Exploring electronic metal and electronic oxide support interactions (EMSI - EOSI)

Pablo Castro-Latorre,[1] Konstantin M. Neyman,[1,2] Albert Bruix[1]

p.castrola@ub.edu

[1] *Departament de Ciència de Materials i Química Física i Institut de Química Teòrica i Computacional - Universitat de Barcelona, Barcelona, Spain*

[2] *Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain*

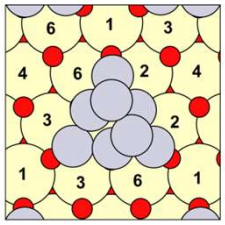
Introduction

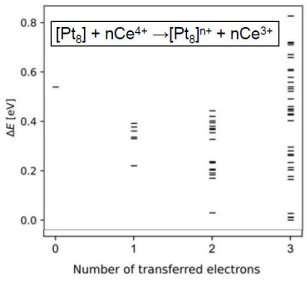
The interaction between metal nanoparticles and their supporting material are important in catalysis. These interactions depend on the size of the metal particle, the nature of the support, and the environmental conditions. On reducible supports such as CeO_2, so-called electronic metal-support interactions (EMSI) may emerge, involving the transfer of electrons from the metal to the support material and altering the electronic and chemical properties of supported species. To evaluate the role of EMSI on chemical properties of various catalytic materials, we characterize the electronic states exhibited by different structural models of Pt/CeO_2, FeO/CeO_2, and $Au/FeO/CeO_2$ as examples of metal and oxide species supported on reducible CeO_2.

4f-core potentials for systematic exploration of EMSI

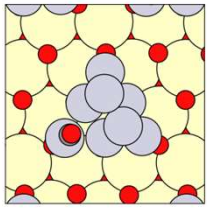
Pt_8 clusters are used as test systems for the systematic evaluation of EMSI on reducible CeO_2 support using 4f-core potentials.

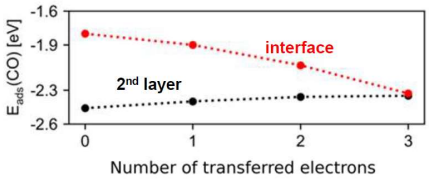
Different electronic states are defined by number and position of Ce^{3+} cations, created upon e^- transfer from Pt 5*d* to Ce 4*f* states.





Adsorption energies are dependent on electronic states.

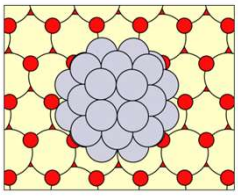




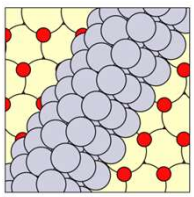
P. Castro-Latorre, K.M. Neyman, A. Bruix; *J. Phys. Chem. C* 2023, 127, 36, 17700–17710

Currently extending this systematic analysis to other Pt/CeO_2 structural models of varying size and dimensionality:

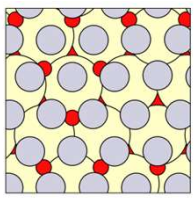
0D particle



1D rod



2D films

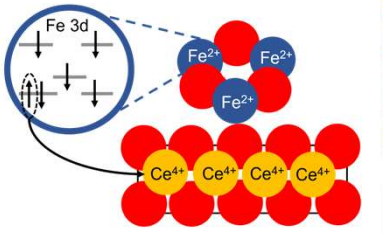


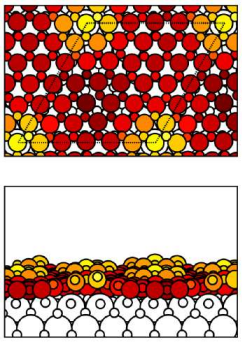
Computational details:

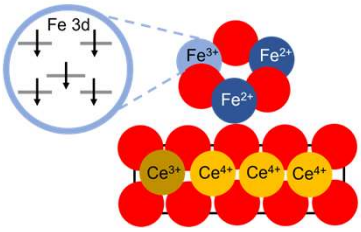
- The systematic characterization of EMSI on ceria-supported nanostructures relies on Ce 4f-core PAW potentials, which include a 4f electron in the fixed core of selected Ce atoms.
- Results with 4f-core potentials are validated with calculations without Ce 4f electrons fixed as core electrons.
- PW91 functional is used in combination with the Hubbard +U correction (U = 4 eV for Ce 4*f*, U = 5 eV for Fe 3*d*).
- VASP software, PAW potentials.

EOSI on Oxide-Oxide Interface: FeO/CeO_2 case

2D FeO supported on CeO_2 is strongly corrugated and exhibits various stable electronic states, with redox processes involving Fe 3*d* and Ce 4*f* states. States with various Fe^{3+}/Fe^{2+} ratios emerge.





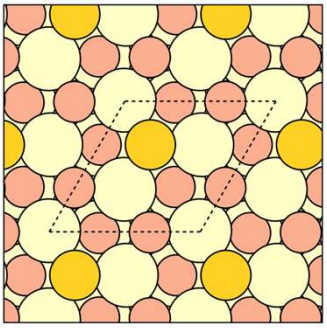


Fe^{3+}/Fe^{2+} ratio	Relative energy [eV]
0	0.40
1/3	0.0
1	0.56

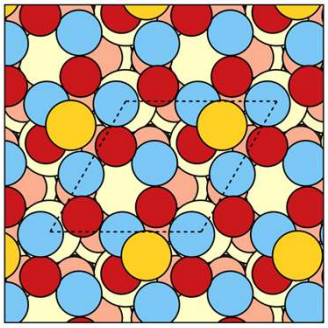
L. Piliai, **P. Castro-Latorre**, K.M. Neyman, P. Matvija, A. Bruix, et. al; *ACS Appl. Mater. Interfaces* 2024, 16, 46858-46871

Effect of the oxide-oxide interface on the adsorption of Au.

$Au\text{-}CeO_2$



$Au\text{-}FeO/CeO_2$



E_{ads} = -0.82 eV ⟶ Au^0

E_{ads} = -0.95 eV ⟶ 0 Ce^{3+}; 1 Fe^{3+}, Au

E_{ads} = -1.23 eV ⟶ 1 Ce^{3+}; 2 Fe^{3+}, Au

Au interacts more strongly with FeO than CeO_2 and FeO reduces both Au and CeO_2. This is promising for catalysts with stable and negatively charged metal centers.

P. Castro-Latorre, K.M. Neyman, P. Matvija, A. Bruix, et. al; In preparation