Ab Initio Investigation of Zr Adatoms on the $CeO_2(111)$ surface

Authors: Johnatan Mucelini
Dr. Yohanna Seminovski
M.Sc. Rafael Costa Amaral
Prof. Dr. Juarez L. F. Da Silva

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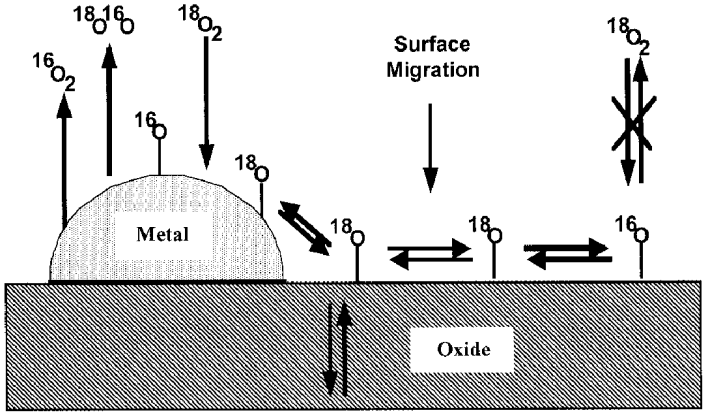
Motivation: CeO_2 catalysts applications

Catalysts support:

- Three way catalysts.
- Steam Reforming.
- Water-gas Shift Reaction.

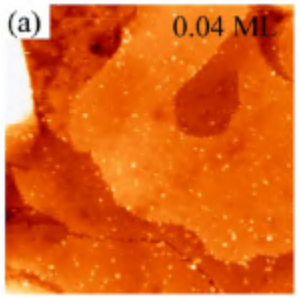
Realistic catalyst:



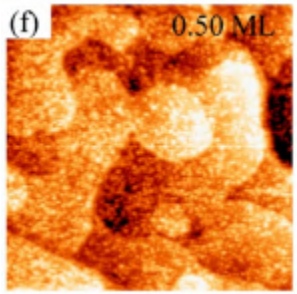
Oxide: CeO_2, $\underbrace{CeO_2{-}ZrO_2}_{\textit{Improvement}!}$.

$Zr–CeO_2$

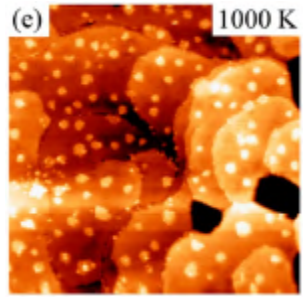
$CeO_2(111) + Zr_{0,04ML}$ — 300 K



$CeO_2(111) + Zr_{0,50ML}$ — 300 K



$CeO_2(111) + Zr_{0,50ML}$ — 1000 K



J. Phys. Chem. C, **2015**, *119* (32), pp 18257–18266

Open problems:

- What is the magnitude and nature of those interactions?
- Will Zr stay above the surface? inside the surface? or in bulk region?
- What changes Zr induce to CeO_2 surfaces?

Top. Catal., **2001**, *16* (1), pp 49–56

J. Catal., **2000**, *193* (2), pp 273–282

Theoretical Approach

- DFT-PBE + $\underbrace{\text{Hubbard U term to Ce } f\text{-states}}_{\text{Correct it localization}}$ in VASP code.

Adsorbed surface. $Zr/CeO_2(111)$ $\longleftarrow$ Clean Surface $CeO_2(111)$ $\longleftarrow$ Bulks Ex.: CeO_2

- Based in our computational parameters testes:

Bulks:

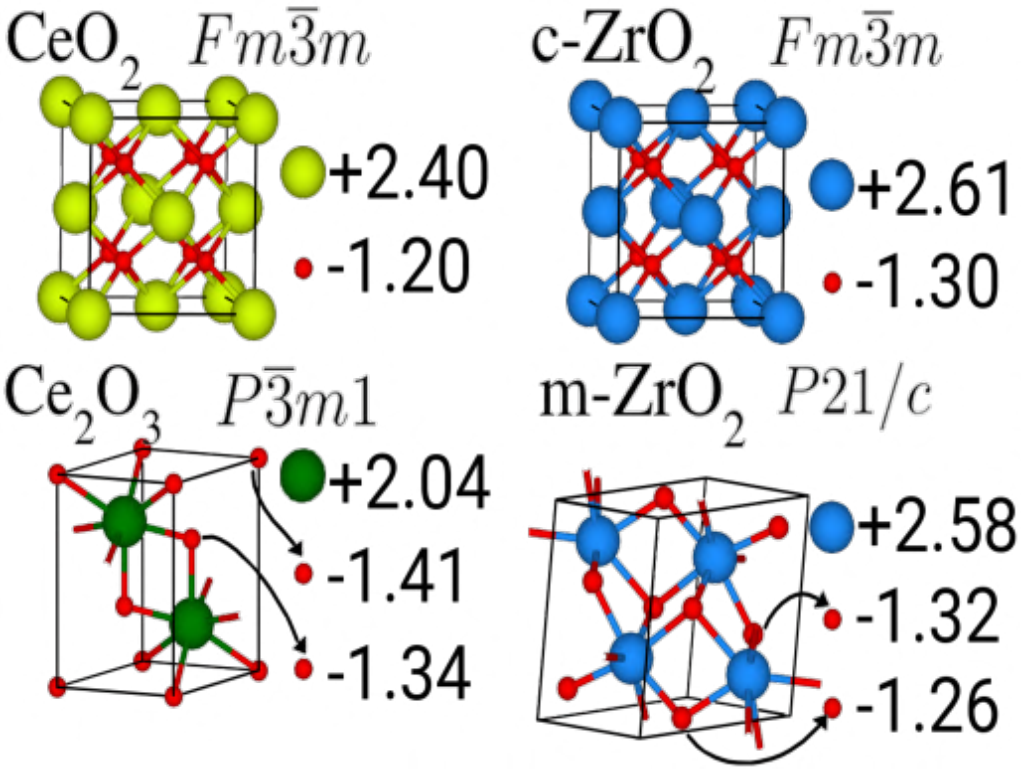
- Stress tensor:
  - Cutoff: 800 eV ($2 \times Emax$).
  - **k**-points: $10 \times 10 \times 10 (l = 30)$.
- Analysis:
  - Cutoff: 450 eV($1.125 \times Emax$).
  - **k**-points: $l = 30 - 45$.

Surface

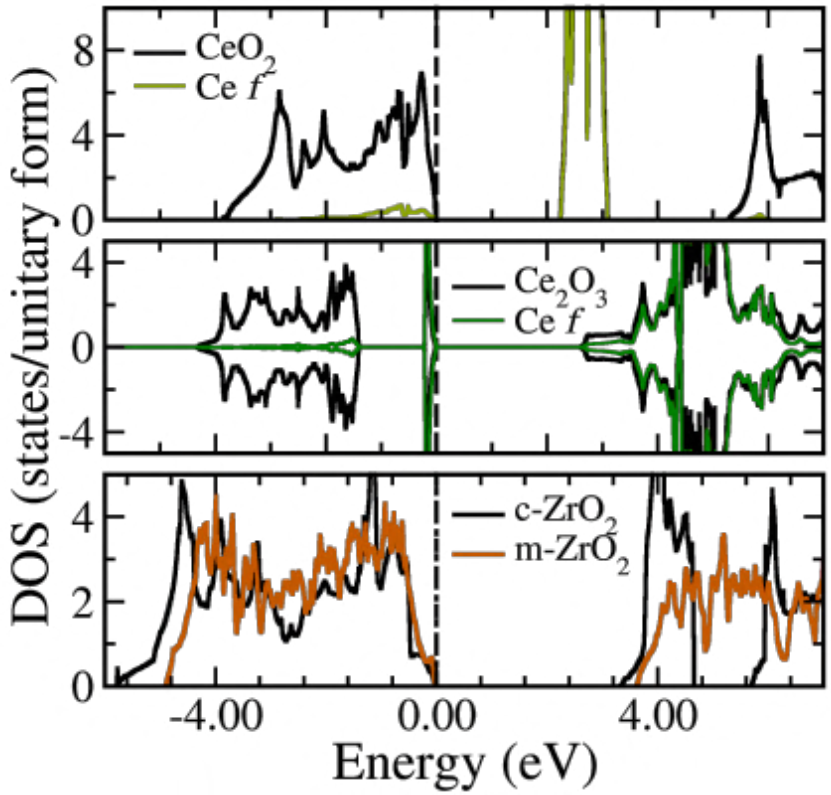
- Geometric optimization:
  - Cutoff: 450 eV ($1.125 \times Emax$).
  - **k**-point: Γ.

Bulks: CeO_2, Ce_2O_3 and ZrO_2

- Low energy bulk structures: cubic CeO_2 (fluorite), hexagonal Ce_2O_3 (lanthana), monoclinic ZrO_2 (baddeleyite).



- Comparison Ce and Zr: cubic ZrO_2.
- Stress tensor calculations.
- DOS, Bader.



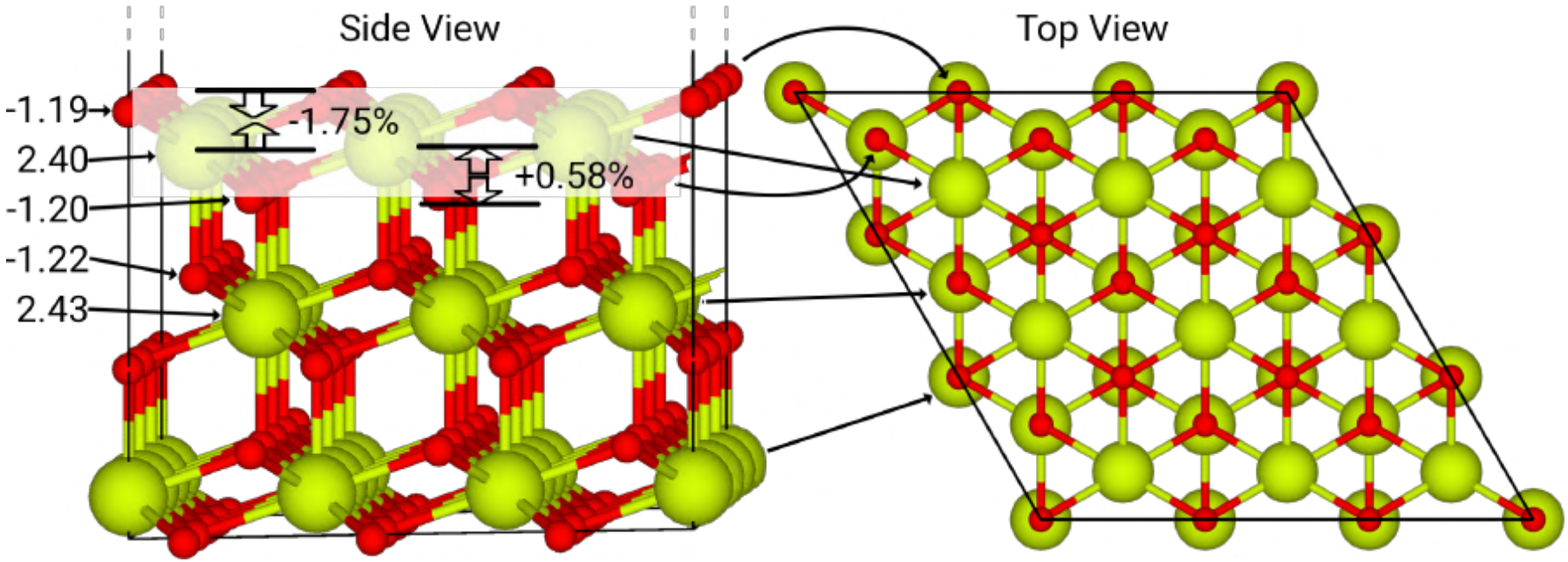
Bulk structure, spatial group, DOS, effective Bader charges in e. Ce^{4+} in **yellow**, Ce^{3+} in **green**, Zr in **blue**, and O^{2-} in **red**.

Unreduced $CeO_2(111)$ Surface and Zr Adsorption Sites

- Size: 3×3 (primitive $CeO_2(111)$).
- Layers: 9 (3Ce + 6O)
- Last 3 layers: kept frozen in this relaxed geometry.

↑ 12 Å vacuum ↑

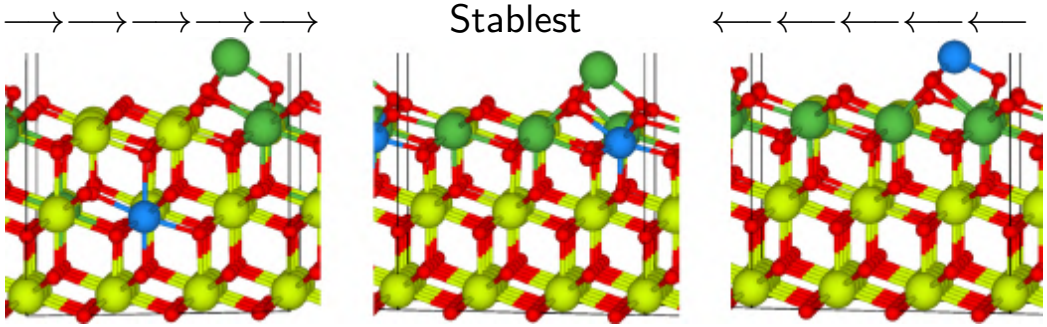
- Zr deposition: hcp-hollow, fcc-hollow, bridge, and top.
- O migration.
- Zr penetration on the surface.



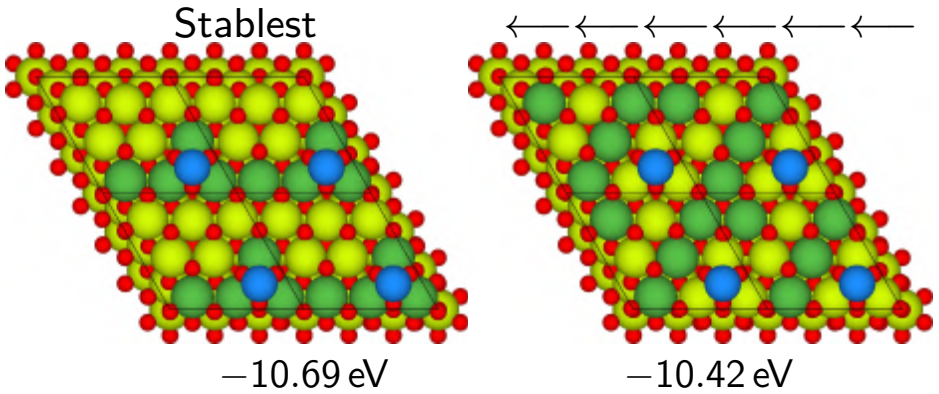
Effective Bader charges and geometrical deformation in relation to solid.

$Zr/CeO_2(111)$: Geometrical and Energetic Analysis

- Low energy coordination site: hcp-hollow!
- Zr oxidize to Zr^{4+} and some Ce^{+4} reduce to Ce^{3+}
- Lowest energy system with Zr in the surface



- Ce^{3+} Trends to stay closer the Zr, and in line.



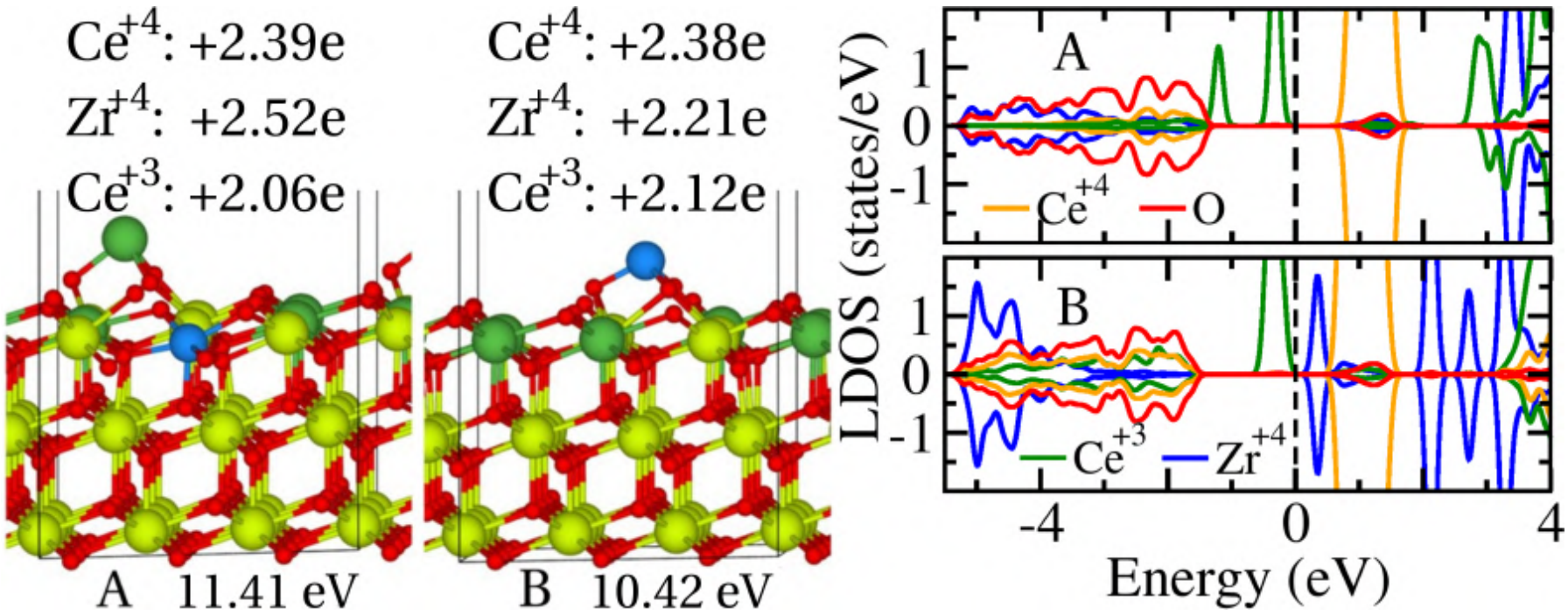
Ionic Interaction:
- Stability: $Ce^{4+}-O < Zr^{4+}-O$
- More coordination if Zr inside the bulk!
- O more reduced: $O-Ce^{3+} > O-Ce^{4+}$

Stress:
- Ionic radius: $Ce^{3+} > Ce^{4+} > Zr^{4+}$
- Ce^{3+} introduce stress.
- Zr^{4+} could reduce it.

Electrostatic Repulsion:
- Cations repulsion: $Zr^{4+}-Ce^{3+} < Zr^{4+}-Ce^{4+}$

- Highness:
  Exp.: 1.4 Å
  J. Catal., **2000**, *193* (2), pp 273–282
  Calc.: 1.58 Å

$Zr/CeO_2(111)$: Electronic Analysis



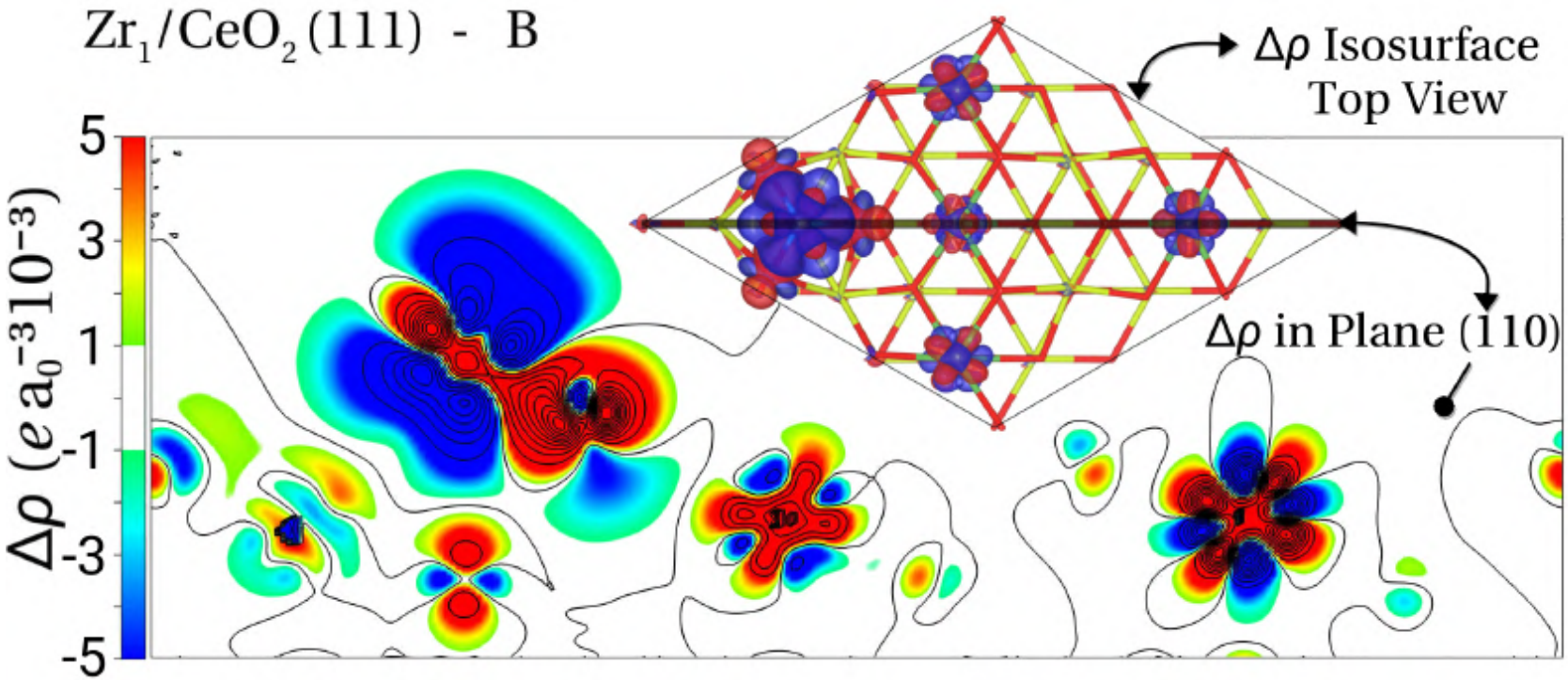
Evidence of:

$$Zr^0_g + 4Ce^{IV}{}_{surf} \longrightarrow Zr^{IV}{}_{ad} + 4Ce^{III}{}_{surf}$$

- Bader charges, DOS, magnetization, and bond lengths.

$Zr/CeO_2(111)$: Electron Density Difference Analysis

$$\Delta\rho = \rho_{Zr/CeO_2(111)} - \rho_{CeO_2(111)^*} - \rho_{Zr}$$



1°: $CeO_2(111) \longrightarrow CeO_2(111)^*$

- 3 O oxidize (close to Zr).
- 4 Ce^{IV} partial reduce to Ce^{III}.

2°: $CeO_2(111)^* + Zr \longrightarrow Zr/CeO_2(111)$

- Zr oxidize to Zr^{IV}
- 3 O reduce.
- 4 Ce^{III} finish to reduce.

Conclusion

- Low energy coordination site to Zr adatom above the ceria surface: hcp-hollow.
- Low energy site to Zr atom in partial reduced ceria surface: in the surface.
- Zr introduction modification in unreduced $CeO_2(111)$:
  - Change in cations nature.
  - Introduce strain in the surface.
- We present several analysis to found Ce^{3+} in partial reduced $CeO_2(111)$.

Acknowledgments to:

Organizer committee, audience,

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