Identification of Intermediates in the Reaction Pathway of SO₂ on the CaO Surface: From Physisorption to Sulfite to Sulfate

Nils Schewe,[a] Farahnaz Maleki,[b] Giovanni Di Liberto,[b] Andreas Gerdes,[a] Hicham Idriss,[a] Gianfranco Pacchioni,[b] and Christof Wöll*[a]

Abstract: The interaction of CaO and Ca(OH)₂ with solvated or gaseous SO₂ plays a crucial role in the corrosion of urban infrastructure by acid rain or in the removal of SO₂ from flue gas. We carried out a combined spectroscopic and theoretical investigation on the interaction of SO₂ with a CaO(001) single crystal. First, the surface chemistry of SO₂ was investigated at different temperatures using polarization-resolved IR reflection absorption spectroscopy. Three species were identified, and an in-depth density functional theory study was carried out, which allowed deriving a consistent picture. Unexpectedly, low temperature exposure to SO₂ solely yields a physisorbed species. Only above 100 K, the transformation of this weakly bound adsorbate first to a chemisorbed sulfite and then to a sulfate occurs, effectively passivating the surface. Our results provide the basis for more efficient strategies in corrosion protection of urban infrastructure and in lime-based desulfurization of flue gas.

Introduction

The interaction of SO₂ with calcium oxide and -hydroxide (CaO/Ca(OH)₂) is of pronounced practical interest. Calcium oxide – derived materials, for example Ca(OH)₂ and CaCO₃, are main constituents of modern building materials such as concrete. These basic urban infrastructure building materials are, unfortunately, rather sensitive to environmental damage. Particularly reactions with SO₂ – either in the gas phase or dissolved in water (acid rain) – are a main source of weathering and corrosion. Whereas in this context the strong chemical affinity of CaO/Ca(OH)₂ towards SO₂ is unwanted, the pronounced reactivity of quicklime towards SO₂ is exploited in the removal of this gas from industrial flue gas mixtures (so called "(dry) desulfurization process"[1–3]) to prevent emission into the atmosphere. The high-purity calcium sulfate (gypsum) formed in this process is also used as raw material in the building materials industry. Thus, quicklime (technical CaO) is a material

well-suited for studying the chemical interaction of sulfur oxide(s) with minerals. Waste gas cleaning processes, where the flue gas is passed through an aqueous suspension or a dry bed of quicklime, have, to this day, substantially gained in importance. Despite SO₂ emission reductions in Germany in the last 25 years (as reported by the German Federal Environment Agency), the environmental effect of this corrosive gas still has a pronounced impact on every-day life. The crucial importance of the environmental impact of SO₂ has led to several governmental measures towards their reduction between 1995 and 2015.[4] The US Acid Rain SO₂ Reduction Program, the Chinese SO₂ emission trading system and the National Emission Ceilings (NEC) Directive employed throughout the European Union (EU 2016/2284) are only a few important examples. The origins of SO₂ emission into the atmosphere are of various nature – both anthropological and natural processes contribute. In nature, especially volcanic activity[5] leads to high atmospheric concentrations of SO₂. On other planets in the solar system, the concentration can be much larger than on Earth, for example, in the atmosphere of Venus SO₂ is the third most abundant gas after CO₂ and N₂, with concentrations up to 150 ppm.[6]

In terrestrial environments, sulfur dioxide as an air pollutant has several unwanted properties. In addition to its toxicity, contact with the human body leads to headaches as well as to severe corrosive injuries in the respiratory system and to mucosae, an autoimmune chronic disease. Furthermore, this gas endangers the long-term structural integrity of urban infrastructure. In this context, in particular the corrosive impact on metals[7,8] and on cement-based materials,[9,10] are of great concern. Despite the huge importance of sulfur dioxide-induced corrosion for calcium oxide- and hydroxide-based construction materials, the detailed mechanism of SO₂ adsorption, reaction,

[a] N. Schewe, Prof. Dr. A. Gerdes, Prof. Dr. H. Idriss, Prof. Dr. C. Wöll
     Institute of Functional Interfaces (IFG)
     Karlsruhe Institute of Technology (KIT)
     76344 Eggenstein-Leopoldshafen (Germany)
     E-mail: christof.woell@kit.edu

[b] F. Maleki, G. Di Liberto, Prof. Dr. G. Pacchioni
     Department of Materials Science
     University of Milano-Bicocca
     20125 Milano, Italy

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and subsequent decomposition of construction materials are still not well known at the atomic scale. This lack of information on elementary steps is in part due to the difficulty in preparing model systems suitable for analyzing concrete surface chemistry but also due to problems in handling the extremely corrosive SO_2 gas under conditions needed for the application of state-of-the art surface science techniques.

Most previous works on the interaction of SO_2 with oxide surfaces have been carried out using XPS, with the information gained limited to the oxidation states of reaction products. For deriving a consistent picture of reaction mechanisms, more detailed information on the nature of the formed intermediates is required. In this context, the non-invasive conditions of infrared-reflection-absorption-spectroscopy (IRRAS) applied to single crystal model systems are better suited. Previously proposed degradation mechanisms of concrete involve the uptake of SO_2 from gas phase into the highly alkaline water contained inside the pores of the hardened cement paste (pore solution).[9] The resulting sulfurous acid is then converted to sulfuric acid, yielding sulfates (e.g., Ettringite in cements). This leads to severe mechanical stress and ultimately destruction of the concrete.[10]

In the present study we have undertaken the first, to our knowledge, concerted experimental and theoretical effort to elucidate the interaction between sulfur dioxide and calcium oxide single crystal surfaces. Previous studies have focused on either CaO powder or CaO thin films or on other gasses.[11–13] Compared to other oxides, such as those of transition metals or aluminum, one should expect striking differences in the surface chemistry of calcium oxide because of its extreme surface alkalinity.[14–16]

Results and Discussion

The CaO(001) single crystal surface was prepared by sputtering/annealing cycles. X-ray photoelectron spectroscopy (XPS) data revealed concentrations of surface impurities of less than 5% (see Supporting Information, Table 1). The as-prepared surface could not be analyzed by low energy electron diffraction (LEED) due to strong charging effects. In Figure 1 we show infrared reflection absorption spectroscopy (IRRAS) data recorded using
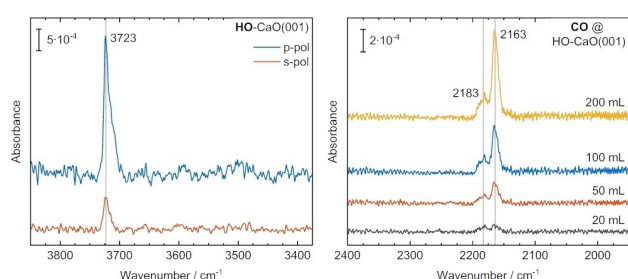
a UHV-compatible multi-purpose apparatus. These results, to our knowledge the first IRRAS data reported for a CaO monocrystal surface, revealed a sharp, slightly asymmetric peak centered at 3723 cm^{-1}, demonstrating the presence of a substantial amount of surface OH-species (Figure 1, left). We explain this observation by the strong reactivity of clean CaO surfaces to water,[13] making the preparation of hydroxide-free surfaces under our experimental conditions virtually impossible. This is supported by our ab initio atomistic simulations and literature studies[17] that show strong interaction of a monolayer of water with the CaO(001) surface. We observed a spontaneous formation of a disordered, hydroxylated surface where most of the water molecules are adsorbed dissociatively. This was confirmed by DFT calculations with PBE[18] and HSE06[19] exchange-correlation functionals and VASP code[20] (see Supporting Information, Figure S11). The frequency reported here is in agreement with literature findings for thin CaO-layers grown on Mo(001),[21] but different from the frequency (ν_{OH} = 3641 cm^{-1}) observed in our reference experiments on Ca-$(OH)_2(001)$ single crystals. Thus, the hydroxylated CaO(001) (in the following referred to as HO–CaO(001)) surface is chemically and structurally different from the $Ca(OH)_2(001)$ surface. Note, that the sign of the OH vibration in s-polarized light is positive. This observation reveals a substantial roughening of the surface.[22,23] Nevertheless, the data shown in Figure 1 clearly reveal that the surface termination with OH groups is rather homogeneous.

Further characterization of the CaO(001) surface was carried out using CO as a probe molecule.[16,24] The IRRAS data (Figure 1, right) reveal the presence of a pronounced peak at 2163 cm^{-1}. On the basis of our DFT calculations (see Supporting Information, Table S5 and S6), we assign this peak to CO adsorbed at the OH groups of the fully hydroxylated HO–Ca(001) surface. A second, substantially smaller peak is observed at 2183 cm^{-1}, which – in agreement with our DFT results – is assigned to CO bound at a second, probably step edge-related OH-species. No signatures possibly related to CO bound to Ca^{2+}- or O^{2-}-ions (expected to show pronounced shifts relative to the gas-phase frequency (2143 cm^{-1})) exposed on hypothetically clean, hydroxy-free patches of the surface, could be observed. This assignment challenges previous reports, which attributed the peak at 2163 cm^{-1} to CO bound at surface calcium ions.[25] Our DFT calculations allow to exclude this assignment, a (hypothetical) CO species bound at Ca^{2+} ions should reveal a strong red shift of −92 cm^{-1}, rather than the blue shift seen in our experiments, see Figure 1 (right). Notice that the computed shift is independent of the exchange-correlation functional used (the shift of −92 cm^{-1} is obtained at hybrid functional level, while a shift of −129 cm^{-1} is found at the PBE level, see Supporting Information, Table S6).

The results obtained using CO as a probe molecule thus reveal a full hydroxylation of the CaO(001) surface obtained using the present preparation procedure.

Further information on the nature of the as-prepared HO–CaO(001) was obtained by exposing the surface to CO_2. The results were found to be consistent with previous reports by Freund and coworkers obtained for CaO thin films grown on Ru

Figure 1. Left: polarized IRRAS data of the as-prepared CaO(001) surface at 62 K referenced versus a well-defined $UO_2(111)$ surface. Right: p-polarized difference spectra of carbon monoxide adsorbed at 62 K on the as-prepared CaO(001) surface.

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and Mo substrates.[11,12] In this previous work the metal supports prohibited the observation of CO_2 vibrational modes for which the transition dipole moments (TDMs) are orientated parallel to the surface (so-called surface selection rule).[22] For the oxide monocrystals used here this limitation does not exist and modes with TDMs oriented parallel to the substrate could be observed, allowing to confirm the band allocations proposed for the surface carbonate species by Freund and co-workers (for details see Supporting Information, Figures S3 and S4).

The exposure of the HO–CaO(001) surface to a mixture of 1% SO_2 in N_2 at 62 K (Figure 2, left, blue line, peaks **A** and **B**) yielded two vibrational peaks at 1328 cm^{-1} and 1149 cm^{-1}, respectively. These are red shifted by $\Delta v = -33$ cm^{-1} and $\Delta v = -2$ cm^{-1} relative to the SO_2 gas phase vibrational frequencies of 1361 cm^{-1} (symmetric stretch) and 1151 cm^{-1} (asymmetric stretch).[26,27] By thorough comparison of this data to literature values from IR-investigations of SO_2-ice at similar temperatures and the results of our calculations for bulk-SO_2, we assign these bands to the asymmetric (1328 cm^{-1}) and symmetric (1149 cm^{-1}) stretching mode of SO_2 in an amorphous SO_2-ice.[27,28] We thus conclude that at low temperatures (62 K), unexpectedly,[14] the exposure of HO–CaO(001) to SO_2 only leads to the formation of physisorbed SO_2 multilayer islands (see Figure 2, comp. Figure 3). The complete absence of add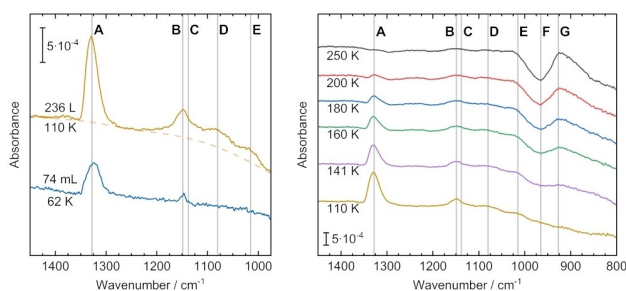itional bands in the IRRAS data allows to exclude the presence of any reaction products and reveals that the chemical transformation of SO_2 on a hydroxylated CaO surface requires a considerable activation energy.

The existence of a physisorbed SO_2 species on this highly reactive CaO surface has not been reported previously. To confirm this somewhat unexpected finding, we have carried out experiments on several reference substrates, i.e. Ca(OH)$_2$(001), CeO$_2$(111) and UO$_2$(111) (comp. Figure 3). The interaction between SO_2 and these other oxides is weakest for Ca-(OH)$_2$(001), showing only the physisorbed islands, while surface-molecule-interactions give rise to one additional set of peaks for UO$_2$(111) and CeO$_2$(111). The complex line shape of the band around 1348 cm^{-1} is due to noteworthy phenomena[29,30] (combination of Berreman effect[31] and Davydov splitting[32]), which will be discussed in a forthcoming publication. Previous theoretical and experimental studies on the interaction of thin film or powdered oxides to SO_2 revealed a strong interaction between the sulfur and surface oxygen atom. Bond formation was reported, leading to sulfite SO_3^{2-} species.[14,33–35] In our experiments, we clearly observe a physisorbed intermediate, while reaction products could only be observed after heating SO_2 island-covered substrate to higher temperatures (Figure 2).

After reaching 100 K, an additional set of broad vibrational bands (**C-E**) appeared between 1150–970 cm^{-1}. To allow for a more precise investigation of this temperature-induced reaction, additional experiments were carried out at an initial substrate temperature of 110 K and higher exposures (Figure 2, left). In addition to the adsorption bands related to the physiosorbed species at 1328 cm^{-1} and 1149 cm^{-1}, three additional broad bands are visible in the spectra, centered at 1138 cm^{-1}, 1080 cm^{-1} and 1015 cm^{-1}. Based on the above presented results, these peaks must belong to a reaction product of SO_2 and HO–CaO(001).

Heating the adlayer consisting of physisorbed multilayered islands and chemisorbed reaction products (located at the island/substrate interface, Figure 2, right) resulted in the desorption of the physisorbed islands. At the same time, two new peaks appeared at 965 cm^{-1} and 927 cm^{-1}, respectively. Above 200 K, the conversion of the first into this second chemisorbate was completed, while the physisorbed islands had fully disappeared.

The positions of the S2p signals in the XPS data revealed the existence of sulfur in the formal +VI oxidation state, direct evidence for the existence of sulfate species (for details see Supporting Information, Figures S1 and S2). According to literature, sulfate is expected to be the most stable form of SO_x adsorbate on oxide surfaces.[33,37–40] Our in-depth DFT study allowed to assign this first chemisorbed species formed by the interaction of SO_2 with the HO–CaO(001) surfaces to a surface-bound (hydrogen)sulfite-species (See Supporting Information, Table S7 and Figure S13 for a compilation of all studied surface-adsorbate-conformations and computational details).

Both, the direct adsorption of SO_2 on surface-oxygen (Figure 4 a and b) and on surface-hydroxide (Figure 4 c) sites lead to species with vibrational frequencies (See Supporting Information, Table S7) similar to the experimentally found bands at 1138 cm^{-1}, 1080 cm^{-1} and 1015 cm^{-1}. Notice that in

Figure 2. s-polarized IRRAS data of the interaction of SO_2 with HO–CaO(001) – left: adsorption at 62 K and 110 K, respectively, with given exposures. Dotted line is a baseline included to improve visibility; right: stepwise desorption by flashing to the indicated temperatures and subsequent cooling/measurement at base temperature (below 120 K).
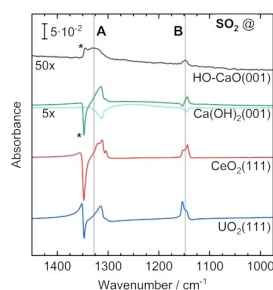

Figure 3. Top to bottom: p-polarized IRRAS data of the interaction of SO_2 with HO–CaO(001) at 74 mL and 62 K, with Ca(OH)$_2$(001) at 0.65 L and 67 K (s-pol spectrum in pale turquoise for comparison), with UO$_2$(111) at 5.4 L and 66 K and with CeO$_2$(111) at 5.05 L and 75 K. Asterisk marks the band at 1349 cm^{-1} with LO-character,[27,30,31,36] only visible in p-polarized light on sufficiently single crystalline samples.

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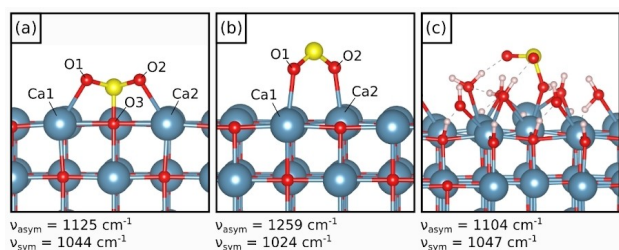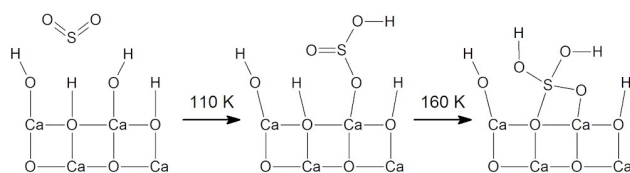Societies Publishing

Figure 4. SO_2 on different CaO(001) surface models. Panels (a) and (b) report two possible isomers on the dry surface. Panels (c) shows the most stable isomer on the hydrated surface.

the species shown in Figure 4c the S atom of SO_2 interacts with a surface O ion that is spontaneously displaced from the surface, thus explaining the similarity of the vibrational frequencies with the sulfite species shown in Figure 4a (see Supporting Information, Table S7). Taking in account our results from the CO adsorption (Supporting Information for details on experiments and supporting DFT-calculations), we exclude the direct adsorption of SO_2 on the CaO(001) regular surface (Figure 4a). This is strongly supported by the observation of three instead of only two vibrational modes. We attribute the considerable broadening to the formation of hydrogen bonds between the adsorbed species and the surface OH groups. We assign the second reaction product formed at higher (160 K) temperatures to a surface-sulfate as shown in Scheme 1. The vibrational modes at 965 cm^{-1} and 927 cm^{-1} observed for this species are in accordance with hydrogen sulfate species.[40–42] We feel we can rule out the presence of symmetrically coordinated sub-surface sulfate since we did not observe the typical high-frequency modes of those sulfate species[40,43] around 1400 cm^{-1}.

The here proposed reaction pathway has the character of two consecutive insertions of SO_2 and HSO_3^-, respectively, into an OH-bond. This can be formally considered as a nucleophilic attack of the hydroxide-oxygen at the sulfur center with subsequent (or concerted) proton-shift.[44] For SO_2, the intermediates and products of this reaction type are typically very difficult to isolate. However, under the conditions of our experiments using model-systems in an UHV environment, their stabilization and characterization was possible. With these results we were able to shed light on the principal reaction of SO_2 with CaO, a reaction with high relevance for technical applications.

Conclusion

Our combination of polarization resolved IRRAS data and state-of-the-art DFT calculations allowed the identification of the reaction mechanism of SO_2 with a hydroxylated CaO(001) single crystal surface. Along the reaction pathway, starting from physisorbed species, two intermediates could be identified, a metastable chemisorbed surface-bound hydrogensulfite and a thereof thermally derived surface hydrogensulfate. The latter species is stable at room temperature. The theoretical vibrational frequencies are in good agreement with the experimental findings. Our experiments reveal a pronounced difference in surface reactivity between $Ca(OH)_2(001)$ and hydroxylated CaO(001), both excellent model systems for lime and hydrated lime, respectively. Our observations have relevant implications for the use of lime in flue gas desulfurization. The presence of OH groups on CaO(001) facilitates the conversion of sulfite into sulfate upon exposure of the surface to SO. Such a passivation of CaO or $Ca(OH)_2$ during the uptake of SO_2 has, to our knowledge, not been discussed in previous literature. We also expect that on the basis of this new insights, advances in the energetically rather costly recovery of CaO particles for flue gas desulfurization by thermal treatment[39] will be made.

Important information can also be taken from the herein presented results for further research into the chemical interactions between $Ca(OH)_2$- or $CaCO_3$-containing building materials and the SO_2-containing atmosphere, which has already led to the deterioration of first-class cultural objects.[45] For instance, the experimental techniques as used here are suitable for characterizing interfacial chemical processes on further model substrates for building materials (e.g. calcium silicate hydrates (C–S–H)) which are still unknown. The presented reaction pathway (Scheme 1) also provides important insight with respect to the chmical processes occurring on real building material surfaces. This is an essential basis for the development of minimally invasive protective (coating/impregnation) measures for endangered artworks and monuments.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Scheme 1. Proposed reaction pathway for the adsorption of SO_2 on as-prepared HO–CaO(001) and subsequent heating. The reaction includes three spectroscopically determinable SO_x species.
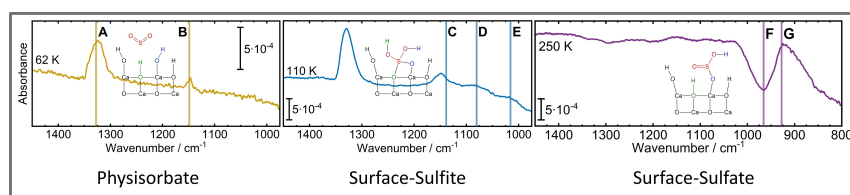
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RESEARCH ARTICLE

N. Schewe, F. Maleki, G. Di Liberto,
Prof. Dr. A. Gerdes, Prof. Dr. H. Idriss,
Prof. Dr. G. Pacchioni, Prof. Dr. C. Wöll*

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Identification of Intermediates in the Reaction Pathway of SO$_2$ on the CaO Surface: From Physisorption to Sulfite to Sulfate

Under ultra-high vacuum conditions, three surface sulfur oxide species were IR-spectroscopically detected on a CaO(001) single crystal surface. Polarisation dependent infrared reflec- tion absorption spectroscopy and density functional theory were used to identify the chemical nature of the adsorbates as a physisorbate and two different chemisorbates.