CO_2 Adsorption on Magnetite $Fe_3O_4(111)$

F. Mirabella,^{*,#,†}[®] E. Zaki,^{#,†} F. Ivars-Barcelo,[†] S. Schauermann,^{‡®} S. Shaikhutdinov,^{†®} and H.-J. Freund^{†©}

[†]Fritz-Haber-Institute, Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

[‡]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Straße 2 24118 Kiel, Germany

ABSTRACT: We monitored the adsorption of carbon dioxide (CO_2) on well-ordered Fe₃O₄(111) films using infrared reflection-adsorption spectroscopy (IRAS) and temperature-programmed desorption (TPD). The results show that CO_2 weakly interacts with the regular Fe₃O₄(111) surface and almost fully desorbs at temperatures above ~140 K. Accordingly, IRA spectra show mainly physisorbed CO₂ species. However, TPD and IRAS features corresponding to a more strongly bound, chemisorbed species were also observed. Their formation required relatively long CO_2 exposure times, which we associated with adventitious coadsorption of residual water from the vacuum background. Since the $Fe_3O_4(111)$ surface is known to be very sensitive toward water, we additionally investigated the correlation between water and CO₂ adsorption process and found that the degree of surface hydroxylation plays a crucial role in CO_2 binding to the $Fe_3O_4(111)$ surface, ultimately leading to the formation of bicarbonate species.



1. INTRODUCTION

The attention to the chemistry of CO₂ at surfaces has increased enormously during the last two decades. This is due, on the one hand, to the role of CO₂ in catalysis, such as methanol synthesis,¹ and, on the other hand, to the recognition of CO₂ as one of the most important greenhouse gases.² Conversion of CO₂ into fuels and other value-added chemicals is a hot topic due to its obvious environmental and economic importance.³ However, CO₂ represents the most oxidized state of carbon and high thermodynamic stability, which render chemical transformations rather difficult. Direct reaction between CO₂ and water towards methanol or, more generally, the use of water as a hydrogen resource (instead of H_2) for CO₂ reduction/hydrogenation would be the ideal process, which, however, remains challenging. Despite certain advances in this field, fundamental studies have to be done which address the interaction of water and CO₂ with catalytically active substrates, in particular transition metal oxide surfaces. Such knowledge could serve as a basis for a rational design of heterogeneous catalytic processes involving CO2. In addition to the studies carried out on single crystal surfaces, recent progresses in preparation of well-defined thin oxide films on metal substrates⁴ made such investigation possible.

A comprehensive review about the surface chemistry of carbon dioxide, following a much earlier one,¹ has recently been published.⁵ The review describes CO₂/surface interaction at elevated pressures on many solids, such as zeolites, sulfides, carbides, and nitrides. However, fundamental studies on welldefined transition metal oxides surfaces are scarce. The general trend seems to be a stronger interaction of CO₂ with oxides rather than with metal surfaces,⁶ and mainly physisorption (e.g., on TiO_{2} , ^{7,8} ZnO, ⁹ and MgO^{10,11}) and formation of carbonates (on CaO, ^{12,13} Cr₂O₃, ^{14,15} Al₂O₃¹⁶) have been observed. Moreover, CO2 adsorption tends to be favored on surface imperfections (i.e., oxygen vacancies, low-coordination sites) rather than on regular surface sites.^{17,18}

Among the transition metal oxides employed in heterogeneous catalysis, iron oxides have proven to be invaluable materials, used not only to catalyze certain reactions, but also as a relatively cheap support for metal nanoparticles.¹⁹ Enormous success has been received on iron oxide-based catalysts employed in the Fenton reaction,²⁰ ethylbenzene dehydrogenation to styrene,²¹ and Fischer-Tropsch synthesis²² as well as in the water-gas shift reaction (WGSR).^{23,24} Despite the role of these materials in catalysis, the CO₂ adsorption on well-characterized magnetite surface has not been extensively studied. A few studies on polycrystal-line Fe_3O_4 , $^{25}Fe_3O_4$ nanoparticles, 26,27 and FeO_x nanoclusters on graphite¹² revealed that, also on iron oxides, mainly physisorption occurs, although the formation of carbonate species are strongly favored in the presence of Fe²⁺ cations.²⁸ Recently, Pavelec et al.¹⁷ investigated CO₂ adsorption on $Fe_3O_4(100)$ single crystal surface, and proposed a model where CO₂ initially adsorbs on Fe²⁺-related defects and then forms a physisorbed monolayer with molecules adsorbed on regular terraces. Density functional theory (DFT) calculations performed on $Fe_3O_4(111)$ surfaces suggest that carbon dioxide chemisorbs via binding to under-coordinated oxygen sites.²⁹ However, to the best of our knowledge, there are no experimental studies regarding CO₂ interaction with welldefined $Fe_3O_4(111)$ surfaces.

Received: August 24, 2018 Revised: November 7, 2018 Published: November 14, 2018

The Journal of Physical Chemistry C

In our recent studies, we characterized surface structures of $Fe_3O_4(111)$ films grown on a Pt(111) single crystal³⁰ using CO as probe molecule, and investigated its interaction with water.^{31,33} This knowledge was used in this work to understand the interaction of CO₂ with well-characterized $Fe_3O_4(111)$ surfaces, by means of infrared reflection absorption spectroscopy (IRAS) and temperature-programmed desorption (TPD). Experimental data show mainly formation of weakly bound species at lower temperatures (120-140 K), although small amounts of chemisorbed species are also detected, which could be assigned to the presence of surface imperfections.^{17,29} At higher temperatures (200-240 K), both TPD and IRAS data show stronger adsorption. However, at these conditions, the sensitivity of the surface toward preparation conditions and residual gas adsorption (in particular of water) $^{30-33}$ has to be taken into account. We found that the hydroxyl groups present on the surface play a critical role in CO_2 binding leading to the formation of surface species consistent with bicarbonate. The results provide a good basis for theoretical calculations and can serve as benchmarks for IR-based characterization of powdered iron oxide materials.

2. EXPERIMENTAL SECTION

The experiments were performed in two UHV chambers with a background pressure below 2×10^{-10} mbar. All setups were equipped with standard facilities necessary to grow wellordered $F_3O_4(111)$ films on a Pt(111) substrate. The quality of the films was checked by low-energy electron diffraction (LEED), showing sharp diffraction spots with low background intensity (at electron energies of 60-70 eV, typically used). No other elements beyond Fe and O were observed by Auger electron spectroscopy. In one chamber, TPD spectra were recorded using a quadrupole mass spectrometer (QMS) having a gold-plated cone shield to minimize signals from the heating stage. Water and CO₂ were dosed using a directional doser. IRA spectra were measured in the second chamber using an FTIR spectrometer (Bruker 66 ivs) at grazing angle 8° with the resolution of 2 cm⁻¹. Carbon dioxide (CO₂, Linde; Carbon-¹³C Dioxide, min 99 atom % 13C, Campro Scientific; Carbon Dioxide-¹⁸O₂, 97 atom % ¹⁸O, Campro Scientific), as well as water (Deuterium Oxide "100", min. 99.96% D, Sigma-Aldrich; ultrapure water, deionized and distilled H₂O) were supplied via an effusive doubly differentially pumped molecular beam.

The $Fe_3O_4(111)$ films, with a thickness of about 5 nm, were grown on a Pt(111) substrate as described elsewhere.^{34–37} The first step includes formation of the FeO(111) monolayer film on the clean Pt(111) surface.³⁸ This step is also used for calibration of the Fe deposition flux. The next step involves several (3-5) cycles of Fe deposition in amounts equivalent to 5-10 monolayers of FeO(111) onto a substrate (kept either at 100 or 300 K), followed by oxidation in 10^{-6} mbar of O₂ at ~930 K for 5-10 min. Oxygen was pumped out at sample temperature around 500 K. The samples were always flashed in UHV to 900 K prior to the water adsorption measurements. Although the precise preparation parameters (Fe flux, oxidation temperature, time and oxygen pressure) may slightly deviate in the UHV setups used, all oxide films under study showed sharp LEED patterns with low background intensity. Note also that the sample temperature readings may slightly deviate in these two chambers.

3. RESULTS AND DISCUSSION

3.1. Temperature-Programmed Desorption (TPD). A series of TPD spectra obtained upon increasing CO_2 exposure at 90 K are shown in Figure 1. Knowing that the $Fe_3O_4(111)$ surface is sensitive to traces of water and CO in the UHV background,³⁰ we also monitored CO (28 amu) and H₂O (18 amu) signals.



Figure 1. CO_2 (44 amu), CO (28 amu), and H_2O (18 amu) massspec signals recorded after increasing dosage of CO_2 at 90 K as indicated. Spectral evolution is highlighted by arrows to guide the eye. CO signals at temperatures below 150 K appearing at high exposures are assigned to CO_2 cracking pattern.

The CO₂ (44 amu) signal is dominated by a peak at 100– 150 K that gradually shifts to lower temperature. A descending edge observed in these spectra suggests that this signal represents solely a cutoff of the desorption signal, having a maximum at a lower temperature than 90 K used in these experiments, which can henceforth be referred to weakly bonded or physisorbed CO₂. A considerably stronger desorption state in the 230–300 K region only develops at higher coverages (see below).

At the lowest CO₂ dosage, the spectra also revealed CO desorbing at the same temperature (~ 235 K) and in amounts as in the γ -state observed upon pure CO adsorption.³⁰ However, this peak attenuates and ultimately disappears at increasing CO₂ exposures. (Note that the signals at low temperatures (<150 K) are caused by the CO₂ cracking pattern in the QMS.) Concomitantly, increasing water desorption signals are found at increasing CO₂ dosage, which bear close similarities in trends to those obtained in water adsorption experiments.³¹

In order to diminish obscuring effects of the strong lowtemperature CO_2 signal on the desorption signal at higher temperatures, we performed adsorption experiments at 140 K, i.e., close to the descending edge of weakly bonded CO_2 . This allowed us to detect a small CO_2 peak at 200 K (Figure 2)



Figure 2. CO_2 (44 amu), CO (28 anu), and H_2O (18 amu) QMS signals recorded at increasing exposures of CO_2 at 140 K, as indicated. (The spectra are offset for clarity.) Colored shaded areas highlight apparent correlation between CO_2 and H_2O desorption states on "water-contaminated" surfaces.

under "water-free" conditions, i.e., only negligible amounts of water were detected (see first two spectra at 1 and 5 L of CO_2). However, CO was still observed in these spectra, even though careful precautions have been taken to minimize parasitic adsorption of residual gases. In principle, the latter finding could be indicative of CO resulting from CO_2 dissociation. To examine this possibility, we performed adsorption of isotopically labeled CO_{2}^{18} on the same film. TPD spectra of three consecutive runs (Figure 3) showed no traces of CO¹⁸ (30 amu) anticipated in the case of CO¹⁸, dissociation. Alternatively, "normal" CO16 (28 amu) was still observed in the same amounts as in the case of CO^{16} adsorption, thus suggesting that CO originates from the UHV background and not from CO₂ dissociation or contamination. Moreover, a closer look at Figure 3 revealed certain relationships between intensities of desorption signals of CO₂ (at 200 K) and of CO (at 235 K) and H₂O (tiny signal at 380 K): (i) the CO₂ signal inversely correlates with the CO signal, whereas the water traces coincide (compare black and red curves); (ii) the CO₂ signal inversely correlates with the signal of water, whereas the adventitious CO signals are equal (compare black and blue curves). These relationships can readily be explained by assuming that CO2, CO, and water molecules, all compete for the same adsorption sites. On the basis of our previous studies,^{30,31} the sites responsible for the most strongly bound CO and water are defects in nature. Bearing also in mind the low intensity of the CO₂ signal at 200 K, we may, therefore, conclude that CO_2 chemisorption on the clean $Fe_3O_4(111)$ surface most likely occurs on defect sites, which, however, more strongly react with CO and water and, hence, may block CO₂ adsorption.

Now we address the TPD results in Figure 2 obtained at CO_2 exposures increasing above 5 L. Clearly, the spectra at high CO_2 dosages are accompanied by quite substantial desorption of water. On the basis of our previous studies,^{20,33} it amounts to about 1 ML after exposure to 40–60 L of CO_2 (1



Figure 3. CO^{18}_2 (48 amu), CO (28 anu), CO¹⁸ (30 amu), and H₂O (18 amu) signals recorded during the three sequential TPD runs (as indicated) following 1 L CO¹⁸₂ adsorption at 140 K. The 30 and 18 amu signals below 220 K follow those of CO₂ and thus belong to the fragmentation pattern.

 $ML = 3.2 \times 10^{14} \text{ cm}^{-2}$ corresponds to the surface density of the Fe atoms in the topmost layer on the Fe₃O₄(111) surface). Such a large amount of water implies its adsorption also on the regular Fe₃O₄(111) sites. Water strongly affects CO₂ bonding such that it starts to desorb at a considerably higher temperature than from the clean surface. Interestingly, CO₂ desorption occurs via several TPD peaks with the envelope centered at ~260 K. Apparently, there is some relationship between CO₂ and water desorption peaks in the spectra, as highlighted by the shaded areas in Figure 2 to guide the eye. This may be indicative of individual CO₂ interaction with different water species on the Fe₃O₄(111) surface.

To shed more light on the interaction of CO₂ with water adspecies using TPD, we performed experiments, in which 1 L of CO_2 was dosed to the surface first exposed to water (Figure 4). Note that for the pristine $Fe_3O_4(111)$ surface CO₂ was found desorbing at ~200 K (see Figure 2) and 3. Preadsorption of 0.1 L D_2O at 140 K immediately leads to CO_2 desorption at 250 K, which would only appear on the pristine surface at dosages above ~50 L (Figure 2). This finding provides solid evidence that strongly bound CO₂ species originate from the reaction of CO₂ with water ad-species formed either by adventitious adsorption from residual gases or by exposure to water. Interestingly, adsorption of 1 L of D₂O, that is sufficient to saturate the entire surface by 2 ML of water species,³³ increases the CO₂ signal by a factor of \sim 3, which is certainly not proportional to the water coverage which increased by a factor of ~10. Note that TPD traces of water in those coadsorption experiments are almost identical to those observed for pure water adsorption.³¹

Therefore, on the basis of the TPD results we may conclude that CO_2 molecules only weakly adsorbs on the regular $Fe_3O_4(111)$ surface sites (desorption temperature below 100 K) and even on defects, from which they desorb at around 200 K. No evidence for CO_2 dissociation is observed in isotopic experiments. CO_2 binds more strongly if the surface is



Figure 4. CO_2 and D_2O traces in TPD spectra recorded after 1 L CO_2 was dosed to the surface first pre-exposed to 0.1 L (black curve) and 1 L (red curve) of D_2O at 140 K.

precovered by water species. The related species desorb as $\rm CO_2$ at temperatures around 250 K.

3.2. Infrared Reflection Absorption Spectroscopy (IRAS). Isothermal adsorption of CO_2 on the $Fe_3O_4(111)$ surface was investigated by means of infrared-reflection-adsorption spectroscopy as a function of surface temperature and carbon dioxide exposure. Figure 5 shows CO_2 related features upon adsorption on magnetite at 120 K (a), 140 K (b), 200 K (c), and 240 K (d). Above 240 K, no signal is detected. As alluded to when discussing the TPD data in the previous section, the detection of CO_2 -related species occurs at relatively high exposures, indicating a certain degree of modification of the surface. Nevertheless, interesting CO_2 behavior at different surface temperatures is observed.

At 120 K (see Figure 5a), the spectra are dominated by a sharp peak centered at 2353 cm⁻¹, which is accompanied by a shoulder at 2338 cm⁻¹, and a small peak at 1258 cm⁻¹. The first peak and its shoulder are characteristic for the asymmetric stretching mode of weakly bound (physisorbed) CO₂ on the surface.¹⁵ On the basis of DFT calculations, CO₂ weakly adsorbs on the terahedrally (Fe_{tet1}) terminated surface, with a calculated adsorption energy of -0.43 eV.^{29} The signal at 1258 cm⁻¹ falls into the range of frequencies assigned to chemisorbed CO₂ species adsorbed in a non-planar geometry. Since we are going to discuss the evolution of several IRAsignals, it is convenient to refer to the above-mentioned peaks as to species A and B. The weakly bonded species A leads to a strong signal already at low CO₂ exposure, and saturates almost immediately without showing further growth in intensity. However, species B gains intensity as the coverage increases on the surface until saturation occurs.

As the temperature increases to 140 K (Figure 5b), major changes in the spectra evolution are observed. At low CO_2 dosages, the spectra are characterized by the weakly bound species A and another more strongly bound one leading to a signal centered at 1249 cm⁻¹. This scenario resembles the one

observed at 120 K, and peak B observed in the chemisorption region seems to be similar in nature to the one observed in Figure 5a. Therefore, we may refer to the latter feature as species B'. However, in contrast to what was observed at lower temperature—at increasing coverage, species B' decreases in intensity and a new peak at 1278 cm⁻¹ (species C) appears. Furthermore, another peak at 1398 cm⁻¹, accompanied by a small one at 1220 cm⁻¹ starts to grow, which we label as species D and E, respectively. The latter species seem to inversely correlate with the amount of species A, which starts decreasing in intensity as D and E grow in intensity.

At further increasing temperature to 200 K (Figure 5c), the spectra are dominated by species A, D, and E. This suggests that species B, B', and C, are stable only at temperatures below 200 K. Under these conditions, species A is considerably lower in intensity and attenuates as species D and E grow, until it completely disappears at higher CO_2 dosages.

Finally, at 240 K (Figure 5d) the spectra are dominated by species D and E, which keep growing in intensity as the coverage increases, and no other peaks are detected. A closer inspection of the spectra evolution in Figure 5b, c, reveals the transformation of species A into D and E, as well as an inverse relationship between species B' and C.

To shed more light on the nature of the observed species and also to rule out the possibility of adventitious CO_2 adsorption, experiments using isotopes have been performed. Figure 6 compares the results of adsorption of regular- (black), ¹³C-labeled- (red), as well as O¹⁸-labeled-CO₂ (blue) at 140 and 200 K, at saturation coverages.

The spectra document substantial shifts for both, weaker and stronger bound adsorbates, as expected upon adsorption of ¹³C-labeled- a well as O^{18} -labeled- CO_2 . This indicates that all the absorption bands observed in the IRA spectra originate from vibrations of carbon dioxide bonds, dosed via the molecular beam, and not from residual gas in the background.

 $\rm CO_2$ chemisorption on metal oxides is primarily associated with the formation of carboxylates (bent $\rm CO_2^{-}$)^{14,15} as well as different types of carbonates ($\rm CO_3^{2-}$).^{14,16} Species B' and C, observed at 140 K, fall in the range of frequencies for the stretching modes of carboxylates and carbonates species. However, the fact that they form after relatively high $\rm CO_2$ exposures and decompose below 200 K, renders their origin and spectral evolution (B' transforming into C) yet unclear. Moreover, TPD results suggest that below 200 K the related desorption signals represent a "desorption tail" of a more weakly bound state associated with physisorption, and therefore the formation of the species B, B', and C might be driven by the presence of surface imperfections.^{17,18,28}

However, species D and E seem to be stable at higher temperature, suggesting that their formation is thermally activated. These two bands may belong either to individual species or to more complex oligomers formed upon CO_2 further aggregation during the adsorption process. Indeed, recent studies of CO_2 adsorbed on a system consisting of Au islands on MgO film assigned bands in this spectral region to dimeric species, such as oxalates.¹¹ To shed more light on the nature of the adsorbates in the present study, we have performed further isotopically labeled experiments.

Hence, when regular \dot{CO}_2 and ^{13}C -labeled $^{13}CO_2$ are simultaneously sent to the surface, two possible scenarios can occur (see sketch on the bottom-left part of Figure 7). If a dimer were formed, then the corresponding IRA features would split into three different peaks with a ratio of intensities



Figure 5. IRA spectra of the CO₂ adsorption on $Fe_3O_4(111)$ as a function of coverage at 120 K (a), 140 K (b), 200 K (c), and 240 K (d).

of 1:2:1. These peaks correspond to the dimer-species formed from two ^{12}C ($^{12}C-^{12}C$), to the one obtained from the statistical combination of the two isotopes ($^{13}C-^{12}C$; $^{12}C-^{13}C$), and to the dimer with two ^{13}C ($^{13}C-^{13}C$), respectively. If the statistical combination of the two Cisotopes leads to two not identical molecules and the experimental setup is able to distinguish between them, then a splitting in four peaks with a ratio of intensity of 1:1:1:1 would be observed. The observations made in the present study do not correspond to the expectations described above: no splitting occurs, and the IRA spectrum is characterized by two well separated peaks, signaling the formation of monomeric species formed with ^{12}C and ^{13}C , respectively.

Figure 7 compares the coadsorption of regular CO_2 and ${}^{13}C$ -labeled ${}^{13}CO_2$ with the coadsorption of regular CO_2 and O^{18} -labeled CO^{18}_{22} , and the adsorption of pure CO_2 on Fe₃O₄(111) at 200 K. In this experiment, only the changes in the 1398 cm⁻¹ peak will be discussed, because the 1220 cm⁻¹ feature is too low in intensity and the shifts concerning it are too small to be appreciated (see also Figure 6). Clearly, upon codosage of CO_2 and ${}^{13}CO_2$ on the magnetite surface, no splitting for the 1398 cm⁻¹ is observed. Instead, two separated peaks appear at 1398 cm⁻¹ and at 1365 cm⁻¹ in correspondence of the molecules formed with regular C and labeled ${}^{13}C$ (with the shift expected for this molecule, ~35 cm⁻¹).

The same behavior is observed when CO_2 and O^{18} -labeled CO_2^{18} are coadsorbed on the surface. Again, no shift but two separate peaks at 1398 and 1382 cm⁻¹ are observed. These experimental findings allow us to rule out the hypothesis of further aggregation of the carbon dioxide on the magnetite surface and suggest that the observed IRA features must be related to some monomeric adsorbates.

To further proceed with the discussion, it must be considered that under the present experimental conditions, the surface temperature is appropriate to dissociate water.³² Since the surface is exposed to CO_2 for relatively long times, the presence of water at the surface from residual gas in the chamber background cannot be neglected. Taking into account the CO_2 TPD measurements, presented above, which revealed considerable amounts of water desorption at high CO_2 exposures, as well as the sensitivity of the $Fe_3O_4(111)$ toward residual gas adsorption (i.e., water),^{30–32} the role of water in the CO_2 interaction with the magnetite surface demands for an investigation using vibrational spectroscopy.

Figure 8a shows an experiment performed to compare CO_2 adsorbed on a "clean" $Fe_3O_4(111)$ surface and on a prehydroxylated one. The magnetite surface was first precovered with H_2O (dosage = 5.4 × 10¹⁴ molec.·cm⁻², which results in a coverage of ca. 1 ML, four molecules/unit cell)³³ at 200 K, and afterwards exposed to different amounts



Figure 6. Comparison of the IRA adsorption features of CO2 and labeled ¹³CO₂ (red spectra) as well as CO¹⁸₂ (blue spectra), obtained at 140 and 200 K at saturation conditions (exposure: 1.4×10^{18} molec. cm^{-2}).

of CO₂ at the same temperature. The presence of hydroxyl groups on the surface (evidenced in the IRA spectra by the peaks at 3690 and 3640 cm⁻¹) has a tremendous effect on CO₂ chemisorption. First, species A is no more observed, showing that water adsorption suppresses CO₂ physisorption, blocking the available sites for its adsorption. Moreover, not only the spectral features resulting from chemisorbed species almost double their intensity, when compared to spectra taken after the same amount of CO2 was adsorbed on the "clean" $Fe_3O_4(111)$, but also, a new broad band appears as a shoulder at 1378 cm⁻¹.

These experimental evidence suggest that the OH groups present on the surface play an important role in the CO₂chemisorption. Moreover, the observed peaks are virtually identical to the one reported by Baltrusaitis et al.³⁹ and Wang et al.⁴⁰ upon CO₂ adsorption on Fe₂O₃ nanoparticles and on Pd/Al₂O₃ catalysts, respectively. These bands are assigned to the symmetric stretching ν_s (1400 cm⁻¹) and bending vibrations δ_{COH} (1220 cm⁻¹) of surface bicarbonates, formed upon reaction between CO₂ and OH of groups present on the surface. To confirm the presence of surface bicarbonate on the surface, CO_2 was then adsorbed on $Fe_3O_4(111)$ surfaces preexposed to deuterated water (Figure 8b). Upon bicarbonate formation involving OD groups, the δ_{COD} mode is expected to red-shift⁴¹ from 1220 to 969 cm⁻¹. Figure 8b shows that, after CO₂ adsorption onto a deuterated magnetite surface, a shift of 9 cm⁻¹ for the ν_s mode, accompanied by a new feature at 1366 cm⁻¹ is observed, while the peak at 1220 cm⁻¹ almost disappears, suggesting that the δ_{COD} mode has shifted to low frequencies, below the cutoff frequency of our IRAS setup. The tiny signal around 1218 cm⁻¹ is related to the formation of



Article

Figure 7. Co-adsorption experiment of pure, and isotopically labeled CO₂ in order to distinguish the formation of monomers versus dimers on the surface. The comparison between the coadsorption of $^{13}\mathrm{CO}_2$ and CO_2 (red), the coadsorption of CO_2^{18} and CO_2 (blue), and the pure CO₂ adsorption (black) is presented. The experiments are performed at 200 K with a CO₂ dosage of 3.6×10^{17} molec. cm⁻².

bicarbonate species involving OH formed from residual H₂O water in the background.

Figure 8 also shows that the stretching mode of the surface bicarbonates results in a peak splitting, which seems to be more evident for OD- rather than for OH- precovered surfaces. This splitting might indicate the formation of species interacting differently with different hydroxyl groups. We have recently reported³¹ that water readily dissociates on regular Fe_{tet1}-terminated magnetite surfaces, forming a terminal O_wD-Fe (on top of a Fe cation) and O_sD involving oxygen from the surface lattice. The two species have different IRA signature and it is, therefore, reasonable that diverse types of bicarbonates are being formed on the surface upon selective interaction with different OD species.

In light of the presented experimental observations, the following mechanism for the bicarbonate formation on the magnetite surface is proposed. In agreement with DFT calculations,¹⁵ the early stage of the CO₂ adsorption on the $Fe_3O_4(111)$ surface results in a weakly bound adsorption (physisorption), characterized by an IRAS peak centered at 2353 cm⁻¹. At 200 K, the surface temperature is high enough for the physisorbed CO₂ to overcome the activation barrier needed to interact with the OH groups present on the surface from the residual gas adsorption and to form bicarbonate.

Certainly, the presence and concentration of surface bicarbonates depends on the extent of hydroxylation of the surface. Figure 9a illustrates the behavior of CO₂ with respect to different amount of OD groups on the surface.



Figure 8. Comparison between the CO₂ adsorption on regular (black) and OH-precovered (blue) $Fe_3O_4(111)$ surfaces (a). Comparison between the CO₂ adsorption on regular (black) and OD-precovered (red) $Fe_3O_4(111)$ surfaces (b). The H₂O (D₂O) dosage on the surface is 5.4 × 10¹⁴ molec. cm⁻².



Figure 9. Panel (a) shows a series of IRA spectra related to the adsorption of a fixed dosage of CO_2 on $Fe_3O_4(111)$ surfaces precovered with different amounts of OD species (black). Panel (b) shows the experiment, where a $Fe_3O_4(111)$ surfaces, precovered with a fixed amounts of OD species, is exposed to two increasing CO_2 dosages. The experiments are performed at 200 K.

When CO_2 is adsorbed on magnetite previously modified by a relatively small amount of OD groups a strong surfacebicarbonate related peak at 1389 cm⁻¹ is detected. As the OD concentration increases, a second peak around 1366 cm⁻¹, which at low exposure develops as a small shoulder, gains considerable intensity. However, when the water starts forming oligomers on the surface which ultimately self-assemble into a 2D network,³¹ no more CO₂ related features are detected. It seems that the accessibility of the "free" OD-Fe on the surface is necessary for the formation of CO_2 adsorbates on the $Fe_3O_4(111)$, and an extended network of H-bonded species passivates the surface.

Interestingly, upon interaction with CO_2 , the intensity ratio of the two water-related peaks changes, in comparison with pure D₂O adsorption on Fe₃O₄(111). The latter observation is more obvious in Figure 9b. Here, the surface is first exposed to a certain amount of D₂O and afterward exposed to two increasing CO₂ dosages. Distinctly, the terminal O_wD-Fe and

The Journal of Physical Chemistry C

the O_sD peaks decrease in intensity asymmetrically, upon formation of surface bicarbonates. This is in quite good agreement with the model of formation of different bicarbonate species upon selective interactions with different OD species proposed earlier. However, further DFT calculations are necessary to confirm such hypothesis.

4. CONCLUSIONS

In this work, adsorption of carbon dioxide on $Fe_3O_4(111)$ surface was investigated by means of temperature-programmed desorption (TPD) and infrared reflection adsorption spectroscopy (IRAS) at different dosages and temperatures. TPD experiments suggest that CO₂ adsorbs very weekly on a regular $Fe_3O_4(111)$ surface. Accordingly, IRA spectra show mainly contribution from CO₂ physisorbed in the range of temperatures between 120 and 140 K, although some features associated with chemisorption are also observed. However, the formation of considerable amounts of the chemisorbed species required relatively long CO₂ exposure times, suggesting that a certain degree of modification of the surface occurred while dosing. The formation of such species might be driven by surface imperfections. This scenario resembles the one found for CO_2 upon adsorption on the (100) facet of magnetite surfaces, recently published by Pavelec et al.¹⁶ However, although the origin of such species remains yet unclear, consistency with carboxylates and carbonates is found.^{14,15}

At higher temperatures (~200-240 K), considerably stronger bound species are consistent with TPD and IRA spectra, respectively. In particular, two IRA features are observed at these conditions: 1398 and 1220 cm⁻¹. Despite these bands have been in the past assigned to dimeric species (e.g., oxalates), a detailed investigation by means of isotopically labeled molecules $({}^{13}CO_2$ and $CO{}^{18}_2)$ allowed us to rule out such a possibility. In order to assign the IRA features, it must be taken into account that, under these temperature conditions, the $Fe_3O_4(111)$ surface is extremely sensitive toward residual gas adsorption (in particular of water).³⁰⁻³² Indeed, all TPD spectra obtained at increasing CO₂ coverage are accompanied by desorption of water in quite substantial amounts which implies its adsorption on the regular $Fe_3O_4(111)$ terrace sites. The apparent correlation between CO₂ and water was investigated in more details via infrared experiments, performed using regular, as well as deuterated water, to precover the surface prior CO₂ adsorption. It was found that the degree of hydroxylation of the surface plays a crucial role in CO_2 adsorption on regular (Fe_{tet1}) tetrahedrally terminated magnetite surface,^{18,28} leading to the formation of adsorbate species identified as surface bicarbonates.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mirabella@fhi-berlin.mpg.de.

ORCID [©]

- F. Mirabella: 0000-0001-8443-3652
- S. Schauermann: 0000-0002-9390-2024
- S. Shaikhutdinov: 0000-0001-9612-9949
- H.-J. Freund: 0000-0001-5188-852X

Author Contributions

[#]These authors contributed equally to the work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been supported by the Deutsche Forschungsgemeinschaft through Collaborative Research Center SFB 1109, and by the Fonds der Chemischen Industrie. F.M. thanks the International Max-Planck Research School "Functional Interfaces in Physics and Chemistry" for a fellowship. Open Access funding provided by the Max Planck Society.

REFERENCES

(1) Freund, H.-J.; Roberts, M. W. Surface Chemistry of Carbon Dioxide. Surf. Sci. Rep. 1996, 25, 225-273.

(2) Lackner, K. S. A Guide to CO_2 Sequestration. Science 2003, 300, 1677–1678.

(3) Yu, K. M. K.; Curcic, I.; Gabriel, J.; Tsang, S. C. E. Recent Advances in CO_2 Capture and Utilization. *ChemSusChem* **2008**, *1*, 893–899.

(4) Freund, H.-J., Kuhlenbeck, H., Staemmler, V. Oxide Surfaces. *Rep. Prog. Phys.* **1996**, *59*, 283–347.

(5) Taifan, W.; Boily, J. F.; Baltrusaitis, J. Surface Chemistry of Carbon Dioxide Revisited. Surf. Sci. Rep. 2016, 71, 595-671.

(6) Burghaus, U. Surface chemistry of CO_2 - Adsorption of Carbon Dioxide on Clean Surfaces at Ultrahigh Vacuum. *Prog. Surf. Sci.* **2014**, 89, 161–217.

(7) Lin, X.; Yoon, Y.; Petrik, N. G.; Li, Z.; Wang, Z.-T.; Glezakou, V.; Kay, B. D.; Lyubinetsky, I.; Kimmel, G. A.; Rousseau, R.; et al. Structure and Dynamics of CO_2 on Rutile TiO_2 (110)-1 × 1. *J. Phys. Chem. C* 2012, *116*, 26322–26334.

(8) Mino, L.; Spoto, G.; Ferrari, A. M. CO_2 capture by TiO_2 Anatase Surfaces: A combined DFT and FTIR Study. *J. Phys. Chem. C* **2014**, 118, 25016–25026.

(9) Funk, S.; Hokkanen, B.; Wang, J.; Burghaus, U.; Bozzolo, G.; Garces, J. E. Adsorption Dynamics of CO₂ on Cu(110): A Molecular Beam Study. *Surf. Sci.* **2006**, *600*, 583–590.

(10) Tosoni, S.; Spinnato, D.; Pacchioni, G. DFT Study of CO_2 Activation on Doped and Ultrathin MgO Films. J. Phys. Chem. C 2015, 119, 27594–27602.

(11) Calaza, F.; Stiehler, C.; Fujimori, Y.; Sterrer, M.; Beeg, S.; Ruiz-Oses, M.; Nilius, N.; Heyde, M.; Parviainen, T.; Honkala, K.; et al. Carbon Dioxide Activation and Reaction Induced by Electron Transfer at an Oxide-Metal Interface. *Angew. Chem., Int. Ed.* **2015**, *54*, 12484–12487.

(12) Kadossov, E.; Burghaus, U. Adsorption Kinetics and Dynamics of CO, NO, and CO_2 on Reduced CaO(100). *J. Phys. Chem. C* **2008**, 112, 7390–7400.

(13) Solis, B. H.; Cui, Y.; Weng, X.; Seifert, J.; Schauermann, S.; Sauer, J.; Shaikhutdinov, S.; Freund, H.-J. Initial stages of CO_2 Adsorption on CaO: A Combined Experimental and Computational Study. *Phys. Chem. Chem. Phys.* **2017**, *19*, 4231–4242.

(14) Seiferth, O.; Wolter; Dillmann, B.; Klivenyi, G.; Freund, H.-J.; Scarano, D.; Zecchina, A. IR Investigations of CO₂ Adsorption on Chromia Surfaces: Cr_2O_3 (0001)/Cr(110) Versus Polycrystalline α -Cr₂O₃. Surf. Sci. **1999**, 421, 176–190.

(15) Seiferth, O.; Wolter, K.; Kuhlenbeck, H.; Freund, H.-J. CO_2 Adsorption on Na Precovered $Cr_2O_3(0001)$. *Surf. Sci.* **2002**, 505, 215–224.

(16) Weilach, C.; Spiel, C.; Föttinger, K.; Rupprechter, G. Carbonate Formation on Al_2O_3 Thin Film Model Catalyst Supports. *Surf. Sci.* **2011**, 605, 1503–1509.

(17) Pavelec, J.; Hulva, J.; Halwidl, D.; Bliem, R.; Gamba, O.; Jakub, Z.; Brunbauer, F.; Schmid, M.; Diebold, U.; Parkinson, G. S. A Multi-Technique Study of CO₂ Adsorption on Fe₃O₄ Magnetite. *J. Chem. Phys.* **2017**, *146*, No. 014701.

(18) Henderson, M. A. Evidence for Bicorbonate Formation on Vacuum Annealed $TiO_2(110)$ Resulting from a Precursor-Mediated Interaction Between CO_2 and H_2O . Surf. Sci. **1998**, 400, 203–219.

(19) Parkinson, G. S. Iron Oxide Surfaces. Surf. Sci. Rep. 2016, 71, 272–365.

The Journal of Physical Chemistry C

(20) Munoz, M.; de Pedro, Z. M.; Casas, J. A.; Rodriguez, J. J. Preparation of Magnetite-based Catalysts and Their Application in Heterogeneous Fenton Oxidation - A Review. *Appl. Catal., B* 2015, 176–177, 249–265.

(21) Weiss, W.; Ranke, W. Surface Chemistry and Catalysis on Welldefined Epitaxial Iron Oxide Layers. *Prog. Surf. Sci.* 2002, *70*, 1–151.

(22) Dictor, R. A.; Bell, A. T. Fischer-Tropsch Synthesis over Reduced Iron Oxide Catalysts and Unreduced. *J. Catal.* **1986**, *97*, 121-136.

(23) Gamba, O.; Noei, H.; Pavelec, J.; Bliem, R.; Schmid, M.; Diebold, U.; Stierle, A.; Parkinson, G. S. Adsorption of Formic Acid on the Fe_3O_4 (001) Surface. *J. Phys. Chem. C* **2015**, *119*, 20459–20465.

(24) Lee, D. W.; Lee, M. S.; Lee, J. Y.; Kim, S.; Eom, H.-J.; Moon, D. J.; Lee, K.-Y. The review of Cr-free Fe-based Catalysts for High-Temperature Water-Gas Shift Reactions. *Catal. Today* **2013**, *210*, 2–9.

(25) Udovic, T. J.; Dumesic, J. A. Adsorptive Properties of Magnetite Surfaces as Studied by Desorption: Studies of O_2 , NO, CO_2 , and CO Adsorption. J. Catal. **1984**, 89, 314–326.

(26) Ramis, G.; Busca, G.; Lorenzelli, V. Low-temperature CO_2 Adsorption on Metal Oxides: Spectroscopic Characterization of Some Weakly Adsorbed Species. *Mater. Chem. Phys.* **1991**, *29*, 425–435.

(27) Hakim, A.; Marliza, T. S.; Abu Tahari, N. M.; Wan Isahak, R. W. N.; Yusop, R. M.; Mohamed Hisham, W. M.; Yarmo, A. M. Studies on CO_2 Adsorption and Desorption Properties from Various Types of Iron Oxides (FeO, Fe₂O₃, and Fe₃O₄). *Ind. Eng. Chem. Res.* **2016**, 55, 7888–7897.

(28) Tamaura, Y.; Tahata, M. Complete Reduction of Carbon Dioxide Using Cation-Eccess Magnetite. *Nature* 1990, 346, 255-256.
(29) Su, T.; Qin, Z.; Huang, G.; Ji, H.; Jiang, Y.; Chen, J. Density

Functional Theory Study on the Interaction of CO_2 with $Fe_3O_4(111)$ Surface. Appl. Surf. Sci. **2016**, 378, 270–276.

(30) Li, X.; Paier, J.; Sauer, J.; Mirabella, F.; Zaki, E.; Ivars-Barcelo, F.; Shaikhutdinov, S.; Freund, H.-J. Surface Termination of $Fe_3O_4(111)$ Films Studied by CO Adsorption Revisited. *J. Phys. Chem. B* **2018**, *122*, 527–533.

(31) Mirabella, F.; Zaki, E.; Ivars-Barcelo, F.; Li, X.; Paier, J.; Sauer, J.; Shaikhutdinov, S.; Freund, H.-J. Cooperative Formation of Long-Range Ordering in Water Ad-layers on $Fe_3O_4(111)$ Surfaces. *Angew. Chem., Int. Ed.* **2018**, *57*, 1409–1413.

(32) Shaikhutdinov, S.; Weiss, W. Adsorbate Dynamics on Iron Oxide Surfaces Studied by ScanningTtunneling Microscopy. J. Mol. Catal. A: Chem. 2000, 158, 129–133.

(33) Zaki, E.; Mirabella, F.; Ivars-Barcelo, F.; Seifert, J.; Carey, S.; Li, X.; Paier, J.; Sauer, J.; Shaikhutdinov, S.; Freund, H.-J. Water adsorption on the $Fe_3O_4(111)$ Surface: Dissociation and Network Formation. *Phys. Chem. Chem. Phys.* **2018**, *20*, 15764–15774.

(34) Ritter, M.; Weiss, W. Fe₃O₄(111) Surface Structure Determined by LEED Crystallography. Surf. Sci. **1999**, 432, 81–94.

(35) Shaikhutdinov, S.; Ritter, M.; Wang, X.; Over, H.; Weiss, W. Defect Structures on Epitaxial $Fe_3O_4(111)$ Films. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *60*, 11062–11069.

(36) Sala, A.; Marchetto, H.; Qin, Z.-H.; Shaikhutdinov, S.; Schmidt, Th.; Freund, H.-J. Defects and Inhomogeneities in $Fe_3O_4(111)$ Thin Film Growth on Pt(111). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *86*, 155430.

(37) Lemire, C.; Meyer, R.; Henrich, V. E.; Shaikhutdinov, S.; Freund, H. J. The Surface Structure of $Fe_3O_4(111)$ Films as Studied by CO Adsorption. *Surf. Sci.* **2004**, *572*, 103–114.

(38) Weiss, W.; Ranke, W. Surface Chemistry and Catalysis on Welldefined Epitaxial Iron-Oxide Layers. *Prog. Surf. Sci.* 2002, *70*, 1–151.

(39) Baltrusaitis, J.; Grassian, V. H. Surface Reactions of Carbon Dioxide at The Adsorbed Water-Iron Oxide Interface. *J. Phys. Chem. B* **2005**, *109*, 12227–1223.

(40) Wang, X.; Shi, H.; Kwak, J. H.; Szanyi, J. Mechanism of CO_2 Hydrogenation on Pd/Al₂O₃ Catalysts: Kinetics and Transient DRIFTS-MS Studies. *ACS Catal.* **2015**, *5*, 6337–6349.