Surface chemistry of carbon dioxide revisited

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Abstract

This review discusses modern developments in CO₂ surface chemistry by focusing on the work published since the original review by H. J. Freund and M.W. Roberts two decades ago (*Surface Science Reports* 25 (1996) 225-273). It includes relevant fundamentals pertaining to the topics covered in that earlier review, such as conventional metal and metal oxide surfaces and CO₂ interactions thereon. While UHV spectroscopy has routinely been applied for CO₂ gas-solid interface analysis, the present work goes further by describing surface-CO₂ interactions under elevated CO₂ pressure on non-oxide surfaces, such as zeolites, sulfides, carbides and nitrides. Furthermore, it describes salient *in situ* techniques relevant to the resolution of the interfacial chemistry of CO₂, notably infrared spectroscopy and state-of-the-art theoretical methods, currently used in the resolution of solid and soluble carbonate species in liquid-water vapor, liquid-solid and liquid-liquid interfaces. These techniques are directly relevant to fundamental, natural and technological settings, such as heterogeneous and environmental catalysis and CO₂ sequestration.

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1 Introduction

Increasing levels of atmospheric CO₂ [1,2] have prompted numerous studies dedicated to solid and liquid surface-facilitated chemical reactions leading to the fixation of carbon from CO₂ as a feedstock. These studies range from natural processes in the atmosphere (CO₂ partitioning into the oceans [3] or on mineral dust aerosols [4] under environmentally relevant conditions of pressure, temperature and co-reactants, such as H₂O vapor [5]) to high temperature and pressure catalytic processes, such as industrial CH₃OH synthesis [6]. CO₂ activation and upgrading to value added chemicals has been extensively reviewed [6–12] with the focus on finding the most feasible catalysts that possess (a) high single pass conversion while (b) selectively yielding desired hydrocarbons or the corresponding oxygenates. Simple thermodynamic considerations (ΔH and ΔG) suggest that a number of catalytic reactions shown in Table 1, below are thermodynamically and exergonically favorable, and even proceed on the same catalysts as the equivalent CO hydrogenation processes (rxn 3 to form CH₃OH on Cu/ZnO based catalysts).

Table 1. Thermodynamic consideration of various reactions of CO₂ to molecules at 298 K.

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Rxn	Reactions	ΔH , (kJ/mol)	ΔG , (kJ/mol)	Catalyst
1	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	41.2	28.6	Cu-, Cu/ZnO-, Fe-, and Ce-based catalysts
2	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{HCOOH}$	-31.2	33	Rh-, Ru-, and Ir-based organometallic catalysts
3	$\text{CO}_2 + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-131	-9	Cu-, Cu/ZnO-, Fe-, and Ce-based catalysts
4	$\text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{H}_2\text{O}$	-164.9	-113.5	Ni-based, supported Ru and Rh catalysts
5	$\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2 \text{CO} + 2 \text{H}_2$	247.3	170.7	Rh-, Ru-, and Ni-based catalysts

Selectivity issues however prohibited practical implementation of catalytic CO₂ conversion. For example, the reverse water-gas shift reaction 1 and methanol formation reaction 3 take place over the same catalyst. Formation of water also presents a challenge to the active catalyst material and the support, in addition to increasing separation costs [7]. Furthermore, converting CO into methanol is much more efficient than CO₂. Even though labeling experiments show that surface carbonate and formate species, resulting from CO₂, not from CO, are the main intermediates, the catalysts for CO to CH₃OH lose their catalytic activity, when CO₂ is used instead of CO [7]. The deactivation of the catalyst is apparently due to the formation of water in the CO₂ case, which is not encountered when one starts with CO [8]. This interesting interplay between favorable thermodynamics and low observed yields suggests catalyst surface controlled reactivity.

The hitherto methods for identifying the best combinations of catalysts have not provided a detailed understanding of the underlying, fundamental surface phenomena. Furthermore, during the recent decades, theoretical methods, such as the Density Functional Theory (DFT), and calculations developed rapidly, now provide a superior tool for understanding the combined reaction mechanism involved. These advances aid in the design of new catalysts, rather than tediously exhausting all the possible combinations of the existing transition metals and oxides. New models and improved algorithms, as well as the introduction of van der Waals contributions to adequately describe weak substrate-adsorbate interactions, are expected to become the main protagonists in understanding CO₂ surface based transformations. Combined with the instrument developments for *in situ* experimental surface analysis at the operating temperature and pressure, advances in theoretical approach could help overcome the selectivity challenges. A comprehensive review of the computational approach for CO₂ upgrade to CO, CH₄, CH₃OH, and

HCOOH, in addition to photocatalysis and electrocatalysis, is provided by Cheng *et al.* [11] and will not be discussed here. Instead, molecular level surface fundamentals in CO₂ adsorption, binding and resulting molecular structure perturbation will be broadly covered using both Ultra High Vacuum (UHV) and controlled temperature and pressure conditions via both experimental and theoretical approaches. At the same time, this review builds upon the one by H.-J. Freund and M.W. Roberts published in 1996 [13] and includes relevant fundamentals pertaining to CO₂ chemistry and techniques needed for resolution of the interfacial chemistry of CO₂ that are of central importance to the topics covered in this review. As such, the overarching goal of this review is to provide an overview of the salient achievements in the interfacial chemistry of CO₂ during the past two decades, yet it cannot fully cover the entirety of the contributions made by the vast and interconnected chemical, geochemical, and atmospheric communities. Still, it is our hope that this review will provide early career to seasoned physical scientists with the necessary overview needed to grasp the rich interfacial chemistry undergone by CO₂, and that it will pave the way for future developments for this engaging greenhouse gas of scientific, engineering and societal importance.

2 Structure and bonding properties of CO₂

2.1 Electronic structure of gas phase CO₂

CO₂ is a linear molecule that has two equivalent C=O bond lengths, with a $\angle$ O-C-O bond angle of 180°. The ground state electronic configuration of a carbon atom is $1s^2 2s^2 2p^2$, whereas an oxygen atom has a ground state electronic configuration of $1s^2 2s^2 2p^4$. This indicates that the carbon atom needs four electrons to reach the octet configuration, while an oxygen atom needs

two more electrons. A linear combination of atomic orbitals can express molecular orbitals of the CO₂ (LCAO-MO) wave function in the general form as

$$\psi = c_1 2s_{O1} + c_2 2s_{O2} + c_3 2s_C + c_4 2px_{O1} + c_5 2px_{O2} + c_6 2px_C + c_7 2py_{O1} + c_8 2py_{O2} + c_9 2py_C + c_{10} 2pz_{O1} + c_{11} 2pz_{O2} + c_{12} 2pz_C. \quad (1)$$

The 1s shells of the C and O atoms are non-bonding orbitals, and hence do not contribute to the bonding of CO₂, as shown in Figure 1, below. The 2p_x and 2p_y orbitals are located in the same plane, hence three doubly degenerate molecular orbitals, 1π_g (non-bonding), 1π_u, and 2π_u^{*}, are formed. The former does not contain a contribution from the C atom, as the 2p orbitals of the O atoms are out of phase and contain lone pairs electrons. The 2p_z and 2s atomic orbitals combine to form six σ molecular orbitals labeled as 3σ_g, 2σ_u, 4σ_g, 5σ_g^{*}, 3σ_u, and 4σ_u^{*}. Not counting the core electrons, the CO₂ molecule shares 16 electrons in the molecular orbitals, with eight electrons occupying four σ orbitals, and the other eight in two π orbitals [13].

Figure 1. Molecular orbital diagram of a linear ($D_{\infty h}$ symmetry) CO_2 .

2.2 Molecular structure and electronic properties of the excited state and anionic CO_2 .

The π_u MOs have contributions from all the atoms involved. However, electron sharing is only permitted when the two orbitals have equal binding energy. Oxygen has considerably greater

electronegativity than carbon, and hence, two lower-energy degenerate π orbitals ($1\pi_u$ and $1\pi_g^*$) are localized on the oxygen atoms, whereas the higher energy one, $2\pi_u^*$, is more localized on carbon [14]. Two of these three MOs, $1\pi_g^*$ (non-bonding) and $2\pi_u^*$, constitute, in turn, the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of this molecule. Bonding electrons are distributed throughout $4\sigma_g$ to $1\pi_u$, where electrons occupying $4\sigma_g$ and $3\sigma_u$ form σ -CO bonds, and those occupying the doubly degenerate $1\pi_u$ form the π -CO bonds. Because the ground-state CO_2 molecule contains 16 valence electrons, it is expected to be linear.

2.2.1 Electronic structure of excited state CO_2

In its first excited state, analogous to NO_2 , the electrons are promoted to the $2\pi_u^*$ molecular orbital, resulting in a smaller population of electrons for stabilizing the linear form. The molecule is consequently expected to be bent. Full-valence Complete Active Space CAS (16,12)/def2-TZVP calculations show that the S_0 ground state of CO_2 possesses minor multi-reference character (92% one reference state). All orbitals are doubly occupied with calculated degenerate HOMO orbitals containing 1.96 e^- and degenerate LUMO containing 0.06 e^- . Calculated CM5 charges are +0.44 on C and -0.22 on each O atom. On the other hand, the S_1 excited state structure exhibits a very different molecular structure with a C-O1 bond of 1.22 Å and a C-O2 bond of 1.46 Å and an O-C-O angle of 150.0° (Figure 2). Still, only a minor multi-reference character is observed (90% one reference state). The singly occupied molecular orbitals (SOMOs) involved in excited state transitions are shown in Figure 2. SOMO1 is mainly localized on the p_z orbital of O2 while SOMO2 is localized on the p_y orbital of C. This is different from the ground state HOMO/LUMO orbital populations also shown in Figure 2, below, where the former is localized on both O atoms equally and the latter, symmetrically on C. Calculated CM5 charges are +0.25 on C, -0.16 on O1 and -0.09 on O2. The CO_2 molecule in the S_1 state should consequently contain a much less electrophilic C, but O1 of nearly the same nucleophilicity as in S_0 , and an essentially neutral O2.

2.2.2 Anionic CO₂ (CO₂⁻) electronic structure

The anionic CO₂ molecule has a negative charge, and 17 electrons in the valence orbitals can form via transfer of an electron from the substrate upon adsorption. It will also exhibit a bent structure (Figure 3).

Figure 3. Electron Localization Function (ELF) domains at an isosurface value of $\eta(r)=0.82$ for the ground state CO_2 (left; $r(\text{C-O}) = 1.16 \text{ \AA}$, $\theta(\text{O-C-O}) = 180^\circ$) and CO_2^{1-} (right; $r(\text{C-O}) = 1.23 \text{ \AA}$, $\theta(\text{O-C-O}) = 138^\circ$) molecules in vacuum. Generated from wave functions obtained at molecular geometries optimized at the B3LYP/6-311+G(3df) level of theory. Calculations were carried out using Gaussian09 [15] and Topmod [16]. Calculations were done at the B3LYP/6-311+G(3df).

B3LYP/6-311+G(3df) level calculations show that CO_2 is indeed linear (22 total electrons total, calculated $\text{C-O} = 1.16 \text{ \AA}$, $\nu(\text{bend})=677 \text{ cm}^{-1}$; $\nu(\text{sym})=1372 \text{ cm}^{-1}$; $\nu(\text{asym})=2405 \text{ cm}^{-1}$). Calculated Electron Localization Function (ELF) [17] domains show electron populations in bonding basins of 2.93-2.85 e^- per basin with electron populations in a valence shell of O = 4.95-4.99 e^- per basin. A strong cross-relation between the electron populations of the valence shell of O and the bonding electrons can also be observed. When CO_2 obtains an additional electron, its structure becomes bent (23 electrons in total; $\text{C-O} = 1.23 \text{ \AA}$, optimal bond angle = 138° , $\nu(\text{bend})=664 \text{ cm}^{-1}$; $\nu(\text{sym})=1213 \text{ cm}^{-1}$; $\nu(\text{asym})=1764 \text{ cm}^{-1}$). Electron populations in the bonding orbitals are 1.80-1.82 e^- per basin, while electron populations in the valence shell of O = 5.73-5.75 e^- per basin. There is also a strong cross-relation between electron populations of the valence shell of O and the bonding electrons. Hence, the CO_2^{1-} molecular anion has an extra

electron which results in the bending of the O-C-O angle to 135° and shifts the electron population from the bonding basin to the O valence basin. This is important because the oxygen atoms in a bent structure are more negatively charged and the carbon is more prone to nucleophilic attack. Both excited state and anionic CO_2 are much more reactive than linear CO_2 and the degree of their apparent reactivity will be elucidated throughout this paper, as inferred from their molecular shape, electronic and vibrational properties.

3 Experimental techniques for CO_2 surface chemistry analysis

The surface chemistry of CO_2 at UHV conditions is a topic of perennial interest [13,18,19], and can be effectively probed by a range of surface sensitive experimental techniques. UHV techniques typically focus on very surface sensitive measurements, where CO_2 is adsorbed as a monolayer coverage. Other techniques, such as infrared spectroscopy, are routinely utilized at CO_2 pressures ranging from a few mTorr to several atmospheres. Similarly, solid-liquid interfaces are probed routinely using various modes of infrared spectroscopy.

3.1 Ultrahigh vacuum (UHV).

Historically, vacuum based techniques have been used extensively to probe CO_2 -surface interactions. UHV is the main prerequisite in these types of studies and is now routinely attained in the laboratory using complex pumping systems, as shown in Table 2. Low vacuum is routinely achieved using rotary vane pumps, although diaphragm pumps are gaining increased popularity because they are cleaner. Momentum transfer based pumps, such as diffusion or turbomolecular, are used to move molecules from the low to the high vacuum side to achieve high vacuums. For UHV studies, pumping systems typically include a combination of pumps for different stages with entrapment pumps, such as ion or cryogenic. To achieve that last stage,

system —baking” – degassing of the chemisorbed water molecules from chamber walls – is necessary.

Table 2. Degrees of vacuum and the pumping equipment employed for attaining them

Vacuum	Pressure, Torr	Pumping equipment
Low	$20 \cdot 10^{-3}$	Rotary vane, diaphragm pumps
Medium	$10^{-3} - 10^{-5}$	Diffusion pumps
High	$10^{-5} - 10^{-9}$	Turbomolecular, diffusion pumps
Ultrahigh	$<10^{-9}$	Ion, cryo pumps (backing required)

The reasons for implementing UHV are typically to:

- Maintain atomically clean surfaces for the duration of the experiment,
- Permit low energy probes, including electrons, photons and ions, to be used without interference due to gas phase scattering,
- Ensure stability, longevity and safety for the typical high energy electronics used.

The *Langmuir* (*L*; where $1L=10^{-6}$ Torr) is a commonly-used unit to quantify the time window available before the surface inside the instrument is completely covered with residual gas. In this context, a sticking coefficient of 1 implies that complete surface coverage (10^{-6} Torr) by residual gases will be achieved in 1s. Hence, for a surface science experiment to be accomplished in the presence of the desired gas molecule, a vacuum of 10^{-8} Torr should provide a time window of at least 100 s. A UHV vacuum of 10^{-10} Torr provides a convenient time window of 10,000 s.

Commonly used techniques for surface-sensitive CO₂ analysis can be grouped into the following probe-surface based interactions between

- Electron and surface,
- Photon and surface,

c. Ion and surface.

They are summarized in Table 3.

Table 3. Conventional UHV CO₂-surface interaction analysis techniques

Electron-surface interactions	Photon-surface interactions
Auger Electron Spectroscopy (AES) High Resolution Electron Energy Loss Spectroscopy (HREELS) Electron-Stimulated Desorption (ESD) Low Energy Electron Diffraction (LEED) Scanning Tunneling Microscopy (STM)	X-ray Photoelectron Spectroscopy (XPS) Photon Stimulated Desorption (PSD) Ultraviolet Photoelectron Spectroscopy (UPS)
Ion-surface interactions	
Secondary Ion Mass Spectroscopy (SIMS) Low Energy Ion Scattering (LEIS)	

UHV techniques based on electron-surface interactions include Auger Electron Spectroscopy (AES), Electron-Stimulated Desorption (ESD), High Resolution Electron Energy Loss Spectroscopy (HREELS), Scanning Tunneling Microscopy (STM), and Low Energy Electron Diffraction (LEED). Those based on photon-surface interactions include X-ray Photoelectron Spectroscopy (XPS), Photon Stimulated Desorption (PSD), and Ultraviolet Photoelectron Spectroscopy (UPS). Those based on ion-surface interactions include Secondary Ion Mass Spectroscopy (SIMS) and Low Energy Ion Scattering (LEIS). This list is not exhaustive, because a plethora of other light and electron based methods typically used to investigate CO₂ interactions in UHV cannot be considered strictly surface techniques, as the signal can originate from the atoms within the bulk. This can be readily seen from Figure 4. Surface sensitivity from within a few monolayers can be achieved utilizing either low energy excitation sources or shallow escape depths, which are based on the inelastic mean free path of the electron. The strongly contrasting penetration depths of photons (1 μm), electrons (20 Å) and ions (10 Å) under a given beam energy also imply that the damage to the sample surface should, in principle, be lowest for ions [20]. The definition of the sampling depth, however, is not straightforward,

nor is that of a monolayer. We will consequently attempt to define this surface sensitivity for the methods to be described in the following sections to compare and contrast their surface sensitivity and analytical capabilities.

Figure 4. Surface sensitive UHV techniques used for CO₂ surface chemistry analysis.

3.1.1 Surface analysis techniques based on electron-surface interactions.

3.1.1.1. AES. Auger electron spectroscopy (AES) is based on the interaction of an electron beam with the sample to initiate the Auger electron emission. The initial step is the excitation of an atom followed by the removal of its core electron. These core electron excitations can be similarly induced by an incident photon or ion. Relaxation ensues by one of the two competing processes. One process can proceed via a less tightly bound electron dropping to substitute for the empty core level followed by a photon emission to compensate for the energy difference between the two levels. This process is X-ray fluorescence and dominates when the excited core levels are of high binding energy, such as for heavier elements. The other process involves the excess energy carried away by a third electron from less tightly bound levels via a radiation-free Auger process. The kinetic energy of the emitted electron is then, for example,

$$E_{KLL} = E_K - E_{L2} - E_{L3} - \Phi, \quad (2),$$

where Φ is the work function of the surface and the peaks are labeled as such (C(KLL)). The Auger de-excitation process is predominant for the lighter elements, with the lightest element detectable being Li due to the need for at least three involved electrons. The resulting emitted electron kinetic energy is measured and shows energy specific peaks superimposed on a large background, due to the

secondary electrons generated via a multitude of inelastic scattering processes. It provides for both qualitative and quantitative elemental analysis with about 1% monolayer sensitivity. First or second derivatives of the spectra with respect to energy can also be used to accentuate spectral peaks. The resulting spectra are most commonly compared with samples of known composition to assess the nature of the surface species formed and their chemical environment by (a) peak position shift and (b) peak shape resemblance. For example, CO₂ adsorption on zirconium alloy

was performed at 150, 300 and 600 K and a 1.4 eV shift was observed in Zr(MNN) with concomitant changes in Zr(MNV) shape [21], as shown in Figure 5. This was attributed to the effect of oxygen on the dissociative CO₂ adsorption. Then, the diffusion of the oxygen formed into the subsurface followed, with the domains of the graphitic (150 K) and carbidic (300 and 600 K) carbon formed on the surface, as confirmed by the C(KLL) peak shapes. The Zr metal feature Zr(MNV)_m decreases in intensity at lower temperatures due to the electron donation from zirconium to oxygen atoms. While such fingerprinting contributes significant knowledge, other spectroscopies, such as XPS, can provide greater levels of detailed molecular (chemical) information. Also, non-conductive surfaces are challenging for Auger, because the negative charge buildup resulting from the electron beam eventually prohibits the flux of the emitted Auger electrons. To this extent, XPS is much more useful, as charging induced with soft X-rays can readily be mitigated by the low energy electron supply. The larger energy of the incoming electrons in Auger also damages the sample more so than in XPS.

3.1.1.2 HREELS. Measuring energy loss of inelastically backscattered, low-energy electrons provides information on vibrational modes of the adsorbed species on the surface. It also provides information on the physisorbed and chemisorbed adsorbate states as well as adsorbate - adsorbate interactions. The process is not restricted by selection rules, and in combination with dipole scattering, all vibrational modes may be discernable. To this extent, in a dipole scattering regime HREELS provides complimentary information to that obtained using infrared spectroscopy. However, very high surface sensitivity, approximately 0.01% of a monolayer, is obtained, which is much greater than that of IR. At the typical electron emitting cathode temperature, ~2,000 K, the width of the thermal energy distribution of the emitted electrons, $k_B T$ is in the hundreds of meV resolution without energy filtering, somewhat akin to the acronym of the technique. Full width at half maxima (FWHM) of a few meV can be achieved by selecting the energy of the beam at a certain pass energy. The highest achievable resolution is 0.5 meV (4 cm⁻¹) for a total spectral range of 0-1,000 meV (0-8,000 cm⁻¹). Importantly, electronic

transitions of both surface and the corresponding adsorbates can be obtained, providing a complete surface picture. However, rather flat and mostly conducting surfaces are needed to fully utilize the advantages provided by HREELS. CO₂ adsorption on RuO₂ (110) at 85 K yields a complex

HREEL spectra with species identified that are difficult to observe using FTIR, including physisorbed CO₂, several forms of chemisorbed CO₂^{δ-}, carbonate CO₃^{δ-} and dimerized modes CO₂·CO₂^{δ-} [22]. At 1L coverage, low temperatures facilitated formation of the CO₂·CO₂^{δ-} dimers, where linear CO₂ is bound to the chemisorbed CO₂^{δ-}, with gradual transition into carbonate species at and above 260 K (Figure 6). Annealing to 350 K resulted in carbonate losses due to the formation of O_{ads} and gaseous CO₂. The formation of adsorbate carbonate is typically observed when CO₂ is exposed to metal oxides [18].

Figure 6. HREELS of 1L CO₂ on RuO₂(110) at various temperatures. Reprinted with permission from [22]. Copyright (2002) American Chemical Society.

3.1.2 Surface analysis techniques based on photon-surface interactions.

3.1.2.1 XPS. Photons of specific energy are used to excite the electronic states of the sample, which results in ejected (photo)electrons. These electrons are filtered in a hemispherical

analyzer and their intensity for the particular energy window is measured by a detector. Binding energy of the electron in eV is then obtained by

$$E_B = h\nu - E_K - \Phi, \quad (3)$$

where E_B is the binding energy of the electron in the atom, $h\nu$ is the energy of the photon and E_K is the kinetic energy of the photoelectron measured. The work function term in equation (3) is important when dealing with solids, whereas gas phase molecule binding energy will be identical to the ionization potential of the particular electron. Importantly, Auger peak kinetic energy is independent of the $h\nu$ term, and altering the photon energy by changing the X-ray anode material will cause Auger lines and photoelectron peaks to change in energy with respect to each other. While X-rays can penetrate several microns into the sample, only electrons from within up to ~ 10 nm can escape from the sample without losing their energy. This is defined as the inelastic mean free path (IMFP) of the electron. IMFPs for the kinetic energies from 20 to 1000 eV is about 5 to 20 Å, while outside that range IMFP values increase [23]. Sampling depth is ~ 3 monolayers with the elemental sensitivity in the order of 0.1 %. Furthermore, the spatial resolution of XPS is by the wavelength of the X-rays (~ 600 nm) compared to that limited by the diameter of the electron beam (~ 5 nm) in AES. Finally, we note that H and He cannot be detected by XPS.

3.1.2.1.1 Qualitative analysis. In principle, XPS relies on the knowledge of well-defined binding energies, as defined by the corresponding electronic state of the atom. These are tabulated for specific compounds and can be found in literature references or online databases [24]. The theoretical models for the calculation of the core-level binding energies (CEBEs) within the DFT approximation have also been used and can be classified in three major groups, namely, (a) based on the complete screening picture, (b) the transition state model and (c) the

initial state approximation [25]. In the initial state approximation, screening of the core hole in the core-excited state is neglected, whereas in the final state approximation, the core hole is completely screened. In a transition state model, partial orbital occupations are introduced to describe the excitation process. Since charge transfer is poorly described by gradient corrected functionals, adsorbed molecule CEBEs can be underestimated so the fraction of Fock exchange needs to be added via PBE0 functional [26].

Of paramount importance in XPS qualitative analysis are so called chemical shifts, which arise due to the changes in binding energy of a core electron. This is caused by the change in the chemical bonding (environment) of that element. Since core binding energy is an electrostatic interaction between the electron and the nucleus, it will be affected by the change in shielding of the nuclear charge by removal/addition of the electronic charge as a result of bonding. In general, withdrawal of the valence charge of electrons will cause an increase in CEBEs, whereas an addition will decrease it. This means that typical binding interactions of CO₂ on solid surfaces can be monitored using XPS and adsorbed species bonding information can be obtained. Conventional XPS is limited to UHV conditions due to the elastic and inelastic scattering of the photoelectrons by the gas molecules. This causes the attenuation of the signal, which is proportional to $e^{(-z\sigma p/kT)}$, where σ is the electron scattering cross-section and z is the distance the electrons have to travel at pressure p . This strongly implies that the electron travel distance in an elevated pressure environment needs to be minimized. Such conditions allow imaging of liquids [27,28]. *Ambient pressure XPS (APXPS)* utilizes a combination of a high intensity X-ray source, differential pumping system and electrostatic focusing, thus allowing operation under elevated pressures of several mbars [29]. Both gas and adsorbed species information can be obtained using modern XPS instruments. Tabulated CEBEs of the species pertaining to CO₂ surface

chemistry in the C1s region are shown in Figure 7. These include adsorbed CO [30,31], CO_3^{2-} [31–36], carboxylate [31,33,35,37], oxalate [33,34], graphite/adventitious carbon [31,33,35], formate [37] and gas phase CO [38] and CO_2 [33,37].

For high-resolution qualitative analysis, a FWHM of the resulting peaks needs to be as small as possible to facilitate their separation and assignment. Spectral peaks are broadened due to the (a) X-ray line broadening, (b) the width of the analyzer energy window, and (c) the natural line width of the orbital in the atom. The latter cannot be altered as it is inherent to the transition considered. The main improvements that can be made come by reducing the line width of the source. Most often used is Al K_α 1486.7 eV radiation with 0.85 eV. With the monochromator it can be reduced to 0.26 eV [39]. A monochromator also removes X-ray satellite peaks and Bremsstrahlung radiation, thus improving the overall appearance of the spectra. On the other hand, it also removes the total X-ray flux to the sample, thus reducing the corresponding photoemission signal. However, to resolve small peak differences due to the chemical shifts in the adsorbed CO_2 products and unambiguously interpret them, a monochromated beam or low temperature experiments are necessary.

3.1.2.1.2 Quantitative analysis. Gathering atomic concentrations from the XPS spectrum involves isolating emission peaks, one per element, and then performing a sequence of corrections to these intensities leading to the normalized values representative of the amount of substance sampled via XPS. Quantification of the XPS spectra needs to account for the electrons belonging to a certain transition. This is typically performed via subtracting the background due to the scattering events other than those of the elastically scattered transition of interest. Background subtraction is typically performed using the Shirley [40] or Tougaard [41] methods. Although for the peaks due to the C1s and O1s electronic transitions for materials which have relatively large bandgaps, where no significant amount of inelastically scattered electrons proceeds, linear subtraction is sometimes acceptable. Exceptions do exist (for example, graphite) where C1s transition is often modeled using the Shirley background. Peak areas are then computed from the background-subtracted data and serve as the basis for quantification. Relative sensitivity factors (RSF) are then used to scale measured peak areas to obtain an atomic concentration. The underlying assumption is that the number of electrons recorded in the spectrum is proportional to the number of the atoms via

$$A_i = \frac{I_i}{T(E_i)RSF_i E_i^n} \quad (4)$$

Here, I_i is the peak area, $T(E)_i$ the transmission function at the peak position, RSF_i is the relative sensitivity factor, E_i is the kinetic energy of the electron and n is the escape depth exponent. RSF values of elements are relative to a specified transition. The purpose of RSF is to correct peak intensities to account for differences resulting from the photoemission process. Traditionally, Wagner *et al.* [42] used RSF values relative to F1s; hence, for Wagner/PHI/Kratos/Thermo tables the RSF values have F1s RSF = 1. Scofield cross-sections [43] used by SPECS/Thermo/Kratos Amicus/Scienta/Omicron are used relative to C 1s, e.g. RSF C1s = 1.

Scofield cross-sections are theoretically derived using Hartree-Slater approximations and do not account for angular distribution variations in the effective cross-section, as a consequence of instruments detecting electrons in a specific direction relative to the photon source. This transmission (ratio of electrons leaving the sample to the number of electrons recorded at the detector) varies as a function of the kinetic energy of the emitted electrons. These are incorporated by specific instrument manufacturers, who have their own RSF values that also account for the transmission function, $T(E)_i$ of that particular instrument. These include Kratos Axis Ultra and Kratos Axis Nova and can have either C1s or F1s as a reference. They are tabulated in Table 4, as follows:

Table 4. Tabulated RSF parameters commonly used for CO₂ adsorption product quantification.

Core level	Wagner [42]	Scofield [43]	Kratos
C1s	0.25	1	0.278
O1s	0.66	2.93	0.78

It is noteworthy that, provided the entire RSF table is converted the same way, the peak selected as the reference (e.g. C 1s or F 1s) for tabulating the sensitivity factors is arbitrary. However, no standard RSF values exist over the XPS instruments. Therefore care must be taken so no RSF values from two different libraries are applied.

3.2 Elevated CO₂ pressures and aqueous solutions

3.2.1 Gas phase FTIR Spectroscopy.

3.2.1.1 Instrumental

Infrared (IR) spectroscopy is based on radiation absorption by the characterized compounds. When an IR beam is passed through a sample, the compound absorbs radiation at a specific wavelength, resulting in a decrease of the transmitted radiation. In the spectra, the absorption is

reflected as a dip in transmission or a peak in absorbance. Upon absorbing the IR radiation, the molecules' oscillation amplitude will increase, hence the molecule is excited to a higher vibrational state. Vibrational states are quantized energy levels, and the particular wavelength of absorption by a specific bond depends on the energy difference between the ground level and the excited state. Thus, different bonds produce different peaks/dips, which also vary depending on the different oscillation modes in the IR spectra at different wavenumbers.

Monitoring the molecular events taking place at a certain reaction temperature or pressure, i.e. *in situ* IR spectroscopy, is now possible and widely used. A substrate, or catalyst, can be put into a reaction chamber, where a reactant is passed over it. IR spectroscopy is then used to continuously monitor the surface species present on the substrate, while the surface is heated up to a certain desired temperature. This characterization method is very powerful, because it provides information about the bonds created or destroyed during the temperature ramping, which, when properly analyzed, can give information on the possible transition states during the reaction.

Vibration spectroscopic measurements of the solid/gas interface can be effectively carried out using a reaction chamber equipped with optical windows enabling measurements in transmission mode, attenuated total reflectance (ATR) and total or diffuse reflectance modes. Fourier transform infrared spectroscopy (FTIR) is generally limited to powdered (submicron-sized) materials, given the limitations in throughput. Single crystals are, on the other hand, best studied by reflectance-based measurements, such as reflectance-absorbance infrared spectroscopy (RAIRS) [44], provided that the sample is conducting. FTIR studies of CO₂ binding with powdered materials have, however, been considerably more popular, given the relative ease with which measurements can be conducted and the relevance of nanoparticles and colloids to

environmental and technological research. Experimental setups using closed or open-loop flow-through cells have facilitated automated measurements of CO₂ adsorption isotherms (Figure 8). Systems for the study of supercritical CO₂ interactions with solid surfaces have also been developed in recent years, with a surge of studies prompted by the prospect of geological storage of CO₂. We note that the study of mixed CO₂-H₂O gases requires careful spectral processing of contributions from atmospheric H₂O and/or gas phase vibrations of the reacting molecules. Dominant strategies include (1) an internal referencing method, by which the gas-phase is monitored by shifting the solid sample away from the optical path [45] and (2) by spectral subtraction using a chemo-metric methodology [46].

The instrumental design shown in Figure 8 has been very widely used in the transmission of FTIR measurements of CO₂ interaction with solid surfaces, with and without the presence of co-adsorbing gases [5,48–52]. The use of this type of spectral subtraction in this particular case was facilitated by the fact that the dominant gaseous CO₂ IR vibration at 2349 cm⁻¹ does not overlap with any dominant adsorption product vibrations, such as adsorbed carbonates (CO₃²⁻), bicarbonates, (HCO₃⁻), adsorbed formate (HCO₂⁻) and others typically observed in the 1700-1000 cm⁻¹ region.

3.2.1.2 Adsorbed CO₂

CO₂ is a linear D_{∞h} molecule with three fundamental vibrations: one is a Raman active symmetric ν_1 stretch at 1388 cm⁻¹ and the other two are an infrared active double degenerate ν_2 (deformation) at 667 cm⁻¹ and a ν_3 asymmetric stretch at 2349 cm⁻¹ [53]. Upon adsorption, IR inactive modes are typically activated, after which double degenerate modes split, resulting in a complex spectral envelope. Isostructural organometallic reference compounds, and vibrations calculated based on first principles, are often used to assign observed IR peaks in complex reactive systems. Various organometallic compounds are readily available for differently configured adsorbed CO₂ species. In particular, there are at least 13 different configurations represented by numerous organometallic compounds, as shown in Figure 9. Distinct trends in fundamental asymmetric and symmetric stretching vibrations are difficult to unambiguously assign between all the species with the apparent asymmetric stretch (2349 cm⁻¹ fundamental frequency) significantly shifting towards lower wavenumbers and symmetric stretch (1388 cm⁻¹ fundamental frequency) becoming IR active. In general, the magnitude of the asymmetric stretch shift can be correlated with the number of metal atoms involved into coordination providing a varying degree of O-C-O bond distortion. Tabulated standard deviations (Table 5) from the pool of organometallic compounds range within ca. ± 60 cm⁻¹, providing confidence that a certain binding mode will take place, regardless of the intrinsic electronic properties of the metal itself. Assignments of the different CO₂ related ligands in organometallic compounds have been discussed extensively by Sumida *et al.*, Gibson, Leitner, and Aresta [54–57]. In this report, we provide a summary of their collective assignments for different types of metal complex-CO₂ ligands.

Table 5. IR peak assignments for CO₂ binding with the corresponding standard deviation provided, where available.

Metal sites	Type	ν as	ν s	Note	Reference
1	I	1780-1751; 2188	1221-1146	Li, Al, U	[57]
1	II	1576±80	1238±84	Li, Cs, Al, Ni, Re, Pd, Mo	
2	III	1341	1174	Cs	
2	IV	1448; 1335	984; 1018	Li, Cs	
1	V	1610; 1550	1230-1210	Ir and Rh	[56,57]

				complexes	
1	VI	1675±40	1135±39	16 organometallic complexes	[56,57]
2	VII	1549±64	1136±63	30 organometallic complexes	[55–57]
2	VIII class I	1372±45	1269±30	19 organometallic complexes	
2	VIII class II	1452±56	1165±42	16 organometallic complexes	
3	IX	1380; 1365	1295-1260	Re, Rh and Co complexes	[55,57]
3	X	1650	1280; 1215	Co complex	[57]
4	XI	1428	1242	Ru water complex	
4	XII	1280	1260-1250	Rh Zn THF complex	
Carboxylate	XIII	1696±66	1339±51	K-Ru and Ir complex	[53,58]

Some of the bridged carbonate ions (*vide infra*) also exhibit vibrations in 1600-1700 and 1200-1300 cm⁻¹ ranges due to the split in double degenerate ν_3 vibrational mode. However, adsorbed CO₂, sometimes referred to as carboxylate or strongly perturbed (bent) CO₂ molecules, also have vibrations in the same spectra regions, as shown in Table 5. Bent CO₂ is of approximately C_{2v} symmetry, with all three vibrations infrared and Raman active [53]. Assignment of the vibrational bands needs to be based on the particular substrate (metal or oxide) and the nature of the corresponding metal ion.

3.2.1.3 Adsorbed carbonate (CO₃²⁻)

Application of IR spectroscopy on CO₂ capture has been in existence for many years. Busca and Lorenzelli compiled and assigned IR vibrations for different CO₂ adsorption configurations on the surfaces of different metal oxides and metal complexes [53]. They did so by comparing them with those on well characterized organometallic compounds. Adsorption of CO₂ on metal oxide surfaces yields mostly carbonates and bicarbonates. Carbonates formed on a surface via reactive CO₂ binding come in different configurations. There are symmetrical (I), monodentate (II-III),

bidentate (IV), bridged (V-VI), and polydentate configurations (VII-XIII), as shown in Figure 10 [53]. Carbonate in its free ion form has a Raman active vibration of 1063 cm^{-1} due to the symmetric C-O stretching (ν_1), an IR active vibration of 879 cm^{-1} due to out-of-plane deformation (ν_2), and two Raman-IR active vibrations of 1415 and 680 cm^{-1} , due to CO asymmetric stretching (ν_3) and in-plane deformation (ν_4), respectively [53]. Changes in molecular symmetry brought by electrostatic, hydrogen and covalent binding induce important shifts as well as the doubly degenerate ν_3 and ν_4 split. These recorded vibrational frequencies can, based on empirical evidence in previous literature data assignments and/or theoretical frequency predictions, be indicators for the coordination environment of the carbonate species, the prevalent CO_2 adsorption product. IR-activation of the symmetric stretching mode, and the splitting of both ν_3 and ν_4 , with each adsorption configuration exhibiting different values of splitting induced by changes in molecular symmetry. The splitting of ν_3 is the one routinely used to identify binding modes, such as monodentate, bidentate, and bridged with the approximate splitting values of 100 , 300 , and $\geq 400\text{ cm}^{-1}$, respectively [53]. For more complicated irregular carbonate structures, i.e., the polydentate configurations, splitting of ν_3 is usually much smaller, sometimes even smaller than that of monodentate, leading to the discrepancy among several authors in assigning specific ν_3 peaks to either monodentate or polydentate carbonates.

With the data presented so far, binding modes of the adsorbed carbonates for the pure metal oxide surfaces can be referenced against those measured for the organometallic compounds and the binding configuration assigned. This was performed and displayed in Table 6. It can be seen that in a prevalent number of cases mono- and bidentate binding modes take place, with just a few exceptions for alumina (Al_2O_3) polymorphs, Ga_2O_3 and yttria.

Table 6. Experimental values for peak assignments of carbonates on various metal oxides.

Oxide	Type										Ref
	Symmetrical	IR modes	Monodentate	IR modes	Bidentate	IR modes	Bridged (V-VI)	IR modes	Bridged Polydentate (VII-XIII)	IR modes	
BeO	1440	ν_3			1640	ν_3 as					[53] and ref therein
					1220	ν_3 s					
MgO			1520/1550; 1506; 1526	ν_3 as	1655/1670/ 1660; 1673; 1778	ν_3 as					[53] and ref therein; [51,59];
	1410	ν_3	1390/1410; 1415-1418	ν_3 s	1325/1320/ 1307/1315/ 1330; 1361; 1243	ν_3 s					
			1050; 1067- 1072	ν_1	1005/1000; 1091; 932	ν_1					
			860	ν_2	850; 847	ν_2					
CaO	1520-1490; 1415	ν_3	1635-1550; 1603	ν_3 as		ν_3 as	1781/1776	ν_3 as			[53] and ref therein; [59]
			1308-1302; 1314	ν_3 s		ν_3 s					
	1060	ν_1	1035	ν_1		ν_1					
	860	ν_4	876	ν_2		ν_2					
α - Al ₂ O ₃			1610-1570	ν_3 as	1710/ 1675-1660	ν_3 as	1810	ν_3 as	1810	ν_3 as	[53] and ref therein
			1385-1350	ν_3 s	1310/1345	ν_3 s	1730	ν_3 as	1730	ν_3 s	
							1310	ν_3			
γ - Al ₂ O ₃			1530	ν_3 as	1730- 1660; 1640	ν_3 as	1900- 1750	ν_3 as			[53] and ref therein;

			1370; 1383	ν_3 s	1270-1230; 1355	ν_3 s	1180	ν_3 s/ ν_1			[50]
			1040	ν_1	1010	ν_1					
η - Al ₂ O ₃			1630-1600	ν_3 as	1710	ν_3 as	1900-1750	ν_3			[53] and ref therein
			1515-1470	ν_3 s	1315	ν_3 s	1180	ν_3 s/ ν_1			
κ - Al ₂ O ₃	1460	ν_3			1652	ν_3 as					[53] and ref therein
					1234	ν_3 s					
SnO ₂			1440	ν_3 as	1580				1760	ν_3 as	[53] and ref therein
			1380	ν_3 s					1740	ν_3 s	
Sc ₂ O ₃	1140	ν_1			1635	ν_3 as					[53] and ref therein
					1220	ν_3 s					
TiO ₂			1461; 1510	ν_3 as	1579; 1691; 1566	ν_3 as					[60,61]
			1392	ν_3 s	1319; 1265; 1355	ν_3 s					
			1076	ν_1							
TiO ₂ Rutile					1485	ν_3 as	1706	ν_3 as			[53] and ref therein; [62]
					1325	ν_3 s					
TiO ₂ anatase			1590-1575	ν_3 as	1580/1670; 1589	ν_3 as					[53] and ref therein; [5,62]
			1370-1320; 1377	ν_3 s	1320/1243; 1315	ν_3 s					
					1055	ν_1					
ZrO ₂			1490/1450	ν_3 as	1575/1550/ 1595/1573/ 1559	ν_3 as			1450	ν_3 as	[63–66]
			1395/1425	ν_3 s	1325/1355/ 1315/1354/	ν_3 s			1430	ν_3 s	

					1310						
					1065	ν_1					
α - Cr_2O_3	1440	ν_3	1490	ν_3 as	1635/1590/ 1560/1650	ν_3 as	1740	ν_3 as			[53] and ref therein; [67]
			1365	ν_3 s	1285/1305/ 1340/1240	ν_3 s					
					850	ν_2					
α - Fe_2O_3	1450	ν_3	1460	ν_3 as	1610/1550/ 1553		1760	ν_3 as			[53] and ref therein; [52]
	850	ν_2	1400	ν_3 s	1290/1340/ 1316						
			1050	ν_1							
Co_3O_4			1440	ν_3 as	1545	ν_3 as					[53] and ref therein
			1408	ν_3 s	1324	ν_3 s					
			876	ν_2	1134	ν_1					
NiO			1640	ν_3 as	1670; 1620; 1625	ν_3 as	1730	ν_3 as			[53] and ref therein; [68]
			1390/1263	ν_3 s			1160	ν_3 s/ ν_1			
			910	ν_2							
CuO	1445	ν_3			1500	ν_3 as					[53] and ref therein
	845	ν_1									
ZnO	1430		1543-1520	ν_3 as	1665- 1580; 1621	ν_3 as			1466	ν_3 as	[53] and ref therein
			1323-1313	ν_3 s	1348- 1303; 1292	ν_3 s			1386	ν_3 s	
					1007-999	ν_1					
					852-841	ν_2					
					680-677	ν_4					
La_2O_3			1500	ν_3 as	1565	ν_3 as					[53] and ref therein,
			1390	ν_3 s	1310	ν_3 s					

			1060	ν_1							[69]
			850	ν_2							
ThO ₂					1610	ν_3 as					[53] and ref therein
					1290	ν_3 s					
					1030	ν_1					
					840	ν_2					
Ga ₂ O ₃					1587	ν_3 as	1680	ν_3 as	1460	ν_3 as	[70]
					1325	ν_3 s	1280	ν_3 s	1406	ν_3 s	
Y ₂ O ₃							1585	ν_3 as			[71]
							1334	ν_3 s			

An interesting comparison of ν_3 vibrational frequencies can be made for the samples where basic oxides (MgO, CaO and Na₂O) are supported on Al₂O₃, as is typical of solid oxide sorbents for CO₂ capture (Table 7). The values observed do not necessarily coincide exactly with those of pure metal oxides shown in Table 6. Also, the exact identity of the binding site cannot be unambiguously determined by FTIR spectroscopy. Some binding modes observed for CaO/Al₂O₃, identified as bidentates, do not typically appear in pure CaO but can instead be associated with Al₂O₃ adsorption of CO₂. Complex polydentate binding can then be postulated due to the availability of inhomogeneous adsorption sites, as in the case of Na₂O/Al₂O₃ (Table 7).

Table 7. Experimental values for peak assignments of carbonates on doped Al₂O₃.

Dopants	Type						Ref
	Monodentate	IR modes	Bidentate	IR modes	Polydentate	IR modes	
MgO	1574/1591	ν_3 as	1708/1610	ν_3 as	1675	ν_3 as	[72–74]
	1420/1506	ν_3 s	1330/1380/1340	ν_3 s			
CaO	1518	ν_3 as	1600	ν_3 as			
	1300	ν_3 s	1350	ν_3 s			
Na ₂ O			1672-1677; 1618-1631	ν_3 as	1571	ν_3 as	[75]
			1361-1376; 1311-1320	ν_3 s	1353/1450	ν_3 s	

3.2.1.4 Adsorbed bicarbonate (HCO₃⁻)

Adsorbed bicarbonate species, as is true of their carbonate counterparts, exhibit several binding configurations. In its solid state bicarbonate is in a dimer form (I) with characteristic IR peaks at 2620-2450 cm⁻¹ ($\nu(\text{OH}\dots\text{O})$), 1655-1615 cm⁻¹ (asymmetric C=O stretch), 1400-1370 cm⁻¹ (symmetric C=O stretch) and 1300 cm⁻¹ (COH...O bending). However, for monomeric bicarbonate species, hydrogen bonding between the two dimers is not necessarily present and the

OH stretch ν_5 is present at much higher wavenumbers (3340-3148 cm^{-1}). At the same time, though, shifts are also expected on the other peaks at 1702-1675 cm^{-1} for the asymmetric C=O stretch (ν_3 as), 1346-1327 cm^{-1} for the symmetric C=O stretch (ν_3 s), and 1252-1205 cm^{-1} for the OH—O bend (δ_4) [53]. There are two main types of surface bicarbonate observed on surfaces: monodentate (II) and bidentate (III). An additional structure, the bridged bicarbonate (IV) species, is rarely recognized, although an FTIR study of isotope labeling of adsorbed $\text{HC}^{16}\text{O}_3^-$, $\text{DC}^{16}\text{O}_3^-$, $\text{HC}^{18}\text{O}_3^-$, $\text{HC}^{16}\text{O}^{18}\text{O}_2^-$, and $\text{HC}^{18}\text{O}^{16}\text{O}_2^-$, combined with quantum chemical calculations, points toward its presence [50]. To facilitate this process, a proton transfer mechanism is likely to occur through an intermolecular process involving either a coadsorbed hydroxyl group and/or a carbonate ion. Figure 11 below depicts the hitherto encountered bicarbonate species.

Figure 11. Various configurations of surface bicarbonate observed.

Table 8. Experimental values for peak assignments of bicarbonates on various metal oxides.

Oxide	Types			IR Modes	Ref
	Monodentate (II)	Bidentate (III)	Bridged (IV)		
PdO/ γ - Al_2O_3	3610			ν_5	[76]
	1645			ν_3 as	
	1485			ν_3 s	
	1235			δ_4	
MgO	1658-1639			ν_3 as	[53,59,77]; [78–80]
	1419-1415; 1480-1420			ν_3 s	
	1250-1210			δ_4	
	1040			ν_1	
	840			ν_2	
CaO	1630			ν_3 as	[59]

	1360-1560			ν_3 s	
Al_2O_3		3620		ν_1	[5,72,75]
	1620	1650		ν_3 as	
	1450	1435; 1436		ν_3 s	
	1230	1228; 1225		δ_4	
$\text{MgO}/\text{Al}_2\text{O}_3$	1650; 1675			ν_3 as	[73,74]
	1403			ν_3 s	
	1220			δ_4	
$\text{CaO}/\text{Al}_2\text{O}_3$		1649		ν_3 as	[81]
		1440		ν_3 s	
		1230		δ_4	
aminopropylsilane functionalized TiO_2		1691		ν_3 as	[82]
		1265		δ_4	
Anatase TiO_2	1434			ν_3 s	[62]
	1222			δ_4	
TiO_2		1623		ν_3 as	[5]
		1423		ν_3 s	
		1222		δ_4	
ZrO_2	3607			ν_5	[63–66]
	1620; 1610; 1613			ν_3 as	
	1453, 1443			ν_3 s	
	1225, 1224, 1243			δ_4	
Ga_2O_3	1619; 1630			ν_3 as	[70,83]
	1456; 1463	1431; 1432		ν_3 s	
	1231	1229		δ_4	
Fe_2O_3		3619		ν_5	[5,52]
		1629; 1622		ν_3 as	
		1410		ν_3 s	
		1222; 1220		δ_4	
		1010		ν_1	
Y_2O_3	3658	3625		ν_5	[71]
	1674	1652	1585	ν_3 as	
	1397	1419	1334	ν_3 s	
	1223	1223		δ_4	
Y-stabilized ZrO_2		1646		ν_3 as	
		1429	1305	ν_3 s	
		1225		δ_4	
ZrO_2	1628			ν_3 as	
	1431			ν_3 s	
	1223			δ_4	

3.2.1.5 Adsorbed formate (HCO_2^-)

As in the case of carbonate and bicarbonate, surface formate species also exhibit different binding configurations, such as monodentate (I), bidentate (II), bridged (III-V), and even more complicated bridged structures (VI-VII), as shown in Figure 12. The characteristic IR peaks of a typical formate ion usually lie at 2841, 1567, 1377, and 1366 cm^{-1} , corresponding to CH stretch, asymmetric CO stretch, CH bend, and symmetric CO stretch, respectively.

The wavenumber value of the peaks in the adsorbed formate should again be referenced in the same, exact manner as the organometallic model compound, thus providing the ability to infer a particular binding mode. However, multiple problems may still persist if several binding configurations are simultaneously present with the peaks in the vicinity of each other. For example, when type XIII carboxylate and type III CO_2 adsorptions are present at the same time a peak at $\sim 1340 \text{ cm}^{-1}$ will appear. This peak could arise from the asymmetric $\nu \text{ OCO}$ ($\nu_3 \text{ as}$) for the former and symmetric $\nu \text{ OCO}$ ($\nu_3 \text{ s}$) from the latter. Another drawback from assigning peaks using organometallic compounds is that organometallic compounds are measured in their non-

adsorbed, rather directly bonded, state. Adsorption of a molecule by a surface can perturb its vibrations to the extent that it is different from that of the direct bonding interaction. *Shifts* of the vibrational frequencies are expected in these cases from the values that are reported for organometallics.

3.2.1.6 Other binding modes.

This subsection deals with CO₂ binding modes encountered in adsorption on a metal organic framework (MOF), where CO₂ adsorbs in a linear fashion using one of its oxygen atoms. Recently, a DFT work combined with IR revealed that on M2L (M=Mg, and transition metals; L=2,5-dioxidobenzene-1,4-dicarboxylate) a blue shift was observed in the CO₂ ν_3 mode for M=Mg, while a red shift took place on M=transition metals [84]. The cause was the perturbation arising from the electrostatic and charge transfer effect typical in transition metal complexes. For this reason, an anomalous blue shift in the case for M=Mg is remarkable. The anomalous blue shift was explained when the binding mode of CO₂ was investigated theoretically. A near-complete cancellation of the opposing local mode contributions to the observed frequency shift was observed in the case of Mg, leaving the shift to originate solely from the electrostatic effect [84]. The absence of d valence electrons in Mg prevented back-bonding (electron density donation to CO₂ π^* orbital) and resulted in anomalously equal red and blue local shifts. The same research group also observed a new peak at a much lower temperature, which they attribute to an alternate, localized orientation of CO₂ adsorbed to the metal site.

Shifts in the ν_3 mode of CO₂ were also observed in MIL-100(Cr), MIL-100(V) and MIL-100(Sc) (where MIL is a metal(III) carboxylate built from trimers of metal octahedra sharing a common oxygen atom and are linked together by trimesate rigid ligands) with respect to the gas phase molecule vibrations of 8, 7, and 11 cm⁻¹, respectively [85]. MIL-100 and MIL-101 (Cr, V, Sc,

Fe) have lately become important for carbon capture purposes [85–87]. Llewellyn *et al.*, reported high uptakes of CO₂ using chromium(VI)-based MIL-100 and MIL-101 as characterized by FTIR [86]. Cr-MIL-100 strongly adsorbed CO₂ gas and produced peaks at 2351 (ν_3) and 1271 cm⁻¹ (2 ν_2 overtone Fermi resonance). These peaks characterized a class of coordination, where the end oxygen atom was bound to the metal site. For MIL-101, there was only one single sharp peak at 2196 cm⁻¹ due to $\nu(\text{CO})$, which was explained by the difference in acidity between the two adsorbing surfaces [86]. Leclerc *et al.* revealed that the oxidation state of the iron metal sites on MIL-100 did not affect the CO₂ uptake, nor adsorbed CO₂ configuration on the surface as demonstrated by the spectra. The spectra exhibited a doublet peak at ca 2333 and 2344 cm⁻¹, characteristic of end-on CO₂ configuration [87].

3.2.1.7 Resolving adsorbed overlapping carbonate/bicarbonate peaks

The spectral region corresponding to C-O stretching vibrations attributable to CO₂ adsorption products spans from 1700 to 1200 cm⁻¹ and very quickly becomes complex and very difficult to interpret. This is due to (a) the variety of the CO₂ adsorption products (*vide supra*) and (b) the close overlap of the resulting peaks that are routinely used to fingerprint the particular species.

Figure 13. Transmission FTIR spectra of nanoparticulate Fe_2O_3 recorded following exposure to increasing pressures of CO_2 (51, 110, 156, 201, 251, and 274 mTorr). All spectra were recorded in the presence of gas-phase CO_2 . Reprinted with permission from [50]. Copyright (2006) American Chemical Society.

For example, CO_2 adsorption on Fe_2O_3 as a function of pressure is shown in Figure 13 [50].

Intrinsically strong and sharp adsorbed bicarbonate ion vibrations at 1622, 1410 and 1220 cm^{-1} interfere with the assignment of the broader adsorbed carbonate peaks observed in the same spectral region. The sharp peak at 3619 cm^{-1} is indicative of the OH stretching vibration in bicarbonate and coincides with the decrease of isolated 3686 and 3664 cm^{-1} surface hydroxyl groups. A combination of temperature programmed desorption with *in situ* FTIR monitoring of the adsorbed species was applied to facilitate adsorbed carbonate peak assignment. Temperature or vacuum treatment can be used interchangeably, while the resulting peaks need to be fit with synthetic components to determine the exact wavenumber value, as well as the relative population, as inferred from the corresponding area under the peak. These experiments can also provide kinetics data on the stability of certain carbonate/bicarbonate species, as shown in Figure 14.

Figure 14. Transmission FTIR spectra recorded for nanoparticulate Fe_2O_3 particles following exposure to 274 mTorr of CO_2 as a function of evacuation time from 0 to 120 min (0, 1, 10, 60, and 120 min). (b) Gaussian curve fit for the transmission FTIR spectrum of nanoparticulate Fe_2O_3 recorded after exposure of nanoparticulate Fe_2O_3 to 274 mTorr of CO_2 and then evacuated for 120 min. The data are fit to three surface species – monodentate carbonate (1383 and 1446 cm^{-1}), bidentate carbonate (1316 and 1553 cm^{-1}), and bicarbonate (1221 and 1411 cm^{-1}). The correlation coefficient for the total fit is 0.99964. Reprinted with permission from [50]. Copyright (2006) American Chemical Society.

A very new approach, recently used to accurately interpret XPS data that is routinely comprised of overlapping peaks in the spectra, was model spectral envelopes created using vector based analysis, thus avoiding synthetic spectral components [88]. Titled *informed amorphous sample model* (IASM), it was created and implemented into Casa XPS analysis software [89]. The concept is however published in a public domain. It creates spectral components by incorporating key information of the sample obtained experimentally. It was tested on the particularly challenging case of elucidating molybdenum oxide oxidation states in the presence of X-ray exposure and resulted in (1) complex shapes for the Mo (VI) and Mo (V) spectral component, accounted for without the need to identify synthetic line shapes and (2) spectral forms introduced as a shape constraint into the model, which guided further introduction of synthetic line shapes necessary to complete data reproduction by the model. Casa XPS is easily

interfaced with FTIR and Raman data and changes in the adsorbed carbonate/bicarbonate envelope as a function of sample temperature, gas partial pressure, and evacuation time can possibly be used so as to utilize IASM to interpret and assign complex overlapping peaks.

3.2.1.8 Computational methods to aid IR peak assignments.

Another method to assign peaks from the complex CO₂ adsorption systems is by using DFT calculations. DFT can calculate every single vibrational frequency that might appear on the spectra. For instance, monodentate and bidentate carbonate species on different defect sites on MgO can be discriminated using this method [90]. This is particularly useful for assigning peaks due to several surface species present simultaneously on the surface (as typically exhibited by the overlapping peaks that need accurate interpretation via peak fitting), even determining at which sites these molecules are adsorbed. However, just like any other assignment method, DFT has its own drawback. Vibrational energy levels calculated using DFT and harmonic approximation will exhibit a parabolic curve. Hence, a correction/scaling factor is needed. Determining the scaling factor itself requires some work and one should apply the same method of computation used on a model compound for which the IR peaks are sophisticatedly characterized. While generic scaling factors are available for the specific functional and basis set used [91], the approach of calculating factors for a specific molecule from the calculated values and the gas phase fundamental vibrational frequencies is preferred [50]. In this procedure, experimental vibrational frequencies (ν_i) and the calculated vibrational frequencies (ω_i) were used to determine the scaling factor c according to this equation:

$$c = \sum(\nu_i \omega_i) / \sum(\omega_i^2) \quad (5).$$

The calculated scaling factor c for the gas phase bicarbonate ion was 0.9506, different from 0.9613 by Wong [92], which was averaged over many compounds at B3LYP/6-31+G(d) level of

theory. Figure 15 summarizes the pros and cons of employing the two different methods. These are organometallic model compound and DFT, intended to assign measured vibrational frequencies.

Figure 15. Pros and cons of the two major methods currently used in vibrational frequency assignment of adsorbed CO₂ products.

DFT based adsorbed CO₂ product peak assignments are relatively new and there are not a lot of publications, as in organometallics. However, several investigators have done work sufficient to give reference for others to assign peaks in the IR spectra, with or without scaling factors [50,90,93–98]. Tables 9 and 10 summarize the assignments of carbonate and bicarbonate IR peaks predicted by DFT calculation on various metal oxide surfaces.

Table 9. Adsorbed carbonate vibrational frequencies on various metal oxide surfaces as calculated by DFT

Oxide	Type						Computational Details	Scaling factor	Ref
	I	II	III	IV-V	VI-XIII	Mode			
MgO		1703; 1440 ^d (1520/1550; 1506; 1526)	1778; 1730-1650 ^d (1655/1670/1660; 1673; 1778)	-	1650- 1600 ^d ; 1560 ^d	ν_3 as	B3LYP, Gaussian 03; 6- 311+G(d) and 6- 31G/6-31G(d) PW91, VASP; PAW-generated pseudopotential ^d	n/a	[90,94]
	(1410)	1327; 1378 ^d (1390/1410; 1415-1418)	1243; 1200-1125 ^d (1325/1320/1307/1315/1330; 1361; 1243)	-	1451; 1300- 1280 ^d ; 1330 ^d	ν_3 s			
		1011 (1050; 1067-1072)	932 (1005/1000; 1091)	-	1084	ν_1			
		849 (860)	847 (850; 847)	-	906	ν_2			
CaO ^a	(1520- 1490)	1664/1603 (1635- 1550; 1603)	1703	(1781/1776)	1461	ν_3 as			
	(1415)	1316/1314 (1308- 1302; 1314)	1257		1423	ν_3 s			
	(1060)	968/1035	944		1080	ν_1			
	(860)	845/876	845		881	ν_2			
Ga ₂ O ₃ ^b	-	-	1775-1755/1655 (1587)	(1680)	(1460)	ν_3 as	PBE, VASP; PAW-generated pseudopotential	n/a	[93]
	-	-	1292-1203/1233 (1325)	(1280)	(1406)	ν_3 s			
ZnO (0001)	(1430)	(1543- 1520)	1713	(1665-1580; 1621)	(1466)	ν_3 as	First principle, VASP; PAW- generated pseudopotential	n/a	[95]
		(1323- 1313)	1281	(1348-1303; 1292)	(1386)	ν_3 s			
				(1007-999)		ν_1			
				(852-841)		ν_2			

				(680-677)		ν_4			
CeO ₂ (331)	-	-	-	1759	-	ν_3 as			
	-	-	-	1183	-	ν_3 s			
ZnO/ CeO ₂ (111)	1556	-	-	-	-	ν_3 as			
	1428	-	-	-	-	ν_3 s			
TiO ₂ anatase		1584 (1590- 1575)	1802 (1580/1670; 1589)			ν_3 as	PBE0, CRYSTAL09; TZ-P/ Hay-Wadt pseudopotential	0.9525	[96]
		1378 (1370- 1320; 1377)	1125/1105 (1320/1243; 1315)			ν_3 s			
		1058	(1055)			ν_1			
		663	610			ν_2			

^a monodentate values represent adsorption on (edge/corner) sites

^b represents vibrational modes on different hydrated surface schemes

^c values in brackets represent experimental values for comparison

^d two calculation results for MgO case

Table 10. Adsorbed bicarbonate vibrational frequencies on various metal oxide surfaces as calculated by DFT

Oxide	Types			Modes	Computational details	Scaling factor	Ref
	Monodentate (II)	Bidentate (III)	Bridged (IV)				
Hydroxylated Fe ₂ O ₃		3619 (3620)		ν_5	B3LYP, Spartan '04, 6-31+G(d)	0.9506	[50]
		1622 (1629)		ν_3 as			
		1410 (1410)		ν_3 s			
		1220 (1220, 1222)		δ_4			
		(1010)		ν_1			
Hydroxylated α -Al ₂ O ₃		3623 (3620)		ν_5			
	(1620)	1648 (1650)		ν_3 as			

	(1450)	1438 (1435; 1436)		v_3 s			
	(1230)	1231 (1228; 1225)		δ_4			
Ga ₂ O ₃	1619; 1630	1595-1586/1591		v_3 as	PBE, VASP; PAW-generated pseudopotential	n/a	[93]
	1456; 1463	1421-1448/1417 (1431; 1432)		v_3 s			
	1231	(1229)		δ_4			
Defective rutile 110 TiO ₂		1804		v_3 as	PBE-TS, VASP; PAW-generated pseudopotential	n/a	[97]
		1240		δ_4			
		1103		v_1			
		873		v_2			
In ₂ O ₃		3677	3653	v_5	PBE, VASP; PAW-generated pseudopotential	n/a	[98]
		1541	1592	v_3 as			
		1460	1421	v_3 s			
		1177	1179	δ_4			
TiO ₂ anatase	1656	1613	1625;1574	v_3 as	PBE0, CRYSTAL09; TZ-P/ Hay-Wadt pseudopotential	0.9525	[96]
	1432 (1434)	1505	1497-1426	v_3 s			
	1052 (1222)	1048	1117-1063	v_1			
	664	713	670-645	v_2			
	1207	1193	1230-1212	δ_4			

^c values in brackets represent experimental values for comparison

As mentioned earlier, FTIR spectroscopy is an important method for characterizing surface species resulting from CO₂ capture over various substrates, metal oxides in particular. Tables 6-10 summarize assignments of prior IR experiments concerning CO₂ adsorption on metal oxides. The assignments made are mostly based on model adsorbing surfaces, such as MgO, organometallic reference compounds, and DFT calculation.

3.2.2 Instrumental designs to monitor CO₂ adsorption and uptake

Experimental detection of CO₂ binding at solid surfaces under ambient atmospheric conditions is essential for assessing environmentally-relevant processes. It should be emphasized that the interfacial chemistry of solids equilibrated to ambient pO₂ levels is dominated by (hydr)oxo terminations that can participate in CO₂ binding in a variety of mechanisms, from weak van der Waals binding, to direct ligand exchange as well as nucleophilic attack. Analytical determinations of CO₂ binding are challenged by the ready exchanges between the solid surface and the gas phase of the solid/gas interface or at the headspace of aqueous suspensions of solids. As such, *in situ* monitoring of CO₂ binding is key for the determination loadings achieved at solid surfaces. Classical methods based on loss of total pCO₂ in a reaction chamber (*e.g.* pressure, gas chromatography, infrared) require highly reactive solids and/or high specific surface area and/or large amounts of materials [99]. The Dynamic Vapor Sorption method [100], which was originally developed for water vapor binding, has extended to CO₂ binding [101–103]. This technique makes use of high precision balances to monitor mass changes [45]. Methods using on ultra-microbalances take samples on the order of mg and those using the Quartz Crystal Microbalance, on the order of a few µg. The latter has a greater sensitivity in the sense that it detects mass changes at the nanogram level, yet it requires a more thorough

preparation of sufficiently viscous (non-rigid) thin solid films on Au-coated quartz electrodes. Congruent serial and parallel resonant frequencies should be achieved throughout the course of an experiment in order to be successful.

Figure 16. System for scCO₂ delivery to optical chamber for *in situ* monitoring by vibration spectroscopy based on a high pressure fluid delivery system. Reprinted with permission from [104]. Copyright (2014), AIP Publishing LLC.

Measurements at the solid/water interface have greater limitations because of the strong absorbance of water. Many studies have thus employed the ATR-FTIR technique to attenuate these contributions, then proceed with careful spectral subtraction of the contributions of the bending mode of water at $\sim 1630\text{ cm}^{-1}$. Work with D₂O provides advantages on this front, as for example in the case of carbonate binding to hematite in the study of Bargar *et al.* [105].

Characterization of CO₂ adsorption in aqueous suspensions of solids also requires monitoring the gas phase as a proxy of the soluble carbonate concentrations via the relationship $\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{CO}_2 \cdot \text{H}_2\text{O}(\text{aq})$ (e.g. $K = 3.4 \times 10^{-2} \text{ M} \cdot \text{atm}^{-1}$ at 298.15 K). Closed reaction vessels, such as in the one shown in Figure 17, enable adsorption experiments to be carried out, not only in a closed system but also in open systems by enabling addition of CO₂ to maintain a given partial pressure [106,107]. Head space CO₂ levels in the reaction vessels can be monitored using an infrared detector [106] or a cavity ring down spectrometer [108], provided the analytical instruments are absolutely air-tight.

Figure 17. Experimental set-up for tracking CO₂ uptake in aqueous suspensions of minerals. Reproduced from [107] with permission from Elsevier.

Molecular-scale resolution of CO₂ species at the solid/atmosphere and solid/water interface has still relied predominantly on vibration spectroscopy. By probing the C-O stretching region of the linear (or bent) CO₂ molecules and of the often-resulting carbonate species, the technique

provides insightful details into the modes of interactions with a solid surface. This approach was very recently extended to supercritical liquids, such as H_2O and CO_2 (sCO_2), both of importance as sustainable solvents. The inherent need for high pressures to attain the supercritical state were circumvented using an attenuated total reflection (ATR) cell as shown in Figure 18 [109]. This cell is based on the commercially available Golden Gate High Pressure ATR accessory from Specac Ltd. It was modified to include an ATR crystal, syringe pump, preheater system, measuring chamber and capillary restrictor. The apparatus can operate at a maximum working temperature of $350\text{ }^\circ\text{C}$ and mixtures can be interrogated up to a pressure of 24 MPa.

In this work phase transitions of alcohols (ethanol and methanol) were monitored owing to the fact that a condensing liquid has a much more intense IR absorption detected by the ATR crystal than a gas phase molecule. While the ATR crystal itself was used as the adsorbent, thin films or slurries of catalyst can potentially be utilized in this setup to extend the analysis beyond monitoring phase change.

4 Surface reactions of CO₂

4.1 Bonding at metal surfaces

4.1.1 UHV

Adsorption of CO₂ on metal surfaces is widely acknowledged to result in two states of adsorbed species: a linear, inert CO₂ and a bent, anionic CO₂, widely recognized as a precursor to CO and O adatoms [110]. A key step for the reaction of CO₂ with hydrogen on Ni(110) is a change in the activated molecule coordination to the metal surface [111]. At 90 K, CO₂ is negatively charged and chemically bonded via the carbon atom [111]. When the temperature is increased and H approaches, the H-CO₂ complex flips and binds to the surface through the two oxygen atoms, while H binds to the carbon atom, thus yielding formate. On a clean Ni (100) surface at 130 K, however, no chemical activity takes place; neither physisorbed nor chemisorbed CO₂ is observed [112].

Copper catalyst surfaces, when in interaction with CO₂, are of paramount importance in catalysis. Polycrystalline copper foil exhibits chemisorption, yielding adsorbed carbonate, bent CO₂, and even C⁰ [37]. On clean Cu, XPS revealed that adsorption under 0.1 Torr CO₂ results in the formation of carbonate species, chemisorbed CO₂⁻, and C⁰. The C 1s peak at 289.3 eV and O 1s peak at 531.9 eV were assigned to a carbonate species; the C 1s peak at 288.4 eV and O 1s peak at 531.4 eV to chemisorbed, negatively charged CO₂ (CO₂⁻) and the C 1s peak at 284.4 eV to a C⁰ species. Co-adsorption with Zn, however, leads to complete conversion of all CO₂ to carbonate. A comparative study between Cu (110) and stepped Cu (311) using AES and temperature desorption spectroscopy (TDS) was conducted by Fu and Somorjai [113]. While the former does not exhibit adsorption of CO₂, dissociative adsorption readily takes place on the

latter, proven by the TDS spectra. The H_2^{18}O is formed due to reaction between labeled C^{18}O_2 and background H_2 , which is the reverse water-gas shift reaction [113]. The TDS spectra obtained from this experiment is shown in Figure 19. These phenomena substantiate increased reactivity of metal surface planes of higher indices (lower stability) that can be prepared and stabilized under vacuum.

Figure 19. CO_2 desorption from Cu (311) and Cu (110). Reprinted with permission from Elsevier [113].

On Cu (332), CO_2 is also found to adsorb by dissociation as CO and O surface species, confirmed by TDS and UPS [114]. The three main desorption states deduced from the experiment are at 110 K, 130 K, and 376 K, while UPS confirmed the presence of adsorbed oxygen with peaks at 6.1 eV and 9.6 eV, corresponding to π_g^* and π_u orbitals, respectively [114]. Different Cu surface preparation methods apparently alter the reactivity of the surface itself, most likely due to the complex surface terminations present. Surface-enhanced Raman spectroscopy (SERS) spectra show CO_2 adsorption on a Cu surface. This surface is prepared

using a cold deposition method and exhibited peaks associated with bent anionic CO_2^- , at 767 and 1182 cm^{-1} corresponding to δ (OCO) and the symmetric stretch mode ν_s (OCO) [115]. At higher coverage, presumably after the surface is saturated with CO, neutral CO_2 peaks intensify, as characterized by peaks at 1261, 1361, and 2292 cm^{-1} assigned to ν_s (OCO), 2δ (OCO), and ν_a (OCO) modes.

Cesium, an alkali metal, has been investigated as a dopant for carbon capture sorbents, especially Cu [116,117]. Adsorption of CO_2 at 80 K on the surface followed by heating up to 110 K was monitored using PES and valence electron energy-loss spectroscopy (VEELS). PE spectra showed two distinct peaks in O 1s spectra, a broad peak at 532 eV and a much weaker one at 536 eV, with the latter corresponding to physisorbed CO_2 . In the VEEL spectra, losses were found at 295, 660, 1460, 1660, and a weaker feature at 1975 cm^{-1} . Assignment of the peaks was as follows: a peak at 660 cm^{-1} was assigned to δ_2 (OCO) of CO_2 , while peaks at 1460 and 1660 cm^{-1} were symmetric and asymmetric vibrational modes of ionic $\text{CO}_2^{\delta-}$. Binding energy at 532 eV was assigned to bent ionic CO_2^- . Peaks at 295 and 1975 cm^{-1} were associated with gaseous and surface CO, respectively, at a very low concentration. Surface carbonate was formed upon heating the system to 298 K as peaks at 1510 (ν_3), 1060 (ν_1), 700 (ν_4) and 350 cm^{-1} ($\nu(\text{Cu-O})$) increased, while the PE spectra exhibited a peak at 531 eV [116]. On a Cs-doped Cu (110) surface, photoelectron spectra revealed the formation of carbonates even after heating up to 350 K, evident from the peaks at 5.54, 9.58 and 12.02 eV corresponding to CO_3^- orbitals [117]. A physisorbed molecule was also detected from a peak found at 15 eV, while a bent CO_2 molecule was represented by the peak at 6.9 eV.

The effect of K promotion on cold deposited Cu film, Cu (110), Cu (115) and Cu (100) changed the reactivity of the supposedly inert surface [115,118–121]. The K-doped, cold deposited Cu

film demonstrated the formation of CO and carbonates, in addition to the other species existing on the surface of its clean counterpart. On this surface, bending mode and symmetric vibration of the bent CO₂ exhibited peaks at 754 and 1197 cm⁻¹, while those of the physisorbed CO₂ molecule were detected at 640 and 1372 cm⁻¹, respectively [115]. The reactivity of alkali metals towards CO₂ resulted in the peaks detected at 280, 368, 2055 cm⁻¹, characteristics of liberation and frustrated translation, as well as stretching modes of carbon monoxide. Those at 1337 and 1424 cm⁻¹ were assigned to ν_3 s and ν_3 as of monodentate carbonate. At higher temperatures, changes in the surface speciation took place with peaks associated with carbonates intensifying above 200K. The only species present were bent anionic CO₂⁻ and carbonates [115]. Photoelectron spectra confirmed the appearance of peaks at 287.4 and 290.4 eV in C 1s spectra for K-doped Cu (110) surface, assigned to CO and bent CO₂⁻, respectively [118]. From the O 1s spectra, a binding state at 531 eV was assigned to bent CO₂⁻, while the presence of a peak at 536 eV indicates CO₂ in the physisorbed state, consistent with previous reports. Carbonate was also detected in some cases. C 1s spectra showed a peak at 290.8 and peaks at 531.9 and 531.0 eV appeared in the O 1s spectra for multilayer coverage and half-monolayer coverage, respectively. The presence of carbonates, CO, and bent CO₂⁻ suggest the reaction $\text{CO}_2^- + \text{CO}_2 \rightarrow \text{CO}_3^{2-} + \text{CO}_a$ [118]. On the Cu (115) surface photoelectron spectra revealed the appearance of peaks at 287.4, 290.3, and 291.2 eV, corresponding to carbon monoxide, surface carbonate, and CO₂ [120]. The latter, however, only appeared at higher coverage of CO₂, presumably due to the preferable chemisorption on the K-doped surface.

On a K-precovered Cu (110) surface, CO₂ adsorption was monitored by photoelectron spectroscopy upon increasing gas exposure at 170 K [121]. Adsorption of CO₂ caused a clear chemical shift of the K 3p core line and a decrease in the asymmetry of the clean K 3p with

increasing CO₂ exposure. Four new peaks also appeared at 8.5 and 11.7 eV after the adsorption and were assigned to chemisorbed CO₂ and at 8.5 and 12.6 eV at higher saturation, indicating the presence of physisorbed CO₂ with some peaks overlapping between the chemisorbed and physisorbed counterparts. Upon heating to 173 K, the physisorbed species was desorbed, while at 233 K CO was released from the surface, as observed from the intensity reduction of the complex peak structure between 6 and 9 eV. This result was also corroborated by HREELS, where peaks associated with physisorbed species at 631 and 2372 cm⁻¹ disappeared at 173 K. Peaks characterizing carbonate and CO appeared at 1512, 1045 and 1704, 2050 cm⁻¹, respectively. Also shown was the effect of the amount of K-coverage on the Cu surface: more CO was adsorbed below monolayer K-coverage due to the free Cu sites [121]. Assignments of both photoelectron spectra and HREELS peaks are provided in Tables 11 and 12.

Table 11. HREELS spectra peaks assignment at different temperatures obtained from CO₂ (10 L) on a K (0.4 ML)/Cu(110) interface. Reproduce with permission from Elsevier [121].

E (cm ⁻¹)					Assignment
107 K	173 K	233 K	400 K	500 K	
627	362				Cu-C stretching
	1045	1045	1045	1045	CO ₂ physisorbed
1375					Carbonate (CO ₃ ²⁻)
1440	1512	1512	1512	1512	CO ₂ ⁻ , CO ₂ physisorbed
1704	1704				Carbonate (CO ₃ ²⁻)
2050	2050				CO
2356					CO
					CO ₂ physisorbed

Table 12. Peak identifications, binding energies (eV) and assignments of structures in the photoemission valence spectra. Reproduced with permission from Elsevier [121].

Interface	Binding energy (eV)	Assignment
4 L CO ₂ on K(0.5 ML)/Cu (110)	8.5, 12.6, 14.2	Physisorbed CO ₂ : 1 π_g , 3 σ_u , 4 σ_g

12 L CO ₂ on K (1.1 ML)/Cu (110)	11.6, 14.3	Cu 3d satellites: ³ F, ¹ G
	5.5, 9.5, 11.7	Chemisorbed CO ₂
	8.5, 11.8	CO: 5 σ /1 π , 4 σ
	8.9, 13.0	Physisorbed CO ₂ : 1 π_g , 3 σ_u
	5.6, 9.8, 11.7	Chemisorbed CO ₂

The importance of alkali doping on a reaction towards adsorbing CO₂ was illustrated on other surfaces. For example, Pt (111) is an inert surface towards CO₂ that is activated by preadsorbing K on its surface [122][123]. The clean surface of the metal demonstrated an inability to adsorb CO₂, as observed using both AES and HREELS. However, when the surface was covered with potassium, an oxygen signal was observed with AES and it increased with higher K-coverage. HREELS studies revealed the peaks associated with CO₂ at 640, 1205, 1355, 1560, 2025, and 2350 cm⁻¹. While the first one is associated with the bending mode of weakly bound CO₂, the last one is assigned to its asymmetric stretching mode. Peaks at 1205 and 1355 cm⁻¹ were assigned to the $\nu_3(s)$ mode. For below monolayer K coverage, the lower spectrum exhibits three peaks indicative of the presence of anionic CO₂⁻ at 780, 1220 and 1520 cm⁻¹ that shifted to 870, 1340 and 1610 cm⁻¹ at the other end of the spectrum. The dissociation of activated CO₂ was confirmed, when the CO peak was spotted at 1670-1660 cm⁻¹. At low K-coverage the anionic species dissociated to CO and O at temperatures above 300 K, while at high K-coverage carbonate was formed with the anion as the intermediate above 200 K. It is also notable that authors tentatively assign some of the CO₂⁻ to be in the oxalate or a cluster ((CO₂)_n)⁻ form, owing to the fact that split peaks are sometimes observed at 1286 and 1388 cm⁻¹ due to a Fermi resonance or accidental degeneracy in the bending and symmetric stretching mode overtone [122]. Computational study using B3LYP functional also confirmed the inability of a Pt (111) surface to adsorb CO₂ molecule. The optimized structure of CO₂ adsorbed on clean Pt (111)

demonstrated a weakly bonded physisorbed binding mode. However, co-adsorbing it with K had activated CO₂ with a mandatory interaction between CO₂ and K required to give anionic CO₂⁻ as the activated form [123]. Llorca *et al.*, however, reported a dissociative adsorption of CO₂ on Pt surfaces supported on silica, in addition to bimetallic phase Sn-Pt/SiO₂ [124]. IR experiment showed that after CO₂ was admitted to the system, a peak developed at 2344 cm⁻¹ and was assigned to CO₂. Gas phase CO was simultaneously detected. After 21 hours, a broad peak at 2061 cm⁻¹ developed extensively. Flushing out the gas phase revealed the removal of the CO₂ peak, while the peak associated with CO remained in the spectra. Deconvolution of the spectra demonstrated that there were actually two peaks at ~2300 cm⁻¹, one at 2339 cm⁻¹ and the other at 2344 cm⁻¹. The latter one, which was also the more prevalent, was associated with coordination of linear CO₂ on a silica support, while the former was due to the interaction with the alloy itself [124].

Another support used as a K promoted CO₂ adsorbing surface was Ru (001) [58]. CO₂ appears to physisorb on Ru (001) surface, whereas K-doped Ru (001) with K present in the form of both monolayer and multilayer chemisorbs CO₂, yielding carbonate and CO in the process. This was confirmed by Fourier Transformed Infrared Reflection Adsorption Spectroscopy (FT-IRAS) and TDMS. Oxalate was also confirmed to appear as an intermediate with peaks at 1716, 1342, and 806 cm⁻¹ for monolayer K coverage, as well as at 1708-1625, 1345, and 765 cm⁻¹ for the multilayer K coverage case. Peaks at 1716, 1342, and 806 cm⁻¹ were assigned to two stretching modes, $\nu_3(\text{as})$ and $\nu_3(\text{s})$ and the bending mode $\delta(\text{OCO})$ of oxalate, respectively [58]. The formation of the carbonate species was also observed as characterized by peak sets for monolayer K (1467 (ν_3), 787 (ν_4) cm⁻¹) for “layer” (1490 (ν_3), 1040 (ν_1), 884 (ν_2) and 764 (ν_4) cm⁻¹ and for multilayer (1447 (ν_3), 1071 (ν_1), 884 (ν_2) and 764 cm⁻¹ (ν_4)) coverage.

Comprehensive analysis of the spectra can be found in reference [58]. However, from the temperature-programmed IR spectra it appears that the mechanism involves reaction between two CO_2 molecules to give C_2O_4 , after which it desorbs to give CO_3 and CO . Spectra of the adsorbates are shown in Figure 20.

Figure 20. Left: vibrational spectra of oxalate species on: (a) monolayer K-Ru(001), (b) K-multilayer, (c) bulk $\text{K}_2\text{C}_2\text{O}_4$; Right: vibrational spectra of carbonate species on: (a) monolayer K-Ru(001), (b) K-bilayer, (c) K-multilayer. Reprinted with permission from Elsevier [58].

Adsorption of CO_2 on pristine and Cu-covered Re (0001) surfaces was studied using XPS by Rodriguez *et al.* [125]. Chemisorption took place on both surfaces where CO_2 dissociated to CO and O . This experiment indicated the augmentation of the dissociative chemisorption due to the effect of Re support that makes the Cu dopant a better electron donor. Surface Re (0001) itself was already active for splitting CO_2 into CO and O atoms as demonstrated via a broad O 1s peak shown in Figure 21 [125].

Figure 21. XPS spectra taken for clean and Cu-doped Re (0001) surfaces after dosing 50 L of CO_2 at ~ 350 K. Reprinted with permission from Elsevier [125].

The dissociation of CO_2 on rhodium surfaces, has been the object of debates in the literature. Several publications have pointed to the inability of the surface to induce chemisorption [126], a result that was supported further by thermodynamics and kinetics calculations on Rh (111) [127]. However, Dubois and Somorjai insisted that CO_2 does dissociate on the Rh (111) surface [128], as HREELS C-O stretching modes at 1870 and 2070 cm^{-1} confirmed the presence of bridged CO and planar-bound CO.

HREELS, coupled with an ELS study, has been conducted on Rh (111) as a potential CO_2 adsorbing surface [129]. No chemisorption is observed (i.e. no peaks associated with CO formation) on clean surfaces. Physisorbed CO_2 was observed only by ELS and not HREELS. On a K-doped Rh (111) surface the adsorption was enhanced, showing energy losses at 820 , 1360 , and 1620 cm^{-1} , which are assigned to the CO_2^- anion. The activated complex dissociated to give CO and O at low potassium coverage, while at higher coverage, CO_3^{2-} and CO were produced

[129]. However, later investigations using a combination of field emission microscopy (FEM) and temperature desorption spectroscopy (TDS) revealed the dissociation of CO₂ on various Rh surface terminations [130]. The elucidation of the O₂ molecule fate, which results from the recombination of oxygen radicals from CO₂ dissociation, was also attained. Chemisorption occurred at temperatures above 165 K, as observed by both FEM and TDS. For low exposure of CO₂ the chemisorbed species recombined to yield CO₂ as a product. Under high CO₂ exposures there was a desorption maximum at 450 K, which was similar to that found after the exposure of Rh surface to CO. The remaining O atoms diffused to the surface of Rh at higher temperatures between 600 K and 1200 K as either O₂ or form surface RhO_x [130].

Recently, a comparative DFT study was conducted that analyzed CO₂ interactions with rhodium nanoclusters (Rh₁₃) supported on unzipped graphene oxide (Rh₁₃/UGO) surface, unsupported Rh₁₃ nanocluster surfaces and Rh (111) surfaces [131]. The calculated CO₂ adsorption energy on an Rh (111) surface was +0.26 eV, supporting the argument that CO₂ might not adsorb. For both Rh₁₃ containing surfaces, dissociation of CO₂ takes place with the UGO-supported, icosahedral Rh₁₃ clustered surface exhibiting the lowest energy barrier. This finding is due to the greater charge transfer from *d* electrons of the Rh atoms to CO₂ adsorbate on the supported Rh cluster, compared to that of the free cluster [131].

The inability of platinum group metals to adsorb CO₂ was also confirmed by *in situ* FTIR measurements of CO₂ over Pd/ γ -Al₂O₃ [76]. At low coverages all peaks observed in the spectra were identical to those found on clean Al₂O₃ surfaces. These peaks were due to the adsorbed CO₂ (2340–2370 cm⁻¹), bridging carbonates (1060, 1410, 1700–1900 cm⁻¹) and bicarbonates (1235, 1485, 1645, 3610 cm⁻¹). However, at higher Pd coverage, peaks decreased in intensity, owing to the fact that Pd metal atoms blocked the adsorption of CO₂ by occupying the defect

sites [76]. HREELS of CO₂ adsorption on Pd (110) metal surface with coadsorbed water confirmed the formation of CO₂^{δ-} [132]. At 110 K no chemisorption was observed on the clean Pd (110) surface and the coadsorption of water significantly changed the chemistry with the bent CO₂ species, a precursor of CO, observed. Adsorption of CO₂ on water-covered surfaces lead to the appearance of two new peaks at 770 and 1200 cm⁻¹, which were respectively assigned to CO₂^{δ-} bending and symmetric stretching modes. Physisorbed CO₂ exhibited unperturbed modes at 667 (bending) and 1298 (stretching) cm⁻¹. The other asymmetric mode of the chemisorbed species would be in the region of ~ 1600 cm⁻¹, which would overlap with the high intensity adsorbed water peaks. Further confirmation of the chemisorbed species formed upon coadsorption with water was attained using TPD, where CO₂ and water are desorbed at the same time. However, TPD also confirmed that water exhibited competitive adsorption. This was also demonstrated by the decreasing concentration of chemisorbed species, when a higher dose of water was introduced [132].

CO₂ undergoes no dissociative adsorption on an Fe (111) surface, as confirmed by time-resolved HREELS [133]. Three adsorbed states were present on the surface at low temperatures of 100 K, two bent and one linear. Bent CO₂ molecules are, however, more prominent than the linear ones, pointing to the saturation of bent states before occupying the linear state [133]. Fe (110) surface, when doped with Cs, however, exhibits a lot of new surface chemistry upon CO₂ adsorption [134]. Adsorption of CO₂ at 85 K yields a variety of surface species resulting from CO₂ chemisorption. Namely, CO, carbonates and oxalates, as confirmed by UPS and XPS, were detected. Temperature ramping demonstrated desorption of CO₂, as well as reaction toward CO, CO₃, and carboxylate species (C₂O₄^{m-}) at temperatures between 85 K to 160 K. At higher temperatures oxalate decomposed to yield CO₂, CO, and surface carbonates. Decomposition of

CO molecules into C and O, and the corresponding recombination to CO, take place at even higher temperature, above 320 K and between 500-700 K, respectively. At low CO₂ coverage linearly physisorbed CO₂ was observed, as confirmed by peaks at 8.8, 12.6, 13.2, and 14.8 eV from UP spectra assigned to $1\pi_g$, $1\pi_u$, $3\sigma_u$ and $4\sigma_g$ molecular orbitals of CO₂. CO was also observed with a peak at 7.1 eV assigned to 1π and 5σ , while the peak arising from the 4σ orbital at 10.5 eV was hidden under the Cs $5p_{3/2}$ core line. The carbonate was characterized by peaks at 4.4, 5.6, and 9.8 eV and assigned to $1a'_2$, $1e''/4e'$ and $1a_2''/3e'$ carbonate orbitals, respectively. XPS binding energies of these molecules can be found elsewhere [134]. Temperature programmed X-ray and ultraviolet photoelectron spectra are shown in Figures 22 and 23, respectively.

Figure 22. X-ray photoelectron spectra taken after subsequent exposure to CO₂ at $\Theta_{Cs} = 0.18$ and $T = 85$ K. Reprinted with permission from Elsevier [134].

Figure 23. UPS spectra of the Cs-covered surface at $\Theta_{\text{Cs}} = 0.13$ after subsequent CO_2 exposure at 85 K. Reprinted with permission from Elsevier [134].

Another alkali metal proven to enhance the reactivity of Fe (110) towards CO_2 is K [135,136]. CO_2 is adsorbed on K-precovered Fe (110) surface, even at low K-coverage with the small amount of CO_2 undergoing dissociation to CO. Upon prolonged adsorption, CO_2 disproportionation takes place with carbonates and CO formation confirmed by UPS and XPS. Oxalate, however, can neither be confirmed nor ruled out. Typically, it is in the form of a C-O-C bridged “iso-oxalate” species or a $\text{CO}_2^{\delta-} \cdot \text{CO}_2$ complex [136]. TPD provides further insight into the chemical activity on the surface of K/Fe (110) [135]. At low K-coverage ($0 < \theta_{\text{K}} \leq 0.20$) in the temperature range 80 to 140 K, desorption and reaction of linear CO_2 to carbonates, CO, and oxalates via $\text{CO}_2^{\delta-}$ occur, while carbonate decomposes within the temperature range of 140 to 330 K. In the higher temperature range from 330 to 500 K, CO dissociation and desorption

occur. At high K-coverage ($0.26 < \theta_K \leq 0.30$), the only differences are in the 140 to 330 K temperature region, where $C_2O_4^{m-}$ is decomposed, as well as at 500 – 600 K, where surface carbonate undergoes decomposition. At higher coverage it is noticeable that carbonates have stronger bonds, presumably due to K atom abundance, which leads to a higher amount of coordinated carbonates [135].

Table 13. Binding energies (in eV) of O 1s and C 1s peaks in XP spectra of CO₂ adsorption on K-precovered Fe (110) surface. Reproduced with permission from Elsevier [136].

Species	θ_K	XPS binding energies		
		O 1s	C 1s	ΔE_b
CO ₂	0.08	535.6		
	0.34	535.9		
CO	0.34	531.6	285.5	246.1
CO ₃ ⁿ⁻	0.08	531.3	289	242
	0.34	531.6	289	242

Surface characterization of the adsorbent is done using XPS, and peak assignments can be seen above. With potassium coverage (θ_K) of 0.34, only with a CO₂ exposure of more than 0.7 L can the peaks associated with CO and carbonates be seen in the spectra. The O1s peaks of both CO and carbonate coincide at ~531.6 eV, while the corresponding C1s spectra shows peaks at 285.5 and 289 eV, respectively. Dissociation of CO₂ on the surface is further corroborated by the presence of a shoulder at 529.5 eV, which can be assigned to oxide from the oxygen. Prolonged exposure to CO₂ results in the appearance of another peak at 535.9 eV in the O1s spectra, which is related to weakly adsorbed linear CO₂ due to the fully occupied surface. The corresponding C1s spectra peak is at 292 eV, which coincides with the K2p_{3/2} signal. At lower K coverage, i.e. $\theta_K = 0.08$, a shift is expected for O1s peaks of both carbonates and linear CO₂, where the values are now 0.3 eV lower than those at a higher θ_K .

The corresponding UV photoelectron spectra for different θ_K is presented in the table below. Linear CO₂ presence is readily confirmed by intense peaks at ~8-9 and ~13 eV. Increasing the CO₂ exposure, i.e. > 0.2 L, results in the formation of two other intense peaks at ~6 and ~10.4 eV, accompanied by several weak peaks at ~7.4 and ~11 eV, depending on the θ_K . The results from XPS and UPS led the authors to conclude that linearly adsorbed CO₂ molecules react to give CO and carbonates.

Table 14. Binding energies (in eV) of characteristic emissions in UP spectra of CO₂ adsorption on K-pre-covered Fe (110) surface; the values in brackets show the difference from the orbital marked by *. Reproduced with permission from Elsevier [136].

Species	θ_K	$h\nu$ (eV)	UPS binding energies			
			$1\pi_g$	$1\pi_g/3\sigma_u$	$5\sigma_g$	
CO ₂	0.05	21.2	8.4 (*)	12.7 (4.3)		
	0.31	21.2	9.2 (*)	13.3 (4.1)		
	0.06	40.8	8.8 (*)	13.0 (4.2)	14.5 (5.7)	
	0.2	40.8	9.3 (*)	13.5 (4.2)	15.0 (5.7)	
			$1\pi/5\sigma$	4σ		
CO	0.18	21.2	7.4 (*)	11.0 (3.6)		
	0.17	40.8	8.1 (*)	11.4 (3.3)		
			$1a'_2$	$1e''/4e'$	$1a''_2/3e'$	$4a'_1$
CO ₃ ⁿ⁻	0.31	21.2	4.4 (-1.6)	6.0 (*)	10.2 (4.2)	12.0 (6.0)
	0.2	40.8	4.4 (-1.6)	6.0 (*)	10.4 (4.4)	12.0 (6.0)

4.1.2 CO₂ interactions with co-adsorbing gas on metal surfaces

While CO₂ adsorption on clean metal surface sites yields either linear CO₂ or bent anionic species, adsorption on precovered gas surfaces, typically hydrogen and oxygen, yields carbonate and even formate. The fate of the carbonate, however, depends on the surface itself; in some cases it gets stabilized [122], while in others it just reacts with CO resulting from CO₂ dissociation to yield CO₂, both bent and anionic [137]. Surface carbonate formed via co-

adsorption of CO₂/O₂ on Ni (100) surface has been characterized using XPS, UPS, and TPR [112]. XPS showed the appearance of new peaks in the C 1s and O 1s spectra at 289.0 eV and a doublet at 529.3 and 531.2 eV, respectively. The doublet indicates the presence of two different O-containing species. The peak from C 1s spectra, along with the first peak in the O 1s doublet, were assigned to surface carbonate, while the peak at 531.2 eV was attributed to either atomically adsorbed O or the atomic O that accompanies the formation of carbonate. It was also demonstrated that pretreating the surface with O₂ is the only way to produce surface carbonate. Flowing O₂ would yield basic surface O sites and resulting chemically adsorbed CO₂ [112].

Polycrystalline Cu foil could potentially be a good candidate for CH₃OH synthesis, because in the presence of 0.1 Torr CO₂ and water, both formate and methoxy species were formed along with the other chemisorbed species. The assignment of the C 1s peaks was reported as carbonate (289.3 eV), CO₂^{δ-} (288.4 eV), formate (287.3 eV), methoxy (-O-CH₃) (285.2 eV) and C⁰ (284.4 eV), respectively. On Zn-pre-covered Cu foil surface, four species were observed: carbonate (289.3 eV), formate (287.3 eV), methoxy (285.2 eV) and C⁰ (284.4 eV). For the O 1s region, overlaps between the formate, carbonate, bent CO₂⁻ and methoxy were prominent, leading to the inability to accurately resolve the peaks [37]. O₂-precovered Cu (311) was more reactive than Cu (110) and exhibited the capability to dissociate CO₂, similar to when it is not pretreated with any gas. Similar to the adsorption without the presence of O₂, water was produced due to the reaction with background H₂ [113]. It is evident from the below C¹⁸O TDS spectra, which are taken by flowing 4L of C¹⁸O₂, that peaks were observed at 200 K and ~480 K, on any Cu (311) surface, but not on any Cu (110) surface.

Figure 24. Decomposition of $C^{18}O_2$ to form $C^{18}O$ and surface atom O on Cu (311) but not on Cu (110). Reprinted with permission from Elsevier [113].

Pre-dosing Cs-doped Cu(110) with hydrogen before CO_2 adsorption resulted in peak shifts on the UP spectra. For instance, carbonate peaks were apparent at 5.3, instead of 5.54 eV, and the peak due to the $4\sigma_g$ orbital of physisorbed CO_2 shifted to 14.7 instead of 15 eV. The peak associated with one orbital molecule of a bent CO_2^- molecule shifted from 6.9 to 6.6 eV, signifying interactions between the adsorbing CO_2 and hydrogen. As expected, formation of surface formate was confirmed by the presence of peaks at 8.56, 10.3, 14.0, and 5.3 eV (overlapping with that of carbonate) [117]. K-promoted Cu(115), when precovered with H gave a complex spectrum resulting from CO_2 adsorption. Photoemission results indicated the presence of hydrogen-induced states, molecular CO_2 , CO, surface formate and carbonates (Figure 25) [120].

Figure 25. Valence band spectra of $(\text{CO}_2+\text{H})/\text{K}/\text{Cu}(115)$ interface obtained at $T=125 - 500$ K. Reproduced with permission from Wiley [120].

Table 15. Peak assignments for valence band spectra of $(\text{CO}_2+\text{H})/\text{K}/\text{Cu}(115)$ interface obtained at $T=125 - 500$ K. Reproduced with permission from Wiley [120].

BE position [eV]	Identification
6.5, 9.0	hydrogen-induced states: β , α
8.6, 12.6, 14.5	$\text{CO}_2(\text{lin})$: $1\pi_g$, $1\pi_u/3\sigma_u$, $4\sigma_g$
8.7, 12.1, 13.0	CO : $1\pi/5\sigma$, 4σ , $4\sigma_{\text{sat}}$
6.0, 9.2, 11.1, 14.2	HCOO^- : $4b_1/6a_1$, $1b_2$, $3b_1/5a_1$, $4a_1$
5.2, 6.2, 9.7, 12.0	CO_3 : $1a_2'$, $1e''/4e'$, $3e'/1a_2''$, $4a_1'$

Pre-covering a K-deposited Pt(111) surface with oxygen atoms yields a similar result, as if the surface

was not pre-dosed with O_2 upon CO_2 adsorption [122]. Bent anionic CO_2^- species forms on the surface and readily reacts with a surface O atom to yield carbonate. Positive shifts in HREELS peak energies were observed for the O-pre-covered surface as compared to the clean K-Pt (111) with the peaks appearing at 955, 1410 and 1710 cm^{-1} assigned to $\delta(\text{CO}_2^-)$, $\nu(\text{CO}_2^-)$, and $\nu(\text{CO}_2^-)$, respectively. The TDS spectra also showed surface O atoms playing a major role in stabilizing the carbonate formed on the surface [122].

An alloyed metal investigated as a CO_2 adsorbing surface was Pd (100)-Mn-c(2x2) [138]. Adsorption on a pristine surface yielded no surface species due to the inactivity of the surface. However, co-adsorption with oxygen significantly altered the outcome. In particular, elemental carbon is detected in photemission spectra at 110K, as characterized by the peak at 283 eV, as well as CO on Pd and CO on Mn at 286.5 eV and the corresponding shoulder, respectively. Upon heating, carbonates and CO_2 were formed on the surface. The increased reactivity was suggested

to arise from the appearance of different oxidation states of the alloy surface caused by pretreatment with oxygen. O₂ pre-dosing destroyed the structure of the metal, creating clusters of Mn-oxides, which were highly reactive towards the formation of surface carbonate [138].

DFT calculations on the reverse reaction of CO₂ dissociation on Ru (0001), i.e., catalytic oxidation of CO, has been carried out [139]. Indirect correlation was inferred from this simulation with two mechanisms for the reaction available depending on the O-coverage. Covering the surface with oxygen reveals the first mechanism, which is a reaction of gas-phase CO with a surface oxygen atom, leading to CO₂. The second one, which is more prominent, is the adsorption of CO on an O-vacancy site of the surface, followed by the reaction of the two adsorbed molecules. The reverse case of the reaction is the dissociation of CO₂ on the surface [139].

Ag appears to be one of the most extensively studied metals [137,140–143] for CO₂ adsorption along with other gases. On an oxygen pre-covered Ag (110) surface, Guo and Madix discovered the formation of carbonate which would react readily with background CO molecules [140]. These were formed when exposing the surface to CO₂ using an ion pump, resulting in a chemisorbed CO₂ state, as confirmed by the desorption temperature of 485 K, remarkably higher than that of physisorbed CO₂ desorbing at 130 K [140]. Dosing a clean Ag (110) surface with Cs results in reconstruction of the surface, as confirmed using STM and AES, and subsequently enhances the adsorption of CO₂, whereas it does not adsorb on a pristine surface [137]. The adsorption leads to the formation of locally ordered (2x1) structures and linear (2x2) structures distributed inhomogeneously on the surface. Desorption of the surface intermediate revealed no oxygen was desorbed, leading to the notion that carbonate was not formed on the surface. Isotope-labeled CO₂ adsorption revealed that even though C=O bond scission could not be

confirmed, extensive isotope exchange took place on the reconstructed surface. One possible surface intermediate was oxalate. However, the oxalate formed is stable on Ag, while on Cs, the oxalate decomposes to give carbonate and CO [137]. The same group also performed STM analysis demonstrating that adsorbed carbonate surface structures are clearly different from those of chemisorbed CO₂ [143]. Figure 26 depicts the difference in the STM images compared for the two distinct surface species (chemisorbed CO₂ and carbonate), along with TPSR spectra to further confirm the gas-phase products.

Figure 26. STM images and TPSR spectra for (top) chemisorbed CO₂ and (bottom) carbonate. Reproduced with permission from Elsevier [143].

The striking difference in both species is that, upon desorbing, carbonate decomposes into CO₂ and oxygen, as can be seen from the TPSR spectra. The images above clearly suggest different morphological forms of the two species. These are round protrusions for chemisorbed CO₂ and rods parallel to $[1\bar{1}0]$ direction for chains of surface carbonates. This finding advocates the

growth of carbonates taking place in the (110) direction, where the carbonate rods accumulate near the step edges, and the surface becomes more reactive due to its low coordination nature. The carbonate formation stages, as observed with STM, can be seen in the Figure 27.

Figure 27. STM images of carbonates on Ag (110) at various carbonate formation stages; (a) - 1.98 V, +365 pA; (b) +304 mV, +333 pA; (c) +2.85 V, +232 pA; (d) +2.85 V, +0.52 nA; (e) +3.26 V, +349 pA; (f) +317 mV, +309 pA. Reproduced with permission from Elsevier [143].

In agreement with Guo and Madix,[143] Stensgaard *et al.*, also confirmed that the reaction is preferentially initiated at steps, and defects, spreading anisotropically along the (001) direction, added Ag-O rows on the surface [141]. At higher oxygen coverage, however, the unreacted rows transform into (2 X 1) structure. In all cases observed by the authors, the reaction to carbonate leads to a new reconstruction of the surface, where the carbonate preferentially sets on top of the (110) triple structure. The transformation into 2x1 structure can be seen in the Figure 28.

Figure 28. Carbonate formation on oxygen precovered Ag (110) surface, as observed using STM under different CO₂ exposure (a-d). Notice that the initial 3x1 phase (a) has transformed into 2x1 phase along with higher exposure of CO₂. Reprinted with permission from [141]. Copyright [2014], AIP Publishing LLC.

Formation of carbonate on Ag (110) with O₂ pre-adsorption was also confirmed using SERS [142]. For the clean surface, a Raman shift of CO₂ peaks was observed at 653, 1276, 1375, and 2329 cm⁻¹, which were assigned to the ν_2 , $2\nu_2$, ν_1 and ν_3 modes of CO₂ deviating about 14-28 cm⁻¹ from those in the CO₂ gas spectra. SERS also confirmed the chemisorption via the appearance of peaks at 1046 (ν_1), 1289 and 1420 (ν_2) and both 682 and 703 cm⁻¹ (ν_4), as well as peaks associated with the physisorbed CO₂ when the clean surface was precovered with O₂. Surface carbonate was formed perpendicularly to the surface, a conclusion drawn from the observed intensities of the peaks in the SERS spectra. On submonolayer alkali metal predosed

silver of undefined surface termination, however, adsorption of CO_2 lead to formation of three new peaks at 750, 1200, and 2130 cm^{-1} . While the latter peak is easily assigned to CO, data analysis by the authors linked the first two peaks to the formation of anionic CO_2^- caused by the presence of alkali metal ions [142]. Figure 29 shows the SERS spectra of CO_2 adsorption on both oxygen precovered and alkali predosed silver metal surface. The main difference between them is that on the spectra of the left of Fig. 29 carbonate peaks are prominent, while those on the right exhibit two intense peaks from bent CO_2 coordinated with the alkali, i.e. potassium.

Figure 29. (Left) SERS spectra of CO_2 on O_2 pretreated silver surface. (a) After 0.5 L O_2 followed by 2.5 L CO_2 , (b) same as (a) with a total of 8 L CO_2 . (right) SERS spectra of CO_2 on a K predosed surface at 50 K with (a) $\theta_K = 0.15$ and (b) $\theta_K = 0.40$. Reproduced with permission from [142]. Copyright (1989), AIP Publishing LLC.

A low reaction pathway to surface carbide or surface formate is available via coadsorption of CO_2 with H_2O vapor on Al (111) surface [144]. XPS showed three peaks in the C1s spectrum during the adsorption of CO_2 on water-precovered surface at 295 K at 292, 285, and 282 eV assigned to surface carbonate, carbon, and carbidic species, respectively. When coadsorbed with

water, however, a peak at 286 eV appeared at the expense of the carbidic peak at 282 eV. The former peak indicates the presence of a C-H species suggesting hydrogenation of CO₂ [144].

Alkali metal surfaces, such as Li, are very reactive toward acids, such as CO₂. When dosed with O₂ at 120 K, XPS showed a major peak at 530.3 eV assigned to a bridged coordination of an oxygen atom with two Li atoms [145]. When the O-precovered Li surface was exposed to CO₂, two other distinct peaks appeared along with two peaks in the C1s spectra at 534.0, 533.2, 290, and 292 eV, respectively. Supported with previous evidence on K and molecular orbital calculations, peaks at 530.3 and 292 eV were assigned to carbonates. The peak at 290 eV existed as a shoulder on the one at 292 eV, C1s peak of carbonate, along with the 533.2 eV peak and were assigned to anionic bent CO₂. Significant spectral changes occurred at temperatures above 370 K, where all the carbonates decomposed into elemental C and O atoms. A different phenomenon was observed for CO₂ adsorption on a clean Li surface, where adsorbed CO was also detected as evident from the appearance of peaks at 288.0 eV in C1s and 534.3 eV in O1s, the latter overlapping with the peak due to the surface carbonate [145]. In this case, temperature ramping to 180 K resulted in decomposition of carbonate to yield CO₂ and CO, which further decomposed into elemental C and O atoms. Four main reactions were tentatively postulated for this system: activation of CO₂, reaction between two anionic CO₂ molecules to yield carbonate and CO, decomposition of CO into elemental C and O, and lastly, the formation of carbonate from O and CO₂ [145]

4.2 CO₂ bonding on metal oxide surfaces

4.2.1 Alkaline Earth Metal Oxides. Carbon dioxide is an acid gas which can readily interact with basic surface sites. Some metal oxides, such as CaO and MgO, possess high basicity and therefore are expected to actively react with CO₂. These two alkaline earth metal oxides are often regarded as model surfaces for the formation of adsorbed carbonates [77]. CO₂ is also used as a surface site, probing molecules in case of MgO, and these interactions have been studied extensively. Aramendia et al., for instance, characterized synthesized MgO particles using DRIFTS to understand the structure/reactivity relationships between the preparation method and the nature of the surface species formed [146]. Philipp and Fujimoto [59] studied CO₂ adsorption using FTIR spectroscopy on MgO and CaO, as well as mixed oxides of these two alkaline earth metal. Busca and Lorenzelli [53] presented a comprehensive account on the IR peak assignments of the surface species observed on various metal oxides, including alkaline earth. Peaks assigned to surface unidentate (monodentate) carbonate as well as bicarbonate arising due to the interaction of CO₂ with surface hydroxyl groups, were observed on the MgO surface upon exposure to CO₂ at 950 °C. On CaO, similar peaks were observed. In particular, unidentate carbonate complexes were formed in addition to bicarbonate and bridging carbonate. Figure 30 represents the IR spectra of CO₂ adsorbed on MgO and CaO. Spectra of the adsorption on the mixed oxides has also been reported [59].

Figure 30. Spectra for CO₂ Adsorption on (a) MgO and; (b) CaO at Room Temperature. Reproduced with permission from [59]. Copyright (1992) American Chemical Society.

Preparation methods for improving the lifetime of CaO/MgO and CaO/ Al₂O₃ surfaces were studied by Luo *et al.* and Sun *et al.*, respectively [147,148]. The methods used were combustion and wet mixing and they successfully increased the lifetime as well as the CO₂ adsorption capacity. After several cycles of CO₂ adsorption the surface morphology was imaged using SEM and compared with the corresponding metal carbonates. Figures 31 depicts the surface before and after CO₂, as well as its comparison with the calcium carbonate. These SEM images suggest that after 20 cycles crystallite size increased from its original state (Figures 31a,b). It can be concluded that the sorbent maintained its CO₂ capture capacity even after 20 cycles, where its bulk structure was still far from the morphology of calcium carbonate and the adsorption is surface limited.

Figure 31. SEM images of CaO/MgO sorbents (a) before CO₂ capture, (b) 20 cycles of carbon capture-calcination, (c) calcium carbonate morphology. Reproduced with permission from Elsevier [147].

Another attempt at utilizing alkaline earth metal oxides for efficient CO₂ adsorption was performed by Shao *et al.* [51] in which the authors synthesized mesoporous MgO nanoparticles applicable for CO₂ capture. *In situ* IR spectroscopy was performed at a constant temperature to investigate the surface species formed during the adsorption process and shown in Figure 32. In addition to an adsorbed complex surface carbonate structure, there was a notable observed peak at 2344 cm⁻¹, due to the linearly adsorbed CO₂. This observation complemented the spectra taken by Philipp and Fujimoto [59].

Figure 32. *In situ* IR Spectra of CO₂ Adsorption on Mesoporous MgO taken at room temperature.

Reproduced from [51] with permission from PCCP Owner Societies.

XPS analysis of CO₂ adsorption on an MgO surface was conducted by Aswal *et al.* [149] and is shown in Figure 33. As received MgO, which already contains CO₂ adsorbed as carbonates due to the inherent MgO reactivity at atmospheric concentrations of CO₂, was analyzed along with a thermally treated MgO. Mg 2p spectra for the pristine crystal resolved peaks at 50.8 eV and 51.6 eV are indicative of hydroxide and carbonate species, respectively. O 1s spectra showed peaks at 531.5 and 533.8 eV also due to the presence of Mg(OH)₂ and MgCO₃. The presence of adsorbed carbonate was further confirmed by the C 1s spectra where two peaks were also detected at 285 eV and 289 eV, with the latter from the carbonate and the former representing physically adsorbed CO₂. At higher temperatures, all peaks assigned to the carbonates disappeared, while those assigned to hydroxide shifted to a lower energy value indicating the formation of pure MgO at higher temperatures.

Figure 33. XPS spectra of MgO treated at different temperatures. Carbonates peaks can be observed on the as-received sample. Reproduced with permission from Elsevier [149].

A similar result on the XPS spectra for the CO_2/MgO system was also presented by Chakradhar and Burghaus [150] where the spectra revealed a carbonate peak on the C 1s spectrum at 289.4 eV, differing by 0.4 eV from the observation from Aswal *et al.* [149], possibly due to the variability in the nature of the neighboring species.

Analysis of another CO_2 interaction with CaO was carried out by Voigts *et al.* [151]. MIES (Metastable Induced Electron Spectroscopy) spectra revealed the ionization of O 2p orbitals in the CaO via the presence of a peak at 5.1 eV, while the triplet carbonate peak appeared in the spectra at 7.4, 12.0 and 14.4 eV. Prolonged exposure to CO_2 results in the disappearance of the O 2p peak associated with CaO, which is related to the consumption of the lattice oxygen to form carbonates when CO_2 is introduced. Furthermore, dissociation of CO_2 is not expected, since CaO has no density of states near the Fermi level. XPS spectra of the system were obtained in O 1s and C 1s regions with two peaks present in the former and only one peak in the latter. The O 1s region showed a peak at 530.8 eV due to CaO and 533.5 eV from adsorbed carbonate. The C 1s

region exhibited a contribution solely from the surface carbonate at 291.9 eV [151]. Comparison among BaO, MgO and CaO with CO₂ adsorption capacity revealed the superiority of the latter [152]. While BaO and MgO demonstrated almost negligible adsorption at 600 °C, CaO adsorbed nearly 12 wt. % during a 1-h equilibrium process. The effects of temperature and dopants on the CaO surface adsorption were further investigated revealing an increased amount of adsorbed CO₂ with increase in temperature and a prominent effect of alkali metal dopants on the adsorption in the following order: Cs >> Rb > K > Na > none > Li. Elucidation of this reactive surface behavior was provided by the XPS spectra of a 20% Cs/CaO surface before and after desorption of the previously CO₂ adsorbed sample. The O 1s spectra show an overlap between the oxygen atom contributions from oxides and carbonates with the latter as a minor component in Figure 34 at ~530.4 eV. The oxygen coordinated to either Ca or Cs, represented by the peak at 532.5 eV, maintains its phase before and after adsorption. On the other hand, both Ca 2p and Cs 3d peaks at ~347 and ~724 eV, respectively, exhibit shifts towards higher binding energy values. These shifts are attributed to the change of phase from the alkali carbonates to their respective oxides at 725 °C. The peak at 530.4 eV was attributed to CaCO₃ and Cs₂CO₃ showing carbonate formation on the particle surface.

Theoretical modeling of CO₂ adsorption using periodic boundary conditions and density functional theory on defect-free alkaline earth metal oxides has been performed previously using VASP computational code [90,153–156]. MgO, CaO, SrO, and BaO were examined and CO₂ was found to adsorb on the basic surface oxygen (O_s²⁻). Adsorption was only physical in magnitude since surface oxygen is relatively less reactive than those of lower coordination, such as on steps, corners, and kinks, where adsorption would generate carbonates. Adsorption on MgO, for instance, did not significantly elongate the C=O bond and the adsorption energy was about -3 kcal/mol [153]. However, Ca and Fe doping in the subsurface layer changed the strength of MgO (001) and CO₂ interaction as shown in Figure 35. In particular, BSSE corrected adsorption energy utilizing periodic boundary conditions, Gaussian basis set and hybrid B3LYP functional using CRYSTAL software [157], $E_{\text{adsorption}}$, for CO₂ decreased by 5.81 and 3.25 kcal/mol from undoped to Ca- and Fe-doped MgO (001) with -8.77, -14.58, and -12.02 kcal/mol, respectively. Hence, showed a lower calculated adsorption energy (stronger

adsorption) of CO₂ on Ca- and Fe-doped MgO than in the undoped case [158]. This is of particular importance in atmospheric chemistry since MgO is an important compound in the environment and is found in the form of mineral periclase at 3.7 % in the continental crust. As natural minerals are rarely pure in the environment, naturally occurring MgO can have varying concentrations of other elements substituted into its crystalline lattice with Ca and Fe reported as the main dopants and concentrations of Fe as high as 5–10 wt % [159].

Figure 35. UB3LYP optimized geometries of CO₂ adsorbed on (a) undoped and (b) Ca- or (c) Fe-doped MgO(001) surfaces. Only relevant atoms are shown. Reproduced with permission from [158]. Copyright (2012) American Chemical

Society.

Adsorption of CO₂ on defect sites, e.g. corners and steps, of CaO resulted in the formation of monodentate carbonate while on MgO, monodentate was formed on the edge sites and bidentate on corner sites [90]. Figure 36 below shows the defect sites of a CaO/MgO slab.

Figure 36. Low-coordination sites on CaO and MgO surface, including step (M_{4c}), corner (M_{3c}), and terrace (M_{5c}); M=Ca/Mg.

GGA (General Gradient Approximation) was also applied using CASTEP (Cambridge Sequential Total Energy Package) [160] for CO₂ adsorption on BaO [154]. CO₂ was found to chemisorb on the surface in a form of carbonate to a large extent. Calculated IR intensities, wavenumbers, and adsorption energies of CO₂ on MgO and CaO are shown in Tables 16 and 17.

Table 16. Calculated Wavenumbers, IR Intensities, and Adsorption Energies of CO₂ at Various MgO Sites. Reproduced with permission from [90]. Copyright (2005) American Chemical Society.

Adsorption mode	ν_3 as (cm ⁻¹)	ν_3 s (cm ⁻¹)	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	E _{ads} (kJ/mol)
terrace, O _{5c} , dih ang 0°	1784	1288	827	821	13
step, O _{4c}	1703	1327	1011	849	-154
corner, O _{3c} , bidentate	1778	1243	932	847	-115
corner, O _{3c} , tridentate	1451	1451	1084	906	-152

Table 17. Calculated Wavenumbers, IR Intensities, and Adsorption Energies of CO₂ at Various CaO Sites. Reproduced with permission from [90]. Copyright (2005) American Chemical Society.

Adsorption mode	ν_3 as (cm ⁻¹)	ν_3 s (cm ⁻¹)	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	E _{ads} (kJ/mol)
terrace,b O _{5c} , dih ang 0°	1708	1298	876	847	-100
terrace,b O _{5c} , dih ang 45°	1692	1304	927	868	-60
step, O _{4c}	1664	1316	968	845	-219
corner, O _{3c} , monodentate	1603	1314	1035	876	-222
corner, O _{3c} , bidentate	1703	1257	944	845	-182
corner, O _{3c} , tridentate	1461	1423	1080	881	-164

Cluster calculations, using the *ab initio* Hartree-Fock approximation and assuming perfect ionicity of MgO and CaO crystals, were carried out. These calculations demonstrated formation of more strongly-bound carbonates on CaO, because to the CaO is a better base. This was resolved from the decomposition of the interaction energy into electrostatic, polarization and charge transfer contributions [155]. The formation of BaCO₃ on a pristine BaO surface after saturating it with CO₂ was confirmed through XPS analysis [161]. Typical peaks that were associated with BaCO₃ were observed, e.g. 289.5 eV in C1s and 531.5 eV in the O1s spectra. The assignments of these peaks was in agreement with those of CaO by Voights *et al.* [151].

4.2.2 Alkaline Metal Oxides. A recent review paper by Wang et al. in 2011 discusses the use of alkaline metal oxides, notably oxides and oxide composites of Na and Li [162], for CO₂

adsorption. The group I oxides are the most basic oxides. Therefore, they should have the highest capability to adsorb carbon dioxide, an acid gas molecule. Duan and Sorescu performed a theoretical study of the structural, electronic and phonon properties of Li_2O and Li_2CO_3 [163]. This VASP simulation led to the notion that Li_2O would not be a good adsorbing surface for CO_2 due to its very strong affinity for the acid gas, allowing desorption to take place only at very low CO_2 pressure or very high temperature, where the carbonate is in a liquid phase. Calculations of all the vibration modes of both IR and Raman spectra of Li_2CO_3 are in a good agreement with earlier theoretical and experimental studies [164]. A comprehensive analysis of CO_2 adsorption on Li_2O , including TGA, SEM and XRD, before and after the adsorption, together with the adsorption isotherms at various temperatures, was carried out by Mosqueda et al. [165]. In agreement with the work of Duan, Li_2O was found to be extremely reactive with the formation of carbonate, but not for the reverse reaction. XRD experiments with the sample during adsorption at high temperatures and post-desorption showed the formation of carbonate without significant desorption taking place even after 22 days. Two models were inferred from the adsorption isotherm curves, including a first-order surface reaction and a diffusional mechanism, controlled by the movement of an interface moving from the surface inward [165]. Other alkaline metal oxide composites, such as lithium silicate, were also studied as CO_2 adsorbing surfaces at room temperature. Research from the Toshiba R&D laboratory revealed that humidity played an important role in promoting CO_2 adsorption [166]. Lithium silicate was confirmed to be superior to another commercially available adsorbent (soda lime) under conditions of controlled humidity. Nakagawa's group performed a body of work in oxide composites of lithium [167]. Lithium zirconate (Li_2ZrO_3) and orthosilicate (Li_4SiO_4) were explored, with the latter being the more promising of the two composite oxides. The use of

composites, as opposed to the bare Li_2O , provided reversible CO_2 adsorption mechanisms that cannot be realized via the use of Li_2O directly. Of the two composites, Li_4SiO_4 generated multiple sites for the lithium ion to hop, which therefore created faster hopping and the stronger CO_2 adsorbing surface, even at room temperature. SEM images of Li_4SiO_4 were recently obtained [168]. The kinetic modeling of the associated surface was also performed, where carbonation, i.e. CO_2 adsorption, and decarbonation, i.e., CO_2 desorption, took place between 500-715 °C and above, respectively. Carbonation of the initially smooth surface resulted in the formation of single particles on the surface, as shown in Figure 37. After decarbonation, however, the surface particles disappear and its roughness changes.

Figure 37. SEM images of Li_4SiO_4 sorbents; (a) pretreated, (b) after carbonation, and (c) after regeneration. Reproduced with permission from Elsevier. [168]

Calculations on alkali carbonates and Raman experiments had been done before and can be found elsewhere [164]. However, not much work has been done to attempt to use these single alkali metal oxides as a CO₂ adsorbing surface, mostly likely due to their high reactivity and stability of the resulting structures with CO₂ desorption being very thermodynamically limited.

4.2.3 Other Metal Oxides (Pure and Doped Al₂O₃, ZrO₂, Cr₂O₃, TiO₂, ZnO, Ga₂O₃)

4.2.3.1 Al₂O₃ Doped Al₂O₃ was also studied for the CO₂ sequestration purpose as an adsorbent. Al₂O₃ is a feasible CO₂ adsorbent because it is inexpensive, has high surface area and possesses good mechanical and thermal stability [5,169]. The adsorption capacities of a typical basic Al₂O₃ surface (98AA1149) at three temperatures were measured in the order of $Q(293\text{K}) > Q(573\text{K}) > Q(473\text{K})$, at 1, 0.62, and 0.35 mmol/g at 1 bar, respectively. To improve CO₂ adsorption capacity of Al₂O₃, other basic metal oxides have been added via surface impregnation before high temperature calcination. Caram's group at Lehigh University studied chemisorption of CO₂ on Na₂O promoted Al₂O₃ and developed a relevant model, where the adsorption isotherm follows the Langmuirian model, but deviating at higher temperatures. The column breakthrough curves for the reversible adsorption-desorption can also be described by the linear driving force (LDF) model in conjunction with the adsorption isotherm [170]. At lower CO₂ pressures of up to 2.0 kPa the adsorption isotherms followed Langmuir behavior, while deviation was observed at higher CO₂ pressures. The column breakthrough curves for both CO₂ sorption from inert N₂ and desorption by N₂ purge fit the linear driving force model in conjunction. This is with the new sorption isotherm, where the mass transfer coefficients were independent of CO₂ feed gas concentration and were a weak function of temperature. IR spectroscopy analysis of CO₂ adsorption on Al₂O₃ was investigated at pressures of 51, 97, 185, 280, 498, and 915 mTorr [5]. Peaks associated with δ_4 , ν_3 s, ν_3 as and ν_5 were observed at 1228, 1435, 1650 and 3620 cm⁻¹, respectively, for adsorbed bidentate bicarbonate. Also present on γ -Al₂O₃ surface were other peaks and they were located at 1383 and 1040 cm⁻¹, for monodentate carbonate (ν_3 s, ν_1) and 1644, 1355, 1010 cm⁻¹ for bidentate carbonate (ν_3 as, ν_3 s, ν_1) [5].

Horiuchi *et al.* impregnated rare earth, alkaline earth and alkaline metal oxides onto Al₂O₃, producing dispersed metal oxide particles on the surface in an effort to increase the CO₂ retention time [72]. As expected, alkaline metal oxides, particularly Cs₂O, gave the highest CO₂ retention time, while rare earth metal oxides were the worst performers. This observation demonstrated the efficacy of metal oxides with low electronegativity in stabilizing the adsorption

of CO₂, thus resulting in a satisfactory CO₂ separation from the feed stream. IR spectra of the adsorbed CO₂ indicated the formation of a monodentate bicarbonate species, which disappeared upon evacuation at 373 K. That formation was observed at 1230, 1450, and 1650 cm⁻¹. Impregnation with MgO gave rise to a more strongly bound bicarbonate species, which was persistent even after evacuation at 473 K and a weak peak at 1330 cm⁻¹ assigned to bidentate carbonate. CaO, BaO, and SrO-modified Al₂O₃ gave similar spectra to those of MgO-doped Al₂O₃, with the only difference appearing in the peaks at 1350 cm⁻¹ and 1600 cm⁻¹ which still remained after evacuation at 573 K and indicated the presence of adsorbed carbonate, as shown in Figure 38.

Figure 38. IR spectra of CO₂ adsorbed on (a) γ -Al₂O₃ and MgO (b) MgO-impregnated Al₂O₃ at various temperatures and (c) IR spectra of CO₂ adsorbed on CaO- impregnated Al₂O₃ at various temperatures. Red, blue, and green dashed lines represent monodentate bicarbonate, monodentate carbonate, and bidentate carbonate, respectively. Reproduced with permission from [72]. Copyright (1998) American Chemical Society.

Keturakis *et al.* investigated the surface chemistry of CO₂ adsorption on γ - Al₂O₃ with and without Na modification [75]. The IR spectroscopy data they obtained on bare Al₂O₃ surface is in accordance with that by Horiuchi *et al.* , indicating the formation of bicarbonate as the only

surface species present. However, the addition of Na to the surface would unselectively bind to the surface hydroxyl groups, replacing the proton as well as activating inert hydroxyl sites, hence, forming bidentate and polydentate carbonates [75]. Prinetto *et al.* studied the use of Pt-K/Al₂O₃ as a NO_x Storage Reduction (NSR) catalyst [171]. In their study, the use of CO₂ as a probe molecule was employed on the substrates allowing further understanding of the interaction between CO₂ and doped Al₂O₃ surface. For a Pt-doped sample few surface species were formed. The peaks at 2345 and 2358 cm⁻¹, in the range of 1780-1860 cm⁻¹ correlated with peaks at 1200-1180 cm⁻¹, and were reversible when outgassing at room temperature. The first doublet is associated with linearly physisorbed CO₂, with the second group of peaks corresponding to strongly bent CO₂ molecules. Other species observed were two surface bicarbonates, indicated by the stable peaks at 1646, 1480, 1440, and 1230 cm⁻¹, and assigned to the ν_3 as, ν_3 s, and δ_4 modes, respectively. Impregnating K on Pt-impregnated Al₂O₃ resulted in an envelope of five strongly overlapping peaks at 1710, 1685, 1660, 1645, and 1610 cm⁻¹, a second envelope centered around 1320 cm⁻¹, and a third one at 1100, 1070, 1010 cm⁻¹. Those three envelopes were assigned to either bridged or bidentate carbonates. The formation of the bridged carbonates was thought to result from the addition of the K phase [171].

The fact that MgO and CaO are strong adsorbents of CO₂ motivated researchers to impregnate them onto pristine γ -Al₂O₃ surfaces [73,74,81]. But conflicting findings were reported on the MgO doped surfaces, where Li *et al.* observed monodentate bicarbonate formed due to the bending vibration at 1220 cm⁻¹ and 1650 cm⁻¹. In addition, there were unidentate and bidentate carbonates, characterized by the peaks at 1420, 1506, 1574, 1591 cm⁻¹, and 1380, 1708 cm⁻¹, respectively [73]. Hu *et al.*, however, only spotted bridged carbonate, free carbonate ions, and bidentate carbonate. These were indicated by the peaks at 1675 and 1403 cm⁻¹ assigned to

surface bridged carbonate species and free carbonate ion, and 1610 and 1340 cm^{-1} due to ν_3 as and ν_3 s of surface bidentate carbonate species, respectively [74]. TPD confirmed the disappearance of bicarbonate at 150 $^{\circ}\text{C}$, while above 450 $^{\circ}\text{C}$ only monodentate carbonate was observed [73].

Figure 39. IR spectra of CO_2 adsorbed over $\text{MgO}/\text{Al}_2\text{O}_3$ surface upon increasing evacuation temperatures: (a) 30 $^{\circ}\text{C}$, (b) 150 $^{\circ}\text{C}$, (c) 300 $^{\circ}\text{C}$, and (d) 450 $^{\circ}\text{C}$. Reproduced with permission from [73]. Copyright (2010) American Chemical Society.

DRIFTS confirmed very different surface interactions between CO_2 and the surface, when $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ was used instead of pristine CaO . On a clean Al_2O_3 surface at 300 $^{\circ}\text{C}$, weakly-bound bidentate bicarbonate (1649, 1440, 1230 cm^{-1}) and carbonate (1518, 1300 cm^{-1}) species. The associated peaks readily vanished upon degassing. On pure CaO the surface species formed was strongly-bound carbonate, differing significantly from those found on $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$, as shown in Figure 40. Only two peaks were observed at 1630 and 1340 cm^{-1} . They were assigned to the ν_3

doublet vibration of a carbonate species, most likely bidentate. The splitting $\Delta\nu_3$ is 135 cm^{-1} and larger, as compared to CO_2 on bulk CaO . The carbonate is loosely-bound and desorbs with time, indicating surface inability to retain the adsorbed CO_2 [81].

Figure 40. DRIFT spectrum of CO_2 on (a) bulk CaO powder and (b) $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ at 300 and 450 °C. Reproduced with permission from [81]. Copyright (2011) American Chemical Society.

The proposed molecular structures of the adsorbed bicarbonate structures were verified using cluster model calculations at the DFT/B3LYP/6-31+G(d) level of theory [50]. The comparison between the experimental and calculated vibrational frequencies of adsorbed $\text{HC}^{16}\text{O}_3^-$, $\text{DC}^{16}\text{O}_3^-$, $\text{HC}^{18}\text{O}_3^-$, $\text{HC}^{16}\text{O}^{18}\text{O}_2^-$, and $\text{HC}^{18}\text{O}^{16}\text{O}_2^-$ indicated that bicarbonate bonds to the surface in a bridged structure. Also, detailed analysis of the mixed isotope bicarbonate data suggested a proton transfer from the surface hydroxyl groups to the adsorbed bicarbonate ion. This was followed by the intramolecular transfer with the MP2/6-311+G(d,p) calculated barrier of 25.78 kcal/mol, a rather high energy. An alternate intermolecular pathway involves neighboring hydroxyl or bicarbonate groups. A similar mechanism involving surface bicarbonate was later believed to take place during carbonic acid (H_2CO_3) formation on $\text{Al}(\text{OH})_3$ clusters using RI-

SCS-MP2/aug-cc-pVTZ//B3LYP/6-311++G(d,p) level of theory [172]. A main point regarding the potential energy surface (PES) enabling a low energy barrier transition state was the stabilization of bicarbonate on the $\text{Al}(\text{OH})_3$ cluster (step III in Figure 41). This is followed by either intra- or intermolecular proton transfer involving bound H_2O molecules (step IV) to yield a stable H_2CO_3 molecule.

4.2.3.2 TiO_2 . TiO_2 was also investigated as an adsorbent for CO_2 capture [5,60–62,82,173,174]. Rasko *et al.* carried out an investigation on the surface facilitated CO_2 adsorption on reduced, oxidized and evacuated rutile TiO_2 , as well as its rhenium-impregnated counterpart using FTIR [82]. From these spectra there was only a slight difference in the region of $2500 - 2200 \text{ cm}^{-1}$. Notable differences were observed for some peaks, namely 3704, 3597, 2364, 2352, 1676 and 1376 cm^{-1} , where these peaks appeared in the presence of CO_2 at 190 K and attenuated when the

system was evacuated. Bent CO₂ was proposed to show peaks at 1630-1640 and 1218 cm⁻¹. The electronic and defect structure of the TiO₂ sample also played an important role on the formation of the bent CO₂ surface species [82]. The absence of CO vibrations at 2180, 2127 and 2206 cm⁻¹ indicated no dissociative adsorption taking place at all times on the pristine surface. The opposite was true for the case where Rh was deposited on the TiO₂ surface, for which the CO₂ dissociation was further enhanced significantly by the presence of H₂. The proposed mechanism of the dissociative adsorption was provided as shown in Figure 42, along with the spectra taken for CO₂ adsorption on clean TiO₂ surface.

Figure 42. Dissociative Adsorption of CO₂ on Rh-doped TiO₂. Notice that the chemistry occurred due to O vacancy. Reproduced with permission from [82]. Copyright (1994) American Chemical Society.

Figure 43. Spectra of Adsorbed CO_2 on Various Pretreated TiO_2 Surfaces at 673 K with CO_2 Flux at 190 K and 300 K. (1)-(3) represent spectra taken at 190 K, for oxidized, evacuated, and reduced samples, respectively; (4)-(6) represent spectra taken at 300 K. Reproduced with permission from [82]. Copyright (1994) American Chemical Society.

To complement the spectra assignment provided previously by Rasko *et al.*, Figure 44 portrays another IR experiment carried out by Liao *et al.* [60] albeit using different experimental set-ups.

Figure 44. Spectra of adsorbed CO₂ on TiO₂ surface (a) in contact with ~0.1 Torr CO₂ at 35 °C, (b) followed by evacuation, (c) and heated up to 70 °C in vacuum. Reproduced with permission from [60]. Copyright (2002) American Chemical Society.

As shown in Figure 44, peaks associated with carbonate appeared at 1319 and 1579 cm⁻¹ for bidentate species and 1461 cm⁻¹ for monodentate carbonate. The peak at 2361 cm⁻¹ was assigned to linearly adsorbed CO₂ with a Ti-O-C-O configuration. Similar to Rasko *et al.* [60], the authors did not observe any peaks associated with the formation of CO. Bicarbonate peaks were also not detected in the spectra. Different phenomena were observed by researchers from Pacific Northwest National Laboratory [173]. IRAS revealed that no chemisorption takes place on the model surface rutile TiO₂ (110)-1×1, which contradicts the findings from Rasko *et al.* and Liao *et al.* [60,82]. Instead, the adsorbate was weakly-bound and of linear geometry. This suggests that any presence of surface defects might contribute to the increased reactivity of the surface. Functionalization of TiO₂ with aminopropylsilane was investigated and shown to yield a strongly CO₂ adsorbing surface [61]. ATR-FTIR spectroscopy revealed through the appearance of

characteristic peaks at 1691 and 1265 cm^{-1} that the functionalization yielded bidentate carbonate when CO_2 was adsorbed on the surface. Adsorption of CO_2 on both rutile and anatase TiO_2 surface was reported in [62]. For the former, the formation of bidentate carbonate, bicarbonate and bridged carbonate was observed, as demonstrated by the peaks measured at 1606; 1416 and 1220; and 1706 cm^{-1} , respectively. The anatase phase, on the other hand, yielded the formation of bidentate carbonate, bicarbonate, monodentate carbonate and carboxylate, as evident from the peaks at 1589, 1315, 1055 cm^{-1} for bidentate, 1434 and 1222 cm^{-1} for bicarbonate, 1377 cm^{-1} for monodentate, and 1670 and 1245 cm^{-1} for carboxylate [62]. Adsorption at low pressure was carried out by Baltrusaitis *et al.* [5]. In their work, the surface species adsorbed was mainly carbonate with some bicarbonate observed. Specifically, the peaks at 1392, 1076 and 1510 cm^{-1} as well as 1355 and 1566 cm^{-1} were assigned to the O–C–O stretching vibrations of adsorbed monodentate and bidentate carbonate, respectively. Bicarbonate and bent CO_2^- were observed by peaks at 1623, 1423, and 1222 cm^{-1} , as well as 1670 and 1251 cm^{-1} , respectively [5].

An *in situ* STM study of CO_2 adsorption on $\text{TiO}_2(110)-1 \times 1$ was recently performed [174]. Two adsorption sites were identified, including bridge-bonded oxygen vacancy sites and Ti^{4+} rows. Adsorption on the former immobilized CO_2 , while on the latter CO_2 was still diffusive even at lower temperatures. DFT calculations showed that CO_2 LUMO was situated above the conduction band onset of TiO_2 by 2.3 eV or 2.7 eV above the Fermi level for both vertical and inclined, yet still linear, adsorption configurations. This LUMO hybridizes with the 3d orbital of Ti making it difficult to excite electrons from the valence band to CO_2 LUMO and for the excited electron to transfer from the TiO_2 conduction band to CO_2 . Figure 45 depicts the STM images taken on the bare $\text{TiO}_2(110)-1 \times 1$ surface, after exposure to CO_2 , as well as after the tip-induced adsorbate dissociation.

Figure 45. STM images of (a) bare TiO_2 (110)- 1×1 surface, (b) after CO_2 exposure at 80 K, and (c) tip-induced dissociation of CO_2 into CO and O. Reproduced with permission from [174]. Copyright (2011) American Physical Society.

4.2.3.3 ZrO₂. The surface chemistry of CO₂ on zirconia has been investigated both by probing a specific catalyst with CO₂ and by directly characterizing a given material for CO₂ capture [63–66]. ZrO₂ surfaces prepared using different synthesis methods have different surface hydroxyl groups and result in different adsorbed CO₂ surface species. IR spectra obtained for monoclinic zirconia with surface terminal hydroxyls revealed the formation of bicarbonate early during the adsorption of CO₂ at room temperature exhibiting peaks at 1625, 1430 (ν_3 as and ν_3 s) and 1220 cm⁻¹ (δ_{OH}) [63]. The bicarbonate species was relatively unstable. It was eliminated upon evacuation at 373 K. However, other peaks related to adsorbed bidentate and monodentate carbonates showed superior stability on the surface, persisting even under evacuation at 573 K. The former was characterized by the peaks at 1575 and 1325 cm⁻¹, while the latter was identified from the peaks at 1490 and 1395 cm⁻¹. For tetragonal/cubic zirconia with no surface terminal hydroxyls, there was no bicarbonate species detected, indicating the necessity of surface terminal hydroxyls for the relevant chemistry to take place. Monodentate and bidentate carbonates were detected as characterized by the peaks at 1450, 1425 cm⁻¹ and 1550, 1355 cm⁻¹, respectively. Figure 46 shows these spectra taken for the two different zirconia samples by Bachiller-Baeza *et al.* [63].

Figure 46. (Left) Spectra taken of clean surface, (a) monoclinic zirconia and (b) tetragonal/cubic zirconia showing the presence of isolated hydroxyl groups; (Right) Evolution of surface species during adsorption and TPD observed by IR Spectroscopy for (a) monoclinic zirconia and (b) tetragonal/cubic zirconia. Reproduced with permission from [63]. Copyright (1998) American Chemical Society.

Similar mechanistic considerations were proposed by Pokrovski *et al.* [64]. Formation of bicarbonate, monodentate and bidentate carbonate was observed during the adsorption and desorption of CO_2 on a monoclinic zirconia surface. However, different conclusions were obtained for the tetragonal zirconia surface. Their IR spectra indicated the formation of bidentate

at 1595 and 1315 cm^{-1} and polydentate carbonate, instead of bidentate and monodentate carbonate, which were observed by Bachiller-Baeza *et al.* [63]. The peaks at 1450 and 1430 cm^{-1} assigned to polydentate carbonate species were essentially the same as Bachiller-Baeza *et al.* assigned to monodentate species. Figure 47 shows the spectra taken by Pokrovski *et al.* [64].

Figure 47. Spectra taken for CO_2 adsorbed on tetragonal zirconia. Reproduced with permission from [64]. Copyright (2001) American Chemical Society.

The formation of bidentate carbonate and bicarbonate on zirconia was also observed by Dobson and McQuillan [65] and Ouyang *et al.* [66]. The former reported peaks at 1573 and 1354 cm^{-1} assigned to bidentate carbonate and 1613, 1443, and 1243 cm^{-1} assigned to adsorbed bidentate bicarbonate. Ouyang *et al.* used CO_2 as a probing molecule, observing the appearance of bidentate carbonate and monodentate bicarbonate, which were characterized by the peaks at 1559, 1310 and 1065 cm^{-1} and 3607, 1610, 1453, 1224 cm^{-1} , respectively. However, unlike Bachiller-Baeza *et al.* [63] and Pokrovski *et al.* [64], Ouyang *et al.* [66] did not observe the formation of either polydentate/monodentate carbonate.

4.2.3.4 ZnO. Noei *et al.* conducted UHV-FTIR analysis of CO₂ adsorption on various ZnO surfaces [175]. Different coordinations of CO₂ were observed on different sites of ZnO. The mixed-termination ZnO (10 $\bar{1}$ 0) facet yields tridentate carbonate. The polar O-terminated (000 $\bar{1}$) facet yields bidentate carbonate on O-vacancy sites and both monodentate and polydentate species on defect sites, such as kinks and steps. A similar work was also done by Buchholz *et al.*, where UHV-IRAS was done on a ZnO (10 $\bar{1}$ 0) surface facet [176]. Tridentate carbonate was detected on the surface, confirmed by peaks at 1584/1591 and 1340/1344 cm⁻¹, corresponding to ν_3 as and ν_3 s, respectively. The orientation of the carbonate species, which is aligned along the [0001] direction, was determined using reflectivity and absorbance relations, taking into account the particular optical properties of the dielectric surface [176]. Cu-doped ZnO was used as a catalyst for methanol synthesis from either CO₂ or CO. IR spectra acquired during the reaction can shed some light on how CO₂ adsorbs and reacts on the surface [177,178]. While ZnO itself contributed to the adsorption of CO₂ and formation of carbonate, Cu as a dopant had increased the adsorption capacity of the carbonate and even catalyzed transformation of carbonates into formate [177], which is an important intermediate in methanol synthesis.

Comprehensive experimental and theoretical work has been done in the past on CO₂ adsorption, particularly on the (000 $\bar{1}$), (0001), and (10 $\bar{1}$ 0) facets. However, no agreement on the adsorption geometries exists, because some studies showed carbonate or bent CO₂⁻ formation, while others argued that the adsorption is mostly physical [176,179–184]. The structure-activity relationship (SAR) of CO₂ adsorption on ZnO surface was studied. most of the time using TDS by Wang and Burghaus [184]. Perfect surface and defective sites were investigated in a study that rejected carbonate formation on the surface. Hydrogen was preadsorbed on the surface to block any defect sites, causing the adsorption to take place only on perfect sites. The resulting binding energies for both cases, i.e., perfect and defective sites, are consistent with physisorption or weak chemisorption. The authors' view is somehow shared by Dutta *et al.*, where, in their DFT study, based on a hybrid, quantum chemical/molecular mechanical (QM/MM) embedded cluster approach, CO₂ is expected to adsorb as bent anionic CO₂⁻ [185]. During adsorption, the CO₂

molecule anchors itself to the surface by orienting one of its oxygen atoms into a vacant site and accepting the localized, trapped electron there. Further bending towards one of the neighboring ions would result in the formation of a carboxylate ion, rather than carbonate [185].

Koßmann *et al.* applied *ab initio* DFT study with an embedded cluster approach to calculate vibrational spectra for various molecules, as intermediates for CO₂ to methanol conversion over a ZnO(0001) surface [183]. Polydentate and monodentate carbonate were expected, along with formate species, as the calculations were carried out using a Turbomole program package with PBE functional [186,187]. Monodentate structures are readily formed on defect free surfaces and F vacancy, while bidentate and tridentate carbonates are observed on F²⁺ vacancies and a V_{2H2O} vacancy, respectively. A stable physisorbed CO₂ molecule, however, is also observed on O-vacancy sites. Figure 48 depicts the formation of all carbonate species along with the IR peak assignments.

Figure 48. Carbonate configurations on various ZnO adsorption sites. Reproduced with permission from [183]. Copyright (2002), AIP Publishing LCC.

The formation of carbonates on various facets of a ZnO surface is also confirmed by another computational work quite recently [180,182]. The first-principles calculation was performed at the DFT+U level of theory using VASP with GGA-PW91 functional. The calculation shows that the adsorption binding strength is ranked in the following order: $\text{ZnO}(0001) > \text{ZnO}(0001) < \text{ZnO}(112\bar{1}) < \text{ZnO}(1120) < \text{ZnO}(1010)$. Interestingly, CO_2 , which is supposedly an electronegative adsorbate, may be positively charged on some ZnO surfaces, such as the stepped $(112\bar{1})$ facet. The calculation clearly demonstrated that physisorption takes place on singly terminated surfaces, while chemisorption is prevalent on mixed terminated surfaces. Similar to Koßmann *et al.*, all monodentate, bidentate, and tridentate carbonates were observed on different facets of a ZnO surface [182].

Experimental work on this sorbent remains scarce, and theoretical chemists have not yet arrived to a unanimous view on binding mechanisms. This area is challenged further by the strong dependence in mechanisms with the nature of adsorption sites, which could yield bent anionic CO_2^- , or carbonate species. [180,182–184,186,187]

4.2.3.5 Cr₂O₃. Cr₂O₃ has also been considered as an active surface for CO₂ adsorption. Seiferth *et al.* discussed the structure/reactivity differences of Cr₂O₃ (0001)/Cr (110) and polycrystalline Cr₂O₃ [67]. On the former, physisorbed CO₂ was observed as characterized by the presence of peaks at 2353 and 2375 cm⁻¹. Bent CO₂^{δ-}, however, was also formed, according to the peaks at 1277 cm⁻¹ that shifted to 1289 cm⁻¹ when CO₂ flux was increased. This surface species was assigned to be a bent species due to the absence of the ν₃ at around 1600 cm⁻¹. Peak assignments for bent CO₂^{δ-} to different vibrational modes on different surfaces is adequately provided elsewhere [67]. IR spectra resulting from CO₂ adsorption products on polycrystalline Cr₂O₃, on the other hand, revealed the formation of surface bidentate carbonates evident from the broadening of peaks at 1240, 1650 and 850 cm⁻¹. Figure 49 show the spectra of CO₂ adsorbed on both surfaces.

temperature, (1) at 100 K, (8) at 300 K. (right) IRAS of CO₂ adsorbed on Cr₂O₃ (0001)/Cr (110) as a function of CO₂ dosage. Reproduced with permission from Elsevier [67].

On stoichiometric Cr₂O₃ (101 $\bar{2}$) CO₂ was found to form bidentate carbonates stable at room temperature [188]. This was due to the five-coordinated Cr³⁺ cations and the three-coordinated O²⁻ anions, leading to an O vacancy on the Cr site on the stoichiometric, nonpolar surface. The chemistry between CO₂ and Na-doped Cr₂O₃ was also investigated [189]. Similar to Cr₂O₃ (0001), formation of bent CO₂⁻ was observed at low Na coverage evident from the peak at 1289 cm⁻¹ in the IRAS spectra. Also, the addition of Na significantly changed the chemistry on the surface with the presence of an Na⁺CO₂⁻ complex formed at low temperatures and regarded as the intermediate for the formation of carbonate on the surface [189].

4.2.3.6 Ga₂O₃. Gallium oxide is a potential catalyst for methanol synthesis from CO₂, just like ZnO, and has been already studied using spectroscopy to analyze CO₂ adsorption/transformations [70,83]. Direct comparison between γ -Ga₂O₃ and its isostructural counterpart, γ -Al₂O₃, is reviewed spectroscopically using CO₂ as a probe molecule [83]. On α -Ga₂O₃, CO₂ adsorption gives rise to the peaks at 3607, 1619, 1456 and 1231 cm⁻¹ associated with monodentate bicarbonate species, compared to the same species on γ -Al₂O₃, with the corresponding peaks at 3608, 1648, 1485, and 1234 cm⁻¹ [83]. Three crystal phases, α -, β -, and γ -Ga₂O₃, were studied elsewhere [70]. Adsorption of CO₂, as shown by the in situ IR spectroscopy experiment, resulted in the formation of various surface species, including carboxylate, bridged carbonate, bidentate carbonate, polydentate carbonate, monodentate bicarbonate, and bidentate bicarbonate. More peaks were observed in the spectra where γ -Ga₂O₃ is used as the reactive surface. For instance, peaks at 1750 and 1170 cm⁻¹ were assigned to carboxylate. This assignment was supported by the fact that the splitting of carbonate ν_3 vibration should not exceed 400 cm⁻¹. The most prevalent surface species was found to be bidentate bicarbonate on all of the surfaces. The associated peaks observed were at 1630, 1431 and 1225 cm⁻¹. The peaks are there due to the ν_3 (as), ν_3 (s) and δ_4 , respectively. The IR spectra

of the adsorbed CO₂ products from all three crystalline phases of Ga₂O₃ can be found in Figure 50.

Figure 50. *In situ* IR spectra of CO₂ adsorption on α -, β - and γ -Ga₂O₃. (a) isothermal adsorption at 323 K with increasing CO₂ pressure; (b) temperature programmed desorption of CO₂ from the surface up to 723 K. Reproduced with permission from [70]. Copyright (2006) American Chemical Society.

A later observation by Tsuneoka *et al.* [190] confirmed the peak assignments on β -Ga₂O₃. The formation of monodentate bicarbonate and bidentate bicarbonate was observed on the β -Ga₂O₃ surface and confirmed by the presence of the peaks at 1432, 1463 for $\nu_3(s)$ mode of bidentate and monodentate species, respectively, while the ones at 1634, and 1229 cm⁻¹ were not resolved due to overlaps between the respective ν_3 as and δ_4 of both species.

4.2.3.7 Iron oxides and oxyhydroxides. Baltrusaitis *et al.* discuss the use of amorphous nanoparticulate Fe₂O₃ as a CO₂ adsorbing surface [5,50,52,191]. Bicarbonate was formed on the Fe₂O₃ surface upon adsorption of CO₂ as characterized by peaks at 1010, 1222, 1410, 1629 and 3619 cm⁻¹, assigned to the ν_1 , δ_4 , ν_3 s, ν_3 as, and ν_5 vibrational modes, respectively [5]. The

formation of bidentate and monodentate carbonate was also observed, signified by the peaks at 1316, 1553, 1590 cm^{-1} for bidentate species, and 1040 cm^{-1} for monodentate carbonate [5]. Surface hydroxyl groups as a proxy of adsorbed bicarbonate formation, as well as the corresponding reactive mechanisms, were investigated in detail using a combination of FTIR spectroscopy, quantum chemical calculations and isotope labelling. Data for Fe_2O_3 nanoparticles following evacuation of the IR cell to $\sim 1 \times 10^{-5}$ Torr overnight are illustrated in Figure 51. These data show a high density of isolated (3687 and 3655 cm^{-1}) and hydrogen-bonded O–H groups on the surface along with a small amount of adsorbed water at 3365 cm^{-1} , as also confirmed by D_2O and $\text{H}_2\text{O}(18)$ experiments [52].

Small shifts in the ν_3 as and ν_3 s vibrations of the adsorbed bicarbonate formed of the isotope labeled surfaces and a large shift for the bending mode in the case of deuterated Fe_2O_3 were observed in the 1800 to 900 cm^{-1} region as δ_{COD} peak shifts to 969 from 1220 cm^{-1} .

Ferrihydrite, a naturally occurring nanoscale iron oxyhydroxide mineral, is a precursor to other iron minerals, such as goethite ($\alpha\text{-FeO}(\text{OH})$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) [192]. A combined experimental ATR-FTIR and B3LYP/6-31G(d) DFT study was performed and a bent – bicarbonate like – adsorbed CO_2 complex was believed to have formed, while hydrated ferrihydrite resulted in no bicarbonate formation, only carbonate due to the hydrogen bound

water competing for surface sites [192]. Further molecular level details of the impact of FeOOH mineral surface structure on adsorbed CO₂ product carbonate speciation were explored by Song and Boily by identifying adsorption sites and geometries of (bi)carbonate species at surfaces of nanosized goethite (α -FeOOH) and lepidocrocite (γ -FeOOH) particles [193]. Monodentate (mononuclear and binuclear) bicarbonate were proposed to coexist. Adsorbed bicarbonate was the dominant species on α -FeOOH, while a mixture of adsorbed bicarbonate and carbonate was present on γ -FeOOH due to the various hydrogen bonding patterns on these mineral surfaces.

Fe₃O₄ decorated-graphene nanoplatelets were found to coordinate CO₂ [194,195]. FTIR analysis showed a complex peak pattern due to the C-O, C=C and C-H vibrations inherently present on graphene. However, an increase in 1402 and 1033 cm⁻¹ peaks was attributed to the vibrational modes of adsorbed bicarbonate and carbonate, respectively. A large shift in the vibrational spectrum was observed for the Fe-O-Fe vibrational mode from 598 to 578 cm⁻¹, suggesting a high degree of interaction between adsorbing CO₂ and the Fe₃O₄ in the composite material.

4.2.3.8 PdO. PdO is one of the least studied surfaces for CO₂ adsorption. A both experimental and theoretical single study was conducted by Hinojosa *et al.* [196]. TPD and quantum chemical calculations using DFT-D3 were performed to analyze the adsorption products of CO₂ on the surface. These calculations revealed no formation of carbonates and bicarbonates. The adsorption was considered physisorption in agreement with some of the work regarding TiO₂, because the structure of the crystal resembled rutile TiO₂ (110). DFT calculations predicted that the initial adsorption of CO₂ is in linear configuration, which will form bent-linear pairs and further, linear-bent-linear trimers on *cus*-Pd rows. At coverage above 0.26 ML, CO₂ begins to physically adsorb on the 4f-Pd sites, and further saturates the sites until total coverage reaches 0.52 ML.

4.2.3.9 NiO. The interaction between CO₂ and a single-crystal NiO (111) surface, as well as hydroxylated NiO (111), were investigated by Matsumoto and coworkers [68]. Adsorption structures of the adsorbed CO₂ species and the effect of hydroxylating the surface were studied

using IRAS under UHV conditions. Two peaks associated with monodentate carbonate were observed during the temperature programmed desorption. These peaks appeared at 1263 (1267) and 910 cm^{-1} and were assigned to ν_3 s and ν_2 and disappeared when the temperature was ramped up to 248 K. The hydroxylated surface exhibited a much less intense deformation peak, which, according to the authors, is indicative of the perpendicular orientation of the molecule to the surface.

4.2.4 CO₂ adsorption on metal oxide surfaces in the presence of coadsorbing molecules

Under O₂-rich and atmospherically relevant conditions, most metal oxides are coordinated by (hydr)oxo groups. These groups can be coordinated to one (-O), two (μ -O) or three (μ_3 -O) metal ions, and consequently have considerably different abilities to bind or exchange with CO₂. Coordination of oxygen moieties of the surface (hydr)oxo groups with incoming CO₂(g) will therefore result in the stabilization of (bi)carbonate species. Gas-phase FTIR spectroscopic studies of CO₂(g) binding to metal oxide and mineral surfaces have thus taken these interactions within, and several have tentatively supported peak assignments with theoretical frequency calculations of (bi)carbonate species bound to (hydr)oxo-bearing clusters (Table 18) [45,105,193,197]. Mixed isotope experiments [50] have also provided insight into the initial nucleophilic attack of surface hydroxo groups, providing evidence that proton transfer is involved in the formation of bicarbonate species at α -Fe₂O₃ and γ -Al₂O₃ surfaces.

Table 18. Theoretical frequency calculations of (bi)carbonate-bound metal (oxy)hydroxide Fe and Al clusters

	ν_3 as	ν_3 s	δ_{COH}	$\nu_3 \text{ as} - \nu_3 \text{ s}$
MBC	1701-1708	1162-1166		539-546
MBC (hydrated)	1517-1523	1323-1329		194
MBB	1590-1620	1414-1435	1193	185-199
MMC	1452	1271		181
MMB	1716-1779	1182-1293		486-534
MMB	1627	1390	1193	237

MMB-a	1589	1204	1038	385
MMB-b0	1575	1372	1177	203
MMB-b1	1701	1325	1173	376

MMC=monodentate mononuclear carbonate; MMB=monodentate mononuclear bicarbonate; MBC=monodentate

binuclear carbonate; MBB=monodentate binuclear bicarbonate. Adopted from [45,105,192,193].

Studies on mixed Al/Fe oxohydroxides [197] using ATR-FTIR with DFT provide evidence for binding at three distinct sites. Al also played an important role in the form of bound CO₂. Thus, while low Al content led to Al- and Fe-bound CO₂ species, larger Al content (> 20 mol%) promoted bicarbonate binding to discrete phases of AlOOH, a result that could possibly be affected by morphological differences controlling site availability in the different mixtures.

The behavior of mixed CO₂-H₂O gases is of particular relevance to environmental studies focused on atmospheric and geochemical processes [198,199]. Work along this front includes vibration spectroscopy and theoretical calculations efforts [45,52,172]) describing the formation of (bi)carbonate species within thin water films at aluminum and ferric iron oxide surfaces. Other work [5], comparing binding at Fe₂O₃, γ -Al₂O₃ and TiO₂ nanoparticle surfaces, also showed that thin water films effectively decreased CO₂ adsorption rates, as water competed for the same CO₂ binding sites. Allen *et al.* [200] also report an *ab initio*-derived phase diagram for the (100), (110), (111) and (310) surfaces of CaO and MgO contacted with mixtures of these gases. Their results underscored the role of water in catalyzing carbonate formation, as well as face-specific products. For instance, carbonate phases preferably form on the (100) face of CaO, while hydration is favored on MgO. The (111) faces of CaO and MgO are, on the other hand, preferentially hydroxylated, while steps of the (310) face promote interactions with carbonate species. DFT investigations also detected considerably stronger CO₂ binding over H₂O on the BaO (100) face [201].

A recent review contrasting the CO₂ binding attributes of different minerals includes the one of Baltrusaitis *et al.* [5] on Fe₂O₃, γ-Al₂O₃ and TiO₂. This work highlighted the roles that sites of contrasting basicity play in CO₂ binding under low levels of humidity. The comparative study showed that Fe₂O₃ and γ-Al₂O₃ favor bicarbonate species, while TiO₂ favors bidentate carbonate species. In another study [193], FTIR measurements of iron oxyhydroxide nanoparticles showed that the actual dispositions of surface OH groups, and their resulting hydrogen bond strengths and populations, impact the speciation of the resulting carbonate/bicarbonate species. This was demonstrated for the case of rows of singly-coordinated (-OH) groups on the (110) face of goethite in contrast to the (100) face of lepidocrocite (Figure 52).

Figure 52. Schematic representation of CO₂(g) adsorption mechanisms and (bi)carbonate formation at lepidocrocite and goethite surfaces. Reproduced with permission from [193]. Copyright (2013) American Chemical Society.

While both faces exhibit highly comparable –OH site densities and are separated by ~3.0 Å, only 25% of those on lepidocrocite donate H-bonds, in contrast to 50% on goethite. The stronger –OH...–OH interactions in the latter prevent H-bonds from forming with neighboring

(bi)carbonate species, and thus favor the stabilization of bicarbonate species of the type $\text{-O-CO}_2\text{H}$. The weaker H-bond in lepidocrocite favor, on the other hand, a co-existence of both $\text{-O-CO}_2\text{H}$ and -O-CO_2 species. Other binding sites to consider include oxygen defects, such as in the proposed case for the (101) face of anatase [202], where CO_2 binding to a V_O defect site leads to a carbonate-like species. Mechanisms of this type have strong implications for interfacial isotopic exchange, as noted in a vibration spectroscopic study [203] building upon these calculations.

A particularly curious case of CO_2 interactions with a nanoparticulate Fe_2O_3 surface in the presence of H_2O as relative humidity, was presented by Baltrusaitis and coworkers as shown in Figure 53 [191]. At the lower relative humidity, there was a decrease in the intensity of the adsorbed bicarbonate peaks at 1622, 1410, and 1220 cm^{-1} for the nanoparticulate Fe_2O_3 as the relative humidity increased (Figure 53, left). The decrease in intensity of the bicarbonate peaks was concomitant with an increase and the apparent shift of the intensity of the absorption peaks near 1511 and 1333 cm^{-1} for nanoparticulate Fe_2O_3 . In addition, in the low relative humidity spectra, the growth of a peak due to the bending mode of adsorbed water, $\delta(\text{H}_2\text{O})$, near 1640 cm^{-1} can be seen. This peak is observed starting at 1 to 2% RH, indicating the presence of molecularly adsorbed water on the surface. These peaks can be attributed to the adsorbed solvated surface carbonate, as apparent from the right side of Figure 53. Here, in (a) the ATR-FTIR spectrum of 1 M NaHCO_3 solution at $\text{pH}=8$ is shown, which remarkably resembles and is almost analogous to the vibrations observed in (b) for $\text{CO}_2 + 40\% \text{RH H}_2\text{O}$. This was confirmed by the D_2O experiments in (c) and $\text{H}_2\text{O}(18)$ experiments in (d) and (e) [52].

Figure 53. (left) FTIR spectra of nanoparticulate Fe_2O_3 following exposure to mixtures of 0.274 Torr CO_2 with increasing relative humidity from 0 to 11% RH (0, 1, 3, 5, 7, 9, 11) in the 1100 to 1850 cm^{-1} region. Reproduced with permission from [191]. Copyright (2007) American Chemical Society. (right) FTIR spectra are shown for Fe_2O_3 in the presence of (a) 1 M NaHCO_3 solution at pH = 8; solution-phase absorptions have been subtracted from the ATR spectrum. The other spectra (b)-(e) are in the presence of gas-phase CO_2 (16) at a pressure of 275 mTorr and 40% RH, (b) $\text{H}_2\text{O}(16)$ on Fe_2O_3 , (c) D_2O on deuterated Fe_2O_3 , (d) $\text{H}_2\text{O}(16)$ on O(18) labeled Fe_2O_3 , and (e) $\text{H}_2\text{O}(18)$ on O(16) labeled Fe_2O_3 . Gas-phase absorptions have been subtracted from the transmission spectra shown in (b)-(e). Reproduced with permission from [52]. Copyright (2005) American Chemical Society.

The remarkable resemblance between the spectra again suggests solvated carbonate species on the surface of nanoparticulate Fe_2O_3 with similar behavior observed for $\gamma\text{-Al}_2\text{O}_3$ [191]. The estimated thickness of the H_2O layer on metal oxides, however, is only about 2 monolayers at 40 % RH without presenting the same bulk solvent properties, such as those for 1.0 M NaHCO_3 [204]. This resulted in a series of works explaining the structure of this partially solvated carbonate ion and how its potential vibrational frequencies can be affected [191]. In particular, vibrational frequency calculations were performed for uncoordinated “free” carbonate ions and compared with those adsorbed on $\text{Al}(\text{OH})_3$, as shown in Figure 54, top left. Cluster models $[\text{M}(\text{OH})_3(\text{H}_2\text{O})_x(\text{CO}_3)]^{2-}$ (where $\text{M} = \text{Al}$ and $x = 0, 1, 2, 3$, or 4) were used and calculations were carried out using B3LYP/6-31G(d) level of theory. The O–C bond in the Al–O–C linkage

decreased from 1.39 to 1.32 Å, because water molecules solvated the coordinated carbonate ion and elongated the C-O bond length of the carbonate ion, showing profound structural (and resulting vibrational) changes of the solvated carbonate ion. The fundamental ν_3 vibrational frequency split also systematically decreased showing that local coordination of H₂O molecules around the carbonate ion can perturb its vibrational properties and need to be accounted for during the vibrational frequency analysis.

function of the amount of outer sphere coordinated water molecules. (bottom) Energy minimized structures for $[M_2(OH)_2(\mu-OH)_2(H_2O)_{11}(CO_3)]$ (where $M = Fe$ and Al) optimized at B3LYP/6-31G(d) level of theory. Atoms of different elements are highlighted with different colors; iron, purple; aluminum, green; oxygen, red; hydrogen, blue; and carbon, yellow. Reproduced with permission from [191]. Copyright (2007) American Chemical Society.

Another calculation attempted to replicate this complex surface coordination/hydrogen bonded H_2O molecule effect on adsorbed carbonate vibrational frequencies using binuclear $[M_2(OH)_2(\mu-OH)_2(H_2O)_{11}(CO_3)]$ clusters, where $M = Fe$ and Al optimized at B3LYP/6-31G(d) level of theory (Figure 53 bottom). Comparison for both Fe and Al unlabeled calculated frequencies, ω , was determined to be in close agreement with experimental values [191]. The proposed structure was that of bridged carbonate, also confirmed by both DFT and experimental $C(18)O_2$ and $H_2O(18)$ isotope measurements.

The proposed reactive mechanism of CO_2 adsorption and chemical transformation on the nanoparticulate Fe_2O_3 surface in the presence of H_2O as relative humidity was presented by Baltrusaitis and Grassian as shown in Figure 55 [52]. In particular, a direct reaction to yield a carbonic acid intermediate was discussed, which would deprotonate to yield bicarbonate. Bicarbonate then displaces the hydroxyl group on an Fe_2O_3 surface followed by the deprotonation, analogous to the solution phase mechanism proposed by Su and Suarez [205], as well as work by Henderson showing the reaction between CO_2 and H_2O occurring on a single crystal of TiO_2 (110) at 110 K in the presence of oxygen vacancies [206]. This work was also later substantiated by the DFT calculations of H_2CO_3 formation on $Al(OH)_3$ [172].

SCHEME 1: Surface Reactions of CO₂ and H₂O on Fe₂O₃

Fig 55. Schematic representation of surface reactions of CO₂ and H₂O at Fe₂O₃ surfaces. Reproduced with permission from [52]. Copyright (2005) American Chemical Society.

Similar hydrated carbonate structures on α -Fe₂O₃ were modelled to agree with their ATR-FTIR air-equilibrated aqueous carbonate data via modelling hydrated monodentate binuclear carbonate surface complexes $\text{Fe}_2(\text{OH})_4(\text{OH}_2)_4\text{CO}_3 \cdot 2(\text{H}_2\text{O})$ and outer-sphere/hydrogen bonded complex $\text{Fe}_2\text{O}(\text{OH})_3(\text{OH}_2)_5 \cdot \text{CO}_3^{2-} \cdot 10(\text{H}_2\text{O})$. While the former was bridged, the latter was perpendicular to the iron site containing cluster and dipole aligned within the interfacial layer [105]. A remarkable similarity between the vibration properties of the bulk solvated carbonate and CO₂ adsorbed in the presence of two monolayers of H₂O condensed from the vapor phase suggests a complex coordination environment governed by the first coordination layer of H₂O and surface atoms and almost inevitably results in a bridge molecule on the surface or similarly distorted one by the first H₂O coordinating sphere.

4.3 CO₂ bonding at other surfaces

4.3.1 Surface/gas interface

4.3.1.1 Zeolites

Study of the interaction of CO₂ with various zeolites was carried out by Stevens *et al.* [207] with five zeolite materials, i.e. 13X, WEG, AGP, 4A, and 5A, investigated. Researchers found that zeolite pretreatment and adsorption temperature affected the adsorbed CO₂ surface species present with carbonates, physisorbed CO₂ and carboxylate ions identified using IR spectroscopy. On 13X surface, pretreatment at 350 °C lead to the formation of bridged carbonate. In addition to bidentate carbonate, physisorbed CO₂ was found on zeolite surface pretreated at 120 °C. Species were characterized by the peaks at 1710 and 1364 cm⁻¹ (bridged bidentate carbonate), 2356 cm⁻¹ (physisorbed CO₂) and 1486 and 1427 cm⁻¹ (bidentate carbonate) with a shift observed for the bridged species to 1688 and 1361 cm⁻¹, when the surface was pretreated at lower temperature. Notable was the loss of OH group intensity on the lower temperature-treated surface, which was not encountered on the higher temperature-treated surface, indicating that the CO₂ interactions with the OH group was not present on the surface treated at the higher temperature. The adsorption behavior on WEG and AGP zeolites, which are also X-type zeolites, was similar to that of 13X [207].

On zeolite 4A a significant difference in adsorbed CO₂ products was observed, when pretreatment was carried out at 350 °C, as evident from the formation of additional peaks in the spectra. When pretreated at a lower temperature only bridged carbonate and physisorbed CO₂ were observed, as characterized by the peaks at 1682, 1377 cm⁻¹ and 2351 cm⁻¹, respectively. Sorbents pretreated at 350°C produce bidentate carbonate (1506 and 1457 cm⁻¹) and two different types of bridged carbonate species. The first one was chemisorbed on a Ca site (1735

and 1245 cm^{-1}) and the second adsorbed on an Na site (1675 and 1373 cm^{-1}). There was also a notable shift in the physisorbed CO_2 peak from 2361 and 2294 cm^{-1} to 2351 and 2285 cm^{-1} , suggesting that there is a dipole-dipole interaction between adsorbed CO_2 molecules. Montanari and Busca studied the same system and observed a peak at 2422 cm^{-1} assigned to a combination of ν_3 with a hindered rotation (libration) mode ($\nu_3 + \nu_{\text{lib}}$) [208]. Upon desorbing, the OCO asymmetric stretching split into 2361 and 2351 cm^{-1} . In the lower frequency region various peaks were observed. The peak at 1382 cm^{-1} was assigned to ν_1 of linearly adsorbed CO_2 due to the activation during the change of symmetry upon adsorption. The other peaks in this region were due to the formation of carbonates or bent CO_2 species. So called “eovalent” carbonate was observed because there were peaks at 1725 and 1248 cm^{-1} , while strong peaks at 1456 and 1390 cm^{-1} appeared after outgassing the system and were attributed to monodentate carbonates. Several other peaks were also present in the spectra at 1693 , 1660 , 1640 , and 1580 cm^{-1} with the corresponding peaks in the range of 1400 - 1250 cm^{-1} . These peaks were assigned to either bidentate or bridging carbonates.

On zeolite 5A, bridged carbonate and physisorbed CO_2 were confirmed using IR spectroscopy by Stevens *et al.*, as characterized by peaks at 1667 and 1384 cm^{-1} (bridged carbonate), and 2353 cm^{-1} (physisorbed CO_2) [207]. An additional insight concerning the system was offered by Montanari and Busca, where a negative peak in the carbonate region was observed [208]. This phenomenon was tentatively attributed to a linear CO_2 molecule adsorbing on the occupied cation site that had originally adsorbed a symmetrical carbonate species. Additionally, several peaks in the same region were also found and were similar to outgassing at room temperature, even though these peaks had lower intensity [208]. The same group also investigated the 3A zeolite system, where they found a peak at 2351 cm^{-1} and assigned it to a linear CO_2 molecule

shifted upward due to the Lewis acidity of the adsorbing center. Sharp peaks were formed at 1653 and 1359 cm^{-1} , while weaker peaks were also present at 1715 and 1246 cm^{-1} . These last two peaks are characteristic of carbonate species and/or bent CO_2^- molecules.

Pillai *et al.* investigated the interaction between CO_2 and an Na-ETS zeolite sample using DRIFTS [209]. Two degassing temperatures prior to CO_2 adsorption were used and compared at 373 K and 423 K. In both, peaks at 2340, 1586 and 1371 cm^{-1} were observed and attributed to physisorbed CO_2 and a ν_3 split of adsorbed carbonates, respectively. For the lower temperature treatment, these peaks disappeared completely upon outgassing the sample, while the higher temperature treated sample retained the peak at 1371 cm^{-1} , even after prolonged evacuation. The author attributed the persistent nature of this peak to the carbonate's coordination to an extra Na^+ ion framework. Also notable in the experiment was the peak at 2340 cm^{-1} that did not completely disappear during the sample treatment at higher temperatures, even after prolonged outgassing [209].

A combined DFT and IR spectroscopy investigation was used to elucidate the interaction between CO_2 and zeolite Na-A [210]. IR spectroscopy revealed no carbonation taking place on the surface since the only peak associated with the CO_2 surface species was present at 2349 and 2360 cm^{-1} , characteristic of physisorbed species. The two peaks were, as confirmed by DFT simulation, associated with two different physisorbed CO_2 species. While the former was present only at very low coverage with the CO_2 molecule preferentially adsorbing on either the S2-S1 or S2-S3 site, interacting with three Na^+ cations in the supercage, the latter was found to take place at a higher coverage range, where the molecule sets on a dual cation site formed by Na^+ cations in S2 and S1 sites. Figure 56 depicts the supercage model used in the calculation along with adsorption configurations at low and higher coverage [210].

Figure 56. (Left) S1-S3 sites with three Na^+ cations (white, blue, and yellow colored) within the supercage used for the calculation. (Mid) CO_2 adsorption sites at low coverage. (Right) adsorption configuration for higher CO_2 coverage, where the molecule is situated on a dual cation site formed by Na^+ cations on S2 and S1 sites. Reproduced with permission from Elsevier. [210].

Adsorption of CO_2 on acidic zeolites, such as H- β and H-FER, was studied by Delgado *et al.* [211,212] using variable temperature IR (VTIR) spectroscopy. Both surfaces possess a high acidity due to the protonic zeolite. Due to this, no carbonate peaks were observed in the 1350-1700 cm^{-1} region. These carbonate species formed most of the time on basic oxygen atoms of zeolite. A physisorbed molecule, however, was observed, as confirmed by peaks at 2348 and 2346 cm^{-1} for H- β and H-FER, respectively, which intensified when the temperature was decreased [211]. Other authors analyzed alkali ion-exchanged H-FER zeolites, too, and also did not detect any formation of carbonates, when CO_2 molecules were adsorbed [213]. For Na^+ and K^+ , exchanged surface peaks at 2370 and 2357 cm^{-1} were observed due to the physisorbed CO_2 species. On Li-exchanged FER a peak was observed at 2353 cm^{-1} . The CO_2 surface species was proposed to be bridged between two cations in all cases. Additionally, the same group also

conducted VTIR of CO₂ adsorption using the alkaline zeolite K-L with only one peak detected at 2346 cm⁻¹ and assigned to a physisorbed CO₂ molecule [214].

Li⁺ modified zeolite SSZ-13 was also investigated and CO₂ adsorption studied using FTIR under near vacuum conditions [215]. The interaction between CO₂ and the surface resulted in the appearance of a peak near 2350 cm⁻¹, which was assigned to linear CO₂. The upward shift due to the ion-dipole interaction between Li⁺ and CO₂ was more pronounced at low pressures where CO₂ had a greater probability of interacting with cations. At higher pressures more peaks between 3598 and 3725 cm⁻¹ were observed due to the combination peaks ($\nu_3 + \nu_1$) and ($\nu_3 + 2\nu_2$). A chemisorbed species was also detected at 1700 and 1360 cm⁻¹ and considered a carbonate-like species, although with lower intensities, indicating the significance of physical adsorption on the surface. Furthermore, while the peaks associated with the physisorbed molecule increased with pressure, the peaks attributed to chemisorbed species did not increase, suggesting that chemisorption only takes place at lower CO₂ loading [215].

Temperature-programmed desorption on alkali-treated zeolite-Y was conducted during CO₂ adsorption in an attempt to elucidate the interaction between the alkali-modified surface and CO₂ [216]. The alkali investigated were Na and Cs, and TPD results clearly showed two desorption peaks taking place during the temperature ramp with the first one, between 200 and 400 °C, related to physisorbed CO₂. The other one took place at significantly higher temperatures of 500-600°C. This second peak was assigned to CO₂ resulting from alkali carbonate decomposition. Between the two dopants Cs was shown to have improved adsorption capacity towards CO₂. On an H-Y zeolite, IR spectroscopy showed the interaction between CO₂ and the surface silanol groups [217]. The native silanol peak at 3747 cm⁻¹ subsequently diminished upon exposure to CO₂, while another peak in the same region ca. 3540 cm⁻¹ simultaneously increased

in intensity. This phenomenon was explained as a native OH group being consumed when CO₂ is introduced, resulting in a different OH group. Physisorbed CO₂ was also observed as characterized by the peak at 2353 cm⁻¹. The carbonate region, i.e., 1300-1700 cm⁻¹, however, was not discussed in that publication [217].

Doping zeolites using alkali metals results in a highly basic surface, which would retain CO₂ at high temperatures [218]. TPD experiments of CO₂ adsorption on zeolite surfaces demonstrated the superiority of alkali-added surfaces to the ion-exchange surfaces, where CO₂ desorption was observed even at 673 K [218]. The alkali-added zeolites were synthesized by soaking Linde13X in an aqueous alkali nitrate solution and then filtered. Ion-exchanged surfaces are essentially alkali-added zeolites that are further washed with deionized water. On the K- and Rb-added surfaces, IR experiments showed the development of several peaks assigned to carbonates at 1670, 1338 and 1570, 1380 cm⁻¹. They were all attributed to bidentate carbonate, with the first two peaks disappearing when the surface was heated up to 500 K. The peaks at 1570 and 1380 cm⁻¹ were stable at the higher temperature possibly due to their bonding to a more basic site of the surface [218].

Modification of zeolites with organic aminosilane has also been studied [219]. IR spectroscopy revealed that adsorption of CO₂ on these functionalized zeolites involved the formation of alkyl ammonium carbamate as characterized by peaks at 1488, 1492, 1484, and 1479 cm⁻¹ on the spectra of zeolites modified with 3-aminopropyltriethoxysilane (APS), N-methylaminopropyltrimethoxysilane MAPS, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS), and 3-trimethoxysilylpropyl)diethylenetriamine (TA), respectively. The C=O stretch was also observed in the spectra at 1563, 1529, 1566, and 1566 cm⁻¹ for each of the organic modifiers, respectively. Upon CO₂ adsorption, negative peaks appeared at 3365 and 3301 cm⁻¹,

characteristic of the NH_2 asymmetrical and symmetrical stretch, respectively. This phenomenon implied that CO_2 interacted with N-H bonds leading to the formation of carbamate. For this particular adsorption system, the presence of water did not affect the binding configuration, as identical spectra were obtained for each surface [219].

4.3.1.2 Carbides

Transition metal carbides have recently attracted a lot of interest in CO_2 adsorption for sequestration and activation purposes [220–228]. The Mo_2C surface shows great promise in replacing noble metals for CO_2 activation [222]. On the Mo_2C surface CO_2 dissociates and adsorbs with better activity than that of its oxide counterpart. AP-XPS investigations of the $\text{Mo}_2\text{C}/\text{Mo}$ (110) surface under CO_2 and H_2 flow showed the formation of oxy-carbide and are shown in Figure 56. In the C1s region the carbide was shown by a peak at 282.9 eV, while small amounts of MoO_x were also present, as evidenced by the peak at 530.4 eV in the O1s region. Another peak in the O1s region at 531.7 eV was attributed to oxycarbide, which appeared after exposing the surface to 150 mTorr of CO_2 . The accompanying peak in the C1s region was present at 283.6 eV. Formates and carbonates, previously reported in metal/ MO_x surfaces upon CO_2 adsorption, were not detected and a different mechanism of adsorption was proposed. On a carbide surface CO_2 was predicted to dissociate and adsorb to form CO and O, with the latter yielding oxycarbide via a reaction with the Mo_2C lattice. The Mo_2C site was determined to be the active site on the catalyst, and for the catalyst to retain its activity, it needs to be in its carburized state, i.e. carbide. Confirmed by in-situ XANES experiments, the catalyst maintains its carburized state, as the linear fit with Mo_2C and MoO_3 standard shows good approximation. However, when the surface is impregnated with Co, the linear fit with the standards no longer holds, suggesting the presence of another phase, likely CoMoC_yO_z [222].

Figure 57. High resolution C1s and O1s XPS spectra of the Mo₂C/Mo(110) surface before and after CO₂ adsorption: (1) Clean Mo₂C, (2) 150 mTorr CO₂ at room temperature, (3) 150 mTorr CO₂ + 550 mTorr H₂ with annealing to 523 K, then cooling to room temperature, 4) 150 mTorr CO₂ + 550 mTorr H₂ at 523 K. Reproduced with permission from Wiley [222].

DFT calculations were performed on α -Mo₂C (0001), β -Mo₂C (001) and δ -Mo₂C (001) using the GGA-PBE level of theory augmented with the van der Waals correction [224,225]. Separate calculations carried out by these two authors predict that either dissociation of CO₂ to CO and O or CO₂ activation to bent anionic CO₂⁻ to be the most stable adsorption configuration. In this case, the dissociated oxygen atom is bonded to two Mo atoms on the top layer, averaging a 2.051 Å bond length. The surface CO species bridges two Mo atoms with its bond length elongated from 1.179 Å to 1.233 Å. In other bonding configurations of adsorbed CO₂, charge transfer is expected to take place from the surface to the molecule's anti-bonding orbital, resulting in the bent structure of the surface species [225]. Figure 58 shows various bonding configurations of CO₂ on the α -Mo₂C (0001) surface.

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Figure 58. CO₂ bonding configurations on terminated α -Mo₂C (0001) surface. Reproduced with permission from Elsevier [225].

On β -Mo₂C (001) and δ -Mo₂C (001) CO₂ adsorbs and reacts differently [224]. Adsorption on the Mo-terminated structure of the former leads to dissociation of CO₂. However, on both C-terminated of the former and the latter, CO₂ is present as a bent structure. As a note of interest, the initial position of the CO₂ determines whether or not the molecule is dissociated. On the Mo-terminated β -Mo₂C (001), when the initial position of CO₂ is not on top of the Mo site, the molecule is solely activated, as opposed to when it is dissociated on top of the Mo site.

Another carbide, e.g. tungsten carbide (WC), has been a subject of a theoretical calculation based on the PAW method with the GGA-PW91 exchange-correlation approximation [228]. On the bare WC surface dissociation is not readily observed. However, on a Co-promoted surface, dissociation of CO₂ takes place when cobalt atoms are layered on the top of the surface. The adsorption energy is actually lowered in the case of Co-doping, where the surface contains CoW_xC_y species decreasing from -0.99 eV for bare surface to -1.61 eV. The activation energy for the dissociation, however, ranges from 0.57 to 1.18 eV for several permutations of the doped surface [228].

The adsorption site for the CO₂-TiC system was identified to be a carbon atom on the carbide surface [226,227]. Using DFT calculations, a C-C bond was established upon adsorbing CO₂ on the surface, with a regular bond length of 1.48 Å. Oxygen atoms preferentially adsorb on top of the nearest Ti sites, establishing a bent geometry, due to charge transfer taking place from the surface to CO₂. Adsorption of CO₂ molecules on Cu and Au-promoted TiC substrates was calculated to have lowered the adsorption energy of CO₂ from -0.62 eV to -0.68 eV and -1.12 eV for the Au-promoted and Cu-promoted substrates, respectively. Both Au and Cu-promoted substrates afford an endothermic dissociation process with the bare surface possessing relatively higher C-O cleaving energy compared to the doped surface. In both cases elongation of the C-O bond takes place upon adsorption with the bond length increasing from 1.17 Å to 1.29 Å, 1.36 Å, and 1.31 Å for bare surface, Cu-doped surface and Au-doped surface, respectively [227].

Figure 59. Bent CO₂ molecule adsorbed on (left) bare TiC surface and (right) Au and Cu-doped TiC surface. Reproduced with permission from [227]. Copyright (2012) American Chemical Society.

4.3.1.3 Nitrides

Nitrides [229–232] and sulfides [233–236] are two classes of compounds rarely used for CO₂ surface facilitated reactions. Boron nitride is a novel nitride for CO₂ adsorption. A DFT calculation using PAW-PBE indicated two adsorption states on boron-rich boron nitride nanotube [229]. The CO₂ molecule initially adsorbs physically on the surface, demonstrating charge transfer from the gas to the surface, before electron backdonation takes place from boron antisite (B_N), distorting the structure and breaking the π -bond, resulting in a carboxylate-like structure, depicted in Figure 60.

Theoretical calculations also demonstrated the existence of two energy barriers between the physisorbed molecule and the dissociated structure on a graphene-like boron nitride with B-vacancy [230]. The first energy barrier connects the physisorbed state and bent CO₂ with a 0.82 eV energy barrier, where the right-hand minimum state refers to the bent CO₂ molecule, in which the carbon is displaced toward the boron vacancy. A lattice-embedded carbon is then obtained

after the second energy barrier is overcome, leading to a dissociated CO_2 product. This atypical dissociation scheme, depicted in the Figure 61, subsequently produces an O_2 molecule [230].

Figure 61. DFT calculation on the catalytic reaction scheme for CO_2 dissociation on B-vacancy sites of boron nitride. Reproduced with permission from Elsevier [230].

To overcome the energy barrier presented by boron nitride, surface dopants such as Al [231] and Ti [232] were tried. DFT calculations show that on a single, Al atom-doped boron nitride surface, the CO_2 molecule dissociates on the surface. This is also true for the Ti case, where the C-O bond is broken and CO and O molecules are produced. To date, surface studies on nitride materials for CO_2 capture are mostly limited to the theoretical calculations reviewed here.

4.3.1.4 Sulfides.

CO_2 adsorption on Cs-promoted MoS_2 has been studied using SIMS [236]. In the SIMS spectra analysis an increase of O^- , m/z 60 (CO_3^- or SCO^-) was observed. The level of MoO_3^- and MoSO^- , which would increase if CO_2 were to dissociate into CO and O, was barely detected, suggesting

that CO₂ does not dissociate on the surface. Increases in CO₂⁻ (m/z 44) and CO signals were not observed, leading to the conclusion that the molecule did not dissociate, although physisorption and carbonate formation cannot be ruled out [236]. Undoped MoS₂ was also tested for CO₂ reduction, along with WS₂ [234,235]. Both pristine sulfide sorbents exhibit good activity for CO₂ dissociation. The gas phase product, recorded using GC-MS, demonstrates the effectiveness of both sorbents to dissociate CO₂ into CO, with selectivity over 99.9% for the case of WS₂ [234]. Another sulfide that might have the capability to reduce CO₂ is Cu₂S [233]. With the help of light, the surface effectively dissociates CO₂ into CO with subsequent desorption. However, scarcity of publications on sulfides suggests that additional work is necessary before a complete understanding of this compound class' efficacy in CO₂ adsorption and transformation is attained.

4.3.2 Other solid surface/fluid CO₂ interface interactions.

Entrapment of CO₂ by cap rocks is of high impact for environmental sciences, as well as for developing CO₂ capture and storage technologies to mitigate industrial emissions. Results from Wdowin *et al.* [237] showed that carbonate rocks have poor adsorptive capabilities for CO₂, on the order of 0.1 mmol/g, while zeolites, with their porous networks, proved to be far superior capture agents and therefore were of further consideration. Other studies have revealed trapping of CO₂ into the intercalation of expandable phyllosilicates with a special emphasis on montmorillonites. Studies have notably pointed to important expansion of the layer-to-layer spacing (XRD-derived d₀₀₁-spacing) of 9% upon exposure of up to 50 bars CO₂ in the presence of small amounts of water [238]. However, no further expansion occurs at greater pressures, tested up to 640 bars. Giester *et al.* [239] and other studies (*e.g.* [240]) have also identified at least a partial irreversibility in these reactions. Giester *et al.* [239] also noted considerably faster

swelling kinetics in Na- (tens of min or less) than Ca- montmorillonite (up to 42 h). The presence of interlayer hydroxo groups, intercalated cations and water are driving intercalation of CO₂ in the form of bicarbonate species. Plausible interactions, probed both experimentally and theoretically, include hydrogen bonding with adjacent basal oxygen planes and hydration by the intercalated water molecules. Calculations, in fact, suggest these reactions are responsible for the greater concentrations of intercalated CO₂ in these systems than in liquid water [241]. Moreover, complexation with intercalated cations also tends to correlate with expected cation-CO₂ bond strength (*e.g.* Na⁺, Li⁺, and even Ni²⁺) as highlighted by Michels *et al.* [242]. This appears to be consistent with the difference in size between the smaller Li⁺ cation versus the larger Na⁺ cation. Li⁺ has a more concentrated charge distribution than Na⁺ and can thus polarize the CO₂ molecule, thereby forming a stronger bond to it. We also note that interactions with surface groups are highly responsible for the formation of these species and that probing clay edge site chemistry is a growing challenge in the community given the importance of these interactions.

The prospect of geological storage of CO₂ for climate warming mitigation has triggered a number of research programs dedicated to the study of mineral-CO₂ interactions and concomitant mineralogical transformations in supercritical CO₂ (scCO₂) [101,243–250]. The interest for scCO₂ lies in the lower density and viscosity of this phase, compared to the fluids that it would displace during injection in deep geologic formations. Experimental and theoretical studies have consequently focused on the surface chemistry of minerals under elevated temperatures (*e.g.* 35–100 °C) and pressures (*e.g.* 90–200 bars) and thus represent a considerable departure from other studies, which focus on environmentally-relevant conditions of atmospheric partial pressures of CO₂, which is where this work is typically carried out. A focus on the reactive basalt-building minerals was motivated by their common occurrence in (*e.g.* continental flood) basalts, which

were targeted host rocks for geological storage [251–256]. The interest in phyllosilicates [101,248,257,258], especially expandable clays, was also motivated by their ability to intercalate and thus lock CO₂ species into their bulk structure. Also, there is a potential means for extracting methane from clay-rich formations, such as nearly depleted shale gas reservoirs [259]. Both experimentation and theory have helped resolve the issue of reactivity of silicates, including olivines (*e.g.* forsterite=Mg₂SiO₄; fayalite=Fe₂SiO₄), pyroxenes (*e.g.* enstatite = MgSiO₃), wollastonite (CaSiO₃), and serpentine (*e.g.* antigorite= Mg₃Si₂O₄(OH)₄) towards scCO₂ [200,201,203,205]. These efforts demonstrate the importance of thin water film thickness in driving the overall reactivity. The films are formed under scCO₂ by hydrogen bonding of water molecules to mineral surface (hydr)oxo groups and/or outcropping cationic centers. Those of several monolayers in thickness (*e.g.* 3.7-7.7 monolayers of 7-15 Å) facilitated carbonation, both as mineral surface complexes (*e.g.* as bidentate Mg-carbonate surface complexes) and also through the formation of hydrated magnesium carbonates (*e.g.* nesquehonite, magnesite) by forsterite (Mg₂SiO₄) and antigorite (Mg₃Si₂O₅(OH)₄) dissolution [251–253]. Thinner layers were, on the other hand, considerably less reactive, possibly due to the restricted mobility of ions under these conditions. These studies thus opened the door for the investigation of new mechanisms involving ion mobility driven by mineral dissolution, nucleation and growth, all within the confines of a thin water film. DFT calculations of a suite of olivine minerals also suggested that water can readily displace carbon dioxide at olivine surfaces and that the ionic character of alkaline earth metal cations outcropping the olivine surfaces facilitates the H₂O and CO₂ adsorption reaction in an exothermic fashion [260].

Important efforts involving clay minerals focus on the impact of H₂O loadings on swelling (*i.e.* XRD-derived d₀₀₁-spacing values) and CO₂ intercalation. Efforts along these lines include CO₂

and H₂O partition studies involving Na-, Ca- and Mg-exchanges montmorillonite, a 2:1 layer phyllosilicate with swelling capabilities, under systematically varied conditions of hydration under scCO₂ [101,248,257,258].

Figure 62. Integrated absorbance of the asymmetric CO stretching peak of the CO₂ molecules that are associated with the Na-SWy-2 as a function of sorbed H₂O concentration from a titration of 0.0441 g of Na-SWy-2 with water at 5 °C and 90 bar. Reproduced with permission from [248]. Copyright (2014) American Chemical Society.

Experimental (X-ray diffraction, vibration spectroscopy and ¹³C nuclear magnetic resonance) and theoretical (DFT) studies point to upper limits in CO₂ incorporation capacities of clays below one monolayer of intercalated water (1W in Figure 62; 12.3-12.6 Å thick). Larger CO₂ loadings are favored at low water content, given the ability for CO₂ to solvate interlayer cations (*e.g.* Na⁺, Ca²⁺, Mg²⁺). This reaction is outcompeted by the more energetically favorable hydration reactions at larger water loadings, thus favoring a larger portioning of CO₂ back to the adjacent scCO₂ phase (*e.g.* [261]) and potentially compromising cap rock integrity for geological storage of CO₂. Other molecular modeling studies (Monte Carlo and molecular dynamics) of related systems point to the thermodynamic stability of expanded montmorillonite spacing, when

exposed to scCO₂ with conformation involving single and double layers of interlayer CO₂ [262]. Those in the center of interlayers containing 1W lie parallel to the clay surface, while those containing the 2W system consist of linear CO₂ molecules close to the surface [262,263]. These authors also point to important decreases in ion diffusion at large intercalated CO₂ loadings. Efforts have also been made to account for vibration spectroscopic observations of intercalated CO₂ in clays. One notable development includes extension of the widely used ClayFF potentials to scCO₂ and to the generation of a theoretical power spectra that can be used to relate simulated molecular structures and molecular flexibility to vibration spectral attributes, as well as diffusion rates [264,265]. Mechanisms through which CO₂ migrates through nano- and micro-porous environments of clays have also called for an understanding of their physical properties in relation to diffusion properties. One small-angle neutron scattering (SANS) and molecular dynamics study, for instance, suggests that 15 Å wide slit pores in muscovite can be filled with a layered structure of low diffusivity/high-density CO₂. Larger pores contain, on the other hand, scCO₂ that cannot be efficiently mobilized. These authors conclude that mobilization of CO₂ in the crystal structure of muscovite requires entrapment as a single layer or through carbonation reactions (surface complexes, mineralization) [266].

Unlike other surfaces, interactions between zeolite 13X and CO₂/H₂O do not result in new adsorbates [207]. While the same interaction on metal/metal oxide surfaces would yield formation of bicarbonates, or some sort of hydroxylated surface species, water and CO₂ compete for the same adsorption site. In the case of 13X, water tends to displace adsorbed CO₂ molecules, as observed using IR spectroscopy. Adsorption of both molecules initially produces several peaks related to hydroxyl groups at 3690 (stretching) and 1652 cm⁻¹ (bending), as well as physisorbed CO₂, bridged carbonate, and bidentate carbonate at 2354 cm⁻¹, 1710 and 1363 cm⁻¹,

1484 and 1429 cm^{-1} , respectively. However, extended exposure leads to the disappearance of all peaks mentioned above, except for the bending mode of the hydroxyl group [207].

4.4 Carbonate/H₂O vapor or fluid interfaces

4.4.1 Solid metal carbonate/gas interface

4.4.1.1 Metal carbonate surfaces in the presence of significant humidity. Metal carbonates are the inevitable products of metal oxide surface interactions with CO₂. They are stable and naturally present in the environment. Solid metal carbonate surfaces exposed to gases are reactive substrates for chemical exchanges. Calcite (CaCO₃) exposed to a humid environment will exhibit a very different surface chemistry from that in bulk aqueous solutions [267–273], as discussed in section 4.4.2. Here H₂O is introduced in a form of a vapor expressed in the water activity range of $0.1 < a < 1$

$$a = \frac{p(\text{H}_2\text{O})}{p^*(\text{H}_2\text{O})} \quad (10)$$

where $p(\text{H}_2\text{O})$ is water vapor pressure and $p^*(\text{H}_2\text{O})$ is the saturation water vapor pressure. FTIR data can be used to quantify the amount of adsorbed water on the surface with 1 ML of water formed at ~20 %RH [268]. The methods of choice in this case are both surface sensitive imaging techniques that can operate under gaseous conditions on non-conducting samples (Atomic Force Microscopy) as well as XPS. This combination provides critical information on structure, morphology and chemical changes induced on a sample surface. One such design is shown in Figure 63 with an Asylum Research MFP-3D AFM instrument, which was coupled with a custom built environmental cell consisting of (i) a gas handling system to control relative humidity; (ii) an environmental cell connected to the scanner head and coupled to a sample heater/cooler; and (iii) an environmental monitor and control system [268,274]. Low force

constant Si cantilevers, with a typical force constant of 1.2 N/m to minimize any tip effects on the surface, are typically used, while relative humidity can be easily adjusted, where 70% RH is routinely used.

Societies. The AFM consists of (i) relative humidity preparation system, (ii) closed environmental cell connected to the scanner head and a sample heater/cooler and, (iii) environmental monitor and control system. The XPS system consists of (i) surface analysis chamber equipped with monochromated X-ray source, (ii) transfer antechamber, and (iii) reaction chamber.

XPS, on the other hand, due to the problems arising from relative humidity with the high voltage electronics, can be performed using a custom-designed reaction chamber after reacting/pumping out the water vapor. A regular monochromatic radiation of 1486.6 eV can be used, so that the sample is transferred under vacuum conditions without exposing it to the environment.

A complex picture (literally speaking) emerges when CaCO_3 ($10\bar{1}4$) is exposed to 70 %RH at 296 K. Surface reconstruction takes place over a period of 180 min, roughening up from 0.32 ± 0.2 nm to micron scale, as shown in Figure 64. Fast nucleation of islands occurs primarily in the vicinity of monoatomic steps, together with the simultaneous growth of etch pits, with the fast growth direction occurring nearly perpendicular to that of the islands [268]. Rates of material

Figure 64. Time sequence topography images of CaCO_3 ($10\bar{1}4$) surface at 70% RH and 296 K. Images were collected at (a) before, (b) after 71 min, (c) 194 min of RH introduction. Corresponding line scans are shown on the right. Full data scale is set to 1.2 nm. Reproduced with permission from Elsevier [268].

transport in nm/min can then be calculated from the image sequence. A two-layer mechanism

was proposed, since the second hydration layer exhibited very different viscoelastic properties from the first one, as shown utilizing force spectroscopy combined with the AFM phase imaging. In particular, exposure to water vapor induces phase changes to hydrated layers composed of amorphous calcium carbonate hydrates and vaterite [268,276,277], as shown in Figure 65. This mobility of the CaCO_3 surface layers (as well as other metal carbonates, including FeCO_3 , ZnCO_3 , MgCO_3 and MnCO_3) [269,276] has a major effect on the reactivity of these carbonate surfaces, beyond those of non-mobile metal oxide surface, as shown in 4.4.1.2.

At the same time, surface contaminants, such as Cd, can inhibit such phase changes [278]. In this case, Cd surface complexes, especially at step edges, inhibit ion mobility and therefore phase change at calcite surfaces. Exposure of humid air to metal carbonates containing redox-active

metals can, on the other hand, lead to the growth of secondary oxides, such as in the case of rhodocrocite (MnCO_3) [279,280]. In this case [268] surface oxidation of Mn(II) was proposed to proceed by surface dissolution followed by oxidation. A solid-state diffusion of Mn(II) then follows, producing an autocatalytic pathway, as illustrated in Figure 66.

4.4.1.2. Metal carbonate surface in the presence of acidic gases. Of particular interest are the reactions with acidic gases, such as HNO_3 , NO_x , SO_2 , during or after the metal carbonate's exposure to H_2O as a relative humidity [281]. Exposure to atmospherically relevant gases, such as SO_x and NO_x , can also induce important phase changes [282–285]. For instance, reactions with SO_x lead to

Rather than leaving homogeneous surface coatings, these reactants produce crystallites, as evidenced by AFM imaging [275]. In the presence of water vapor, exposure to SO_2 or NO_2 also produces surface-bound sulfate and nitrate species, alongside crystalline hydrates of CaSO_3 and $\text{Ca}(\text{NO}_3)_2$ [267]. The S2p:Ca2p ratio monotonically increased with RH in the presence of 100

mTorr SO₂ , as evidenced by XPS analysis of CaCO₃ surfaces [275]. When exposed to 10 mTorr NO₂ at 70% RH for 210 min, XPS analysis showed the presence of a single peak in the N1s region at 407.5 eV, indicative of nitrate, NO₃⁻ and analogous with that scanned for a nitrocalcite (Ca(NO₃)₂·4H₂O) surface. A proposed surface reaction sequence entailed an adsorbed ~15 Å H₂O layer yielding surface hydroxyl/bicarbonate groups, via H₂O dissociation, followed by NO₂ reaction with surface oxygen or hydroxyl sites via

Evidence for related reactions in the field was also noted in a study by Laskin *et al.* [286]. This noteworthy study demonstrated complete conversion of calcite particles to calcium dinitrate by exposure to humid atmospheres of nitric acid. Such reactions, which incidentally result from the industrial production of NO_x gases, can have important implications on atmospheric cloud chemistry and physics. A comparison has to be made between the hygroscopic metal carbonates, such as CaCO₃ and metal oxides, such as α-Fe₂O₃ and α-FeOOH [287]. It has been shown and discussed in 4.4.1.1 that the former undergoes dramatic reconstruction in the presence of RH and surface adsorbed SO₂ has been measured to increase five- to ten-fold [275]. The latter, on the other hand, exhibits negligible changes in the amount of adsorbed SO₂ product, providing a detailed background on the underlying reactivity of adsorbed H₂O modified metal oxide and carbonate surfaces. In particular, increased ion mobility on CaCO₃ opens up new surface regions for further adsorption and uptake of SO₂, while on α-Fe₂O₃ and α-FeOOH, the reaction is limited to the very top surface layer due to the low ionic mobility. Another observation emerging from Figure 65 is the surface area effect. In particular, CaCO₃ exhibited greater

reactivity towards SO₂ at all relative humidities. Since the S2p:Ca2p ratio accounts for the number of available Ca sites, enhanced particulate CaCO₃ reactivity can be attributed to the intrinsic reactivity and inhomogeneity greater than in the cleaved single crystal CaCO₃ (10 $\bar{1}$ 4), which also shows greater reactivity towards adsorbing SO₂.

4.4.2 Aqueous carbonate ion/solution interface

The dissolution of carbon dioxide in water via

is a process of paramount importance in environmental, biological and technological systems [288–294]. Examples include the key roles that soluble carbonate species play in ocean geochemistry [291,292], buffering of blood pH and CO₂ transport as a key physiological process in organisms [295] and the (geo)engineered sequestration of CO₂ in geological fluids. Henry's law ($p = k_H c$) is a very well-known formulation, which predicts the amount of dissolved gas (c)

in a fluid at a given temperature based on its partial pressure (p) in the gas-phase. As an example, incorporation of the current-day $\text{CO}_2(\text{g})$ level of ~ 397 ppm to water at ambient conditions leads to about $13.4 \mu\text{M}$ total $\text{CO}_2(\text{aq})$. Prediction of the pressure and temperature dependence of $\text{CO}_2(\text{g})$ solubility and for the $\text{CO}_2\text{-H}_2\text{O-NaCl}$ system [296–299], are performed with Equations of State, which have been under development for several decades [296,300–305], Diamond and Akinfiev [306] proposed a general formulation of Henry's law based on a critical review of 520 data points from 25 literature studies and it is valid from -1.5 to 100°C and from 0.1 to 100 MPa CO_2 (Fig. 68). This formulation was later extended to NaCl solutions [307]. Another formulation also predicts densities and volumes in $\text{CO}_2\text{-H}_2\text{O-NaCl}$ systems up to 374 and 100 MPa [308].

Figure 68. P-T diagram of solubility isopleths of CO_2 . Reproduced with permission from Elsevier [306].

Models predicting the temperature and pressure dependence of the first and second dissociation constants of carbonic acid have also been the object of development throughout several decades [309–322]. The more recent model of Li and Duan [322] predicts the speciation of H^+ , HCO_3^- , CO_3^{2-} and $\text{CO}_2(\text{aq})$ in aqueous solutions of 0–5.0 mol/kg NaCl at temperatures in the 0–225 °C range and pressures in the 0–1000 bar range. We note that these models have built a secured foundation upon which multicomponent systems, such as interfacial systems to be described in this review article, can be studied in a detailed manner.

While thermodynamics offers a reliable means for predicting air/water partitioning of CO_2 , the actual mechanisms of the incorporation of CO_2 into the fluid phase continue to be elusive. Most particularly, the air/water interface plays a primordial role in this process. Surface tension and surface potential studies have looked into the interfacial distribution of (bi)carbonate ions. A theoretical study [323], for example, classifies the carbonate ions as a strongly hydrated kosmotropic ion that ought to be depleted at the air/water interface. This was corroborated further experimentally by heterodyne detected phase-sensitive sum-frequency [324] in sodium carbonate and by X-ray photoelectron spectroscopy [325] in potassium carbonate. Both studies also show that sodium and potassium ions are located near the air/water interface. It also suggests that bicarbonate is more closely involved in the hydrogen bonding network of the interface and at the same level of sodium atoms. Thus, while these studies do not directly address the mechanisms of $\text{CO}_2(\text{g})$ adsorption at the air/water interface, this interfacial distribution of ions could possibly suggest that it proceed first via an interfacial transformation to bicarbonate. Current-day knowledge on the mechanisms of bicarbonate formation [326–328], to be detailed in the latter part of this section, could in fact fall in line with this concept, although the potential involvement of cations ought to be addressed. Along these lines, recent molecular modeling

work by Galib and Hanna [329] suggests faster dissociation rates for carbonic acid at the air/water interface. This may be caused by a greater structured solvation of water at the interface facilitating the solvation of the transition state species involved in the dissociation reaction (Fig. 69). This remains, however, an area that is in dire need of development.

Figure 69. Simulation of H_2CO_3 dissociation along a representative metadynamics trajectory. Clockwise from top left: hydrogen bond formation between H_2CO_3 and water molecule; formation of Zundel-like structure; formation of a metastable contact ion pair; complete dissociation. Reproduced with permission from [329]. Copyright (2014) PCCP Owner Societies.

The hydration assimilation of CO_2 into the matrix of aqueous solutions has also been studied. Recent notable developments in this area show that aqueous CO_2 can be regarded as hydrophobic: namely, with a small hydrogen bond number (0.56 bond/ CO_2) [330,331] as shown in Figure 70.

Figure 70. Theoretical RDF of aqueous carbonic acid and dissolved carbon dioxide. Reproduced with permission from Elsevier [330].

The $CO_2(aq)$ molecule is embedded in a cylindrical void which forces a slightly larger local ordering of water. Carbonic acid, formed via

, is an instable species [332–334] representing ~1% of the total $CO_2(aq)$ under ambient and acidic conditions. It has consequently long eluded unambiguous experimental detection of the first dissociation constant, as has been described through

with a well-known $pK_a = 6.35$ in pure water at 25 °C. This overall reaction thus accounts for energetic contributions from (de)hydration and (de)solvation reactions of $CO_2(aq)$. Theoretical studies [330,331,335] suggest that the hydroxyl, and not the carbonyl, group of carbonic acid is strongly hydrated in aqueous solutions. Building upon multiple efforts attempting to isolate carbonic acid [336–341], the study of Adamczyk *et al.* [340] measured the proton transfer rate to the bicarbonate anion upon electronic excitation of photoacid. They proposed a more realistic pK_a value of 3.45 for the reaction

corroborating earlier suggestions for values in the 3.4-3.8 range [326,334,342,343]. An *ab initio* molecular dynamics study [344] shortly after predicted comparable pKa values for (*anti-anti*, *anti-syn*) conformers of carbonic acid. The femto-second infrared spectroscopy measurements of Adamczyk *et al.* [340] also pointed to a lifetime of the order of ~300 ns for carbonic acid. They also suggested deprotonation and not dissociation to CO₂ and H₂O, as often stated in textbooks, is responsible for the instability of carbonic acid in solutions. Concomitantly, the Saykally group [330,345] added further insight into the aqueous chemistry of carbonic acid via near absorption fine structure (NEXAFS) spectroscopy of aqueous H₂CO₃ using a high velocity liquid microjet mixing system combining a bicarbonate and a hydrochloric solution. This approach took advantage of the slow dehydration rate of carbonic acid ($k=26.3 \text{ s}^{-1}$; $t_{1/2}=26 \text{ ms}$) and the fast protonation rate of bicarbonate ($k=4.7 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $t_{1/2}=21.3 \text{ ps}$) to produce carbonic acid. These measurements produced the first NEXAFS data of the C(1s) $\rightarrow \pi^*$ transitions for CO₂, HCO₃⁻ and H₂CO₃, whose spectral assignments were substantiated by DFT calculations. MD simulations from the same group suggested, at the same time, hydration numbers of 3.17 for H₂CO₃, 4.26 for HCO₃⁻ and 0.56 for CO₂ in the presence of sodium as a counterion.

Other studies focused on the mechanisms of carbonic acid decomposition. These include the theoretical studies [326,327] showing that hydration of CO₂(aq) involves a (1) hydroxylation of CO₂ to form HCO₃⁻, followed by (2) protonation. Recent *ab initio* metadynamics simulations of the converse reaction [328] suggest that the deprotonation involves a metastable solvent-separated HCO₃⁻/H₃O⁺ pair part of a Zundel-type structure (H₅O₂⁺). A similar concept was pursued in gas-phase cluster calculations [346]. The rupture of the remaining C-OH bond then proceeds via hydrogen bonding to a hydrogen-bonded H₃O⁺, such that

Finally, we note that the second dissociation reaction

has also been studied along such lines. For instance, *ab initio* molecular dynamics resolved a plausible Grotthus-type (proton shuttling) protonation of the carbonate ion that involved a cooperative network of water responding in the time scale of picoseconds (Fig. 71). [347]).

Figure 71. Recombination of carbonate via a Grotthus-type transfer of protons in a cooperative network of waters. Reproduced with permission from [347]. Copyright (2014) American Chemical Society.

A classical molecular dynamics study by Bruneval *et al.* [348] also suggests that in aqueous calcium carbonate solutions, the ion forms 12 long-lived (36 ps relaxation time under ambient conditions) hydrogen bonds with a highly organized first water shell. The second hydration shell adopts a three-dimensional structure creating a hydrophobic-like hydration exclusion area on top of the carbon atom. The *ab initio* molecular dynamics study of Kumar *et al.* [331] (Fig. 72) also adds further insight into the hydration environment of carbonate in pure aqueous solutions. In particular, their study points to an average of 2.85 hydrogen bonds per O site in carbonate, and to

a slight fall in the number of water-water interactions. Their study also points to slow rates of structural relaxation of water and rates of hydrogen-bond reorganization.

Collectively, these recent sets of studies pave the way for a new understanding of CO₂ hydration and hydrolysis reactions in confined aqueous systems, such as thin water films bound to solid surfaces.

Figure 72. Atomic density distribution of hydrogens (gray) and oxygens (red) of water near (a-b) carbonic acid, (c) bicarbonate, (d) carbonate, (e) CO₂ and (f) pure water. Reproduced with permission from [331]. Copyright (2009) American Chemical Society.

4.4.3 Carbonate/Water Interfaces

While this review does cover the extremely vast literature on carbonate crystal growth, we note that interfacial carbonate species are key players in crystallization reactions. These species are binding sites for crystal growth and also for foreign ions, which may ultimately alter or poison growth, or give rise to solid-solutions. Surface carbonate species have, for instance, been identified through various chemical [349,350] and/or isotopic exchange methods [351] and vibration spectroscopy [352]. Carbonate surface structures have been mapped by AFM

[353,354], probed by crystal truncation rod [355], modeled by *ab initio*/DFT [356], and their hydration layers mapped by amplitude-modulation AFM [293]. Carbonate surface species (*e.g.* $\equiv\text{CO}_3\text{H}$, $\equiv\text{CO}_3^-$, $\equiv\text{CO}_3\text{Mg}^+$, $\equiv\text{MgHCO}_3$) have also been explicitly accounted for in thermodynamic models as potential-determining species accounting for the complex reactivity of carbonate phases [350,357,358].

Figure 73. Conceptual molecular representation of possible protonation/deprotonation reactions at the $(10\bar{1}4)$ rhombohedral carbonate mineral surface. Reproduced with permission from Elsevier [350].

Metal-carbonate ternary complexes can also have considerable effects on carbonate surface chemistry. This was, for instance, denoted in the case of calcite dissolution contacted with

soluble Mn(II), where manganese-carbonate complexes stabilized reactive sites and consequently worked against surface step movement and defect nucleation [359].

The flotation properties of trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), a mineral mined for sodium carbonate production, investigated by contact angle and bubble attachment studies, suggested that Na_2CO_3 surfaces are considerably more hydrated and structured than their NaHCO_3 counterparts, a finding tentatively ascribed to the greater water-making structure of the interfacial carbonate ion species [360]. Carbonate mineral surfaces are hydrophilic, with small (e.g. $< 10^\circ$) contact angles in distilled water [361]. Commonly occurring alkaline earth ions, such as Ca^{2+} and Mg^{2+} , surface bindings contribute to positive charges on carbonates and could be a cause in the preferential separation of huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$) from magnesite (MgCO_3).

While this review shall neither cover the extremely vast literature on carbonate crystal growth, dissolution [362] and solubility [312] in aqueous solutions, nor its broad geochemical and atmospheric implications [198,199,363], it cannot ignore the rich interfacial chemistry of carbonate minerals. Thus, in this section, we will limit our review to interfacial species of carbonate. Carbonate species outcropping metal carbonate surfaces are not only binding sites for crystal growth and dissolution [364,365], but also for binding foreign ions, which may ultimately alter or poison growth, or produce solid-solutions [366–371]. Surface carbonate species (e.g. $\equiv\text{CO}_3\text{H}$, $\equiv\text{CO}_3^-$, $\equiv\text{CO}_3\text{Ca}^+$, $\equiv\text{MeHCO}_3$, $\equiv\text{MeOH}$; where $\text{Me}=\text{Ca}^{2+}$, Mg^{2+}) have been inferred through various chemical [349,350] and/or isotopic exchange methods [351], as well as through vibration spectroscopy [352,372]. At the same time, X-ray reflectivity [373] results favored the concept that metal-bound hydroxo groups (e.g. $\equiv\text{CaOH}$) are the protonation sites of the calcite/water interface, and that interfacial exchange of calcium and carbonate ions should predominantly occur at step-edge kink sites. Surface carbonate and metal-bound hydroxo species

have also been explicitly accounted for in thermodynamic models as potential-determining species that may account for the complex reactivity of carbonate phases [350,357,358,374,375]. More recently, amplitude modulation atomic force microscopy (AM-AFM) has provided direct visualization of single ions coordinated to interfacial carbonate species, such as in the case of the $(10\bar{1}4)$ face of calcite [353], as shown in Figure 74.

Figure 74. Amplitude modulation atomic force microscopy imaging of the $(10\bar{1}4)$ face of calcite in (left) 10 mM NaCl. Schematic representation of sodium species is shown at the right. Reproduced with permission from [353]. Copyright (2013) American Chemical Society.

A surface diffraction study by Heberling *et al.* [376] also provided evidence for a layering of electrolyte ions at the $(10\bar{1}4)$ face of calcite, as shown in Figure 75, a finding that contrasts with classical views of the electric double layer and that potentially highlights the direct involvement of electrolyte ions in the charging process.

Figure 75. Schematic representation of calcite (10 $\bar{1}$ 4)-H₂O interface in the presence of Rb⁺. Reproduced with permission from [376]. Copyright (2014) PCCP Owner Societies.

Still, a recent X-ray reflectivity study [377] underscored continuing uncertainties with respect to key structural and dynamic properties of the calcite-water interface, and offered a means to benchmark molecular dynamics parameters to improve modeling of this important system. In a very recent study on dynamics of a propagating dissolution front at the calcite/water interface, Laanait *et al.* [362] also reported the prevalence of anisotropic front velocities, and therefore of no preferential control from defects or pits. These latest efforts consequently highlight further the complexity of the surface chemistry of carbonate minerals.

4.4.4 Metal Oxide/Aqueous Carbonate Ion Interface

Carbonate species are ubiquitous in many aqueous solutions exposed to the atmosphere. A great deal of studies focused on fundamental surface chemical aspects of metal oxides and minerals (*e.g.* hydroxyapatite [378] or iron oxides [379]) go, in fact, to great lengths to avoid carbonate contamination. Interfacial carbonate species, which are stabilized by electrostatic, hydrogen or covalent bonds, can not only block adsorption sites, but also alter the proton budgets of solid/solution suspensions [380], inhibit mineral (*e.g.* forsterite [381]) dissolution, depress mineral flotation [382] in alkaline solutions, and lower the point of zero charge (pzc) and

isoelectric (*ise*) points. Thermodynamics calculations, moreover, suggest that carbonate surface complexes do not considerably affect the inner-Helmholtz potentials of mineral surfaces, but rather impact those of the diffuse layer, which are manifested in the *ise* [379].

Studies directly addressing carbonate binding at metal oxide and mineral surfaces are of particular relevance for atmospheric, groundwater and even industrial water (*e.g.* mine flotation waters or Bayer liquors) studies, where this ion is of great abundance. Adsorption experiments are carried out in both open and closed atmospheres. Work by Villalobos and Leckie [107] on goethite provided one of the few available experimental constraints of carbonate loadings achieved at mineral/water interfaces (Fig. 76).

Focusing on submicron-sized synthetic goethite (α -FeOOH) surfaces, these authors report carbonate loadings of up to 0.3 sites/nm² (0.5 μ mol/m²) at circumneutral pH under close conditions (133 μ M CO₂). Under open conditions (0.24-0.41 atm CO₂), loadings are up to 0.7-0.8 sites/nm² (1.2-1.4 μ mol/m²); namely, about one-fourth of the reactive site densities on these surfaces. The authors also detected an ionic strength dependence on the surface loadings below pH 7 only, suggesting that outer-sphere complexes predominate under these conditions. The

same authors also characterized surface complexes by FTIR spectroscopy [106] and interpreted a split of 155 cm^{-1} between ν_3 s and ν_3 as evidence for monodentate inner-sphere complexation reactions. Other ATR-FTIR studies of carbonate binding at hematite [105], magnetite [384], aluminum and iron oxide surfaces [205] have identified key (bi)carbonate species. The study of Bargar *et al.* [105], comparing ATR-FTIR spectra and DFT frequency calculations, notably revealed coexisting carbonates at the hematite surface. These complexes include a monodentate binuclear inner-sphere and a symmetry-broken hydrogen-bonded complex alongside an additional one located in the diffuse layer. In a more recent study of CO_2 binding at the hematite/water interface, Chernyshova *et al.* [385] constrained plausible binding mechanisms by use of rhombohedral nanoparticles predominantly terminated by the {014} facet. Vibration spectroscopic measurements notably suggest a Langmuir-Hinselwood type of binding for CO_2 , involving nucleophilic attack from neighboring $\mu_3\text{-OH}$ sites.

Thermodynamic adsorption models accounting for a molecular-level representation of carbonate interfacial species have been developed using the surface complexation modeling approach, one that accounts for complexation and ligand exchange reactions involving surface (hydr)oxo/aquo groups [106,386,387]. The model developed by Villalobos and Leckie [106] predicts experimental carbonate loadings achieved on goethite in both closed and open conditions involving a monodentate inner-sphere proposed from concurrent ATR-FTIR spectra. A sodium-carbonate ternary complex accounts for ionic strength effects. Their model was also used to suggest carbonate loadings that can be achieved in groundwater under circumneutral conditions up to 1.8 site/nm^2 ; namely, about half of the -OH site densities at typically iron oxyhydroxide surfaces. Hiemstra *et al.* [386] later developed an alternative complexation model from the same

data set, arguing that the FTIR absorption band splitting of the C-O stretching region may be more representative of bidentate complexes as shown in Figure 77.

Using a charge-distribution modeling strategy [388] these authors assigned 2/3 of the charges of inner-spherically bound carbonate species to an inner-Helmholtz plane and the remaining to an outer-Hemlholtz plane and proposed that the proton co-adsorption response to carbonate, and by extension oxyanion, binding is strongly correlated to these distributions. Both models were used to describe sorption in competitive systems. The one of Villalobos *et al.* [383] was used to describe how interfacial carbonate species enhanced Pb(II) uptake by mineral surfaces through the formation of "type A" ternary

surface complexes, $(\equiv\text{FeO})_2\text{H-Pb-OCO}_2^-$ (where $\equiv\text{FeO}$ is a surface oxo site). The formation of a comparable complex for uranyl, $(\equiv\text{FeO})_2^{2-}\text{-UO}_2\text{-(CO}_3\text{)}^{2-}$, was, in turn, used to explain the greater loadings achieved under alkaline systems contacted with atmospheres of $\text{CO}_2(\text{g})$. The study also accounts for competitive adsorption effects in mixed carbonate-chromate systems, effectively decreasing chromate loadings at goethite surfaces. Hiemstra, on the other hand, developed a model accounting for the competitive sorption of carbonate and phosphate [387]. Other competitive systems of noteworthy interest include the cases of sulfate and selenite [389] on aluminum oxide surface. These authors demonstrated the protonation of additional surface hydroxo groups that would be otherwise proton silent under these conditions. In other studies,

carbonate ions were shown to competitively displace Sb (V) at surfaces [390] of boehmite and corundum, yet they could be readily displaced by the formation of five-member chelates of the Al-oxalate surface species [391].

Interfacial species of carbonate also play key roles in actinides (geo)chemistry. These affect actinide binding modes and strengths [392–400]. EXAFS studies of uranyl-carbonate species [401] [402] revealed the presence of uranyl-carbonato ternary surface complexes on minerals. These have also been the focus of theoretical studies, for example, on quartz [403], underscoring the co-existence of inner- and outer-sphere species involving carbonate in the equatorial shell of uranyl. Such complexes can enhance U(VI) uptake in some situations, such as has been shown in the case of iron oxide coated quartz surfaces [378], but decrease adsorption on negatively charged surfaces, such as on kaolinite [400] or low-charged clays like montmorillonite [404]. The impact of carbonate in contaminated soils is more complex, as mineral (*e.g.* U(VI) phosphate) dissolution, *i.e.* U(IV) oxidation, U(VI) complexation and desorption of U(VI)-organic matter complexes under alkaline conditions, can act independently or concurrently. One study suggested that these effects may be responsible for the enhanced leaching and mobilization of uranyl by carbonate in soils [405], as well as diffusivity at interfaces and within (*e.g.* clay) pores [406] and fractures [407]. Neptunyl(V) biscarbonato inner-sphere complexes have also been shown to inhibit calcite growth rates [408].

Carbonate species can also play key roles in solid synthesis/growth and transformation mechanisms in aqueous solutions. A study by Zhang *et al.* [409], for instance, demonstrated carbonate ions effectively alter the coordination environment in fresh short-range ordered Al hydroxides precipitates. Carbonate interactions with incipient metal (oxy)hydroxide clusters/nuclei during synthesis can even alter solid formation pathways. In goethite, for

example, carbonate ions favor the formation of nano-sized particles (*cf.* nanogoethite), and incipient interactions are also responsible for the formation of carbonate-goethite solid solutions [410,411], which can contain up to 4 % C [412]. The stability of such goethite and even gibbsite [413] solid solutions of carbonate has also lead to the use of the ^{13}C isotopic composition of goethite in paleosols, when determining atmospheric CO_2 levels in the context of paleoclimatological studies [412,414,415].

Finally, we note that interfacial species of carbonate have even broader implications for environmental processes involving more complex systems. For instance, analogous forms of interactions can also occur in the cases of organic adsorption on mineral surfaces. Demonstrated cases include those of thiram disulfate pesticide adsorption on corundum and montmorillonite surfaces where a thiram- HCO_3 complex shows enhanced adsorption abilities, and even alters the electronic structure and UV-Vis spectrum of the molecule [416]. Another example is a study demonstrating that carbonate binding at goethite surfaces promoted virus attachment, while inactivating their infectivity from neighboring protonate groups [417].

5. Outlook

Two decades after the review of H.-J. Freund and M.W. Roberts in *Surface Science Reports* [13] the scientific literature on the interfacial chemistry of CO_2 continues to grow at a rapid pace. This field becomes even more relevant now that the Earth's atmospheric CO_2 levels have exceeded 400 ppm and that 185 nations and the European Union have engaged in a common goal to mitigate emissions of carbon dioxide and other greenhouse gases in the recent 2015 Paris Climate Change Conference. A Chemical & Engineering News article [418] even foresees that the *Success of Climate Deal Will Hinge on Chemistry*. When it comes to CO_2 chemistry, this will call for a new generation of studies that will not only push forward current boundaries in our

fundamental understanding of the electronic and molecular structures of CO₂-related species, but also in their (photo)chemistry atmosphere and linkages with terrestrial processes, as well as in new technologies aimed at capturing, sequestering CO₂ and even converting it to useful forms of carbon. Advancing this knowledge will rely on a concerted effort in the chemical, geochemical, and atmospheric communities to develop new experimental and theoretical approaches that will probe the interfacial chemistry of CO₂ in unforeseen ways in the days the original H.-J. Freund and M.W. Roberts [13] was printed and even hopefully as this review is written.

The vast literature of the *in vacuo* interfacial chemistry of CO₂ is serving as a sound stepping-stone to a new generations of studies focused on environmentally relevant systems at ambient and even to industrially relevant systems at elevated pressures. As such, as classical UHV methods are adapted to emulate such conditions, as for example seen in the increasing usage of Ambient Pressure XPS, Time Resolved Sum-Frequency Generation Spectroscopy, Cavity Ring-Down Spectroscopy, Environmental Molecular Beam Spectroscopy and Environmental Electron Microscopy, new knowledge on the interfacial reactivity of CO₂ should be gained. On the modeling front, we anticipate that new advances allowing bond formation and breaking (e.g. new reactive force fields for MD, *ab initio* and hybrid *ab initio* MD methods) will allow the community to resolve more precisely conversion mechanisms in settings as varied as solid/air, solid/water and even solid/water/air interfaces.

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