

CeO₂(111) Electronic Reducibility Tuned by Ultra-small Supported Bimetallic Pt-Cu Clusters

Lauro Oliver Paz-Borbón^{*1}, Fernando Buendía¹, Ignacio L. Garzón¹, Alvaro Posada-Amarillas², Francesc Illas³ and Jun Li^{4,5}

¹Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, 01000 CDMX, Mexico

²Departamento de Investigación en Física, Universidad de Sonora, Blvd. Luis Encinas & Rosales, 83000 Hermosillo, Mexico

³Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), de la Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

⁴Department of Chemistry, Tsinghua University, Haidian District, Beijing 100084, China

⁵Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China

*oliver_paz@fisica.unam.mx

Introduction

Cutting edge experimental and computational work on the deposition of size- and composition- selected clusters over oxide surfaces helps to narrow down the current gap between gas-phase cluster studies and the traditional field of heterogeneous catalysis [1]. This study aims further at the advance of frontier research areas such as single-atom (SAC) catalysis [2]. Furthermore, understanding Ce⁴⁺ to Ce³⁺ electronic reducibility in CeO₂ supported metal particles has enormous implications in heterogeneous catalysis. This is particularly true in attempting to predict supported metal catalysts' chemical reactivity and selectivity, where knowledge at the atomic level is still largely lacking [3].

Materials and Methods

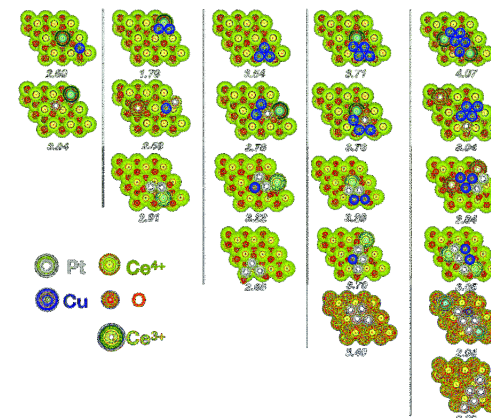
Density Functional Theory (DFT) based calculations are carried out using the periodic plane-wave Quantum ESPRESSO code. The gradient-corrected Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional is used along with Rappe–Rabe–Kaxiras–Joannopoulos and Vanderbilt type ultrasoft pseudopotentials for Pt, Cu and Ce, and O atoms respectively. The DFT+*U* formalism, with a *U* parameter for the Ce(4f) level set to 4.5 eV as recommended in the literature [4], is used to correctly describe the highly localized Ce atom f-electrons. We use our recently implemented global optimization routine based on the Basin Hopping Monte Carlo (BH-DFT) methodology [5]. It allows one to thoroughly explore the bimetallic Pt_{*m*}Cu_{*n*}/CeO₂(111) potential energy surface (PES) up to *N* = 5 (*N* = *m* + *n*) and to locate putative global minima (GM) configurations and high energy isomers. Performing global optimization searches on bimetallic systems is always a difficult task as the number of possible low-energy isomers increases with size due to the presence of “homotops”. In order to increase the efficiency of our BH-DFT code, we introduce an atom-exchange (“swap”) routine (SWAP.PY) to search for low-energy permutations of atoms A and B (*i.e.* “homotops”).

Results and Discussion

Our PBE+*U* global optimization calculations indicate a preference for Pt-Cu clusters to adopt 2D planar geometries parallel to the oxide surface, due to the formation of

strong metal bonds to oxygen surface sites and charge transfer effects. Calculated adsorption energy values (*E*_{ads}) for both mono- and bimetallic systems are of the order of 1.79 up to 4.07 eV, implying a strong metal cluster interaction with the oxide surface. Our calculations indicate that at such sub-nanometer sizes, the number of Ce⁴⁺ surface atoms reduced to Ce³⁺ cations are mediated by the amount of Cu atoms within the cluster, reaching a maximum of three Ce³⁺ for supported Cu₅ cluster [6].

Figure 1. Calculated BH-DFT lowest energy configurations for supported mono-metallic Cu_{*N*} and Pt_{*N*}, and bimetallic Pt_{*m*}Cu_{*n*} clusters supported on the (3×3) periodic CeO₂(111) surface. The size range considered varies from 1 to 5 atoms, including all compositions. The adsorption energy (*E*_{ads}) values are shown in eV. The location of the reduced Ce⁴⁺ to Ce³⁺ cations is also displayed. Our calculations indicate that the location of the reduced Ce³⁺ cations are always in the vicinity of the metal cluster, while the Ce⁴⁺ to Ce³⁺ charge transfer process is mediated by neighbouring O_{surface} atoms, thus completing the redox process between the oxide surface and the supported metal cluster. Colour labelling: grey (Pt), blue (Cu), light green (Ce⁴⁺), dark green (Ce³⁺) and red (O) atoms, respectively.



Significance

Our computational results have critical implications on the continuous understanding of the strong metal-support interactions over reducible oxides such as CeO₂, as well as the advancement of frontier research areas such as heterogeneous single-atom catalysts (SAC) and single-cluster catalysts (SCC).

References

1. S. Vajda and M. G. White, *ACS Catal.*, 2015, **5**, 7152
2. B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li and T. Zhang, *Nat. Chem.*, 2011, **3**, 634
3. H. Kuhlenbeck, S. Shaikhtudinov and H.-J. Freund, *Chem. Rev.*, 2013, **113**, 3986
4. P. Ghosh, M. Farnesi Camellone and S. Fabris, *J. Phys. Chem. Lett.*, 2013, **4**, 2256
5. L. O. Paz-Borbón, A. López-Martínez, I. L. Garzón, A. Posada-Amarillas and H. Groenbeck, *Phys. Chem. Chem. Phys.*, 2017, **19**, 17845
6. L. O. Paz-Borbón, F. Buendía, I. L. Garzón, A. Posada-Amarillas, F. Illas, J. Li, *Phys. Chem. Chem. Phys.*, 2019, **Advanced Article**, DOI : 10.1039/c9cp01772k