

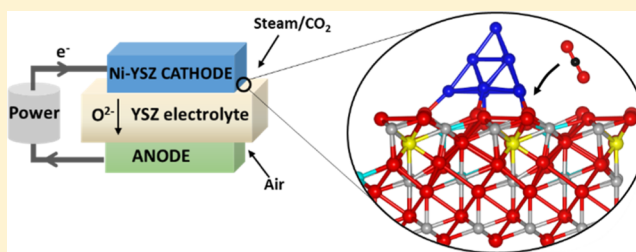
CO₂ and H₂ Adsorption and Reaction at Ni_n/YSZ(111) Interfaces: A Density Functional Theory Study

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ABSTRACT: To recycle CO₂ into sustainable fuels and chemicals, coelectrolysis of CO₂ and H₂O can be achieved in solid oxide electrolysis cells, where the molecules are supplied to the Ni/YSZ electrode (YSZ = yttria-stabilized zirconia). Oxygen diffusion along the electrode has been identified as the critical step in the process, where YSZ is the common catalyst support. We have investigated the interaction of a CO₂ molecule with the clean YSZ(111) surface and with Ni_n/YSZ(111) ($n = 1, 4-7, 10,$ and 20) interfaces, using a spin-polarized density functional theory and a long-range dispersion correction. Here, we have considered up to six initial adsorption sites and two orientations for the CO₂ molecule, which showed that the adsorption is stronger at the Ni_n/YSZ(111) ($n = 4-7, 10,$ and 20) interface than on the clean YSZ(111) and Ni₁/YSZ(111) systems. Additionally, we have determined that the preferential adsorption site of CO₂ is at the interface between the Ni clusters and the YSZ(111) surface. We have observed a bending and stretching of the molecule, demonstrating its activation upon adsorption, because of charge transfer between the metal cluster and the molecule and a mixing between Ni orbitals and CO₂ orbitals. In this work, we show that although the electronic structure of the clusters depends on the cluster size, the interaction strength of CO₂ with the interface is independent of the size of the supported nickel particle. Finally, we have considered the reverse water gas shift reaction and determined the hydrocarboxylic intermediate in the reaction mechanism over Ni₅/YSZ(111).



1. INTRODUCTION

Significant efforts have been dedicated to the identification of a catalytic system, which is capable of sustainably converting CO₂ to liquid fuels and chemicals, where the activation of CO₂ is a key step in the conversion process.¹ For instance, coelectrolysis of CO₂ and H₂O could be used in solid oxide fuel cells (SOFCs) to recycle CO₂ into sustainable hydrocarbon fuels.²⁻⁹ During the cell operation, both CO₂ and H₂O are supplied to the anode of the fuel cell,⁴ where they interact with the catalyst.

SOFCs have three main components: two porous electrodes separated by an oxygen ion-conducting electrolyte. As the working temperature of the SOFC is high, from 773 to 1173 K, these devices present several advantages, including efficiency, reliability, modularity, fuel flexibility, and low pollutant emission.¹⁰⁻²¹ Ni/YSZ (YSZ = yttria-stabilized zirconia) is an appropriate anode for the SOFC, as this system is stable at high temperatures, is electronically conducting, and has porosity to maximize the contact area with the fuel.¹¹ Ni/YSZ is a cermet, which is a ceramic matrix, here YSZ, containing supported metal (Ni) nanoparticles. The Ni nanoparticles and YSZ provide electronic and oxygen-ion conductivities, respectively.^{4,22-25}

YSZ is obtained from doping cubic zirconia (c-ZrO₂) with yttria (Y₂O₃). At atmospheric pressure, pure zirconia (ZrO₂) has three polymorphs: below 1400 K, the stable phase is

monoclinic; between 1400 and 2650 K, ZrO₂ is tetragonal; and between 2650 and 2950 K (polymorph melting point), cubic ZrO₂ (c-ZrO₂) is the most stable structure.^{26,27} However, c-ZrO₂ is the stable phase at a lower temperature (below 800 K) when it is doped with Y₂O₃ to form YSZ, which increases the ionic conductivity of the material and is therefore the phase employed in SOFCs.

In the SOFC, the key reactions occur at the triple phase boundary (TPB) where the anode, the electrolyte, and the fuel meet,²⁸⁻³⁰ hence our interest in the interaction of Ni/YSZ with gas molecules such as CO₂, CO, H₂O, and H₂. H₂/CO mixtures can be used as a fuel in the SOFC, and therefore, reactions such as the water-gas shift reaction (WGSR) can take place.³¹⁻³³ Following other authors, who have used density functional theory (DFT) calculations to study the interaction of CO₂ with metal-oxide interfaces,^{34,35} we have used a similar methodology to focus on the interaction of CO₂ with different cluster sizes of the nickel particle supported on YSZ.

Studies of the adsorption and activation of CO₂ on other metal-oxide systems,^{36,37} such as M₂/γ-Al₂O₃ (M = Sc-Cu), have shown a charge transfer from the oxide-supported metal to the CO₂ molecule, leading to the adsorption and bending of

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CO₂.¹ Pan et al.³⁸ have studied CO₂ hydrogenation on Ni/ γ -Al₂O₃, where they adsorbed separately CO₂ and H adatoms on supported Ni₄ clusters before describing the coadsorption of both molecules. On the clean Ni₄/ γ -Al₂O₃, they found that CO₂ interacts with two Ni atoms via its C atom and both O atoms, where the molecule is activated as shown by the bending and elongation of C–O bonds upon adsorption. They have also explored the elementary steps in CO₂ conversion, typically to formate and carboxyl groups, on both dry and hydrogenated Ni/ γ -Al₂O₃ surfaces. Here, they showed that on the clean surface, the formation of formate is kinetically feasible, whereas the pathway leading to CO is thermodynamically more favorable. However, on the hydroxylated surface, CO formation is preferred both kinetically and thermodynamically.

Another CO₂ hydrogenation study on Cu/ZnO(000 $\bar{1}$)³⁹ has confirmed the importance of the supported metal cluster in the reaction mechanism: the authors showed at a theoretical level that the reaction is faster on the supported Cu clusters than on the Cu(111) surface, owing to low-coordinated Cu sites that contribute to the stabilization of the reaction intermediates. Similarly, Vidal et al.⁴⁰ showed that CO₂ activation is more favorable on Cu/TiC than on the Cu(111) surface. The adsorption of CO₂ over Cu–Co supported on γ -Al₂O₃ showed CO₂ activation upon adsorption, where the hydroxylated surface stabilized the adsorbed CO₂ by either hydrogen bonding or protonating CO₂.⁴¹ Tang et al.⁴² used first principles kinetic Monte Carlo simulations to study the hydrogenation of CO₂ on the Cu/ZrO₂ interface. In their investigation, the authors described the interaction of CO₂ with Cu/ZrO₂, where they showed that CO₂ prefers to adsorb on the naked ZrO₂ surface, rather than at the Cu/ZrO₂ interface. They calculated an adsorption energy of 0.69 eV and also described the bending of the molecule upon adsorption. They also noted a stretching of the C–O bonds and charge transfer from the ZrO₂ surface to the antibonding $2\pi_u$ orbital of CO₂.

Despite these studies, a systematic investigation of the effect of the size of the supported metal clusters on CO₂ adsorption and potential activation is still lacking. Here, we have studied the interaction of eight systems [YSZ(111) and Ni_{*n*}/YSZ(111) (*n* = 1, 4–7, 10, and 20)] with a CO₂ molecule, and we have analyzed the geometric structure and vibrational frequencies to describe the configuration of the adsorbed molecule at the interface. We have also characterized the electronic structure to evaluate the charge transfer between the interfacial systems and the CO₂ molecule. Finally, we have investigated the reverse WGS mechanism, which is the reaction between the adsorbed CO₂ molecule and H₂ to generate water and carbon monoxide.

2. COMPUTATIONAL METHODS AND MODELS

Cubic zirconia (*c*-ZrO₂) has the fluorite structure and therefore a face-centered cubic (fcc) unit cell (space group *Fm*3*m*). The Zr atoms constitute the fcc cube, and each Zr atom is coordinated to eight oxygen atoms which are located on the diagonals of the cube. To model the most stable cubic zirconia surface, the ZrO₂(111) O-terminated surface,^{43,44} we have cleaved the *c*-ZrO₂ bulk using the METADISE code⁴⁵ and created a slab model, similarly to our previous investigation.⁴⁴ The ZrO₂(111) slab contains nine atomic layers (three O–Zr–O trilayers), where the five top atomic layers were relaxed during geometry optimization and the four

layers in the bottom were kept fixed to represent the bulk crystal. The YSZ(111) surface was built by the substitution of two Zr layers (from the top and the sub O–Zr–O trilayers) by two Y atoms (9.1 w % of yttria) with the consequent removal of one oxygen atom from the third atomic layer (the next-nearest neighbor of Y atoms). The side and top views of ZrO₂(111) and YSZ(111), respectively, are shown in Figure 1.

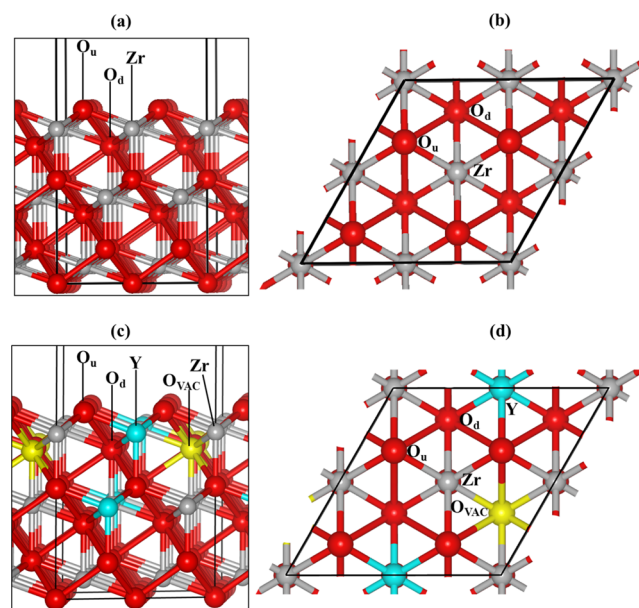


Figure 1. (a,b) Side and top views, respectively, of the oxygen-terminated ZrO₂(111) surface. (c,d) Side and top views, respectively, of the YSZ(111) surface. Color key: O, Zr, and Y are represented by red, gray, and cyan spheres, respectively. The yellow spheres represent the oxygen vacancy.

The location of the Y dopants and oxygen vacancy were determined in previous works.^{44,46,47} We have described all the nonequivalent positions of the Y atoms and oxygen vacancy, and here, we show the most stable structure (Figure 1c,d). The unit formula represented in Figure 1c,d is Zr₁₀Y₂O₂₃. In this structure, the Y atoms are located in the top and sub O–Zr–O trilayers, whereas the oxygen vacancy is positioned in the lower oxygen layer of the top O–Zr–O trilayers.

We have repeated the unit cell in the *x* and *y* surface directions to avoid lateral interactions between the Ni_{*n*} clusters; thus, our YSZ(111) surface is modeled by a Zr₄₀Y₈O₉₂(111) slab. We first tried several nonequivalent geometries and initial adsorption sites for the Ni_{*n*} clusters,⁴⁸ which showed that the most stable configuration for the clusters is a pyramid shape, rather than a flat shape on top of the YSZ(111) surface, indicating that the binding between the Ni atoms is stronger than the interaction to the surface. Tosoni et al.⁴⁹ have adsorbed Ni₁₀ clusters on top of a similar surface, i.e., tetragonal ZrO₂(101), and they also showed that the metal clusters prefer to adopt a three-dimensional shape rather than a flat configuration.

In addition, we observed that the Ni_{*n*} clusters adsorb away from the Y atoms. Figure 2 shows the most stable Ni_{*n*}/YSZ(111) (*n* = 1, 4–7, 10, and 20) configurations, which we have considered for the adsorption of the CO₂ molecule, where the average size of the Ni_{*n*} clusters ranges from 3.63 Å² (*n* = 4) to 41.10 Å² (*n* = 20).

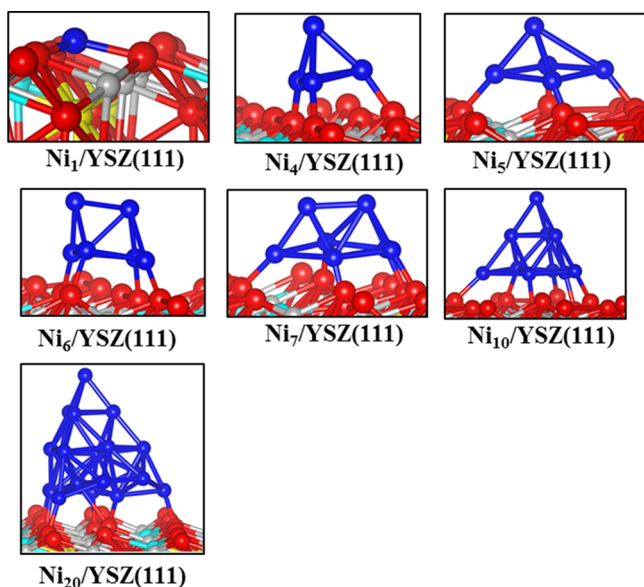


Figure 2. Stable configurations of Ni_n ($n = 1, 4-7, 10,$ and 20) clusters adsorbed on the YSZ(111) surface. Color key: O, Zr, Y, and Ni are represented by red, gray, cyan, and blue spheres, respectively. The yellow spheres represent the oxygen vacancy.

The calculations in this study are based on spin-polarized DFT and performed by solving the Kohn–Sham equations⁵⁰ in a periodic system, as implemented in the Vienna Ab-initio Simulation Package.^{51–54} Exchange–correlation potentials are modeled by the general gradient approximation⁵⁵ using the Perdew–Burke–Ernzerhof density functional. The long-range dispersion interactions were described by the semiempirical method of Grimme,⁵⁶ which showed an improvement in the description of the molecular adsorption.^{57–59} The C (2s, 2p), O (2s, 2p), Ni (3d, 4s), Zr (4d, 5s), and Y (4s, 4p, 4d, 5s) electrons have been treated explicitly as valence states, whereas the inner electrons were considered as core electrons and kept frozen. The core–valence electron interaction has been treated with the projected augmented wave method.⁶⁰ A plane-wave kinetic energy cutoff of 500 eV has proven to accurately describe the geometry and electronic structure.^{61–63} Geometry optimization has been performed using the conjugate gradient technique with an interatomic force threshold of 0.01 eV/Å. Monkhorst–Pack grids of $3 \times 3 \times 1$ k -point sampling were used for the 2×2 slab calculations. In our previous study,⁴⁴ we

calculated the band gap of $\text{ZrO}_2(111)$ to be 3.14 eV, which, as expected from the DFT calculations, is lower than the experimental bulk values ($\sim 5-6$ eV),^{64,65} but in good agreement with previous computational investigations.^{62,66} The gas-phase CO_2 molecule was placed in a large box ($14 \times 15 \times 16 \text{ \AA}^3$) in order to avoid lateral interactions using $1 \times 1 \times 1$ k -point sampling.

The vibrational frequencies of CO_2 (in the gas phase and adsorbed on the surface) were calculated by finite displacements of every coordinate, where the eigenvectors of the Hessian matrix correspond to the vibrational normal modes. The CO_2 frequency changes, upon adsorption, reflect an alteration of interatomic bonds. For example, a shift toward higher frequency values indicates stronger bonds. To evaluate the atomic charges in the system, we employed Bader analysis as implemented in the Henkelman algorithm.⁶⁷

3. RESULTS AND DISCUSSION

3.1. Geometry. We have first evaluated the interaction of CO_2 with both the bare YSZ(111) and the $\text{Ni}_n/\text{YSZ}(111)$ surfaces and have calculated the binding energy (E_B) of CO_2 on the surfaces as follows (eq 1)

$$E_B = E_{\text{CO}_2\text{-surface}} - (E_{\text{surface}} + E_{\text{CO}_2}) \quad (1)$$

where $E_{\text{CO}_2\text{-surface}}$ is the energy of the YSZ(111) surface (with or without the Ni_n cluster) and the adsorbed CO_2 and E_{surface} and E_{CO_2} are the energies of the surface system without CO_2 and the CO_2 molecule in the gas phase, respectively. A positive binding energy reflects an endothermic CO_2 adsorption, whereas a negative binding energy reflects an exothermic CO_2 adsorption and therefore a favorable interaction between CO_2 and the $\text{Ni}_n/\text{YSZ}(111)$ interface.

We have tried several initial adsorption sites for CO_2 on the clean YSZ(111) surface and on the supported Ni_n clusters on YSZ(111). On $\text{Ni}_n/\text{YSZ}(111)$, CO_2 has been initially adsorbed on the top and edge of the Ni_n cluster, at the interface between the Ni_n cluster and the oxide surface, and away from the Ni_n cluster. We have considered at least two CO_2 orientations for each initial adsorption site, and Figure 3 shows the energetically most favorable adsorption geometries. We have also investigated the adsorption of CO_2 -derived carbonates on the clean YSZ(111) surface, where the CO_2 molecule is activated, and the carbon and oxygen interact with the surface oxygen and metal (Zr and Y) atoms, respectively (Figure 3).

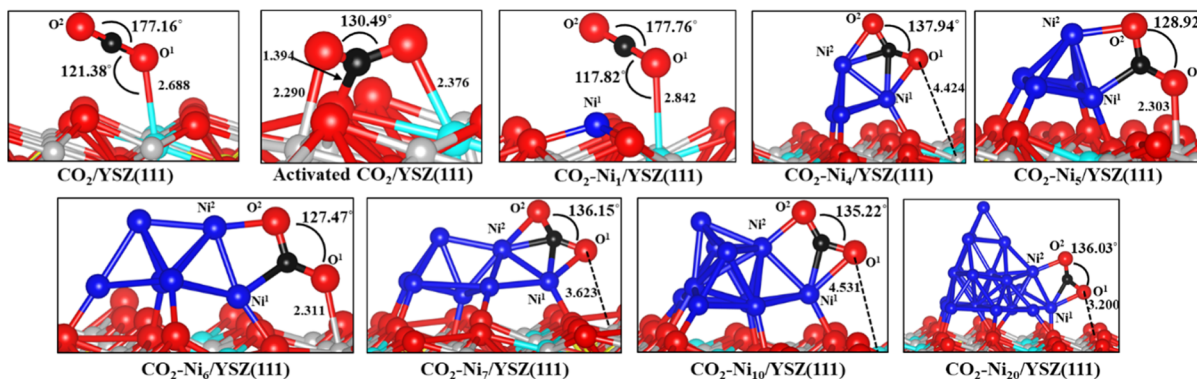


Figure 3. Most stable configurations of $\text{CO}_2/\text{YSZ}(111)$ and $\text{CO}_2\text{-Ni}_n/\text{YSZ}(111)$. Color key: O, Zr, Y, Ni, and C are represented by red, gray, cyan, blue, and black spheres, respectively. The yellow spheres represent the oxygen vacancy. All distances are in angstrom.

Table 1. Calculated Binding Energy (E_B , in eV), Distances (in Å), O–C–O Angle (θ_{OCO} , in Degrees), and Charge (q , in e^-) of CO_2 Adsorbed on the YSZ(111) and Ni_n /YSZ(111) ($n = 1, 4-7, 10, \text{ and } 20$) interfaces

surface	E_B	CO internal bonds		CO_2 -surf atom distance	CO_2 - Ni_n distance				θ_{OCO}	total charge before CO_2 adsorption		total charge upon CO_2 adsorption	
		C–O ¹	C–O ²		C–Ni ¹	C–Ni ²	O ¹ –Ni ¹	O ² –Ni ²		q_{Ni}	q_{O_1}	q_{Ni}	q_{CO_2}
YSZ(111)	−0.37	1.183	1.170	2.688					177.16				0.0
Ni_1 /YSZ(111)	−0.32	1.181	1.172	2.842	3.655		4.555		177.76	+0.3		+0.3	0.0
Ni_4 /YSZ(111)	−1.16	1.253	1.256	4.424	1.971	1.981	2.075	2.065	137.94	+0.1		+0.7	−0.7
Ni_5 /YSZ(111)	−1.20	1.265	1.274	2.303	1.884	2.430	2.706	2.019	128.92	+0.2		+0.8	−0.8
Ni_6 /YSZ(111)	−1.66	1.260	1.288	2.311	1.859	2.451	2.757	1.895	127.47	+0.2		+0.8	−0.8
Ni_7 /YSZ(111)	−1.24	1.263	1.260	3.623	1.939	1.984	2.083	2.051	136.15	+0.2		+0.8	−0.8
Ni_{10} /YSZ(111)	−1.20	1.247	1.268	4.531	1.899	2.141	2.230	1.971	135.22	+0.2		+0.9	−0.7
Ni_{20} /YSZ(111)	−1.49	1.265	1.256	3.200	1.888	2.108	2.091	2.029	136.03	+0.2		+1.0	−0.7

On the clean surface, the linear CO_2 prefers to adsorb near the Y atom with a binding energy of -0.37 eV (Table 1) and adopting a tilted position. The activated CO_2 adsorbs with a binding energy of -0.49 eV. However, we will not discuss any further about the different activated CO_2 isomers on the clean surface, as we are primarily interested in CO_2 adsorption at the Ni /YSZ interface, which is our model for the TPB in SOFCs. Upon adsorption, CO_2 remains linear with an angle between the molecule and the surface of 121.38° . The CO_2 -surface distance is 2.688 Å, and the average internal C–O bond is 1.177 Å, which is similar to the C–O distance calculated for the gas-phase molecule, indicating that the CO_2 -surface interaction is weak and the molecule remains nonactivated. This CO_2 -YSZ(111) interaction has been discussed in detail in our previous work.⁶⁸ Chen et al.⁶⁹ found a weaker adsorption for linear CO_2 on top of the (111) surface of pure tetragonal ZrO_2 (-0.05 eV) because of the non-consideration of the dispersion forces.

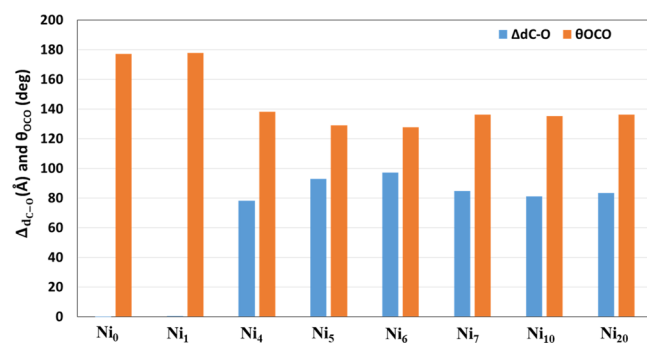
In Figure 3, we observe that CO_2 -YSZ(111) and CO_2 - Ni_1 /YSZ(111) have a similar geometry and comparable binding energies: -0.37 and -0.32 eV, respectively (Table 1). On Ni_1 /YSZ(111), CO_2 adsorbs at a distance of 2.842 Å from the yttrium atom and the average internal C–O bond is 1.177 Å; the molecule also remains linear and forms an angle of 117.82° with the oxide surface. Thus, one Ni atom does not affect significantly the CO_2 adsorption properties of the YSZ(111) surface.

From Table 1, we note that for Ni_n ($n \geq 4$) clusters supported on the YSZ(111) interface, E_B is -1.16 eV or larger, which is approximately 3 times stronger than the binding energies found on either CO_2 /YSZ(111) or CO_2 - Ni_1 /YSZ(111), indicating that the Ni_n ($n \geq 4$) clusters stabilize CO_2 adsorption. Our calculated binding energies for CO_2 - Ni_n /YSZ(111) ($n \geq 4$) are in the same range as the one obtained by Pan et al.³⁸ (0.93 eV) in their study of CO_2 hydrogenation on $Ni/\gamma-Al_2O_3$. From Figure 3, we note that CO_2 adsorbs on the edge of the cluster, at the interface with the YSZ(111), where the C atom binds at least one Ni atom: the C–Ni distance ranges from 1.859 to 2.451 Å for the Ni_n /YSZ(111) ($n = 4-7, 10, \text{ and } 20$) interfaces (Table 1). These calculated C–Ni distances at the Ni_n /YSZ(111) ($n = 4-7, 10, \text{ and } 20$) interfaces are comparable to the study by Hahn et al.,³⁵ where they found a C–Ni distance of 1.89 Å and showed that CO_2 adsorbs on top of the $Ni_{10}/CeO_2(111)$ surface with similar geometries to the ones presented in Figure 3.

We find that CO_2 further interacts with Ni_n clusters through its oxygen atoms (O^1 and O^2) at distances ranging from 1.8 to

1.9 Å (Table 1). The YSZ(111) surface also plays a role in the CO_2 adsorption because the CO_2 oxygen atom that points toward the surface interacts with Zr atoms, as shown in Figure 3. The O^1 -surface distance varies depending on the cluster shape: for the geometries where the cluster is slightly tilted toward the surface, i.e., CO_2 - Ni_5 /YSZ(111) and CO_2 - Ni_6 /YSZ(111), the O^1 -surface distance is shorter than the one found in the geometries where the cluster adopts a configuration parallel to the surface, i.e., CO_2 - Ni_n /YSZ(111) ($n = 4, 7, 10, \text{ and } 20$) (Table 1 and Figure 3).

In Figure 4 we have plotted the average of the difference between the internal C–O¹ and C–O² distances in the gas

**Figure 4.** Elongation ($\Delta_{d_{C-O}}$, in Å) and angle (θ_{OCO} , in deg) of CO_2 adsorbed on the YSZ(111) and Ni_n /YSZ(111) ($n = 1, 4-7, 10, \text{ and } 20$) interfaces. Note that we have multiplied by 10^3 the elongation $\Delta_{d_{C-O}}$ to facilitate the reading of the graph.

phase and after adsorption of CO_2 on the YSZ(111) and Ni_n /YSZ(111) ($n = 1, 4-7, 10, \text{ and } 20$) interfaces from $\Delta_{d_{C-O}} = \frac{(d_{C-O^1} - 1.177) + (d_{C-O^2} - 1.177)}{2}$, where 1.177 Å is the internal C–O distance in the gas phase. We have also plotted the molecule's angle for the latter configurations, and the calculated values of C–O¹, C–O², and θ_{OCO} are shown in Table 1.

Figure 4 clearly shows that the internal C–O bonds vary only weakly upon CO_2 adsorption on both the YSZ(111) (Ni_0) and the Ni_1 /YSZ(111) interfaces. However, on the Ni_n /YSZ(111) ($n = 4-7, 10, \text{ and } 20$) interface where CO_2 chemisorbs, the internal C–O elongation is more notable: $\Delta_{d_{C-O}}$ ranges from 0.078 to 0.097 Å. Additionally, we note that the stretching of the C–O internal bonds is asymmetric as shown in Table 1: generally, the C–O² distance (involving the

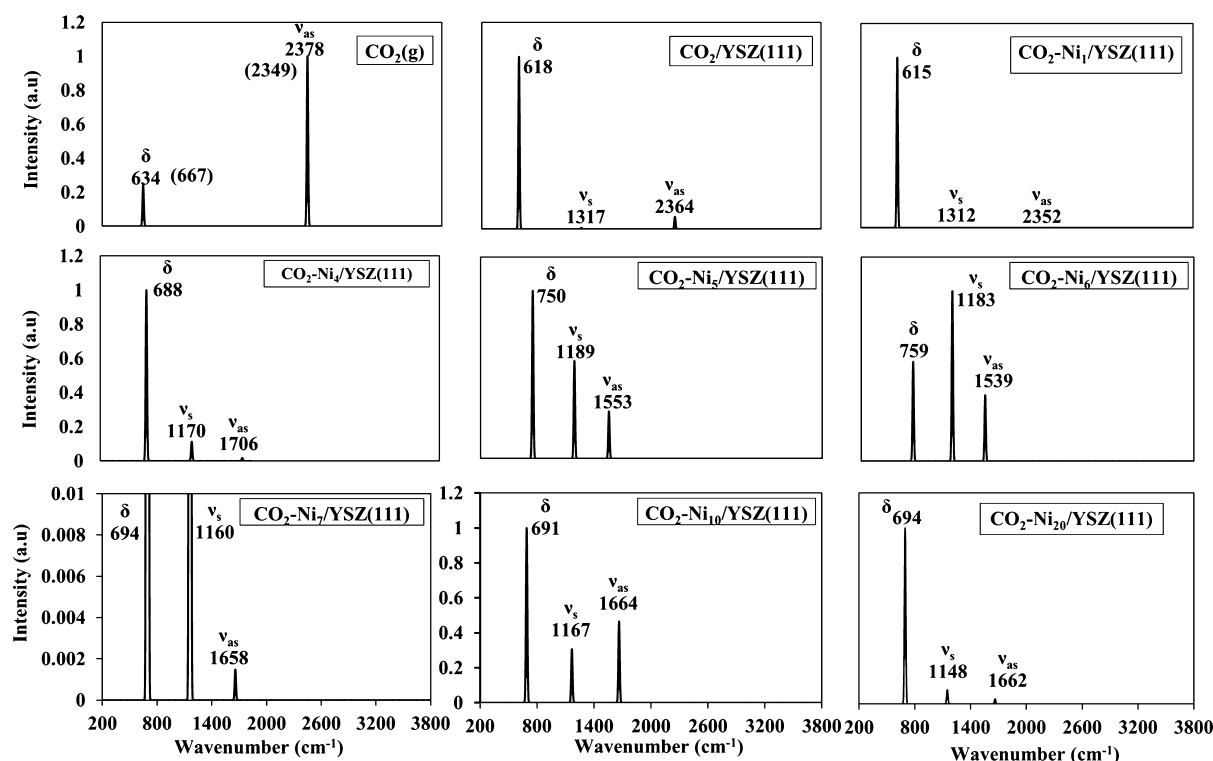


Figure 5. Modeled IR spectra of CO_2 in the gas phase and on the naked YSZ(111) and on the $\text{CO}_2\text{-Ni}_n/\text{YSZ}(111)$ ($n = 1, 4-7, 10, \text{ and } 20$) interfaces. The insets in parenthesis are the IR experimental values from the literature.⁷⁰

oxygen pointing toward the gas phase) is larger than the C–O¹ distance, except on the Ni₇/YSZ(111) and Ni₂₀/YSZ(111) interfaces. This asymmetric stretching upon CO_2 adsorption on the Ni_{*n*}/YSZ(111) interfaces suggests that O² would dissociate more easily than O¹ from the molecule, as was also suggested by Hahn et al.³⁵ This asymmetry provides insights into the mechanism of the CO_2 reduction in SOFCs: the hydrogenation of O² may lead to CO + H₂O, yielding CH₃OH, whereas HCOOH may be the product of the hydrogenation of O¹.

The CO_2 activation is confirmed by the O–C–O angle analysis (Figure 4). CO_2 bending is more pronounced upon adsorption on supported clusters than on the clean YSZ(111) surface or on a single Ni atom catalyst. As expected, for the strongest adsorption, we obtained the smallest angle ($\text{CO}_2\text{-Ni}_6/\text{YSZ}(111)$) and most pronounced bending. This CO_2 activation has also been observed on similar systems,¹ where the authors showed that CO_2 prefers to adopt a bent geometry on top of its most favorable adsorption site: the interface between the oxide support ($\gamma\text{-Al}_2\text{O}_3$) and the transition metal dimer (Sc–Cu).

3.2. Frequency Analysis. In Figure 5 we have plotted the infrared (IR) spectra of CO_2 adsorbed on pristine and Ni_{*n*}-decorated YSZ(111) surfaces and compared them with the IR spectra of CO_2 in the gas phase. The variation in the peak position upon the adsorption of the molecule confirms the change in the CO_2 geometry and weakening of the intramolecular bonds. We have also compared the IR spectra of the adsorbed molecule with the experimental data to characterize the structures determined in this work and validate the geometries of the CO_2 adsorbed on the Ni_{*n*}/YSZ(111) interfaces.

In the gas phase, CO_2 has two calculated vibrational modes active in IR: the asymmetrical stretching ($\nu_{\text{as}} = 2378 \text{ cm}^{-1}$) and

the bending ($\delta = 634 \text{ cm}^{-1}$) modes. As shown in Figure 5, our calculated values of CO_2 IR in the gas phase are in good agreement with the experimental values from the literature (667 and 2349 cm^{-1} for δ and ν_{as} , respectively).⁷⁰

Upon adsorption on YSZ(111) and Ni₁/YSZ(111), the average shift of the asymmetrical stretching is 20 cm^{-1} , which is in good agreement with the weak adsorption energy and small internal bond elongation of CO_2 upon adsorption. Our calculated IR values for CO_2 on YSZ(111) are in good agreement with the experimental study made by Ramis et al., who studied the weak adsorption of CO_2 species on ZrO₂ (2362 and 1378 cm^{-1} for ν_{as} and ν_{ss} , respectively).⁷¹

On the Ni_{*n*}/YSZ(111) ($n = 4-7, 10, 20$) interfaces, where CO_2 adsorbs strongly, we note an average shift of 748 cm^{-1} of the asymmetrical stretching mode. The reason for this decrease is the weakening of the CO_2 internal bond upon adsorption. This shift confirms the geometrical analysis, where we showed an increase of the C–O distances and an increase of the θ_{OCO} bending. Mudiyansele et al.⁷² have studied WGRS on a similar system, i.e., the CeO_{*x*}/Cu(111) interface. They showed experimentally and theoretically by DFT a 700 cm^{-1} shift in ν_{as} upon CO_2 adsorption at the interface, which is in the same range as our value (748 cm^{-1}). Graciani et al.⁷³ have also shown experimentally that the CeO_{*x*}/Cu(111) interface activates CO_2 , as they observed two IR peaks at 1288 and 1610 cm^{-1} corresponding to the presence of a carboxylate species ($\text{CO}_2^{\delta-}$) on the surface.⁷⁴ These values agree with our findings on the Ni_{*n*}/YSZ(111) ($n = 4-7, 10, 20$) interfaces, where ν_{s} and ν_{as} are at 1170 and 1630 cm^{-1} , respectively.

Figure 5 also indicates that the symmetrical stretching (ν_{s}) of adsorbed CO_2 becomes active in IR as a consequence of the dipole perpendicular to the surface, which increases once the molecule bends. In addition, the bending of the molecule upon

adsorption leads to an increase in the value of the bending mode (δ) with an average calculated shift of 79 cm^{-1} .

3.3. Electronic Structure. In Table 1, we have included the Bader charge analysis of the Ni_n clusters before and after CO_2 adsorption. The average calculated charge for Ni_n clusters supported on YSZ(111) is $+0.2\text{ e}^-$ (i.e., loss of 0.2 e^-). However, the charge distribution within the cluster is not uniform: the Ni atoms located at the interface with the surface are positively charged (an average of $+0.1\text{ e}^-$), whereas the Ni atoms at the top are negatively charged (an average of -0.1 e^-). Once CO_2 adsorbs, the Ni atoms interacting with CO_2 lose an average of 0.3 electrons: the top Ni atom (Ni^2 —Figure 3) oxidizes from -0.1 e^- to $+0.2\text{ e}^-$, whereas the charge of the bottom Ni atom (Ni^1 —Figure 3), directly interacting with CO_2 , increases from $+0.1\text{ e}^-$ to $+0.4\text{ e}^-$.

As to the CO_2 molecule, we have evaluated an average charge gain of 0.8 e^- upon adsorption on the Ni_n -YSZ(111) ($n = 4-7, 10, \text{ and } 20$) interface, which comes mainly from the Ni_n clusters because the charge of the surface atoms neighboring CO_2 remains unchanged.

We have characterized the adsorbed CO_2 species by plotting the electron density difference as $\Delta\rho = \rho_{(\text{CO}_2\text{-surface})} - (\rho_{(\text{surface})} + \rho_{(\text{CO}_2)})$ in Figure 6, which shows charge accumulation

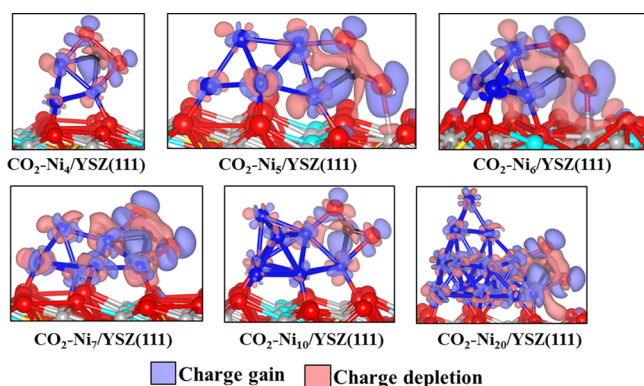


Figure 6. Calculated electron density differences for the most favorable CO_2 adsorption on the Ni_n ($n = 4-7, 10, \text{ and } 20$)-decorated YSZ(111) surfaces. Color key: O, Zr, Y, Ni, and C are represented by red, gray, cyan, blue, and black spheres, respectively. The yellow spheres represent the oxygen vacancy.

between the CO_2 oxygens and the cluster. The strong CO_2 - Ni_n /YSZ(111) ($n = 4-7, 10, \text{ and } 20$) interactions come mainly from C-Ni bond formation, as shown by the accumulation of charge density between the C and the metal cluster. We have observed a polarization of the CO_2 oxygen atom by the surface oxygen and zirconium in CO_2 - Ni_n /YSZ(111) ($n = 5 \text{ and } 6$), since there is a depletion of charge between the CO_2 oxygen and the surface atoms. This finding is in good agreement with the charge transfer from the surface atom to the molecule discussed previously. The electron density difference analysis confirms our previous observation, i.e., that the CO_2 - Ni_n /YSZ(111) ($n = 4-7, 10, \text{ and } 20$) interaction is mainly due to the interaction of the CO_2 molecule with the Ni_n cluster.

The representation of the projected DOS of CO_2 - Ni_n /YSZ(111) ($n = 4-7, 10, \text{ and } 20$) (Figure 7) reveals peaks in the band gap of the YSZ surface corresponding to d-type Ni orbitals. The number of the d-type orbitals in the band gap increases with the cluster size, as it has also been shown previously on the Ni_n/CeO_2 surface.³⁵ There is metal d mixing

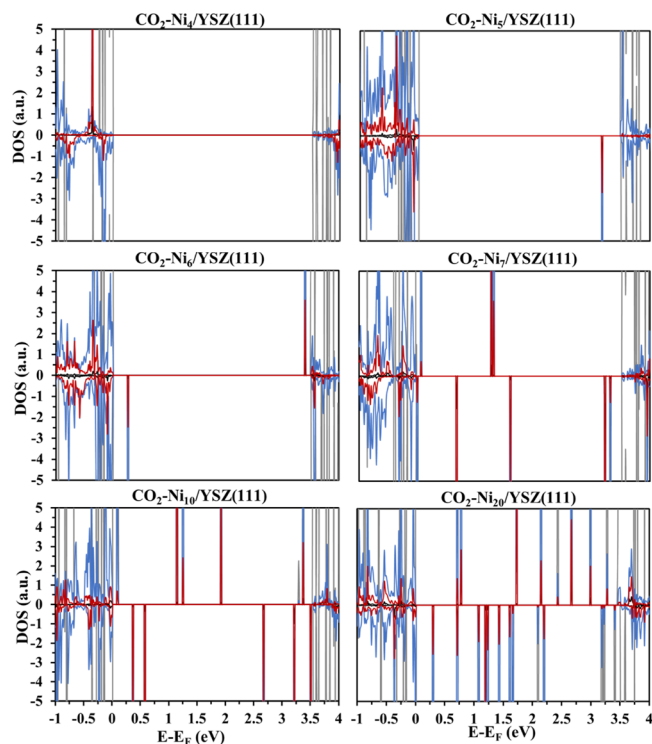


Figure 7. Total density of states (DOS) of CO_2 - Ni_n /YSZ(111) in gray and projected DOS on C of CO_2 , O of CO_2 , and Ni_n clusters in black, red, and blue, respectively.

with the CO_2 orbitals, leading to bonding and antibonding states related to the bending of the molecule upon adsorption. This behavior is similar to that found by Choe et al.,⁷⁵ in their investigation of the adsorption of CO_2 on Pt(111) and Fe(111). They used the atom superposition and delocalization molecular orbital theory to show the relation of the bending of CO_2 on the surfaces with the mixing of the d metal orbitals and the CO_2 orbitals. They have calculated the binding energies of 3.73 and 1.70 eV on Fe(111) and Pt(111) surfaces, respectively. Thus, CO_2 adsorption is stronger on these metallic surfaces than on the Ni/YSZ(111) surface, as the largest binding energy calculated here is 1.66 eV for the Ni_6 /YSZ(111) surface.

3.4. Reverse WGSR. We have studied the catalytic properties of the Ni_n /YSZ interface for the reverse water gas shift (RWGS) reaction (eq 2) by proposing one of the possible reaction paths



We have chosen to study the RWGS reaction for a relatively small cluster size, i.e., Ni_5 /YSZ(111), based on the above findings that the CO_2 adsorption geometry is similar regardless of the Ni cluster size. The adsorbate binds at the edge of the cluster with a minimal interaction with the YSZ surface.

We have tried several adsorption sites and orientations of the H_2 molecule and show the most stable geometry of H_2 - Ni_5 /YSZ(111) in Figure 8.

From Figure 8, we see that H_2 adsorbs dissociatively on Ni_5 /YSZ(111), and each hydrogen sits on a facet of the triangular pyramid Ni cluster. The homolytic dissociation of H_2 upon adsorption on Ni_5 /YSZ observed in this investigation is in good agreement with previous studies.^{63,76-78} The calculated binding energy is -1.51 eV , and we note a charge transfer from

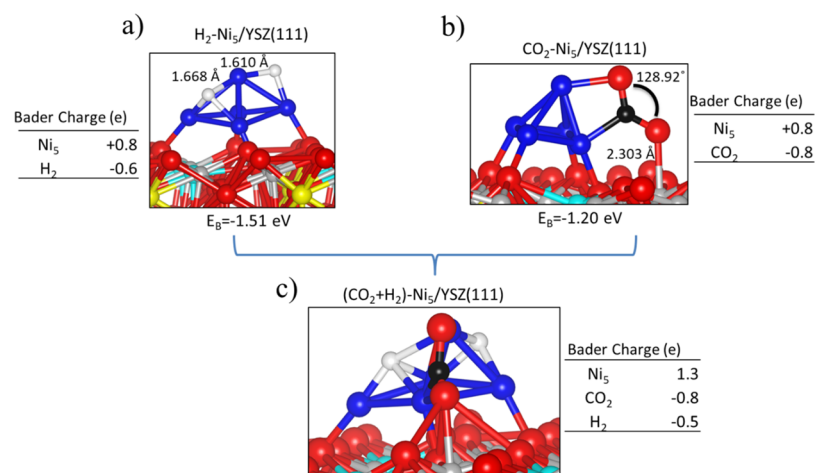


Figure 8. Representation of the most stable configurations of (a) H₂, (b) CO₂, and (c) CO₂-H₂ on Ni₅/YSZ(111). The Bader charges of the adsorbed molecules are shown next to each configuration. Color key: O, Zr, Y, Ni, C, and H are represented by red, gray, cyan, blue, black, and white spheres, respectively. The yellow spheres represent the oxygen vacancy.

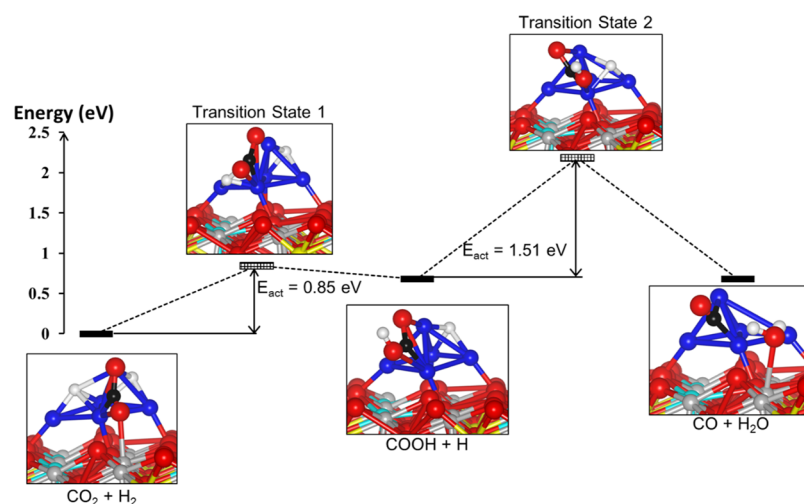


Figure 9. Energy profile showing reactants, intermediates, transition states, and final products for the RWGS reaction on the Ni₅/YSZ(111) interface. E_{act} corresponds to the activation energy between the initial and final states and the intermediate state. The energy of the reactants is set to zero. Color key: O, Zr, Y, Ni, C, and H are represented by red, gray, cyan, blue, black, and white spheres, respectively. The yellow spheres represent the oxygen vacancy.

the Ni₅/YSZ(111) to both hydrogen atoms (Figure 8 a). H₂ and CO₂ adsorb on Ni₅/YSZ(111) with a similar binding energy (Figure 8). However, we did not find competition of the adsorbates for the same adsorption sites. This led us to consider a geometry where hydrogen atoms are adsorbed on the faces of the metal cluster and the CO₂ molecule on its edge. Figure 8c corresponds to the most stable geometry of the (CO₂-H₂)-Ni₅/YSZ(111) system, which is the starting point of the RWGS reaction (eq 2).

During the RWGS reaction, one of the H atoms can either go toward the CO₂ oxygen or carbon atom. In the first alternative, the reaction proceeds through a hydrocarboxylic intermediate (COOH), whereas in the second case, the intermediate is a formate (HCOO). We have investigated the hydrocarboxylic pathway of the RWGS reaction by identifying the structures and calculating the energies of the intermediate state and two transition states (Figure 9), which had been identified using the dimer method.⁷⁸

Figure 9 shows the first step of the RWGS reaction pathway, where a hydrogen atom migrates toward its nearest CO₂

oxygen to form the hydrocarboxylic intermediate (COOH). The energy difference between the first transition state and the initial state ((CO₂ + H₂)-Ni₅/YSZ(111)), i.e., the activation energy, is equal to 0.85 eV. The second step involves the protonation of the hydrogenated CO₂ oxygen, allowing the formation of H₂O (adsorbed on the surface) and the CO molecule (adsorbed on the Ni cluster). This step goes through a transition state with an activation energy of 1.51 eV, which is higher than the previous barrier (0.85 eV) and the latter is thus the rate-limiting step of the overall pathway. This large activation energy (1.51 eV) explains the high temperature needed (above 810 °C) to achieve the RWGS reaction. Previous theoretical investigations of CO₂ hydrogenation on similar metal-oxides interfaces have also determined high barriers to form the transition states in their reaction pathways.^{36–38}

4. CONCLUSIONS

We have used DFT+D calculations to investigate the interaction of CO₂ with the clean YSZ(111) surface and

with the interface of YSZ(111) and supported Ni_n (*n* = 1, 4–7, 10, and 20) particles. The molecule adsorbs weakly on the clean YSZ(111) surface and at a single supported Ni atom. However, it bends and activates at the interfaces between the Ni_n (*n* = 4–7, 10, and 20) particles and the YSZ surface. The C–O distance, as well as the vibrational stretching and bending modes, confirms the activation of the molecule along the bending mode and a shift of the asymmetrical stretching mode. The Bader charge analysis demonstrates a charge transfer from the Ni_n cluster to the molecule, with the electron density difference plot, indicating a charge accumulation between the Ni atoms and the CO₂ molecule, which is further evidenced by the mixing of the metal d orbitals with the CO₂ molecule, as described in the DOS analysis. These observations led us to conclude that the CO₂ interaction with the Ni_n/YSZ(111) (*n* = 4–7, 10, and 20) interfaces is similar and independent of the Ni particle size beyond a minimum size. Next, we have studied the hydrocarboxylic pathway for the RWGS reaction including the thermodynamic and kinetic analysis of the energy profile. Our calculations showed that the second transition state, from COOH intermediate to CO and H₂O products, is the rate-limiting step of the overall reaction with a barrier energy of 1.51 eV.

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Notes

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