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A Density Functional Theory Analysis on Syngas Interaction (Adsorption) on Ceria (001) Surface

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Abstract : Amidst the pressing demand for effective carbon capture technologies, understanding the nuanced behavior of Oxygen Carriers (OCs) like Ceria is crucial. This study employs a Density Functional Theory (DFT) analysis to probe into the interaction of syngas on the CeO2 (001) surface, which has implications for carbon capture and storage. Capitalizing on Ceria's notable characteristics as an OC in the Chemical Looping Reforming (CLR) process, this research decodes the microscopic intricacies involved during the adsorption phase. An exploration into vital parameters, including the adsorption energy and electronic properties of the Ceria surface, was conducted. The findings underscore the pivotal role of neighboring effects in determining the adsorption trajectory. While DFT computations furnish invaluable theoretical insights, it is vital to recognize that these insights stem from idealized material models and might not encompass the full spectrum of real-world experimental conditions.[1]

Introduction - The realm of CO2 capture has witnessed the prominence of Oxygen Carriers (OCs) like NiO and Ceria, albeit with limited theoretical insights to support their applications. Ceria, in particular, captures attention owing to its exceptional attributes such as high oxygen storage capacity, rapid oxygen transfer kinetics, and adaptability through doping. These unique features elevate its potential as a catalyst, enhancing reaction rates and ensuring durability, positioning Ceria as a versatile and potent OC in the Chemical Looping Reforming (CLR) process. [2]

However, while empirical studies have explored these characteristics, there is a noticeable deficit in theoretical explorations, especially ones that investigate the impact of neighboring atoms on the ssssadsorption of fuel molecules on OC materials. This research endeavors to bridge this gap by presenting a comprehensive Density Functional Theory (DFT) analysis of syngas adsorption on Ceria. The focus lies not just on the primary interaction but extends to the nuanced effects exerted by neighboring atoms. Through a deep dive into the adsorption energy and electronic properties of the Ceria surface, this work strives to shed light on the microscopic intricacies that govern the behavior of this OC.

It is, however, pertinent to underscore that while DFT offers a wealth of theoretical insights, these are rooted in idealized representations of materials and may not always mirror the intricacies presented under real-world experimental conditions.

Computational Details: The Quantum Espresso software was employed to analyze syngas adsorption on a ceria slab. Initially, a periodic Ceria slab model was created, featuring 3-4 layers, with the bottom layers fixed. Using the Projector-augmented Wave (PAW) method, core electrons were described, and atomic coordinates and lattice parameters optimized. Given its stability, a cleaved Ceria (100) surface was chosen for the adsorption studies. The adsorption mechanisms of CO and H2 molecules were then investigated. CO presented a vertical bond relative to the Ceria surface, whereas H2 exhibited a similar orientation at the top of the Ce atom. DFT calculations were executed using the Generalized Gradient Approximation(GGA) of Perdew-Burke-Ernzerhof (PBE), considering a specific energy cut-off and Brillouin-Zone configuration. The syngas molecules' geometry was optimized using DFT, and the adsorption energy was subsequently calculated. The findings were then aligned with experimental data and other theoretical research for validation and in-depth understanding.

Results and Discussion

Structure Characterization

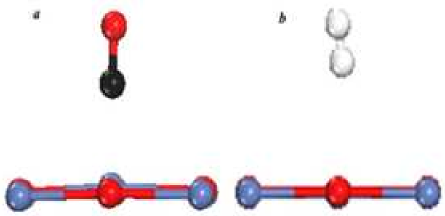

Figure 3-1: The used adsorption configurations for simulation. (a) CO adsorbate (b) H adsorbate above ceria

100 surface. Blue (Ce), red (O), black (C), white (H).

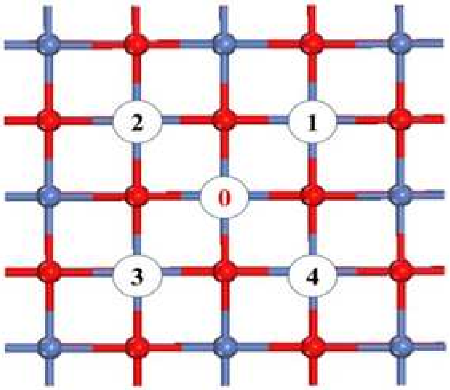

Figure 3-2: Studied nearest neighbor sites on (001)on the surface of Ceria labeled as 1, 2, 3 and 4, adsorption site labeled as 0. Blue (Ce), red (O), * means vacant position i.e. no CO or H_2 molecule is present above that site. Example of this notation is that **C*H means CO is being adsorbed at 3rd spot and H_2 at 0th or 5th spot.

Adsorption Energy Analysis with neighboring effect

Adsorption Energy: Adsorption energy measures the energy needed to detach a molecule from a material's surface. For syngas on ceria, this energy is determined by comparing the energy of standalone syngas to when it's on ceria. This metric helps in refining ceria-based catalyst designs for syngas reactions. The formula involves Esystem (the energy with adsorbed CO or H2), Efreefuel (energy of unattached CO or H2), and Esurface (energy of the OC surface).

$\Delta E_{absorption} = E_{system} - E_{freefuel} - E_{surface}$

Neighboring effect overall : The neighboring effect reflects how surrounding adsorbed entities affect adsorption at specific surface sites. In ceria-based carriers, elements like oxygen vacancies can greatly influence adsorption and reaction properties. They can boost CO and H2 reactions, enabling electron transfers and creating oxygenated compounds. But excessive CO or H2 can block syngas adsorption. This effect is complex and depends on factors like the carrier's surface and gas composition. Understanding it can optimize CLR processes. The discussion will proceed with a comparison of Adsorption energy values on Ceria.[3][4]

Now let us look at the comparison of Adsorption energy values at different configurations of syngas over Ceria.

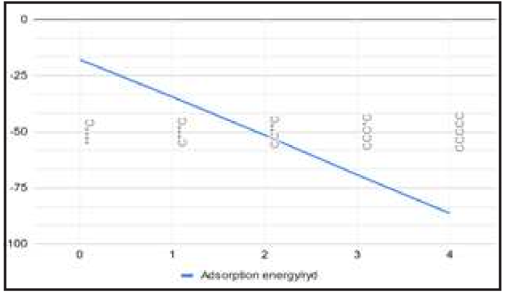

Figure 3-3 Adsorption energy of uniform loading molecules (CO)

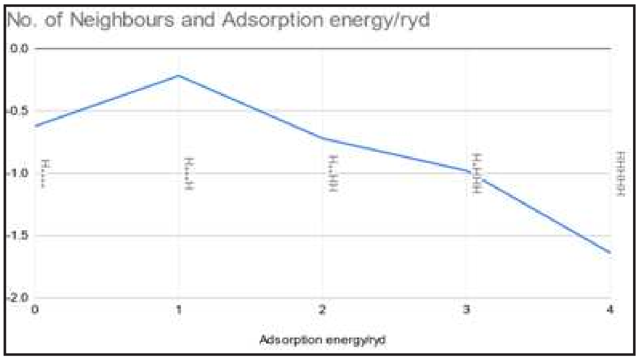

Figure 3-4 Adsorption energy of uniform loading molecules (H_2)

To understand the adsorption dynamics of syngas (CO and H2) on the Ceria (100) surface, we first examined CO and H2 adsorption with uniform neighboring molecules. Generally, a negative adsorption energy signifies a spontaneous exothermic adsorption, with a larger negative value indicating more heat released during the process. Figures 3-3 & 3-4 display the adsorption energy for CO with CO neighbors and H2 with H2 neighbors. Notably, CO has a more negative adsorption energy than H2. As similar neighboring atoms increase, the released adsorption energy also rises. The consistent slope for CO suggests no bond breaking between CO and the slab, with negligible symmetry effects. However, for H2, symmetry effects are present, and H2 tends to shift towards CO's position during reactions.

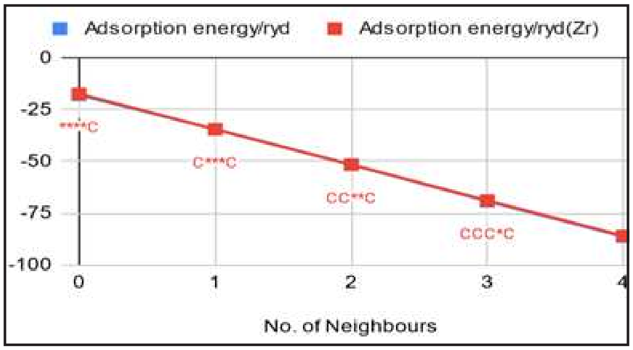

Figure 3-5 Adsorption energy comparison of Ceria and Zr-doped Ceria (6.25%), in case of uniform loading molecules (CO)

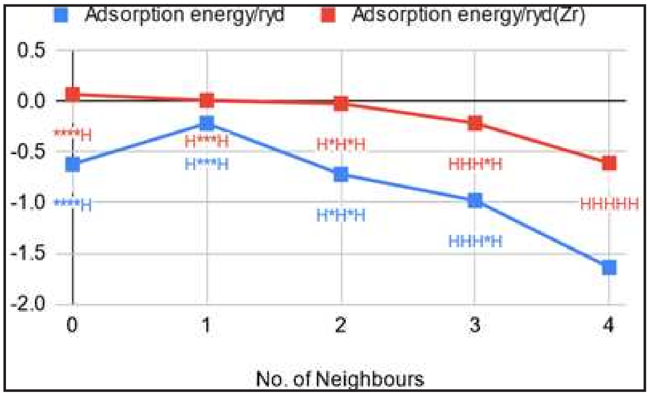

Figure 3-6 Adsorption energy comparison of Ceria and Zr-doped Ceria (6.25%), in case of uniform loading molecules (H_2)

Uniform adsorption analysis incorporating a 6.25% Zr doping (1 Zr atom replacing 1 out of 16 Ce atoms) was presented in figures 3-5 & 3-6. While CO's adsorption energy remains more negative than H2's in Zr-doped Ceria, the trend mirrors undoped Ceria. Notably, Zr-doped Ceria consistently exhibits less negative adsorption energies than undoped Ceria, even becoming endothermic at times. The graphs suggest Zr-doped Ceria is less stable but more reactive than its undoped counterpart. Also, the motion of H_2 to the position of CO during the reaction will be easier in the case of Zr-doped Ceria. Similarly, ****H's positive adsorption energy value indicates very less interaction between H_2 and Zr. H2's positive adsorption energy with Zr implies minimal interaction. Evaluating the stability across ceria surfaces (100, 110, 111) reveals the 111 surface as most stable, followed by 110, then 100. As Zr doping rises from 6.25% to 25%, stability reduces uniformly across configurations.

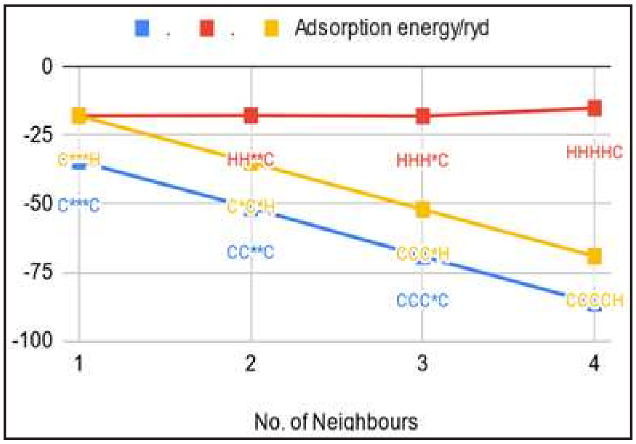

Figure 3-7 Overall Adsorption energy comparison of Ceria in case of uniform loading molecules and hybrid adsorption (H_2& CO)

The Figure 3-7 above compares CO uniform adsorption and CO hybrid adsorption as a function of the number of nearest neighbors. Uniform adsorption energy with the same number of neighbors is also presented for comparison purposes. The neighboring occupied geometry sharing the same x value means that they have the same number of occupied neighboring molecules and the same degree of symmetry. Hybrid adsorption is distinguished from uniform adsorption by the different neighboring occupied molecules with the studied adsorption molecule. For example, the CO hybrid adsorption considers the neighboring sites occupied by H_2, while the H_2 hybrid adsorption estimates the neighboring sites employed by CO.

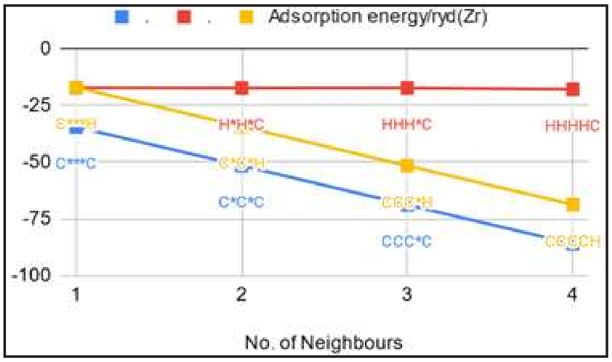

Figure 3-8 Adsorption energy comparison of Zr-doped Ceria (6.25%), in case of uniform loading molecules and hybrid adsorption (H_2& CO)

We can observe that Adsorption Energies in the case of non-uniform are less negative. And HHHHC in the case of Zr-doped ceria is more negative, i.e., less stable. It can be concluded overall that the Effect of symmetry on adsorption is negligible whenever adsorption of CO is involved, and CO with H_2 as its closest neighbor is more prone to undergo oxidation reaction. Similarly, CO surrounded by 4 H_2 will undergo a reaction more easily than H_2 surrounded by 4 CO molecules. And finally, More H_2 adsorption will always favor our CO->CO_2 oxidation reaction.

DOS based calculation on Undoped, Zr, Nd, Sm, La Doped Ceria and Ceria with Oxygen Vacancy

The density of states (DOS) indicates the number of permitted electron states per volume for a specific energy, stemming from fundamental quantum mechanics. The DOS vs. Energy Graph reveals the hybridization of bonding and anti-bonding orbitals, the HOMO-LUMO gap, and any changes due to hybridization or the substance's behavior. The DOS graph for syngas on ceria illustrates the interaction dynamics and subsequent changes in ceria's electronic properties. By contrasting ceria's DOS graph with that of syngas-adsorbed ceria, alterations in ceria's electronic attributes become evident. These graphs, marked with a vertical line at 0.256 eV representing the Fermi Level, differentiate between valence and conduction bands. [5]

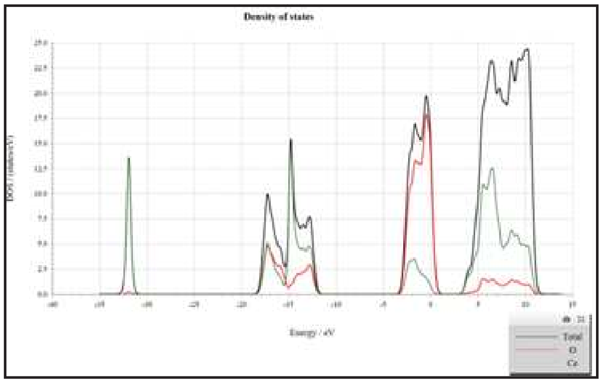

Figure 3-9 Density of State graph of undoped Ceria. Black(Total), Red (Oxygen atoms in Ceria) & Green (Cerium atoms in Ceria).

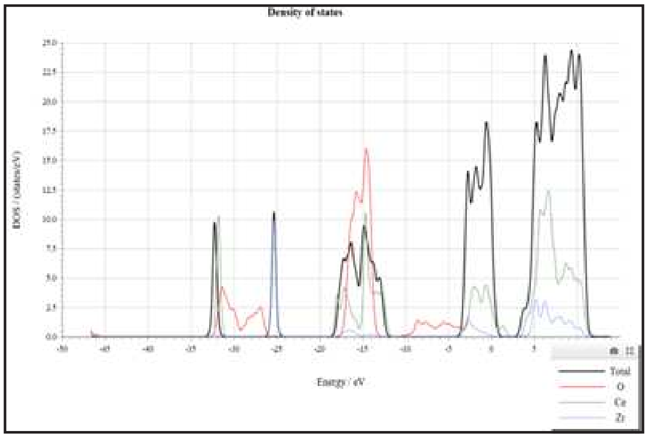

Figure 3-10 Density of State graph of Zr-Doped Ceria (6.25%). Black(Total), Red (Oxygen atoms in Ceria), Blue (Zr atoms in Ceria) & Green (Cerium atoms in Ceria).

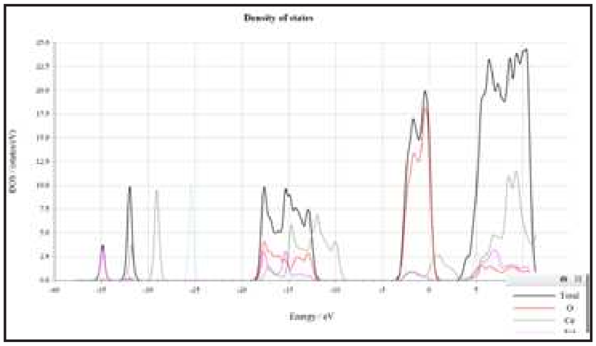

Figure 3-11 Density of State graph of Zr, Nd simultaneously-Doped Ceria (6.25% both). Black(Total), Red (Oxygen atoms in Ceria), Blue (Zr atoms in Ceria), Pink (Nd atoms in Ceria)& Green (Cerium atoms in Ceria).

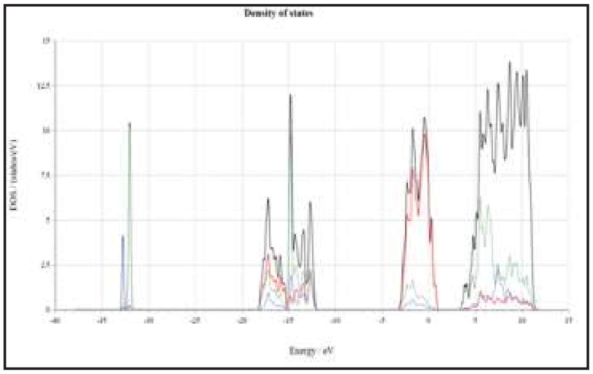

Figure 3-12 Density of State graph of Nd-Doped Ceria (6.25%). Black(Total), Red (Oxygen atoms in Ceria), Blue (Nd atoms in Ceria) & Green (Cerium atoms in Ceria).

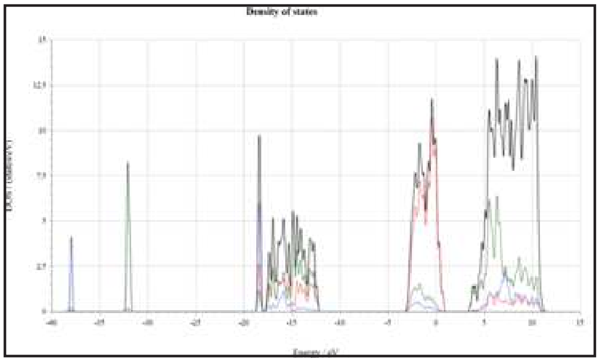

Figure 3-13 Density of State graph of Sm-Doped Ceria (6.25%). Black(Total), Red (Oxygen atoms in Ceria), Blue (Sm atoms in Ceria) & Green (Cerium atoms in Ceria).

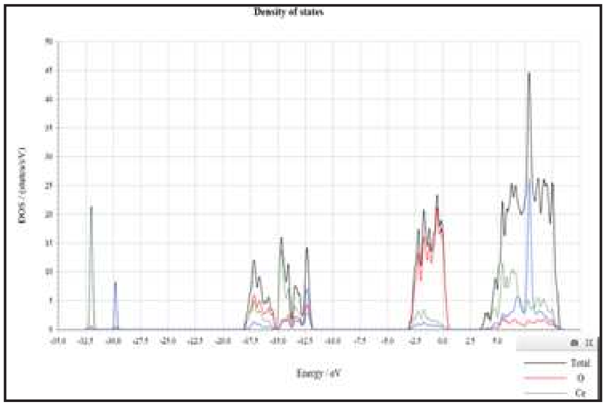

Figure 3-14 Density of State graph of La-Doped Ceria (6.25%). Black(Total), Red (Oxygen atoms in Ceria), Blue (La atoms in Ceria) & Green (Cerium atoms in Ceria).

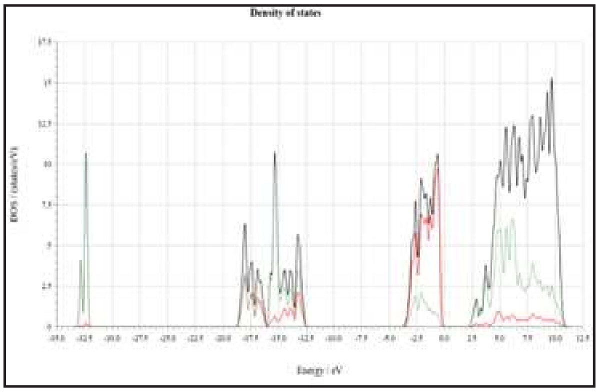

Figure 3-15 Density of State graph of Ceria (Ce6O12 Lattice) with 1 oxygen vacancy. Black(Total), Red (Oxygen atoms in Ceria) & Green (Cerium atoms in Ceria).

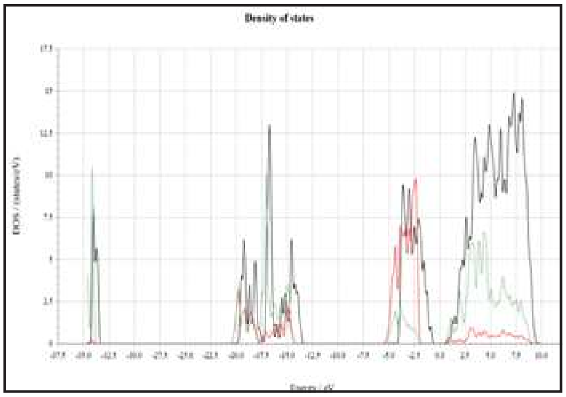

Figure 3-16 Density of State graph of Ceria (Ce6O12 Lattice) with 2 oxygen vacancy. Black(Total), Red (Oxygen atoms in Ceria) & Green (Cerium atoms in Ceria).

S.	Structure	HOMO	LUMO	HOMO-LUMO GAP
1	Undoped Ceria	-0.9	6	6.9 (6.2 reported)
2	Ceria- Zr Doped	-1	5.5	6.5
3	Ceria- Zr, Nd Doped	-1	6.2	7.2
4	Ceria- Nd Doped	0.3	3.8	4.1
5	Ceria- Sm Doped	-0.1	3.9	4
6	Ceria- La Doped	-0.5	4	4.5
7	Ceria- 1 Oxygen vacancy (Ce_6O_{11})	-1	2.9	3.9
8	Ceria- 2 Oxygen Vacancy (Ce_6O_{10})	-0.8	1.5	2.3

The electronic configurations for various materials are given as: Ceria: [Xe](5d1)(6s2), Oxygen: [He](2s2)(2p4), Zirconium: [Kr] $4d^2$ $5s^2$, and Neodymium: [Xe] 4ft $6s^2$. The valence band, starting around –4eV, is primarily made of O atoms with an spdf hybrid. Below “10 eV, the hybridized d, s, and p orbitals of both Ce and O atoms dominate, with Ce(6s) and Ce(4f) orbitals present. O's p orbital, beyond the Fermi level at 6 eV, interacts mainly with cerium's pdf hybrid. Dopants can either increase or decrease the band energy gap. Comparing Undoped Ceria, Zr-Doped Ceria, and Zr-Nd-doped Ceria, it's evident that Zr's addition destabilizes Ceria's phase structure. Zr-doped Ceria introduces a new electron band near –25 eV, signifying Zr's Zr(5s2) orbital, and shifts O's peak from -15 to -2 eV. Nd's addition to Zr-doped Ceria flattens the conduction band in the high energy region. The study uses the HOMO-LUMO gap to describe the energy difference between peaks below and above the Fermi Level.

Now look at the table below which tells us about homo-lumo gap from the DOS Graphs. Now we know that the Homo-Lumo gap relates to the energy difference between occupied and unoccupied molecular orbitals in a molecule, while the band gap refers to the energy difference between the valence band and conduction band in a solid material. Here in this study HOMO-LUMO gap is being used as a quantitative description of energy difference between the sharpest peak just below & just above the Fermi Level.

The table indicates that Zr and Sm doping decrease ceria's band gap, while La & Nd doping exhibit minimal impact on the HOMO-LUMO gap. Oxygen vacancies boost electron movement due to a reduced energy gap, displaying metallic attributes. Lower energy levels can aid in electron transfer and enhance methane's adsorption, but a smaller band gap might limit the material's redox activity. The HOMO-LUMO gap, indicative of kinetic stability, for undoped Ceria is approximately 6.9 eV. Doping with a single element makes Ceria more reactive. However, double doping with Zr and Nd returns properties similar to the undoped Ceria.

3.3.4 Band Energy Graph Analysis of Undoped, Zr, Nd, Sm, La Doped Ceria

It is reported that Cerium oxide, CeO_2, is an n-type semiconductor with a band gap of 2.9 eV. [6]

The Quantum Espresso band energy graph illustrates a material's electronic structure by showcasing allowed electron energy levels. In this graph, the horizontal and vertical axes represent electron momentum and energy, respectively. The gap between occupied and unoccupied energy levels, known as the band gap, provides insights into the material's conductivity: a large gap indicates insulators, while a small one suggests conductors or semiconductors. In the provided Ceria graph, blue lines represent energy bands, with the 0 eV level denoting the Fermi Level. Vertical lines highlight high symmetry points in Ceria's FCC lattice, critical for understanding its band structure.

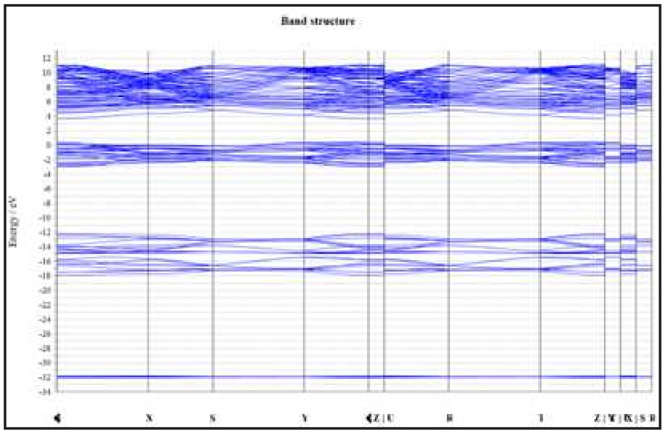

Figure 3-17 Band energy graph of Ceria (110).

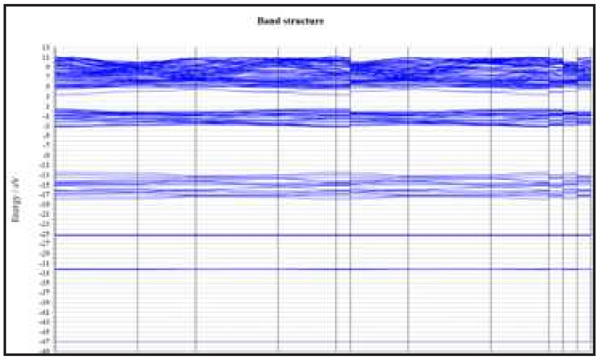

Figure 3-18 Band energy graph of Zr-doped Ceria (110) surface (6.25%).

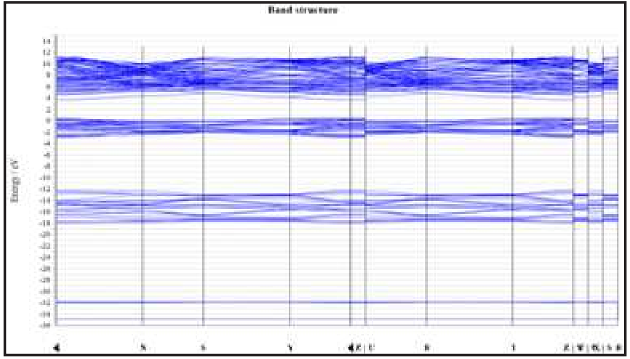

Figure 3-19 Band energy graph of Nd-doped Ceria (110) surface (6.25%).

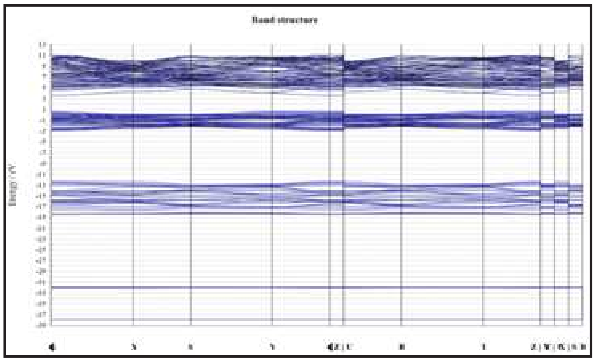

Figure 3-20 Band energy graph of Sm-doped Ceria (110) surface (6.25%).

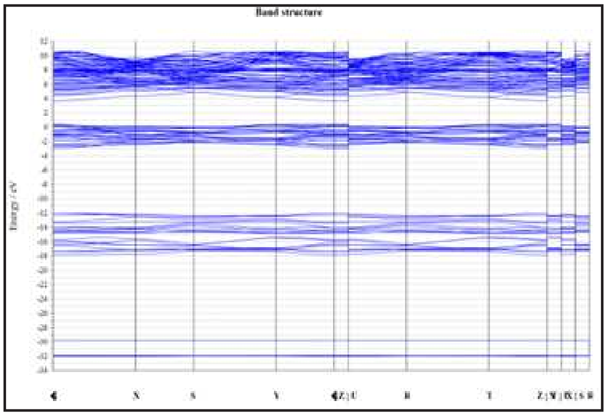

Figure 3-21 Band energy graph of La-doped Ceria (110)

surface (6.25%).

S.	Structure	Band Gap
1	Undoped Ceria	3.2 eV (2.9 reported)
2	Ceria- Zr Doped	2.5 eV
3	Ceria- Nd Doped	3.0 eV
4	Ceria- Sm Doped	2.7 eV
5	Ceria- La Doped	3.2 eV

The forbidden gap represents the energy difference between the highest valence band and the lowest conduction band. When ceria is doped with different elements, its band gap varies:

1. **Zr-doped Ceria**: Zirconium doping narrows ceria's band gap from its usual 2.8 to 3.2 eV to a range of 2.5 to 2.8 eV, depending on the Zr concentration.
2. **Nd-doped Ceria**: Neodymium doping typically reduces the band gap or leaves it unchanged. Nd introduces additional energy levels in the band gap, altering the material's electronic structure.
3. **Sm-doped Ceria**: Samarium doping's effect on the band gap isn't consistent and depends on factors like doping concentration. In general, its band gap is similar to Nd-doped ceria, showing a slight decrease or no change based on DFT studies.
4. **La-doped Ceria**: Lanthanum doping often results in a slightly larger band gap, increasing by about 0.1 to 0.3 eV compared to undoped ceria due to the introduction of additional energy levels by La dopants.

Summary and further work: DFT calculations were utilized to study the interaction of syngas (carbon monoxide and hydrogen) with the Ceria (100) surface. This exploration is vital for understanding catalytic processes, like CO2 capture and hydrogen production on Ceria-based materials. The research examined adsorption energies, molecular geometries, and electronic properties. Both carbon monoxide and hydrogen exhibited a preference for adsorption on Ceria's oxygen sites. Oxygen vacancies and surface defects significantly impacted these adsorption energies. Electronic structure investigations, including DOS and band energy analysis, detailed the changes in electronic properties and charge distribution upon syngas adsorption. These analyses provided deeper knowledge about the electron density redistribution and band energy level alterations.[7]

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