

Small Molecule Activation on Spinel-Type Oxides

Density Functional Theory Studies on CO₂ and N₂ Activation on Cobalt and Iron Oxides

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Kurzgefasst

- Atomic level characterization of CO₂ and N₂ adsorption on spinel-type oxide surfaces.
- Understanding electron transfer reactions on reducible oxides.
- Support effects involving cobalt and iron oxides.

Being able to convert very stable and hence chemically nearly inert molecules like CO₂ and N₂ into so-called value-added products, such as alcohols, ammonia, or amides is beneficial from many point of views. CO₂ is a greenhouse gas and its concentration in the atmosphere currently exceeds 410 ppm, a frightening value, largely due to industry and traffic. Consequences are apparent climate changes. N₂ is industrially turned over into ammonia in the energy-consuming Haber-Bosch Process. Thus, knowledge on sustainable, energy-efficient ways to convert (activate) these molecules into chemically versatile compounds will certainly affect the global population, economy, as well as ecology [1]. But this represents a formidable task and requires fundamental research focusing on the elucidation of reaction mechanisms at the molecular level.

Herein, we report results obtained within the framework of this project. So far, the approved computing time lead to two publications. The first one discusses results confirming the structure of the outermost atomic layers of the (111) surface of magnetite (Fe₃O₄). These results were obtained combining surface action spectroscopy (SAS) and density functional theory (DFT) calculations carried out on the HLRN-IV compute cluster [2]. The other relevant paper discusses the adsorption characteristics of CO₂ on that very surface [3] and compares DFT results with recent TPD and IR experiments [4]. This work is central in terms of fundamental characterisation and represents a cornerstone of the project before we go ahead addressing more complex systems.

[3] discusses two essential aspects helping to understand the complex magnetite (111) surface structure at the atomic level. First, how does CO₂ interact with the regular surface termination of Fe₃O₄(111), and how is that interaction affected, for instance by defects like additional Fe ions? These defects could be triggered applying reducing conditions favoring metal rich surfaces. Secondly, what happens if water

is on the surface? Our previous work clearly showed that the (111) surface of magnetite interacts strongly with water [5], and it is therefore expected that water affects the surface reactivity. Figure 1 shows molecu-

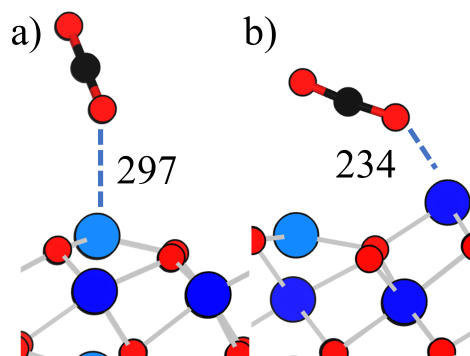


Abbildung 1: Structures obtained using PBE+U for molecular adsorption of CO₂ on the Fe_{tet1} terminated (a) and Fe_{oct2} terminated (b) Fe₃O₄ (111) surface. Bond distances in pm.

larly adsorbed CO₂ on magnetite (111). The molecule binds with ca. 0.2 eV (including approximations for van der Waals-type dispersion interactions). Calculated vibrational wavenumbers amount to ca. 2377 cm⁻¹. Additional relevant structures are shown in Fi-

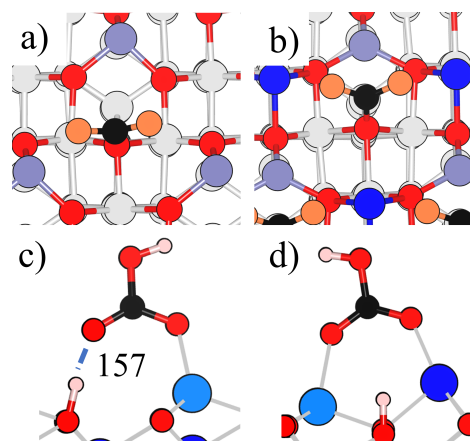


Abbildung 2: Most stable carbonate structures for the Fe_{tet1} (a) and Fe_{oct2} (b) terminated Fe₃O₄ (111) surface. Same applies for the most stable bicarbonate species for respective surface terminations (c,d). Note that for the Fe_{oct2} termination no hydrogen bond is formed. Bond distance in pm.

gure 2, which shows very stable carbonate and bicarbonate species formed on the two relevant surface terminations. Bicarbonate is formed in the presence of water, however traces of water are always present on that surface. It is known as "background water". Figure 3 shows a stick chart of calculated wavenumbers of relevant species (shown below the chart

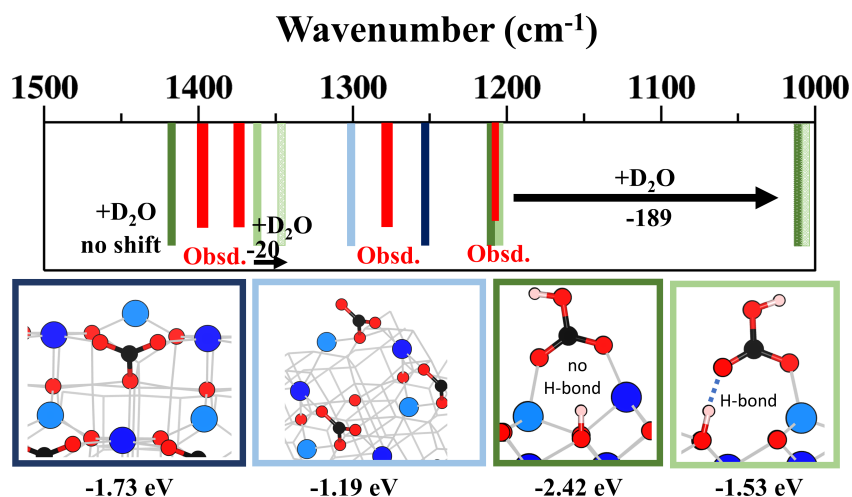


Abbildung 3: Wavenumbers obtained for the most relevant structures given below the stick chart. The OH bending mode in bicarbonates suffers a substantial red-shift of ca. 190 cm^{-1} upon dosing D_2O . Corresponding adsorption energies (eV) are given below structures. Red bars indicate observed wavenumbers.

and associated with correspondingly colored figure frames). Moreover, effects upon dosing deuterated water (D_2O) are also displayed (black arrows) and adsorption energies for each structure are provided below (correction for vdW dispersion is included).

These results represent a careful characterisation of the regular and metal-rich magnetite (111) surface, because the $\text{Fe}_{\text{tet}1}$ “single metal” and $\text{Fe}_{\text{oct}2}$ “double metal” terminated surfaces are thermodynamically comparably stable over wide ranges of the chemical potential of oxygen. Preparation conditions decide, which one will be accommodated. The latter may serve as a model for more complex surfaces involving defects, as e.g. line defects or steps (island formation, see [6]), which may expose metal-rich edges.

On the $\text{Fe}_{\text{tet}1}$ terminated surface, the CO_2 adsorbs molecularly with an adsorption energy ranging between -0.1 and -0.2 eV . This result is consistent with recent TPD experiments (see [4]). The thermodynamically slightly less stable, hence competing, $\text{Fe}_{\text{oct}2}$ terminated surface binds the CO_2 stronger and forms carbonate species. Results for this part of the project confirm the $\text{Fe}_{\text{tet}1}$ termination as the regular surface structure [6] when applying established preparation conditions.

Regarding the formation of carbonate at the so-called O_b position in the $\text{Fe}_{\text{oct}2}$ terminated surface (note the “cup-like structure” in Figure 2), computed wavenumbers agree well with observed band positions. Very stable bicarbonate species are shown to exist on the surface, given the presence of adventitious water or especially when water is intentionally co-dosed. The precise structure of bicarbonate, i.e., bidentate, bridging, or H-bonded motifs, affects the eigenenergies of vibrations noticeably. These results provide important characterisation of pristine, metal-

rich, and hydrated $\text{Fe}_3\text{O}_4(111)$ surfaces and could only be obtained by virtue of DFT.

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Weitere Informationen

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Förderung

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