Transition-Metal Clusters Supported on the CeO$_2$(111) Surface: A Density Functional Theory Investigation

Polina Tereshchuk[1] (PQ), Yohanna Seminovski[1] (PQ), Rafael L. H. Freire[2] (PG), Maurício J. Piotrowski[3] (PQ), Adam Kiejna[4] (PQ), and Juarez L. F. Da Silva[1,*] (PQ)

[1]*São Carlos Institute of Chemistry, University of São Paulo, São Carlos, SP, Brazil,* [2]*São Carlos Institute of Physics, University of São Paulo, São Carlos, SP, Brazil,* [3]*Department of Physics, Federal University of Pelotas, Pelotas, RS, Brazil,* [4]*Institute of Experimental Physics, University of Wrocław, Wrocław, Poland*

Key words: *Cerium oxides, Surfaces, Ab-initio Quantum Chemistry*

Introduction

A typical catalyst employed for ethanol steam reforming is composed of transition-metal (TM) particles supported on oxides (e.g., Al$_2$O$_3$, CeO$_2$, and etc.), where the catalytic activity and hydrogen selectivity are dependent on the TM particles (chemical species, size, shape, etc.) and substrate properties (stability, surface orientation, oxygen vacancies, etc.), as well as on synergetic effects that might arise in the combination of TM with oxide systems. Although several studies have been reported for TM particles supported on ceria, our atomistic understanding of the TM-CeO$_2$ interactions is still far from complete. To address this problem, we performed a systematic investigation of the interaction of TM$_4$ (TM = Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au) and TM$_{13}$ (TM = Rh, Pd, Pt, and Au) clusters with the unreduced CeO$_2$(111) surface.

Theoretical Approach

In this work, we employed spin-polarized density functional theory calculations within the Perdew-Burke-Ernzerhof functional and taking into account on-site orbital-dependent Coulomb interactions for the Ce 4f-states as implemented in the Vienna Ab-initio Simulation Package (VASP). For the on-site Coulomb 4f-interactions, we used an effective parameter of 4.50 eV, which have been employed for a large number of cerium oxide studies. For the 4-atom clusters, we employed a (2x2) surface unit cell, while for the 13-atom clusters, we employed a (4x4) surface unit cell. To obtain the atomic structure of the TM clusters supported on the (111) surface, we employed ab-initio molecular dynamics simulations to selected atomic structure models, which were then optimized at zero-temperature using conjugated gradient algorithms.

Results

We found two structure patterns for the 4-atom clusters supported on CeO$_2$(111), namely, two-dimensional (2D) arrays with zig-zag orientation for Ru, Rh, Os, and Ir and tetrahedral 3D configurations for Cu, Pd, Ag, Pt, and Au. The 13-atom clusters form pyramidal-like structures on CeO$_2$(111) in the lowest energy configurations following stacking sequence, TM/TM$_4$/TM$_8$/CeO$_2$(111), while they adopt 2D structures at high energy structures. Our analyses indicate that the occupation of the antibonding d-states and the hybridization of the TM d-states with O p-states play a crucial role in the magnitude of the TM-TM and TM-O interactions and determine the formation of the 2D and 3D configurations on CeO$_2$(111). The interaction of the TM atoms with the CeO$_2$(111) surface changes the nature of the occupied Ce 4f-states from itinerant (Ce^{IV}) to localized (Ce^{III}) behavior. For example, the Ce^{IV} cations can be found in the bulk CeO$_2$ and unreduced surfaces, while the Ce^{III} cations are found in systems such as Ce$_2$O$_3$, CeVO$_4$, and reduced surfaces. Because of the charge state change, there is a change in the atomic radius of the cations. For example, the localization of the Ce 4f-states increases the atomic radius of the III cation by about 4.4% compared with the IV cation. The change in the oxidation state is induced by the charge transfer between the TM atoms and the oxides surface due to the large difference of the electronegavity, which will be discussed based on the Bader analysis.

Conclusions

We identified few trends in the formation of the atomic structures of small clusters supported on the CeO$_2$(111). We identified the role of the TM atoms in the change of the oxidation state of the Ce atoms based on the charge transfer among the different atoms (TM, Ce, and O). Further details are discussed elsewhere [1,2] or feel free to contact Juarez L. F. Da Silva (juarez_dasilva@iqsc.usp.br).

Acknowledgments

———————————————

[1] M. J. Piotrowski, P. Tereshchuk, J. L. F. Da Silva, J. Phys. Chem. C **2014**, 118, 21438–21446.

[2] P. Tereshchuk, R. L. H. Freire, C. G. Ungureanu, Y. Seminovski, A. Kiejna, J. L. F. Da Silva, paper submitted in **2015**.