

Elucidating Cerium + H₂O Reactivity through Electronic Structure: A Combined PES and DFT Study

Josey Topolski, Jared Kafader, Manisha Ray, Caroline Jarrold, Indiana University at Bloomington

Abstract

Ceria (CeO₂) has been established as a good support in heterogeneous catalysts for the water gas shift reaction. This study looks into cerium's reactivity with water, a water gas shift reagent, and aims to build an understanding of the three reactions which can occur: direct oxidation, -OH abstraction, and H₂O addition. Through the use of anion photoelectron spectroscopy and density functional theory calculations we have been able to determine that the reactivity is dependent on (1) the oxidation states of the metal centers, (2) the availability of 5d orbitals to form metal oxide bonds, and (3) the presence of electrons in the 6s* orbital. The results of this study can be used to inform design of catalytic materials for the water gas shift reaction.

Experimental Methods

Clusters were generated using a laser ablation/pulse molecular beam valve assembly.

Time of Flight Mass Spectroscopy

Clusters were exposed to increasing concentrations of water seeded in helium gas through a second pulse molecular beam valve. By varying the reaction channel temperature and the introduced water concentration a kinetic analysis of the reactions was completed.

Photoelectron Spectroscopy

Prior to colliding with the ion detector, a second laser was used to detach an electron from the cluster. The electron travels up a field free drift tube and hits a second detector. The kinetic energy of the electron can then be related to the binding energy through the following relationship:

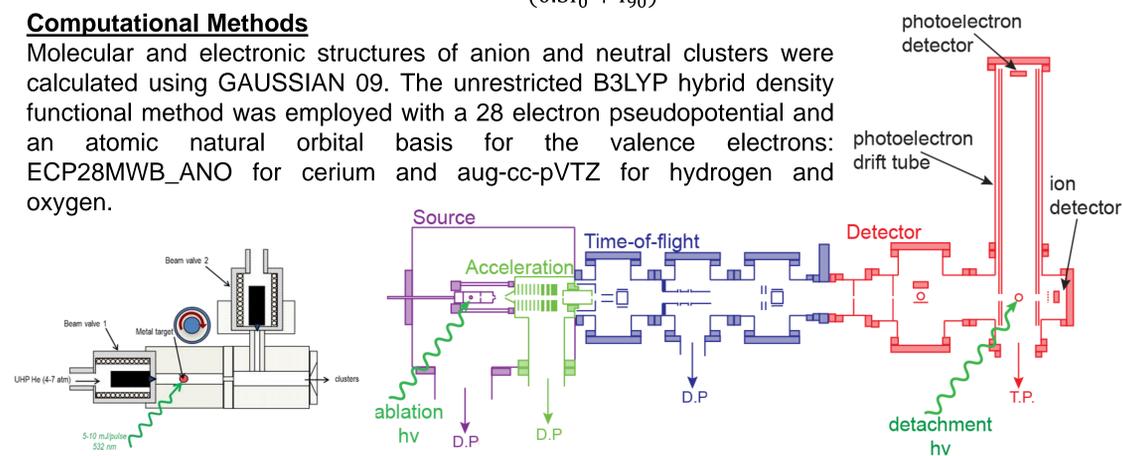
$$e\text{BE} = h\nu - e\text{KE}$$

The experiment was completed with laser polarizations of $\theta = 0^\circ$ and $\theta = 90^\circ$. The resulting intensities can be related by the following equation in order to gain insight about the detachment cross section.

$$\beta = \frac{(I_0 - I_{90})}{(0.5I_0 + I_{90})}$$

Computational Methods

Molecular and electronic structures of anion and neutral clusters were calculated using GAUSSIAN 09. The unrestricted B3LYP hybrid density functional method was employed with a 28 electron pseudopotential and an atomic natural orbital basis for the valence electrons: ECP28MWB_ANO for cerium and aug-cc-pVTZ for hydrogen and oxygen.



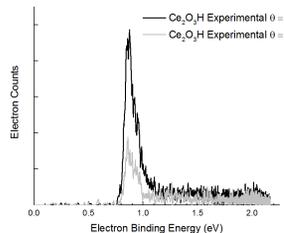
DFT v. Experiment Test Case: Ce₂O₃H⁻

Experiment

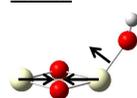
Binding Energy: 0.84 eV
Polarization Dependence: $\beta = 0.87$: consistent with e⁻ p-wave
Peak Width: e⁻ from bonding or antibonding orbital

DFT Calculation

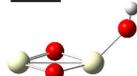
Binding Energy: 0.77 eV
Detachment Orbital: 6s – like (distorted due to hybridization, bonding, etc.)



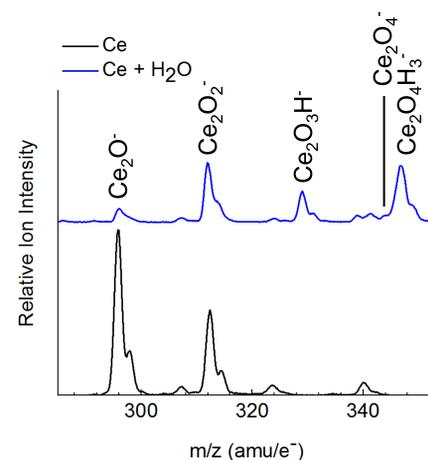
Neutral



Anion

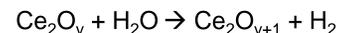


Cerium + H₂O Reactivity Studies

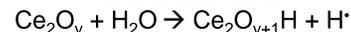


Possible Reaction Pathways

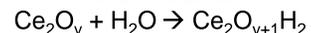
Direct Oxidation



-OH Abstraction



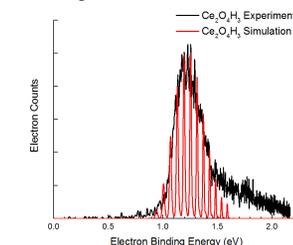
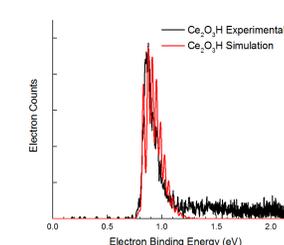
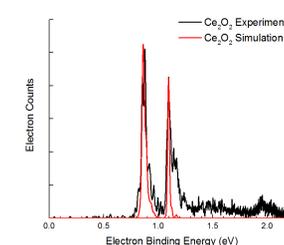
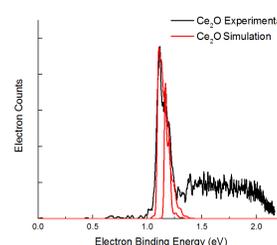
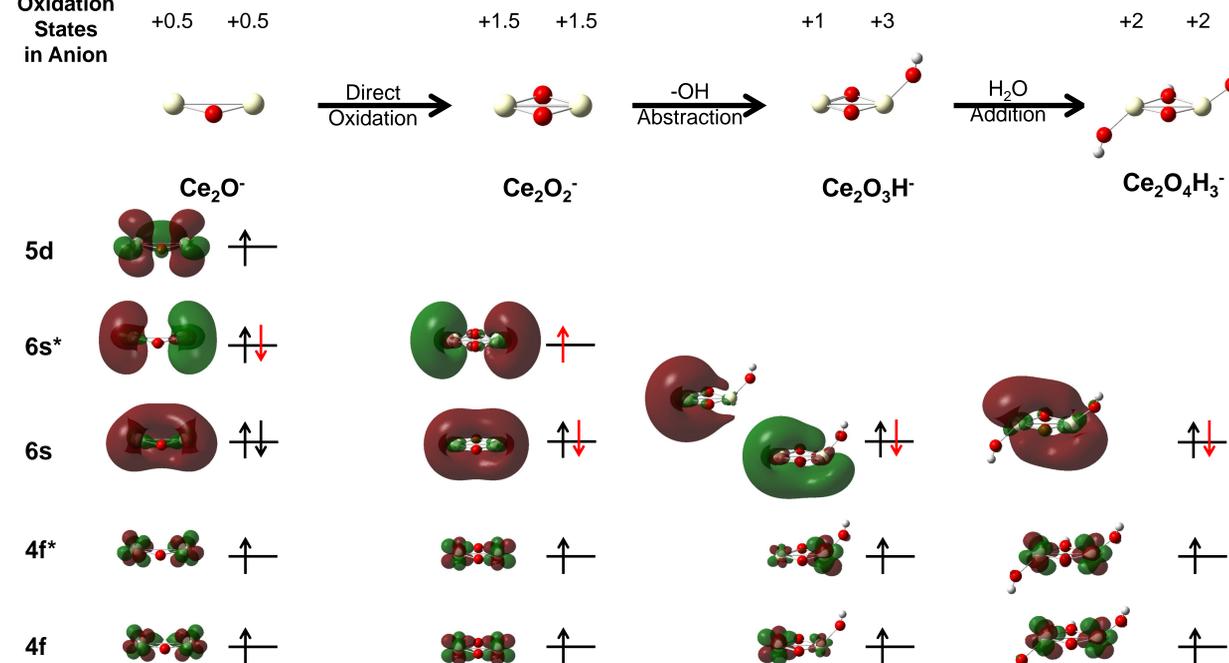
Water Addition



Felton, J. A.; Ray, M.; Waller, S. E.; Kafader, J. O.; Jarrold, C. C., *J. Phys. Chem. A* **2014**, *118* (43), 9960-9969.

Combined PES and DFT Results

Cerium Oxidation States in Anion



Key Findings

Oxidation States

As the reaction sequence proceeds the cerium metal centers are oxidized. It is believed that reactivity should be continuous until all metal centers are in a +4 oxidation state in the neutral cluster. This sample of data demonstrates cerium's oxidation from +1 to +2.5 for the neutral cluster.

Electronic Structure

The reactivity of cerium oxide clusters has been found to be heavily dependent on the electronic structure. The availability of molecular orbitals to form bonds with water is the directing factor for which reaction will occur. Direct oxidation will occur as long as there are at least two electrons beyond the 6s orbital with bonding occurring through the 5d orbitals. Two electrons are needed in order to create a bond with oxygen. If the sequence of direct oxidation yields an unpaired electron in the 6s* orbital, -OH abstraction will occur. Once all electrons beyond the 6s orbital are used, the cluster will undergo water addition. Water addition does not consume electrons from the 6s orbital, resulting in the highest occupied molecular orbital remaining the same.

Future Directions

Mixed Metal Systems

This study has provided much insight into cerium's reactivity with water, but it is essential to study mixed metal systems in order to fully understand heterogeneous catalysts. Some mixed metal systems which have been used for the water-gas shift reaction are: Pt/CeO₂, Au/CeO₂, CuO/CeO₂, and Ni/CeO₂.

Acknowledgements

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