbon monoxide are probably the most actively studied areas of CO_2 conversion at present; for details please consult the above listed reviews. CO_2 has been in the focus of the research of the Chemical Physics department for a long time [28] which, together with its environmental and technological relevance, triggered this study of carbon dioxide adsorption on V_2O_3(0001). Temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS) were employed in this study. An overview of adsorption studies of CO_2 from the surface science perspective was recently collected by Burghaus [29].

2 Experimental

The data were recorded in a chamber equipped with facilities for LEED, TPD, and IRAS. Infrared absorption spectra were obtained with a Bruker IFS 66v/S FTIR spectrometer. The angle of incidence of the IR light relative to the sample normal was about 85°. IR spectra were usually obtained by accumulating 500 scans with a resolution of 2 cm^{-1}.

For TPD measurements, the sample was placed at a distance of 0.5 mm in front of the nozzle of the pumped housing ('Feulner cup', see Ref. [30]) of a quadrupole mass spectrometer (Hiden HAL RC 201). Spectra were recorded with a heating rate 0.5 K/s using a feedback temperature controller (Schlichting Instruments).

The samples were mounted using tantalum and tungsten wires attached to a hollow rod which could be filled with liquid nitrogen for cooling purposes. Temperatures of 88 K could be reached with an estimated temperature measurement accuracy of $\pm$5 K. Heating was possible by passing an electrical current through the wires holding the sample. In addition, a tungsten filament was mounted behind the sample for electron beam heating. The latter was applied only in the course of the sample preparation procedure but not in the course of the adsorption experiments to prevent unintentional surface reduction and electron induced reactions. The temperature of the Au(111) crystal was measured with a chromel/alumel thermocouple inserted into a small hole drilled into the crystal's side.

Au(111) was cleaned in UHV by cycles of argon sputtering and annealing at 1050 K. After sample cleaning the $V_2O_3(0001)$ film was prepared by evaporation of metallic vanadium (using an Omicron EFM3 electron beam evaporator) in an oxygen atmosphere (1×10^{-7} mbar) at 600 K followed by annealing at 670 K in 1×10^{-7} mbar of oxygen and annealing in vacuo at 850 K. Deposition rates (calibrated with a quartz microbalance) between 0.5 and 1 Å/min were employed in the experiments. The prepared V_2O_3 (0001) films were usually about 100 Å thick.

Surface reduction of the oxide layers was performed with a tungsten filament in front of the sample at a distance of some millimeters. The electron energy was set to 500 eV and the electron current was in the range of some 10 µA to some mA. For full reduction the surface was irradiated with an electron dose of 40 mC; for partial reduction a dose of 10 mC was used. A recent I/V–LEED study has shown that a dose of 40 mC is sufficient to reduce the surface essentially completely [23].

3 Results and Discussion

Figure 1a shows a set of TPD spectra of CO_2 on V_2O_3 (0001)/Au(111). Carbon dioxide desorbs from the vanadyl terminated oxide surface at temperatures below ~200 K [spectrum (I)]. The desorption features may be attributed to molecular CO_2 in contact with the oxide surface. Multilayer adsorption cannot be expected at 100 K [31] and therefore the sharp peak at the beginning of the spectrum may be assigned to a compressed physisorbed monolayer phase (desorption from the sample holder is also conceivable, but this should not lead to a very intense signal in the TPD spectrum due to the presence of the Feulner cup.) In the case of the reduced oxide surface [spectrum (II)] additional features show up. There is a low temperature regime which ends at about 250 K and a high temperature regime which extends from 250 to 425 K. When a second TPD run is performed [spectrum (III) in Fig. 1] the spectrum is essentially identical to the one of the vanadyl terminated surface [spectrum (I)], which demonstrates that re-oxidation of the sample takes place in the course of the first TPD run. This may be explained by a surface reaction involving CO_2 dissociation into CO and O, where the oxygen atoms

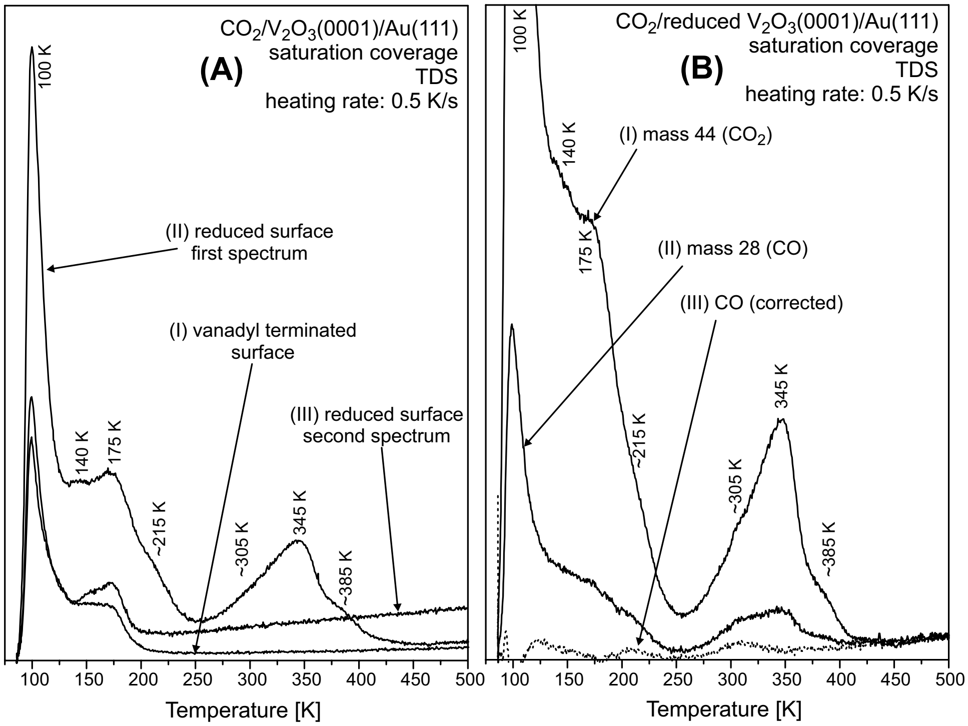

Fig. 1 **a** TPD spectra (mass spectrometer set to mass 44) of CO_2 on vanadyl terminated $V_2O_3(0001)$ [(I)] and on reduced $V_2O_3(0001)$ [(II) and (III)]. Spectrum (III) was recorded directly after spectrum (II). **b** CO_2 (mass 44) [(I)] and CO (mass 28) [(II)] TPD spectra of a carbon dioxide adsorbate on reduced $V_2O_3(0001)$. Spectrum (III) was computed from spectrum (II) by subtraction of part of the intensity of spectrum (I). For details see text

re-oxidize the surface via formation of vanadyl groups according to the reaction:

$$V - CO_2 \rightarrow \text{some surface complex} \rightarrow V = O + CO^{\uparrow} \quad (1)$$

Figure 1b exhibits TPD spectra of CO_2 on vanadium terminated $V_2O_3(0001)$ where CO_2 [mass 44, spectrum (I)] and CO [mass 28, spectrum (II)] desorption were recorded within the same run. Since CO is part of the mass cracking pattern of CO_2, the CO spectrum largely follows the CO_2 spectrum, but it is obvious that there are differences between the line shapes in the high temperature regime between 250 and 425 K, demonstrating that the CO spectrum is not completely due to CO_2 being cracked in the mass spectrometer but also to CO desorption from the oxide surface. In order to determine the extent of the latter, part of the intensity of the CO_2 spectrum was subtracted from the CO spectrum [spectrum (III)]:

$$I_{CO(corrected)} = I_{CO(measured)} - C \times I_{CO_2(measured)} \quad (2)$$

Of course, the outcome of this procedure depends crucially on the value of the constant C which is defined by the mass cracking pattern of CO_2. Published values for CO_2 (http://www.hidenanalytical.com/reference/cracking.html) did not give satisfactory results, probably due a different mass spectrometer calibrations and therefore the value of C was chosen such that the intensity of the corrected CO spectrum was about zero at low temperature where desorption of CO_2 reaction products was assumed to be unlikely. Such a subtraction procedure does not necessarily yield the accurate CO desorption spectrum since the probability that the CO_2 molecules are cracked in the mass spectrometer and the distribution of fragments depend on the rotational, vibrational and electronic state of the desorbing CO_2 molecules. However, together with other data (discussed later) it may support conclusions drawn from these data.

Common products formed by the interaction of carbon dioxide with surfaces are carbonate (CO_3^{2-}) and a bent charged CO_2 species (CO_2^-). The carbonate species may be viewed as a CO_2^- group attached to a surface oxygen ion. Other compounds considered sometimes are oxalate ($C_2O_4^{2-}$) and formate ($HCOO^-$) with the latter being formed via interaction with hydrogen.

IRAS was employed to study the nature of the adsorbed species. Figure 2 displays spectra of CO_2 on fully and partially reduced $V_2O_3(0001)$ surfaces after annealing at different temperatures. The intense band at 1043 cm^{-1} is due to the V=O vibration of the surface vanadyl groups. The IRAS data of the CO_2 covered surface exhibit bands between 2300 and 2400 cm^{-1} which are visible directly after adsorption at 88 K and survive until about 270 K. This correlates well with the low-temperature desorption feature in Fig. 1, which extend up to ~250 K. The vibrations between 2300 and 2400 cm^{-1} are attributed to the CO_2 asymmetric stretching vibration which is found at 2349.3 cm^{-1} for CO_2 in the gas phase [32]. They are the signature of an intact molecule and the existence of different levels in this energy range may be viewed as an indication of CO_2 molecules in different chemical environments.

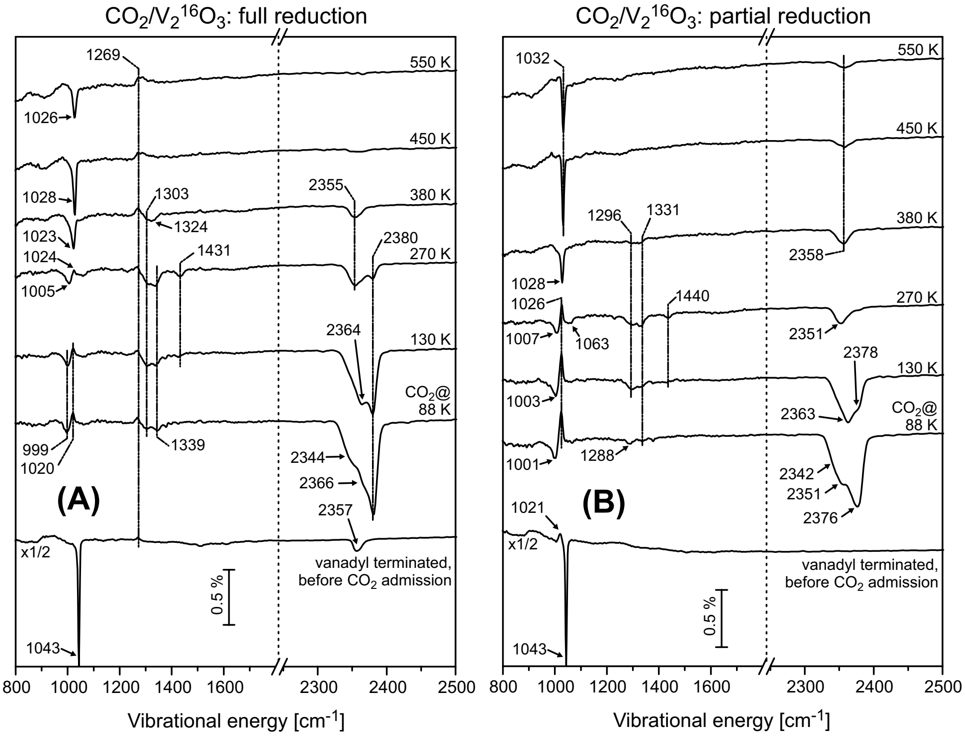

Fig. 2 IRAS spectra of CO_2 on $V_2{}^{16}O_3(0001)$. CO_2 was adsorbed at 88 K. The sample was annealed at the temperatures given in the figure and after cool-down the spectra were taken. The graphs shown here are obtained by dividing spectra of the CO_2 covered or vanadyl terminated surface by the spectrum obtained from the reduced surface before CO_2 adsorption

The complexity of the desorption features between ~130 and ~250 K in Fig. 1 mirrors the complexity of the levels in the IR data. Weak IR bands of molecular CO_2 are also identifiable at higher temperatures which may be attributed to CO_2 adsorption from the residual gas atmosphere. There was a significant carbon dioxide contribution to the residual gas atmosphere due to the slow desorption of CO_2 adsorbed on the cooling system.

The bands at ~1440 and ~1330 cm^{-1} are in an energy range where the vibrations of carbonate and CO_2^- are found. Since this would involve an interaction with substrate oxygen, especially in the case of a surface carbonate, IRAS data were also recorded for CO_2 on $V_2O_3(0001)$ prepared with $^{18}O_2$ instead of $^{16}O_2$. This permits to identify such bonds via the isotopic shift of their vibrational frequencies.

Figure 3 displays spectra of CO_2 on such isotopically labeled surfaces. The oxide layers were prepared with $^{18}O_2$, but due to the interaction of the reactive reduced layers with molecules from the residual gas atmosphere the layers also contained a certain concentration of $^{16}O_2$. In this context especially the interaction with carbon dioxide as discussed later in this text has to be considered. Therefore the oxide layer contained a mixture of the oxygen isotopes ^{18}O and ^{16}O which is the origin of the two vanadyl vibrations at 1000 and 1034 cm^{-1} in the spectra of the vanadyl terminated surfaces in Fig. 3. The energy shift with respect to the level in the spectra of the layer prepared with $^{16}O_2$ (Fig. 2) can be attributed to vibrational dipole coupling as observed before for $V_2O_3(0001)$ [14]. Crossley and King [33] have treated the frequency shifts of molecular vibrations in isotopic mixtures for the case of ^{13}CO and ^{12}CO on Pt(111) theoretically and measured the molecular vibrational energies with IRAS, finding a downward shift of the ^{12}CO band in the isotopic mixture, similar to what we find for the $V{=}^{16}O$ vanadyl vibration. A point to note is that the intensities of the $V{=}^{16}O$ and $V{=}^{18}O$ vanadyl vibrations in the bottom spectra in Fig. 3 are not proportional to the concentrations of ^{16}O and ^{18}O in the oxide layer since there is an intensity transfer from the low energy band to the high energy band [33–36]. This can be a significant effect [35] so that the concentration of ^{16}O in the oxide layer whose data are presented in Fig. 3 is probably just a few percent.

There is some fine structure especially in the feature around 1300 cm^{-1} which points towards a number of slightly different adsorption states, but there are no indications that the states are significantly different for CO_2 on the oxide which contains mainly ^{18}O and the one prepared with ^{16}O, which may be viewed as an indication that it is not carbonate which is formed on the surface since this would involve a bond of CO_2 to surface oxygen. Another observation that points into the same direction is that CO_2 does not react with the vanadyl terminated surface, for which only molecular adsorption is found (see Fig. 1). This means that CO_2 does neither react with the vanadyl oxygen atoms nor with the oxygen layer below the topmost vanadium layer which might be accessible to the CO_2 molecules since the distance between the vanadyl groups on the surface in ~5 Å. Therefore we conclude that surface vanadium

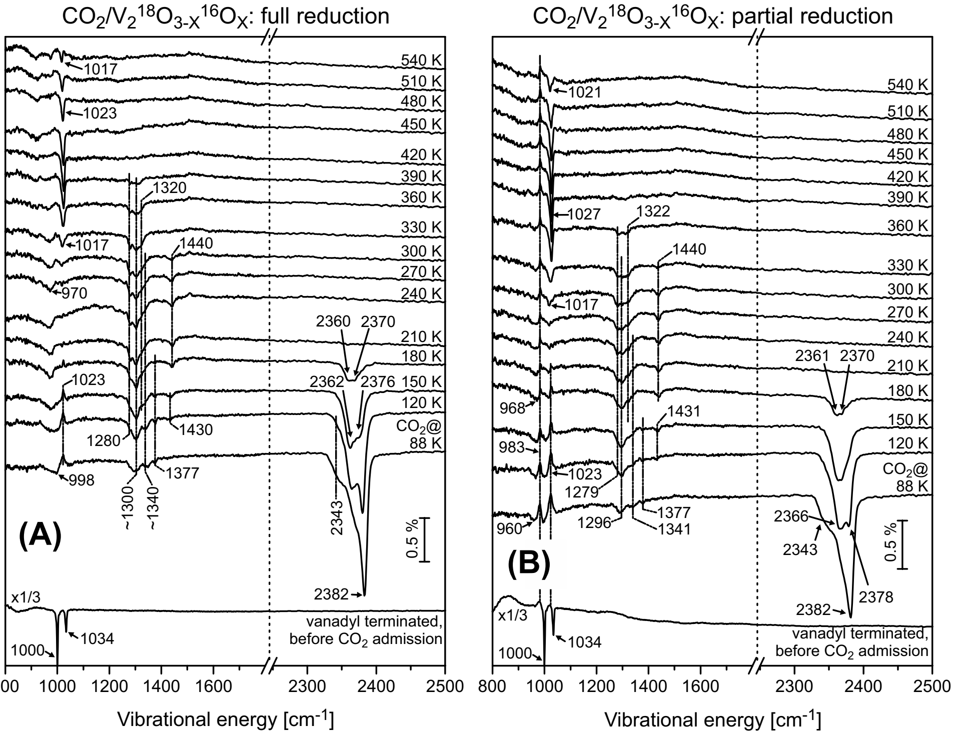

Fig. 3 IRAS spectra of CO_2 on $V_2{}^{18}O_{3-X}{}^{16}O_X(0001)$. CO_2 was adsorbed at 88 K. The sample was annealed at the temperatures given in the figure and after cool-down the spectra were taken. The graphs shown here are obtained by dividing spectra of the CO_2 covered or vanadyl terminated surface by the spectrum obtained from the reduced surface before CO_2 adsorption

atoms accessible to CO_2 must be present on the surface to induce a reaction between CO_2 and the oxide layer. A comparison of the vibrational spectra of CO_2 on fully reduced $V_2O_3(0001)$ with spectra of CO_2 on partially reduced V_2O_3 (0001) (Fig. 3a vs. b and Fig. 2a vs. b) reveals that the vanadyl groups on the partially reduced also do not a play a role for the reaction of CO_2 with the oxide layer since the shape and energy of the CO_2 derived vibrational features essentially do not depend on the presence of vanadyl groups [the feature at 1269 cm^{-1} in Fig. 2a is likely to be assigned to a water contamination in the reference spectrum as concluded from spectra of water on $V_2O_3(0001)$ (not shown here)]. It appears that the features attributed to products of the reaction of CO_2 with the oxide surface are somewhat weaker in the spectra of CO_2 on the partially reduced oxide, which is probably to be attributed to the smaller number of available surface vanadium sites, again indicating that the surface vanadium sites are the ones which are responsible for the reaction with CO_2.

An interesting topic is the behavior of the intensity in the range of the vanadyl vibrations (~995 to ~1043 cm^{-1}). At temperatures where molecular CO_2 is on the surface, bands with positive intensity appear in this energy range due to a removal of vanadyl vibrational intensity. The interaction with CO_2 derived species leads to a broadening and shift of the vanadyl vibrations so that a positive feature appears at the original position of the vanadyl vibration. The positive features vanish together with the vibrations of molecular CO_2, indicating that they are due to an interaction with this species. Starting at about 300 K in Fig. 3 an absorption band at ~1020 cm^{-1} grows which is attributed to vanadyl groups formed on the surface. The oxygen for the vanadyl groups comes from the CO_2 derived species on the surface and not from oxygen in the oxide bulk since the latter would lead the formation of two absorption bands ($V{=}^{16}O$ and $V{=}^{18}O$). However, the topmost spectrum in Fig. 3a indicates that diffusion does occur at elevated temperature since here a weak feature due to vanadyl with ^{18}O shows up.

We note that there is also some positive intensity in the spectra of the fully reduced surfaces showing that there are some vanadyl groups on the surface before CO_2 adsorption. Figure 3a reveals this is not due to an incomplete reduction but to a slight contamination of the highly reactive reduced surface since there is only one positive peak and not two (for ^{18}O and ^{16}O). This band may be attributed to a $V{=}^{16}O$ vibration with the ^{16}O originating from a reaction with molecules from the residual gas atmosphere.

Similar IRAS spectra as reported here for CO_2 on vanadium terminated $V_2O_3(0001)$ were observed for CO_2 on chromium terminated $Cr_2O_3(0001)$ [37]. However, neither CO_2 induced chromyl formation nor a CO_2 induced state near 1440 cm^{-1} were reported. This is an indication that the CO_2 derived surface compound giving rise to the vibrational line at 1440 cm^{-1} is at least partly responsible for the re-oxidation of the vanadium terminated V_2O_3 (0001) surface. Spectrum (III) in Fig. 1b exhibits a CO desorption peak at ~305 K. This temperature is near to the temperature where the state at ~1440 cm^{-1} in the IRAS spectra vanishes and where the CO_2 induced vanadyl vibration starts to show up. Therefore it may be assumed that the species characterized by the vibration at ~1440 K dissociates on the surface into oxygen and CO. The oxygen atoms bind to surface vanadium atoms forming vanadyl groups and the CO molecules desorb as described by Eq. 1. Spectrum (III) in Fig. 1a reveals that the vanadium terminated surface is fully re-oxidized after one CO_2 TPD run. It is unlikely that this is exclusively due to a re-oxidation of the surface by CO_2 decomposition since the CO desorption peak at ~300 K is rather weak, as is the vibrational band at ~1440 cm^{-1} in the vibrational spectra. However, as already noted (and also reported by Feiten et al. [23]), diffusion of bulk oxygen to the surface, where it forms vanadyl groups, does occur at elevated temperature.

Seiferth et al. [37] assign the infrared bands in the regime around 1300 cm^{-1} to the symmetric stretching vibration of a CO_2^- species with a local C_{2V} symmetry. For such a symmetry the dynamic dipole moment associated with the asymmetric stretching vibration would be mostly parallel to the surface which would result in a rather small cross section for infrared excitation and thus to a rather weak band in infrared spectra. The absence of such a band in the vibrational data of CO_2 on $Cr_2O_3(0001)$ was used to conclude that the CO_2^- species should have a local C_{2V} symmetry. This may also apply to the case of CO_2 on V_2O_3 (0001) since vibrational bands related to the asymmetric stretching vibration could not be identified also in this case. A tentative schematic model of the structure of CO_2^- on $V_2O_3(0001)$ is shown in Fig. 4.

The reduced $V_2O_3(0001)$ exhibits a number of different adsorption sites as revealed by STM [23, 38]. We assume that the species responsible for the infrared band at ~1440 cm^{-1} is a minority species related to special yet unidentified surface sites.

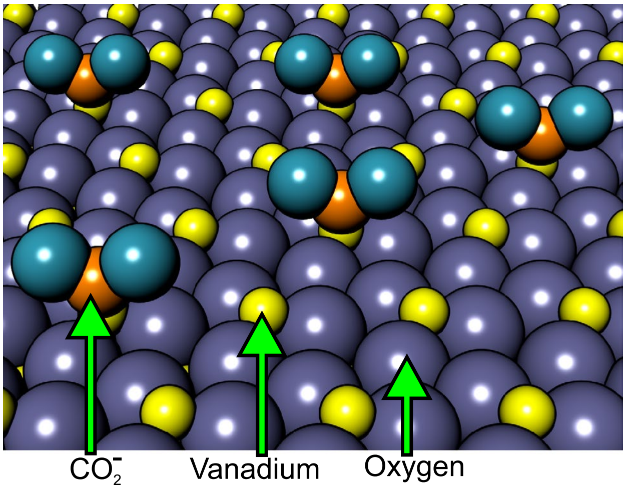

Fig. 4 Schematic model of the structure of CO_2^- on $V_2O_3(0001)$, assuming that the carbon atoms bind to substrate vanadium atoms

4 Summary

We have investigated the adsorption of CO_2 on $V_2O_3(0001)$ with TPD and IRAS. Carbon dioxide adsorbs only molecularly on vanadyl terminated $V_2O_3(0001)$ from which it desorbs below 200 K. If vanadyl oxygen atoms are removed by electron irradiation such that vanadium atoms become accessible, then CO_2 binds to these atoms, forming a surface CO_2^- species. Part of the CO_2 derived species dissociates at the surface, leading to the production of vanadyl groups and CO. The results are very similar to the results obtained for CO_2 on $Cr_2O_3(0001)$ [37] with the difference that surface reoxidation was not observed in the latter case.

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