Coverage Effect of the CO2 Adsorption Mechanisms on CeO2(111) by First Principles Analysis

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Abstract: The adsorption of carbon dioxide on CeO2(111) has been studied using density functional theory. At low coverage (1/9 monolayer), CO2 is found to preferably adsorb in a monodentate configuration forming a carbonate species with a surface O atom. In this configuration, the CO2 molecule is bent with an O-C-O angle of 129 degrees and a remarkable elongation (to 1.27 angstrom) of the C-O bond length compared to the gas phase molecule, indicating a high degree of CO2 activation. A similar activation is observed when the CO2 molecule adsorbs as bidentate carbonate; however, this configuration is less stable. Linear configurations are found to adsorb very weakly at low coverage by physisorption. Increasing the coverage leads to a decrease of the stability of mono- and bidentate configurations which can be attributed to repulsive interactions between adjacent adsorbates and the limited capacity of the CeO2(111) surface to donate electrons to the adsorbates. In contrast, the binding energy of linearly adsorbed CO2 is shown to be coverage independent. At coverages >1/4 monolayer, we have also addressed the stability of mixed configurations where monodentate, bidentate, and linear species are present simultaneously on the surface. The most stable configurations are found when 1/3 monolayer CO2 is bound as monodentate species, and additional molecules are physisorbed forming partial layers of linear species. Analysis of the projected density of states has shown that the orbitals of linear species in the first partial layer lie at lower energies than the ones of the second partial layer suggesting stabilization of the former through interactions with preadsorbed monodentate species. These findings provide fundamental insight into the CO2 adsorption mechanism on CeO2 and potentially assist the design of new Ce-based materials for CO2 catalysis.

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Coverage effect of the CO$_2$ adsorption mechanisms on CeO$_2$(111) by first principles analysis

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ABSTRACT

The adsorption of carbon dioxide on CeO$_2$(111) has been studied using density functional theory. At low coverage (1/9 monolayer), CO$_2$ is found to preferably adsorb in a monodentate configuration forming a carbonate species with a surface O atom. In this configuration, the CO$_2$ molecule is bent with a O-C-O angle of 129° and a remarkable elongation (to 1.27 Å) of the C-O bond length compared to the gas phase molecule, indicating a high degree of CO$_2$ activation. A similar activation is observed when the CO$_2$ molecule adsorbs as bidentate carbonate, however, this configuration is less stable. Linear configurations are found to adsorb very weakly at low coverage by physisorption. Increasing the coverage leads to a decrease of the stability of monodentate and bidentate configurations which can be attributed to repulsive interactions between adjacent adsorbates and the limited capacity of the CeO$_2$(111) surface to donate electrons to the adsorbates. In contrast, the binding energy of linearly adsorbed CO$_2$ is shown to be coverage independent. At coverages >1/4 monolayer, we have also addressed the stability of mixed configurations where monodentate, bidentate and linear species are present simultaneously on the surface. The most stable configurations are observed when 1/3 monolayer CO$_2$ is bound as monodentate species and additional molecules are physisorbed linearly. Analysis of the projected density of states has revealed that the orbitals of linear species in the first partial layer on top of monodentate ones are shifted to lower energies compared to the second partial layer suggesting stabilization of the former. These finding provide fundamental insight into the CO$_2$ adsorption mechanism on CeO$_2$ and potentially assist the design of new Ce-based materials for CO$_2$ catalysis.
INTRODUCTION

Rare earth metal oxides such as CeO\(_2\), La\(_2\)O\(_3\), Yb\(_2\)O\(_3\) and Lu\(_2\)O\(_3\) are highly interesting materials for a wide range of applications, for example as gate insulators\(^1,2\), abrasive materials\(^3,4\), catalysts in automotives\(^5\) or for syngas production\(^6\). The most interesting and studied metal oxide among these is ceria. Due to its potential to store and release oxygen depending on the process conditions it is a superior catalyst for CO oxidation and NO\(_x\) reduction reaction\(^5,7,8\) but also for hydrogenation of CO\(_2\)\(^9,10\).

Hydrocarbon production from CO\(_2\) is in particular interesting since it provides high energy density fuel from CO\(_2\) which is omnipresent in our environment. The dominating mechanism for this process is the Sabatier reaction (I). The reaction itself is exothermic. However, remarkable activation barriers are present due to the high thermodynamic stability of CO\(_2\)\(^12\). The activation barriers can be decreased when the linear CO\(_2\) molecule transforms into a bent configuration prior to the hydrogenation reaction. The bent CO\(_2\) is ca. 0.5 eV\(^12\) less stable than the linear molecule facilitating subsequent reactions such as CO\(_2\) dissociation or hydrogenation.

Numerous studies have been conducted on the adsorption and activation of CO\(_2\) on metal surfaces such as Cu\(^13-16\), Pt\(^17,18\), Pd\(^19,20\) and Fe\(^16,21,22\) where the Fe(110) surface has been identified to be most suitable for CO\(_2\) activation\(^23\). This has been attributed to the elongation of one of the C-O bonds (to ca. 1.30 Å) and a remarkable charge transfer (0.83 e\(^-\)) from the surface to the CO\(_2\) molecule\(^23\). The most widely used metals for CO\(_2\) methanation, however, are Ni and Rh\(^11\). Using DFT calculations, it has been verified, that the reaction on Ni involves the formation of the bent CO\(_2\) intermediate\(^24\).

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad (\text{-252 kJ/mol}^{11}) \quad (\text{I})
\]
Density functional theory (DFT) calculations of the adsorption mechanism on metal oxides have revealed that CO$_2$ adsorbs preferably in a linear configuration on most monoxides such as TiO, CrO, VO and MnO.\textsuperscript{25} The same behavior has been observed on TiO$_2$\textsuperscript{26,27} and LaMnO$_3$\textsuperscript{28}. In contrast, favorable bent geometries were determined on CaO and FeO.\textsuperscript{25} The different adsorption mechanisms can be attributed to the acidity of the metal oxide surface.\textsuperscript{29,30} In this scheme, a molecule adsorbing on the metal oxide surface is regarded as Lewis base when reacting on the metal cation and as Lewis acid when reacting on the O$^{2-}$ site. Most metal oxide surfaces react as Lewis acids on which organic molecules are adsorbed without dissociation. Basic metal oxides, on the other hand, rather lead to dissociation of organic molecules and, in the case of CO$_2$, promote the formation of a bent CO$_2^-$ species including a charge transfer from O$^{2-}$ sites to the CO$_2$ species.

In experimental studies using IR and X-ray photoelectron spectroscopy the presence of bent carbonate species on CeO$_2$ upon CO$_2$ adsorption has been observed\textsuperscript{31} suggesting the CeO$_2$ surface to react as Lewis base in the CO$_2$ adsorption process. Theoretical evidence from DFT calculations on the adsorption processes on CeO$_2$, however, is rare. This is mainly due to the complex electronic structure of CeO$_2$ exhibiting highly localized 4f states about 3 eV above the valence band.\textsuperscript{32,33} Upon reduction of Ce$^{4+}$ to Ce$^{3+}$ these states become occupied\textsuperscript{34-36} and an accurate description of the electronic structure with standard DFT gets problematic\textsuperscript{37}. Nevertheless, standard DFT calculations have shown to correctly describe the stoichiometric CeO$_2$ bulk and surface\textsuperscript{37-39} as long as no reduction of Ce$^{4+}$ to Ce$^{3+}$ is involved. In fact, comparing standard DFT with DFT+U calculations it has been shown that even CO adsorption on the (111) and (110) surface can be accurately treated with standard DFT.\textsuperscript{7} Results of both standard DFT and DFT+U methods were in reasonable agreement with experimental studies.\textsuperscript{40,41} While CO
physisorbed on the (111) surface, a carbonate species with two adjacent surface O atoms was formed when adsorbed on the (110) surface. Calculations based on the DFT+U method have been applied recently for the investigation of CO$_2$ adsorption on stoichiometric and reduced CeO$_2$(110) showing the formation of a bent CO$_2$ species on the reduced surface. Only weak adsorption without geometric deformation has been observed on the stoichiometric surface.

In this study, CO$_2$ adsorption has been investigated on the CeO$_2$(111) surface using standard DFT calculations. Different adsorption mechanisms are examined for CO$_2$ molecules at coverages ranging from 1/9 to 1 monolayer (ML). The coverage effect for the most stable configurations is discussed in terms of stability, geometry and electronic structure. The results are further compared to CO$_2$ adsorption on other metal and metal oxide surfaces giving an estimate of the degree of CO$_2$ activation. Selected adsorption modes are additionally simulated using hybrid functional (PBE0) calculations and compared to the results of standard DFT verifying the qualitative accuracy of the later.
THEORETICAL METHODS

The calculations of this study are based on DFT and are carried out with the Quickstep\textsuperscript{44} module of the CP2K program package, a suite of programs developed for efficient electronic structure calculations and molecular dynamics based on the Gaussian and plane waves formalism\textsuperscript{45}. Valence electrons are treated explicitly whereas interactions with the frozen atom core are described with norm-conserving pseudopotentials.\textsuperscript{46} Here, 4, 6 and 12 electrons are explicitly considered in the valence shell for C, O and Ce atoms, respectively. A triple-zeta valence plus polarization (TZV2P) basis set, optimized according to the Mol-Opt method\textsuperscript{47}, is adopted for C and O atoms. The basis set for Ce is optimized with the atomic ground state\textsuperscript{45} and has the form of a double-zeta valence (DZV) basis set without polarization. For auxiliary plane wave expansion of the charge density, the energy cutoff is set to 1000 Ry. Exchange-correlation potentials are modeled within the general gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional.\textsuperscript{48} The GGA formalism has been shown to yield reasonably accurate results for the CeO\textsubscript{2} bulk\textsuperscript{37} and its (111) surface\textsuperscript{38,39}. To confirm the suitability of the standard DFT method for the simulation of CO\textsubscript{2} adsorption on CeO\textsubscript{2}(111), selected configurations were additionally calculated hybrid functional calculations are conducted for selected configurations using the PBE\textsuperscript{43} hybrid functional with 20% exact exchange and DFT+U calculations with the PBE functional and a U value of 5 eV. Some configurations are further optimized introducing a Grimme D2\textsuperscript{49} potential to account for van der Waals interactions between adsorbates and surface slab. It has been verified that 15 Å are sufficient to eliminate effects of the van der Waals interactions on the binding energy. All calculations are performed with periodic boundary conditions.
The size of the simulated supercell is a critical parameter in real space calculations. It defines the accuracy of the physical properties of the system and the computational time frame needed. The supercell size has been optimized to reach convergence of the bulk properties such as lattice parameter and total energy per CeO2 unit. A supercell containing 81 atoms has been found to be sufficient for the evaluated bulk properties. In this supercell, the primitive unit cell of fluorite CeO2 is repeated three times in all spatial directions. The optimized lattice parameter for this set-up resulted in 5.48 Å which is in good agreement with previous calculations (5.47 Å)\(^{37}\) and experiments (5.41 Å)\(^{50}\) (Table 1). The (111) surface is realized by introducing a vacuum of 15 Å along the [111] direction to avoid interaction with the periodic images of the slab. Convergence of the surface energy within 0.02 J/m\(^2\) with respect to the slab thickness is reached with six O-Ce-O trilayers. In a p(3x3) expansion of the (111) surface unit cell, the surface energy is calculated to be 0.74 J/m\(^2\) in excellent agreement with previous calculations using the DFT+U method (0.72 J/m\(^2\))\(^{51}\) (Table 1). The band gap between the O-2p and Ce-4f states of the clean CeO\(_2\)(111) slab is calculated to be 1.99 eV, which is again in good agreement with previous calculations using the PBE exchange-correlation functional (2 eV)\(^{37}\).

Depending on the CO\(_2\) coverage, different surface dimensions are used: slabs with p(3x3), p(4x3) and p(4x4) expansions of the surface unit cell corresponding to a total of 9, 12 and 16 active Ce-sites, respectively. In all cases, the slab consists of six trilayers of which the top three are allowed to relax while the three bottom trilayers were fixed to simulate the bulk properties. Adsorption of CO\(_2\) was simulated on one exposed surface. The CO\(_2\) binding energies \((E_B)\) is calculated according to:

\[
E_B = \frac{E_{\text{slab+}n\text{CO}_2} - \left(E_{\text{slab}} + n \cdot E_{\text{CO}_2, g}\right)}{n},
\]

(II)
where \( n \) is the number of adsorbed species on the described surface and \( E_{\text{slab}+n\text{CO}_2} \) denotes the energy of the surface slab plus \( n \) adsorbates. Equation (II) implies that negative values for \( E_B \) indicate exothermic desorption processes. The energy of an isolated \( \text{CO}_2 \) molecule \( (E_{\text{CO}_2,\text{g}}) \) is calculated in a periodically repeated cell of 15x15x15 Å. Optimization of the geometry of the \( \text{CO}_2 \) molecule in gas phase resulted in an O-C-O angle \( (\alpha_{\text{OCO}}) \) of 180° and a C=O bond length \( (d_{\text{C}-\text{O}}) \) of 1.17 Å in good agreement with experiments (1.16 Å)\(^{52} \) (Table 2). Geometrical properties of adsorbed \( \text{CO}_2 \) are characterized by \( \alpha_{\text{OCO}} \), the C-O bond length \( (d_{\text{C}-\text{O}} \text{ or } d_{\text{C}-\text{O}1} \text{ and } d_{\text{C}-\text{O}2}) \) and the adsorption height which is indicated by the distance of C to the closest surface O atom \( (d_{\text{C}-\text{Osurf}}) \) for carbonate species and by the height of C above the first layer of Ce \( (\Delta z_{\text{CO}_2}) \) for linear species (Figure 1).

Mulliken population analysis\(^{53} \) is used to determine the charge transfer between surface and adsorbate. Further analysis of the electronic structure is carried out by projection of the Kohn-Sham orbitals at single atoms (projected density of states, PDOS) and the summation of the projections at the relevant atoms when multi-atomic groups are of interest such as the \( \text{CO}_2 \) molecule or selected slab atoms. In this respect, the PDOS denoted as “total” as in Figure 2 and Figure 9 corresponds to the summation of the projections at all atoms of the system. The DOS is shifted so that the upper edge of the valence band of the \( \text{CeO}_2(111) \) slab is positioned at 0 eV.
RESULTS AND DISCUSSION

Adsorption Mechanisms of Isolated CO₂ (1/9 ML). Stability and Geometry. The adsorption mechanism of isolated CO₂ is simulated on a CeO₂(111) slab with a p(3x3) surface unit cell at a CO₂ coverage of 1/9 ML. At this coverage, it is expected that interactions between adsorbates are negligible and the adsorbed species can be assumed to be isolated. Optimization of the geometry leads to three stable configurations: i) mono- (Figure 1a,d) and ii) bidentate (Figure 1b,e) carbonate species in a bent conformation and iii) linearly adsorbed CO₂ (Figure 1c,f). The monodentate bent CO₂ forms spontaneously from a linear configuration located 1.7 Å above the surface indicating that no activation energy is required for the formation of the bent CO₂ molecule (see Figure S1 for initial configurations of all stable species). However, using nudge elastic band (NEB) calculations, an energy barrier of 0.2 eV is observed for the transition from the linear to the monodentate configuration (Figure S2). Geometric properties of the transition state can be found in the Supporting Information (Figure S2). Among the calculated configurations, the monodentate species configuration is most stable with a binding energy of -0.31 eV, followed by the bidentate one with $E_B = -0.12$ eV. Both mono- and bidentate configurations are additionally optimized with PBE0 calculations resulting in a binding energy of -0.68 eV and -0.42 eV, respectively (Table 2, Figure S3). The lower values of the binding energy indicate stronger binding compared to standard DFT calculations. Using the DFT+U approach, binding energies are determined to be -0.28 and -0.04 eV for the mono- and bidentate species, respectively, and thus reasonably close to the PBE results (Table 2, Figure S3). Results of the two methods are in qualitative agreement with the monodentate species being more stable than the bidentate one and it can be concluded that the results obtained with standard DFT calculations are qualitatively correct. Moreover, no reduced cerium ions are involved in the CO₂
adsorption on stoichiometric CeO$_2$(111) additionally justifying the use of standard DFT calculations.

Remarkable conformational changes are observed in the bent configurations compared to the linear CO$_2$ molecule in gas phase (Table 2). In the mono- and bidentate configuration, $a_{OCO}$ decreases remarkably to 130° and 129° (Table 2), respectively. At the same time, both C-O bonds elongate to 1.27 Å in the monodentate configuration which is close to the literature value of a regular C=O bond of carbonyl (1.23-1.26 Å)$^{54}$. Asymmetric bond elongation is observed in the bidentate configuration with 1.22 Å for $d_{C-O1}$ and 1.30 Å for $d_{C-O2}$ (see Figure 1 for definition of geometrical quantities). Both distances are in the range of a (partial) double C-O bond. Due to the longer $d_{C-O2}$, we suggest that, in this case, separation of one O atom is facilitated.

Previously, it has been shown that CO$_2$ adsorption on pure metal surfaces is only stable and highly activated in the case of Fe$^{23}$, whereas endothermic binding energies have been determined for various other metals such as Ni, Rh, Co and Pd$^{23}$. The exothermic binding energies found here for mono- and bidentate configurations indicate that the CO$_2$ bond strength on CeO$_2$ is comparable to the one on Fe(110). Furthermore, the geometry of the monodentate configuration is similar to the most stable one found on a Ni(110) surface.$^{55}$ In contrast to metal surfaces, most metal oxides such as TiO$_2$$^{56}$, TiO, ScO and MnO$^{25}$ favor a linear CO$_2$ adsorption over the formation of bent mono- or bidentate species. Different behavior has only been shown on FeO where monodentate adsorption and on CaO where bidentate adsorption is favored.$^{25}$ It is thus suggested, that CeO$_2$ induces catalytic reaction mechanisms similar to the latter materials.

The distance of C ($d_{C-O\text{surf}}$) to the closest surface O atom (O$_\text{surf}$) in the monodentate configuration is found to be 1.38 Å indicating a partial double bond between the C atom and the
surface O atom. For bidentate species it is 1.41 Å, thereby somewhat larger and corresponding to a single C-O bond. This explains its weaker bond strength.

Computational investigation of CO adsorption on CeO$_2$(110)$^7$ has revealed bond characteristics comparable to the one found here for the monodentate configuration. There, carbon monoxide has been shown to form a carbonate species with two surface O atoms, where the bond length between the C atom and the O atoms of the surface has been determined to be 1.35 Å.$^7$

Geometrical properties obtained with PBE0 are represented in Table 2. Using hybrid functional calculations the bond lengths tend to be smaller compared to PBE results. However, in general, only marginal deviations are observed between the different methods.

Adsorption of linear CO$_2$ (Figure 1c,f) is endothermic with a binding energy of +0.02 eV. This result is obtained without consideration of dispersion interactions. Introducing a D2 Grimme-potential$^{49}$ to account for van der Waals interactions, the binding energy of the reoptimized linear configuration is found to be -0.07 eV indicating the adsorption of linear CO$_2$ to be exothermic. Hardly any changes in geometry compared to the gas phase CO$_2$ molecule are observed for the linear configuration. For the simulation without D2, the O-C-O angle decreases slightly to 177.6° whereas $d_{C-O}$ remains at 1.17 Å for both C-O bonds. The height of the molecule above the surface ($\Delta z_{CO2}$, Figure 1c) is 3.52 Å (Table 2). These results indicate weak interactions between the linear CO$_2$ molecule and the CeO$_2$(111) surface.

Electronic Structure. A significant charge transfer from the CeO$_2$ surface to the CO$_2$ group was observed in both carbonate configurations resulting in a total charge of -0.46 and -0.40 for the mono- and bidentate species, respectively (Table 2). This is comparable to the charge transfer observed from Pd and Cu surfaces to CO$_2$$^{23}$ and is an indication of the basic character of the CeO$_2$ surface.$^{29}$ On various other metal oxides such as TiO$_2$$^{56}$, TiO, SeO and MnO$^{25}$ a different
behavior has been observed. Linear adsorption has been found to be favored demonstrating an acidic character of these surfaces. Similar behavior is observed here in the case of linear adsorption of CO\textsubscript{2} on CeO\textsubscript{2}(111) where the CO\textsubscript{2} molecule has a minor positive charge (+0.03). In other words, depending on the adsorption mechanism, the CeO\textsubscript{2}(111) surface can act both as Lewis base or weak acid, however, its basic character is predominant.

Further analysis has been done on the DOS, shown in Figure 2 for monodentate adsorption. The adsorption leads to the evolution of one additional state at the top of the valence band attributed to hybridization of the p-type orbitals of the surface O atom with the orbitals of the CO\textsubscript{2} molecule (see Figure S4 for further details). In the monodentate configuration, this state is located 0.33 eV above the valence band (Figure 2). This was confirmed by PBE0 calculations where this state was found 0.21 eV above the valence band (Figure S5). In general, the DOS obtained with the PBE0 method is similar to the one with PBE (see Figure S5). However, the binding orbital between C and O\textsubscript{surf} found about 6 eV below the valence band are shifted by 0.67 eV to lower energies. Furthermore, the split between binding and anti-binding CO\textsubscript{2} orbitals is enlarged using the PBE0 method. This explains the lower binding energy that was found with PBE0 for the monodentate configuration.

Upon formation of a bidentate species, it is found at higher energy (0.62 eV above the valence band, Figure S6) rationalizing the weaker bond of bidentate CO\textsubscript{2} on the CeO\textsubscript{2}(111) surface. The evolution of additional CO\textsubscript{2} states above the CeO\textsubscript{2} valence band has been reported previously as well for the adsorption of CO on CeO\textsubscript{2}(110).\textsuperscript{7} In the latter case, the additional states are formed 0.3 eV above the valence band.

The acidic nature of the bent CO\textsubscript{2} molecule has been described previously\textsuperscript{12} and it promotes the basicity of the CeO\textsubscript{2} surface. Bending of the CO\textsubscript{2} molecule leads to splitting of the
unoccupied \( \Pi_u \) orbital of the linear CO\(_2\) molecule holding \( C_{2\infty} \) symmetry into two orbitals, one of which is found at remarkably lower energy.\(^{12}\) This favors the transfer of substrate electrons to the CO\(_2\) molecule accompanied by the occupation of this orbital. The DOS of gas phase CO\(_2\) and adsorbed species obtained from our calculations confirm this behavior (Figure 3). Upon bending, the HOMO of the linear CO\(_2\) molecule splits into two distinguishable orbitals at slightly different energies (Figure 3). The same is true for the LUMO. Here, the splitting results in a significant shift of one of the non-degenerate orbitals to lower energies (Figure 3a, state 2). HOMO and LUMO of the bent gas phase CO\(_2\) are shown in Figure 3b. When CO\(_2\) is adsorbed on CeO\(_2\)(111) as either of the bent species, the shape of HOMO is similar to the one of the gas phase (Figure 3b). However, several states of the valence band resemble the shape of the LUMO of CO\(_2\) and can be attributed to hybridized carbonate states.

Furthermore, the PDOS of the adsorbed CO\(_2\) species shows a shift of the orbitals of the bidentate species by 0.29 eV to higher energies compared to the monodentate species (Figure 3). This value is in line with the difference in binding energy of the two adsorption mechanisms indicating that it is the major driving force for the higher stability of the monodentate species. The bonding mechanism of the two species, however, is identical.

It has been proposed previously that charge transfer to the bent CO\(_2\) molecule and thus formation of an anionic species leads to the occupation of the hybridized LUMO.\(^{12}\) The resulting orbitals have bonding character between C and O\(_\text{surf}\) and anti-bonding character between C and the O atoms of the molecule. The anti-bonding character leads to the elongation of the intramolecular C-O bonds which has been found for both mono- and bidentate species and is responsible for the activation of the CO\(_2\) molecule.\(^{23}\)
Bond formation between O$_{\text{surf}}$ and C is additionally confirmed by the charge density difference shown in Figure 4. Yellow lobes represent excess of electrons which are mainly found between O$_{\text{surf}}$ and C and suggest the occupation of the LUMO of the bent gas phase CO$_2$ (Figure 3b, state 2). This is further supported by the electron excess around the O atoms of the CO$_2$ molecule, which resembles the shape of the gas phase LUMO. On Ni(110), being one of the best metal-based catalysts for CO$_2$ methanation, similar bond characteristics between CO$_2$ and the surface have been reported based on charge density differences for CO$_2$ on Ni(110) suggesting similar CO$_2$ reaction mechanisms on CeO$_2$(111) and Ni(110). This demonstrates comparable chemical interaction of Ni and CeO$_2$ with CO$_2$ and it is thus proposed that mechanisms and properties of reactions involving CO$_2$ are similar on these surfaces.

The charge density difference of the bidentate species observed between O$_{\text{surf}}$ and C (Figure 4b) is equivalent to the one of the monodentate species (Figure 4a). Additionally, the electron excess around the O2 atom is shifted towards the interacting surface Ce atom (Ce$_{\text{surf}}$) indicating polarization of O2 and Ce$_{\text{surf}}$ orbitals. However, no chemical bond between O2 and Ce$_{\text{surf}}$ is evident from the charge density difference.

In contrast to the bent CO$_2$ species, the partial DOS of the linearly adsorbed CO$_2$ is identical to the one of the free molecule lacking any indication of hybridization of the surface orbitals (Figure S63). Thus it can be concluded that the linearly adsorbed molecule does not form chemical bonds and does not cause any perturbation to the surface.

**Coverage Effect on Single-Phase Adsorption Mechanisms. Stability and Geometry.** In addition to the investigation of mechanisms of isolated CO$_2$ at 1/9 ML, adsorption is simulated at higher coverages (1/4, 1/3, 1/2, 2/3, 1 ML) in the mono-, bidentate and linear configuration. The resulting binding energies as a function of the CO$_2$ coverage are shown in Figure 5a.
coverage effect is observed when CO$_2$ is exclusively physisorbed in a linear configuration. The binding energy is between 0.0 and +0.05 eV for all calculated coverages (1/9-1 ML). The intramolecular geometry of linear CO$_2$ is not affected by the coverage. However, an increase of the average distance ($\Delta z_{CO2}$) from the surface (Table 2) is noticeable with increasing coverage from 1/2 (3.43 Å) to 1 ML (3.92 Å), which can be attributed to repulsive interactions between adsorbates and the formation of a second partial layer of linear CO$_2$.

In contrast to linearly adsorbed CO$_2$, a significant influence of the coverage on the binding energy is observed for both carbonate configurations. The bond strength for monodentate species decreases monotonously from $E_B=-0.31$ to +0.36 eV with increasing coverage from 1/9 to 2/3 ML. This is, similar to the case of linear adsorption, an indication of repulsive interactions between the adsorbates. In fact, no stable configuration for monodentate species at 1 ML is found. Relaxing the geometry of such a configuration results in a mixed state with linear CO$_2$ and carbonate species. The change in binding energy of the monodentate configuration is nearly linearly dependent on the coverage up to 1/2 ML ($E_B=-0.08$ eV) followed by a remarkable increase (loss of bond strength) at 2/3 ML ($E_B=+0.36$ eV) (Figure 7). The diminishing bond strength is accompanied by notable changes in the geometry of the configurations, especially at high coverages. This is in particular observable in the monodentate configuration at 2/3 ML due to the oversaturation of Ce surface sites. In the stable monodentate configuration CO$_2$ interacts with two Ce surface atoms (Figure 1d). Thus, all active sites are occupied already at a coverage of 1/2 ML resulting in a rotation of adsorbed CO$_2$ away from the corporate surface Ce atom at 2/3 ML (Figure 6a,d) and a drastic decrease in bond strength (increase of $E_B$, Figure 5a). Furthermore, the distance between the C atom (Ce$_{surf,2}$) and O$_{surf}$ ($d_{C-Osurf}$) of monodentate species increases from 1.38 (1/3 ML) to 1.41 Å (2/3 ML) (Figure 5b). No change in $d_{C-Osurf}$ is observed
at lower coverages. Thus, we conclude that no interactions between adjacent adsorbates are present at coverages <1/3 ML.

Similar trends are observed in binding energy and geometry of the bidentate species. Here, $E_B$ increases linearly from -0.12 to +0.71 eV with increasing coverage from 1/9 to 1 ML indicating a loss in bond strength at high coverages. Caused by repulsive interactions between adsorbates this leads to a change from exothermic to endothermic adsorption between 1/3 and 1/2 ML coverage (Figure 5a). Bidentate species interact only with one Ce surface atom which implicates saturation of active sites not until 1 ML coverage and allows for a stable configuration even at 1 ML (Figure 6b,e). In the bidentate configuration, $d_{C-O_{surf}}$ increases only marginally up to 1/3 ML (1.41-1.42 Å) followed by a remarkable increase to 1.48 Å at 1 ML. This suggests a limited capacity of the CeO$_2$(111) surface to interact with CO$_2$ molecules.

Electronic Structure. The charge transfer between CeO$_2$ surface and CO$_2$ adsorbates as a function of the coverage is depicted in Figure 7. When CO$_2$ is adsorbed as monodentate species the charge transferred per CeO$_2$ surface unit increases linearly with the coverage up to 1/3 ML. At higher coverages, it shows a convex behavior converging towards ca. 0.18 e$^\prime$/CeO$_2$ and demonstrating the limits of CeO$_2$ as e$^\prime$ donor. Thus, at coverages >1/3 ML, the CeO$_2$ substrate is no longer capable to donate the optimal amount of electrons to each adsorbed CO$_2$ species which contribute to the occupation of LUMO of the unbound species (Figure 3b), resulting in a loss of bond strength (Figure 5a). It is suggested that interactions between CO$_2$ adsorbates influence the capacity of each single CO$_2$ to uptake electrons and thus also contribute to a limited charge transfer. This is further supported by the behavior of bidentate species. At low coverage (1/9 ML), basically the same charge is transferred to mono- and bidentate species. However, the convex behavior of the charge transfer already at low coverages causes the curve of bidentate
species to lie below the one of monodentate species. Moreover, the charge transfer to bidentate species converges to 0.13 $e^-$/CeO$_2$ at higher coverages which is about 0.05 $e^-$/CeO$_2$ lower compared to monodentate species.

In summary, a CO$_2$ molecule adsorbed in a bent configuration (mono- and bidentate) acts as Lewis acid accepting electronic charge from the surface at all coverages. The limitation of charge transfer given by the value at the convergence at high coverage can act as an analyzer of the degree of basicity of the CeO$_2$ surface. In contrast, for linear adsorption, minor charge transfer (0.009±0.005) is observed from the CO$_2$ molecule towards the CeO$_2$ surface. In this case, the surface acts as a weak acid.

**Mixed Adsorption Mechanisms at High Coverage (>1/4 ML). Stability.** In addition to the simulations where all CO$_2$ are adsorbed in the same configuration, calculations are performed at coverages >1/4 ML for mixed adsorption mechanisms where different configurations of CO$_2$ exist at the same time. At 1/4, 1/2 and 2/3 ML coverage, mixed configurations with monodentate and either linear (mono+lin) or bidentate (mono+bi) species are simulated. At 1 ML, additional configurations are investigated with all three adsorption configurations present simultaneously. The average binding energy for both types of mixed configurations at 1/4 ML shows a linear behavior with increasing fraction of CO$_2$ adsorbed as monodentate species (Figure 8a). In fact, the pure monodentate adsorption is found to be the most stable configuration at 1/4 ML. The linear decrease in binding energy (increase in bond strength) with increasing amount of monodentate species evidences unperturbed superposition of the binding energies of single-phase configurations (monodentate ratio equal to 0 or 1) indicating negligible interactions between adsorbates.
A similar behavior is observed at 1/2 ML coverage in the mono+bi configuration (Figure 8b, triangles). In contrast, in the mono+lin (Figure 8b, circles) configuration, the bond strength is maximal (minimum in $E_B$) when 2/3 of the CO$_2$ molecules are adsorbed in a monodentate configuration, having a binding energy of -0.17 eV. This ratio of monodentate species corresponds to a coverage of 1/3 ML. This is identical to what is found at 2/3 and 1 ML for the mixed configurations: the bond strength is maximal for a fraction of monodentate species of 1/2 and 1/3, respectively. Again, in both cases, this fraction corresponds to a total of 1/3 ML of monodentate species. At 1 ML, additional configurations are calculated at the minimum, where 1/3 ML monodentate species are adsorbed together with both bidentate and linear species. The coverage of bidentate species in these configurations is 1/9, 1/4 and 1/3 ML. The highest value of $E_B$ (least stable) is found at 1/3 ML bidentate and it decreases monotonously with decreasing amount of bidentate species.

In summary, at all investigated coverages a configuration with 1/3 ML monodentate species and additional linear adsorption is most stable. This suggests that CO$_2$ initially binds as monodentate carbonate to the CeO$_2$(111) surface up to 1/3 ML and further CO$_2$ adsorption results in the formation of linear species.

*Geometry.* Geometry of mixed adsorption mechanisms will be discussed here only for the most stable configurations. These are the mixed configurations where 1/3 ML is adsorbed as monodentate carbonate and additional CO$_2$ is adsorbed linearly (Table 3). For completeness, results for the configuration with monodentate and linear species at 1/4 ML total coverage are reported as well in Table 3.

The C-O bond length ($d_{C-O}$, Figure 1) is significantly larger in the monodentate (1.27 Å) than the linear (1.17 Å) species at all coverages, similar to the results for homogenous adsorption
mechanisms. It is independent of the total CO$_2$ coverage demonstrating that the monodentate species remain in an activated conformation upon further adsorption of linear CO$_2$ species. Linear species adsorb at different heights depending on the coverage. Linearly adsorbed CO$_2$ molecules in the first partial layer (1/3 ML) align along the [11\bar{2}] direction in between the monodentate species (Figure 6f) and are in average $\Delta z_{\text{CO}_2} \approx 4$ Å above the surface. Starting the optimization from different initial configurations of the first partial layer of linear CO$_2$ always results in this configuration demonstrating attractive interactions with the monodentate species. Additional CO$_2$ molecules adsorb at ca. 5 Å above the surface.

As discussed above, the $d_{\text{C-Osurf}}$ distance for homogenous adsorption of monodentate species remarkably increases from 1.38 to 1.41 Å with increasing coverage from 1/3 to 2/3 ML (Figure 5b). In contrast, for a mixed adsorption of monodentate and linear species, it remains constant at 1.38 Å. This again indicates that the additional linear molecules do not affect the configuration of the chemisorbed monodentate species.

Electronic Structure. As discussed above, the average charge of a CO$_2$ molecule in the monodentate configuration increases steadily with increasing coverage. In contrast, in the mixed mono+lin configuration, the average charge CO$_2$ in a monodentate configuration decreases slightly when linear species are additionally adsorbed (Figure S74) at a total coverage >1/3 ML. This is accompanied by a marginal increase in charge of the linear CO$_2$ species and indicates a charge transfer from the linear to the monodentate species.

Figure 9 shows the PDOS on the orbitals of the different CO$_2$ species observed in the most stable mixed (mono+lin) configuration at 1 ML (Figure 6c,f) where 1/3 ML is adsorbed as monodentate species and two partial layers of linear CO$_2$ can be distinguished. The orbitals of monodentate CO$_2$ lie at the same energy as the ones for the isolated monodentate configuration.
(Figure 2). On the other hand, the DOS of the two different linear species shows the characteristic bands of the gas phase CO$_2$ molecule. Interestingly, the bands of the linear CO$_2$ molecules closer to the surface are shifted to slightly lower energies compared to the more distant CO$_2$ species by ca. 0.4 eV. This demonstrates a stabilization of the first partial layer of linearly adsorbed CO$_2$ molecules due to the pre-adsorption of monodentate carbonate species and is confirmed by the charge transfer from linear CO$_2$ to the bent species and the alignment of the linear species in their geometry [11$ar{2}$] (Figure 4f).
CONCLUSIONS

Adsorption properties of CO$_2$ on a CeO$_2$(111) surface have been investigated with standard DFT calculations using the PBE exchange-correlation functional. Three stable configurations have been distinguished of isolated CO$_2$ (1/9 ML) species adsorbed on the CeO$_2$ surface: (i) monodentate carbonate, (ii) bidentate carbonate and (iii) linear species. In both carbonate configurations the CO$_2$ molecule is bent with the C atom forming a chemical bond to a surface O atom. The chemical bond formation has been confirmed by the change of geometry of the CO$_2$ molecule and the hybridization of its orbitals with the orbitals of the surface O. Analysis of the PDOS and the differential charge distribution suggest the occupation of the LUMO of a bent CO$_2$ in gas phase upon adsorption. In contrast to the bent configurations, the linear species is physisorbed. Geometry and electronic structure of the latter have been found to be identical to the ones of a gas phase CO$_2$. Among these three configurations, the most stable one is the monodentate species with a binding energy of -0.31 eV.

Upon formation of monodentate carbonate, the C-O bond elongates to 1.27 Å. This bond length is comparable to the one found for bent CO$_2$ on several metal surface such as Rh, Pd and Pt, indicating a similar CO$_2$ activation. A charge transfer of 0.46 e$^-$ has been observed from the CeO$_2$(111) to the monodentate CO$_2$ species demonstrating the basic character of the CeO$_2$(111) surface. It is in contrast to what has been observed on some other metal oxides such as TiO$_2$ where linear adsorption was favored.

The coverage effect has been investigated for the three stable configurations. It has been observed that the bond strength of both monodentate and bidentate species decreases with increasing coverage of CO$_2$, which can be attributed to the restricted charge transfer capacity of the CeO$_2$ substrate. This leads to a drastic loss of bond strength at coverages >1/3 ML. It has
been observed that the limit for electron donation per CeO$_2$ surface unit from the substrate to the adsorbate is lower for bidentate than for monodentate species.

Furthermore, mixed configurations have been investigated at coverages $>1/4$ ML where monodentate and either bidentate or linear species are adsorbed simultaneously. At 1 ML, additional tri-structural configurations have been examined where mono-, bidentate and linear species are present at the same time. It has been observed that mixed configurations with monodentate and linear species are most stable at all coverages. Different fractions of monodentate species have been simulated yielding a minimum of the binding energy when an absolute amount of 1/3 ML of monodentate specie is present on the surface.

These results lead us to the conclusion that CO$_2$ adsorbs as monodentate carbonate on the CeO$_2$(111) surface up to a coverage of 1/3 ML. At higher coverages, mixed CO$_2$ configurations are formed where multilayers of linear species adsorb above the monodentate species. The binding energy of such configurations has been shown to increase marginally to -0.11 eV at 1 ML. Analysis of the density of states has revealed that the first partial layer of linear CO$_2$ is stabilized by the pre-adsorbed monodentate species.

This study provides fundamental insight of the adsorption properties of CO$_2$ on CeO$_2$(111) demonstrating that CeO$_2$(111) is capable of activating CO$_2$ up to a certain coverage (1/3 ML). It is a basis for further investigation of CO$_2$ reaction mechanisms with hydrogen on CeO$_2$-based catalytic surfaces. Furthermore, dynamic studies, such as molecular dynamics or meta-dynamic simulations, are planned to be directly compared to experimental results of IR-spectroscopy at finite temperatures and pressure$^{31}$. These are expected to give a more realistic picture of the different adsorption mechanisms and properties of mixed adsorption at specific process parameters.
ACKNOWLEDGMENTS

We gratefully thank K.-H. Ernst for fruitful discussions from the experimental point of view. This work is financially supported by the Forschungskredit 2012 of University of Zurich under grant 57170203. Computational resources were generously provided by University of Zurich and a grant from the Swiss National Computer Center (CSCS) under project ID s89.

SUPPORTING INFORMATION

Supporting information contains the binding energies of CO$_2$ on CeO$_2$(111) for selected configurations calculated with the PBE0 method, the PDOS on s-, p- and d-type orbitals of CO$_2$ and O$_{surf}$ of the monodentate species, the PDOS of mono-, bidentate and linear species and the average charge per CO$_2$ molecule as a function of the coverage.

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REFERENCES


**Table 1.** Lattice parameter $a$ of CeO$_2$ bulk and surface energy $E_{\text{surf}}$ of its stoichiometric (111) surface calculated with different methods and compared to literature values.

<table>
<thead>
<tr>
<th>Method</th>
<th>$a$ [Å]</th>
<th>$E_{\text{surf}}$ [J/m$^2$]</th>
<th>reference</th>
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<tr>
<td>PBE</td>
<td>5.48</td>
<td>0.74</td>
<td>this work</td>
</tr>
<tr>
<td>PBE0(20%)</td>
<td>5.44</td>
<td>0.78</td>
<td>this work</td>
</tr>
<tr>
<td>PBE</td>
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<td>Ref$^{48}$</td>
</tr>
<tr>
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<td>Ref$^{51}$</td>
</tr>
<tr>
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<td>1.02</td>
<td>Ref$^{51}$</td>
</tr>
<tr>
<td>exp</td>
<td>5.41</td>
<td></td>
<td>Ref$^{50}$</td>
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Table 2. Binding energy ($E_B$), geometric properties (explained in Figure 1) and total charge of CO$_2$ in the gas phase and adsorbed in different single-phase configurations on the CeO$_2$(111) surface at 1/9, 1/2 and 2/3 ML coverage.

<table>
<thead>
<tr>
<th>Coverage</th>
<th>Configuration</th>
<th>$E_B$ [eV]</th>
<th>$d_{C-O1}(d_{C-O2})$ [Å]</th>
<th>$d_{C-Osurf}$ [Å]</th>
<th>$\Delta z_{CO2}$ [Å]</th>
<th>$\alpha_{COC}$ [$^\circ$]</th>
<th>Charge</th>
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<td>-</td>
<td>-</td>
<td>180.0</td>
<td>0.00</td>
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<tr>
<td>1/9 ML</td>
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<td>1.27</td>
<td>1.38</td>
<td>-</td>
<td>129.7</td>
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<tr>
<td></td>
<td>DFT+U</td>
<td>-0.28</td>
<td>1.27</td>
<td>1.38</td>
<td>-</td>
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</tr>
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<td>1.26</td>
<td>1.36</td>
<td>-</td>
<td>129.4</td>
<td>-0.54</td>
</tr>
<tr>
<td></td>
<td>PBE0(20%)$^a$</td>
<td>-0.65</td>
<td>1.26</td>
<td>1.36</td>
<td>-</td>
<td>129.4</td>
<td>-0.54</td>
</tr>
<tr>
<td></td>
<td>Bidentate</td>
<td>-0.12</td>
<td>1.22 (1.30)</td>
<td>1.41</td>
<td>-</td>
<td>129.2</td>
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<td>DFT+U</td>
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<td>-</td>
<td>3.52</td>
<td>177.6</td>
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<td>1/2 ML</td>
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<td>-</td>
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<td>-</td>
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<tr>
<td></td>
<td>Linear</td>
<td>0.00</td>
<td>1.17</td>
<td>-</td>
<td>3.43</td>
<td>177.8</td>
<td>0.03</td>
</tr>
<tr>
<td>2/3 ML</td>
<td>Monodentate</td>
<td>0.36</td>
<td>1.25</td>
<td>1.41</td>
<td>-</td>
<td>131.4</td>
<td>-0.27</td>
</tr>
<tr>
<td></td>
<td>Bidentate</td>
<td>0.43</td>
<td>1.20 (1.29)</td>
<td>1.46</td>
<td>-</td>
<td>131.6</td>
<td>-0.19</td>
</tr>
<tr>
<td></td>
<td>Linear</td>
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<td>-</td>
<td>3.92</td>
<td>178.6</td>
<td>0.01</td>
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</table>

$^a$ spin-polarized calculations
Table 3. Binding energy ($E_B$), geometric properties (see Figure 1) and total charge of CO$_2$ molecules adsorbed in mixed configurations (mono+lin) on CeO$_2$(111) surface at different coverages.

<table>
<thead>
<tr>
<th>coverage [ML]</th>
<th>$E_B$ [eV]</th>
<th>$d_{C-O}$ [Å]</th>
<th>$\alpha_{COC}$ [$^\circ$]</th>
<th>charge</th>
</tr>
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<tbody>
<tr>
<td>total</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/4</td>
<td>1/8</td>
<td>1/8</td>
<td>-0.12</td>
<td>1.27</td>
</tr>
<tr>
<td>1/2</td>
<td>1/3</td>
<td>1/6</td>
<td>-0.17</td>
<td>1.26</td>
</tr>
<tr>
<td>2/3</td>
<td>1/3</td>
<td>1/3</td>
<td>-0.17</td>
<td>1.27</td>
</tr>
<tr>
<td>1</td>
<td>1/3</td>
<td>2/3</td>
<td>-0.11</td>
<td>1.27</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Figure 1. (a, b, c) Cross-sectional and (d, e f) top view of stable configurations of isolated CO$_2$ adsorbed on a CeO$_2$(111) surface. In the most stable configuration (a, d), CO$_2$ forms a monodentate carbonate with the surface O atom resulting in a binding energy of -0.31 eV. The binding energy of the bidentate and linear configurations was found to be -0.12 and +0.02 eV, respectively.

Figure 2. PDOS summed over all atoms (black) and on specific species (Ce$_{slab}$, O$_{slab}$, O$_{surf}$ and CO$_2$) of isolated (1/9 ML) CO$_2$ adsorbed on CeO$_2$(111) in a monodentate configuration. The grey and red lines indicate the PDOS projected on the orbitals of Ce and O atoms, respectively, of the CeO$_2$ substrate. The orange line shows the PDOS on the orbitals of the surface O atom interacting with the CO$_2$ molecule (O$_{surf}$). The green line shows the PDOS on orbitals of the adsorbed CO$_2$ molecule. Filled curves indicate occupied orbitals and the reference 0 eV energy was set to the edge of the valence band of the CeO$_2$(111) slab. Upon adsorption, the HOMO of the CO$_2$ molecule forming a carbonate species with the O$_{surf}$ atom, is found at 0.33 eV above the valence band of CeO$_2$(111).

Figure 3. (a) PDOS of linear CO$_2$ in gas phase, bent CO$_2$ in gas phase and projected DOS of CO$_2$ adsorbed on CeO$_2$(111) as mono- and bidentate species and (b) selected electronic states derived from the molecular orbitals of the CO$_2$ species. Upon adsorption, the LUMO (2) of gas phase CO$_2$ hybridizes and the binding orbital becomes occupied. Occupied molecular orbitals of both adsorbed species corresponding to the LUMO of the gas phase CO$_2$ were found in the valence band between ca. -2.5 and 0 eV (4, 6).
**Figure 4.** Charge density difference at 0.067 e/Å$^3$ for (a) monodentate and (b) bidentate CO$_2$ species. Yellow lobes indicate electron excess and cyan lobes indicate loss of electron density. The excess of electrons between O$_{surf}$ and C demonstrates the filling of the LUMO (see Figure 3) of gas phase CO$_2$ and the binding character between the two atoms.

**Figure 5.** (a) Binding energy $E_B$ and (b) $d_{C-O_{surf}}$ distance as a function of the CO$_2$ coverage of linear (circles), bidentate (triangles) and monodentate (diamonds) species and for a mixed configuration (filled diamonds) with 1/3 ML monodentate species and additional linear CO$_2$. At 1 ML, the most stable configuration consisted of 1/3 ML monodentate and 2/3 ML linear species.

**Figure 6.** (a, b, c) Cross-sectional and (d, e, f) top view of (a,d) monodentate species at 2/3 ML and (b,d) bidentate species and (c,f) a mixed configuration of monodentate and linear species at 1 ML. The two adjacent rows in [01 $\bar{1}$] direction of monodentate species at 2/3 ML in (d) share one surface Ce site (Ce$_{surf,2}$) leading to a rotation of the CO$_2$ molecules away from this Ce atom. When CO$_2$ is adsorbed in a bidentate configuration at 1 ML, the molecules arranged in a zig-zag pattern (e). CO$_2$ molecules of the mixed configuration are represented with different green spheres to differentiate between various species. The first partial layer of linear CO$_2$ (green spheres) arranged in [11 2] direction in between the monodentate species (dark green spheres) at $\Delta z_{CO2}=$3.84 Å. Linear CO$_2$ adsorbed in a second partial layer (light green spheres) were found at $\Delta z_{CO2}=$5.01 Å.

**Figure 7.** Charge transfer per surface CeO$_2$ unit from the surface to CO$_2$ adsorbates as a function of the CO$_2$ coverage for linear (circles), mono- (diamonds) and bidentate (triangles) species and for a mixed configuration (filled diamond) with monodentate and linear species.
**Figure 8.** Average binding energy of CO$_2$ adsorbed simultaneously in different configurations at a total CO$_2$ coverage $\theta$ of (a) 1/4, (b) 1/2, (c) 2/3 and (d) 1 ML. The binding energy is shown as a function of the fraction of CO$_2$ adsorbed as monodentate species at each specific total coverage. At $\theta > 1/2$ ML, the binding energy has minimum when 1/3 ML (green line) of CO$_2$ is adsorbed as monodentate species. Additional mixed configurations where simulated at 1 ML (d) where all mono-, bidentate and linear species were present. Here, the amount of monodentate species was fixed to 1/3 ML and the amount of bidentate species was varied from 1/9 to 1/3 ML. Nevertheless, the most stable state (lowest binding energy) was found when only monodentate (1/3 ML) and linear (2/3 ML) species existed.

**Figure 9.** PDOS for the mixed configuration with monodentate (1/3 ML) and linear (2/3 ML) species at 1 ML. The pDOS of monodentate CO$_2$ (dark green) was identical to the one of isolated species (Figure 2) whereas the linear CO$_2$ showed the same bands as the gas phase molecule (Figure 3). Molecular orbitals of linear CO$_2$ adsorbed in the first partial layer (linear low) were shifted by ca. 0.40 eV to lower energies compared to linear species in the second partial layer (linear high) indicating stabilization of the CO$_2$ molecules closer to the surface.
FIGURE 1

(a) $d_{C-O_{surf}}$

(b) $d_{C-O_{surf}}$, $\alpha_{OCO}$

(c) $\Delta z_{CO_2}$

(d) monodentate

(e) bidentate

(f) linear
FIGURE 2

PDOS

Energy [eV]

-10  -5  0  5  10

0.33 eV

monodentate

total

Ce_{slab}

O_{slab}

O_{surf}

CO_2
FIGURE 3
FIGURE 4

(a) monodentate  (b) bidentate

O1  O2  Ce_{surf}
FIGURE 5

(a) $E_B$ [eV]
- ○ linear
- △ bidentate
- □ monodentate
- ■ mono+lin

(b) $d_{C-O_{surf}}$ [Å]
- ○ linear
- △ bidentate
- □ monodentate
- ■ mono+lin

CO$_2$ coverage [ML]
FIGURE 6
FIGURE 7

![Graph showing charge transfer/CeO$_2$ vs CO$_2$ coverage [ML]. The graph includes lines for linear, bidentate, monodentate, and mono+lin. The x-axis represents CO$_2$ coverage in monolayers, and the y-axis represents charge transfer/CeO$_2$. Different markers are used to indicate the type of bonding.](image-url)