A Density Functional Theory Investigation of the Reaction of Water with Ce_2O^-

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Abstract

Cerium suboxide clusters have been shown to react with water to yield H_2 . Since reactions of metal oxides with water are of great fundamental and practical importance in energy science, detailed study of this reaction can provide new key knowledge for future catalyst design. Using density function theory calculations, we identified and report complete reaction pathways for two spin-states of Ce_2O^- reacting with H_2O . Additionally, examining the molecular orbitals of initial and final cerium oxide clusters, we found that metal d electrons facilitate the reduction of water. This work provides new understanding of this reaction and insights to the reactivity enhancements for cerium-doped surfaces.

Introduction

Water, being one of the most abundant substances in nature, has been the subject of intense interest for scientists to study its physical and chemical properties.¹⁻¹¹ In addition to the various roles water plays in different families of chemical reactions and biological systems, H_2O has been a key focus in energy related research. Of particular interest are catalysts facilitating the four-electron $2\text{H}_2\text{O} \longrightarrow 2\text{H}_2 + \text{O}_2$ reaction.¹²⁻¹⁷ Cerium oxides attracted special interest recently due to their ability to efficiently catalyze a wide range of oxidation and reduction reactions, including water-gas shifting reactions.¹⁸⁻²² Several studies have also shown that cerium oxide-supported metal surfaces exhibit increased catalytic activity relative to their non-cerium oxide supported analogues.²³⁻³⁵

Surface defects due to metal or oxide deficiencies possess unique electronic properties and facilitate increased reactivity. As with other metal oxides, the catalytic activity of lanthanide oxide surfaces is most active at surface defect sites. However, studying extended surfaces is complicated by the low concentration of surface defects and the continuous structural changes along the surfaces. Defect sites exhibit incomplete valencies and localized electronic structures,³⁶ thus they pose as model systems to study reactivity on surface defects on

catalytic surfaces.

While the partially filled f-manifold in most lanthanide complexes lies close to the 5d and 6s orbitals of the lanthanide centers, it is non-bonding in nature and exhibits core-like behavior. Several studies have shown that the orbitals involved in chemical processes on lanthanides and lanthanide-based clusters involve 6s and 5p orbitals, while the occupation number of 4f orbitals remains intact.³⁷⁻⁴³

Several experimental and computational studies have been performed on cerium oxide clusters in order to better understand the electronic structure features that pave the way to a thorough understanding of their reactivity and catalytic activity. In addition, various experimental and theoretical studies have explored the reactivity of classes of cerium-based clusters with various gas-phase small molecules.^{17,19,39,42,44-56} Of particular interest here are computational studies conducted by Zhou and co-workers on the reactivity of Ce_n ($n=1-3$) with up to six water molecules.^{44,45} Their results indicate high reactivity of these cerium clusters and their efficiency in decomposing multiple water molecules. Recently, Jarrold and co-workers reported mass spectra of $Ce_xO_y^-$ systems ($x=2,3$, $y=1-4$) and their respective products of the clusters and water.¹⁷ Their results indicate that cerium oxide clusters undergo three types of reactions: hydrogen gas production, water abstraction, and hydroxide abstraction. The relative selectivity of one reaction type over the others is highly dependent on the stoichiometry of the cluster. For example, Ce_2O^- , Ce_3^- , $Ce_3O_2^-$, and $Ce_3O_2^-$ preferentially produce H_2 gas, while clusters with equal stoichiometric ratios of Ce and O undergo $-OH$ abstraction, and clusters bearing more oxygens than ceriums undergo water abstraction.

In order to investigate the mechanism of water reactivity with cerium oxide clusters, we consider the simplest stoichiometric cluster that is capable of efficiently producing H_2 gas, namely Ce_2O^- . We first examine the geometric and electronic structure of different gas-phase clusters potentially involved in the reaction. Obtained experimental results include data from mass-spectrometry and photoelectron spectroscopy which supply us with valuable

information on the geometric and electronic structures of the studied molecules. To this extent, we map the potential energy surface of the studied reaction by altering the relative positions of cerium, oxygen, and, when necessary, hydrogen atoms as well. In addition, for each conformation, we optimize the geometry under several spin-states and investigate the relative stabilities of these states. In this paper we present an exploration of the reaction of Ce_2O^- with water to provide a clear mechanistic explanation of the overall chemical process.

Computational Methods

Calculations were performed using a development version of the GAUSSIAN suite of electronic structure programs.⁵⁷ The B3PW91 density functional was employed.^{58–62} The unrestricted formalism was used for all calculations.⁶³ The Stuttgart relativistic small core atomic natural orbital basis set and corresponding effective core potential (ANO/ECP) basis set with 28 core electrons and a contracted valence basis set (14s13p10d8f6g)[6s6p5d4f3g] for cerium center.⁶⁴ The Dunning style correlation-consistent basis set aug-cc-pVTZ was used for oxygen and hydrogen centers.^{65,66} Geometry optimizations were carried out using standard methods and the nature of all located potential energy surface stationary points were confirmed by vibrational frequency analysis.⁶⁷ Intrinsic reaction coordinate (IRC) calculations were performed to ensure that optimized transition structures connect appropriate potential energy surface minima.^{68,69} For all stationary points along the reaction pathways, all reasonable spin-states were calculated. The stability of all calculated Kohn-Sham determinants was verified.^{70–72} Reported enthalpies of reactions were calculated at 298 K. Relative energies including zero-point corrections at 0 K are reported in the supporting information.

Results and Discussion

In what follows, structures are labeled as X - n , where $X=A,B,C\dots$ represents a particular molecular structure, and the value of n indicates the multiplicity of the cluster. Transition

structures are labeled as TS1- n and TS2- n , where n also represents the spin multiplicity of the transition structure. As shown in Scheme 1, the reaction proceeds via the addition of water to a cerium center (**A** $\longrightarrow$ **G**), followed by formation of a hydride bridge between cerium atoms (**G** $\longrightarrow$ **H**). This is followed by formation of complex **I**, which features a bridging hydroxide ligand. The last step yields evolution of H_2 and formation of Ce_2O_2^- .

Scheme 1: Overview of the proposed mechanism

Reactant and Product Cerium Oxide Clusters

The first step of exploring the mechanism of $\text{Ce}_2\text{O}^- + \text{H}_2\text{O} \longrightarrow \text{Ce}_2\text{O}_2^- + \text{H}_2$ is to determine the initial structure of Ce_2O^- . In order to do so, various molecular structures and electronic configurations were studied. For a Ce_2O^- molecule, two general structures can be considered: (1) the oxygen atom can bridge the two cerium atoms; or (2) the oxygen can be a terminal and bound to one cerium only. In addition to the molecular structure, we accounted for the possible existence of several spin-states. We performed our calculations on the ground-state quartet in addition to doublet and the sextet multiplicities.

Our calculations showed that several different structures of Ce_2O^- species exist. Figure 1 shows all competitive Ce_2O^- species. The ground state of Ce_2O^- , shown in Fig. 1 as **A-4**, is a quartet state featuring a bridging oxide. In this structure, the two Ce–O bonds are equivalent with a bond length of 2.06 Å and a Ce–O–Ce angle of 120.8°. Two other closely lying states, both having bridging oxides were located. The first is the sextet (**A-4**), lying 3.92 kcal/mol higher than **A-4** and the doublet state (**A-2**) which is 9.88 kcal/mol higher in energy than the ground state. These results are in agreement with the anion photoelectron spectroscopy results published by Kafader et al.³⁹ Another located structure, **B-6**, features

a terminal oxide rather than bridging and has a sextet spin ground state. This structure is much higher in energy than the others; it is 48.40 kcal/mol higher than **A-4**. Quartet and doublet states were not found for this structure. Despite the fact that **B-6** is much higher in energy than the other three structures, we still considered the possibility of its role in the reaction with water and consequent H_2 production. Yet, calculations that considered **B-6** to be the structure for the initial Ce_2O^- reactant did not yield any conclusive results.

Figure 1: Optimized structures of Ce_2O^- and their relative energies given in kcal/mol.

In order to determine the various geometric structures of the product cluster species **C**, Ce_2O_2^- , we consider different variations in the positions of oxygens relative to the cerium centers. As for **A** and **B** above, each oxide can either be at terminal positions relative to a cerium atom or bridging the two cerium centers. We have calculated various combinations of terminal and bridging geometric configurations.

Figure 2 shows the various identified Ce_2O_2^- structures and their relative energies. The ground-state structure, **C-4**, is a quartet planar structure where both oxygens are bridging the two cerium atoms. Another closely lying state is doublet **C-2**, which has a geometry similar to the ground-state. **C-2** lies only 0.63 kcal/mol higher than **C-4**, and the geometries of the two structures are quite similar.

Compounds **C-6** and **F-2** lie approximately 25 kcal/mol higher in energy than **C-2** and **C-4**. **C-6** is a sextet and is 24.94 kcal/mol higher in energy than **C-4**. Although the structure of **C-6** is similar to **C-4** and **C-2**, **C-6** is not a planar structure. In fact, the $\text{Ce}-\text{O}-\text{Ce}-\text{O}$

torsion angle is 20.3° , unlike **C-4** and **C-2**, which have Ce–O–Ce–O torsion angles of 0° .

An additional set of higher energy Ce_2O_2^- isomers have also been found and are labeled **D-n**, **E-n**, and **F-n**. The geometry of **F-2**, which is only 2.2 kcal/mol higher in energy than **C-6**, is quite different. Specifically, one oxide is terminal while the other one is bridging. Given that **D-2**, **D-4**, **D-6**, **E-2**, **E-4**, **E-6**, and **F-6** are all much higher in energy (58.73 - 162.47 kcal/mol) we presume that they do not contribute to the mechanistic study presented in this paper and do not consider them further.

Figure 2: Optimized structures of Ce_2O_2^- and their relative energies given in kcal/mol.

In their study, Kafader et al. reported the anion photoelectron spectra of Ce_2O^- and Ce_2O_2^- is reported alongside a computational analysis to fully characterize the observed structures.³⁹ DFT calculations and Franck-Condon simulations were used to determine that the ground-state configuration of Ce_2O^- is a $^4\text{A}_2$ state with the Ce–O–Ce bridge bonding being the favored structural motif, resulting in C_{2v} symmetry. Another close-lying state was found, a $^2\text{A}_2$ with a bonding motif resembling the ground-state quartet. These two structures correspond to **A-2** and **A-4** structures reported in Fig. 1. Using the same approach, Kafader et al. determined the ground-state configuration for Ce_2O_2^- to be a $^4\text{A}_g$ state with the $^2\text{A}_g$ state being slightly higher in energy. Both structures exhibit D_{2h} symmetry and Franck-

condon simulations confirmed their contributions to the photoelectron spectrum. These two structures resemble **C-4** and **C-2** shown in Fig. 2, respectively. As far as the starting materials and the final products are concerned, our computational results are in good agreement with the results reported by Kafader and coworkers. Thus, the two potential energy surfaces to be explored are the 4A_2 and 2A_2 routes leading to 4A_g and 2A_g , respectively. Following up on this, we aim to explore the mechanistic studies of the reactions of **A-2** and **A-4** with water to produce **C-2** and **C-4** alongside H_2 .

Water Addition

We have identified one unique mode for water addition to **A-2** and **A-4** clusters. This mode is best described as an interaction between the water oxygen and a terminal cerium atom, while the second cerium atom does not directly engage in this step. Water addition to the Ce_2O^- clusters forms structures **G-2** and **G-4**. A distinctive feature about both adduct structures is that a water hydrogen is oriented towards the distant cerium, suggesting the feasibility of proton transfer to the remote cerium center.

Figure 3: Quartet G-4 (left) and doublet G-2 (right) with intermolecular distances given in Angstroms and relative energies given in kcal/mol.

The relative heats of reactions of the water adducts are also shown in Fig. 3. Formations of both adducts resulting from water addition to Ce_2O^- are exothermic, with ΔH values of -23.3 and -12.2 kcal/mol for the doublet and quartet states, respectively. For the two formed intermediates the distance between the water oxygen center and the cerium atom is 2.56 Å

(**G-4**) and 2.49 Å (**G-2**). Moreover, as the oxygen approaches Ce_2O^- , one of the hydrogens from the water molecule orients towards the position of the cerium atoms, indicating the first step towards breaking the O–H bond and consequent formation of a new Ce–H bond. An interesting aspect of water addition to the cerium oxide cluster is the activation of the aqua-oxygen by the Ce center, which precedes O–H bond cleavage. Instead, the interaction of the lone pairs on the oxygen of the water with the electron-deficient cerium center provides an incentive to proceed with an energetically-favored water addition to Ce_2O^- through direct addition via the water oxygen onto the cluster. Unlike the behavior of transition metal oxides and their reactions with water,⁷³ the mode of water addition in Ce_2O^- does not involve initial interaction between the water hydrogens and a cluster oxide site. Instead, the interaction of the water lone pairs with the electron deficient cerium center initiates an energetically favorable water addition to Ce_2O^- through direct addition via the water oxygen to the cluster.

Hydride Bridge Formation

Following water addition, the reaction undergoes Ce oxidation as a water O–H bond is cleaved and leads to formation of a bridging hydride. Structures **H-2** and **H-4** correspond to these intermediates, $\text{Ce}_2\text{HO}(\text{OH})^-$ that form from O–H bond cleavage in **G-2** and **G-4**, respectively. Figure 4 shows the structure and relative energies of two identified spin states that correspond structure H. Both doublet and quartet states of structure H bear the same geometry. The oxygen and hydrogen centers in the ring are both in bridging positions relative to the two cerium atoms. The bridging hydride binds to the Ce centers with bond lengths of 2.29 Å and 2.30 Å for both the doublet and quartet species. The structure of **H-2** and **H-4** is best described as a four-membered planar ring consisting of two cerium atoms, an oxygen, and a hydrogen, with a bound hydroxide ligand. The O–H bond cleavage in both the quartet and doublet states is exothermic with heats of reaction of -73.0 kcal/mol (quartet state) and -81.6 kcal/mol (doublet) relative to their respective starting materials.

Such exothermicity suggests the formation of each of **H-2** and **H-4** is highly favorable.

Figure 4: Structures of quartet **H-4** and doublet **H-2**, Ce–O distances are shown in units of Angstroms and relative energies are shown in kcal/mol.

Transition structures connecting **G-2** to **H-2** and **G-4** to **H-4** have been identified and verified by calculating analytic frequencies and intrinsic reaction coordinates. These transition structures are shown in Fig. 5. The identified transition structures are geometrically similar to their respective precursors, **G-4** and **G-2**, with the water hydrogen oriented towards the two cerium centers. The Ce–H bond distances are 2.34 and 2.80 Å (quartet) and 2.38 Å and 2.79 Å (doublet), respectively. The transition state between structures **G-2** and **G-4** on one side and **H-2** and **H-4** on the other side is essentially barrierless, with a calculated activation energy of only 0.6 kcal/mol (quartet) and 1.3 kcal/mol (doublet) and relative enthalpies of reaction of -11.6 kcal/mol (quartet) and -21.0 kcal/mol (doublet).

H₂ Production

The relative positions of the two hydrogen centers is critical for the final H₂ formation step. For this reason, we explored a series of possible rearrangement steps. Of the identified structures, **I-2** and **I-4** feature molecular orientations that act as reasonable precursors to the formation of H₂ (Fig. 6). Structures **I-2** and **I-4** include a new hydroxide bridge between the cerium centers, resulting in the two hydrogens being in close proximity to one another (H–H

Figure 5: Structure TS1-4 that connects G-4 and H-4 (left) and TS1-2 that connects G-2 and H-2 (right) with relative energies given in units of kcal/mol.

distance is ~ 3 Å). These structures directly lead to subsequent release of H_2 and formation of product clusters **C-2** and **C-4**. By comparing the Ce–H bond lengths of structures **H-2** and **H-4** with **I-2** and **I-4**, we observe a decrease in bond distance as the hydroxide binds to the second cerium atom. Thus the bond formation between the hydroxide and cerium plays a role in decreasing the bond distance between one of the cerium atoms and the other hydrogen center.

Our calculations identified transition structures connecting **H-2** and **H-4** to **I-2** and **I-4**, shown in Fig. 7. These transition structures lead to bond formation between the hydroxide and a cerium center. Both doublet and quartet transition structures were confirmed as first-order saddle points by identifying one imaginary frequency. Further confirmation of the nature of the potential energy surface was done using IRC calculations (see supporting information for more details). In both cases, the transition structures present small reaction barriers (7.6 kcal/mol for the quartet and 6.5 kcal/mol for the doublet). In support of experimental interpretations,^{39,53} these transition structures feature an electron rich hydroxide attracted by the electron-poor cerium center resulting in diffuse multi-centered bonds

Figure 6: Front and side view of the geometry of structures quartet I-4 (left) and doublet I-2 (right) with relative energies given in kcal/mol.

involving the hydroxide and both cerium atoms.

Figure 7: Structures of TS2-2 and TS2-4 that connect H-2 and H-4 to I-2 and I-4, respectively and their relative energies (in kcal/mol).

Figure 8 shows structures of the last step of the mechanism, which involves H_2 production and formation of **C-2** and **C-4**. The relative energies of the separated products (shown in Fig. 8) indicate the exothermic nature of the last step as well as the overall reaction. The enthalpy of reaction for hydrogen gas evolution via a quartet starting material is -91.3 kcal/mol, while ΔH calculated for the doublet is -100.5 kcal/mol. Moreover, the relative

energies of the separated products with respect to their precursors, structures **I-4** and **I-2**, are -24.7 kcal/mol and -25.0 kcal/mol, respectively.

Figure 8: Structures and relative energies (in kcal/mol) of **I-4** and **C-4** (left) and **I-2** and **C-2** (right).

Reaction Profiles

Figure 9 shows the full energy profile of the doublet and quartet mechanistic routes. In both cases the overall reactions are barrierless, in agreement with the experimental data provided by Jarrold and coworkers.^{39,53} Again, the reaction can be summarized by four steps: (1) addition of water onto a cerium center of Ce_2O^- ; (2) hydride transfer from water into a bridging position between the two cerium atoms; (3) bond formation between hydroxide and the far cerium atom; and (4) evolution of H_2 .

There are features of the Ce_2O^- catalyzed reaction that are different from reports published for transition metal oxide cluster analogues. Three such examples include tungsten oxide, molybdenum oxide, and mixed manganese-molybdenum oxides.^{73–76} The overall reaction barriers for those cases is similar to the case reported in this work, but a key difference lies in the mode of addition of water to the clusters. Indeed, previous reports found that the initial steps of water addition occur via a concerted step involving simultaneous addition of hydroxide (from water) to the metal center and O–H formation at an oxo site. As discussed

Figure 9: Energy profile for the proposed $\text{Ce}_2\text{O}^- + \text{H}_2\text{O} \longrightarrow \text{Ce}_2\text{O}_2^- + \text{H}_2$ quartet (orange) and doublet (green) mechanisms

above, our calculations identified a different pathway for the reaction with cerium oxide that occurs via a two-step process: water adds to the cerium center to form structures **G-2** and **G-4** (Fig. 3), then the hydrogen transfers to a bridging position between the two cerium centers.

In the reaction of Mn_xMoO_y anions with water, both Mn and Mo are involved in the initial cluster-water formation.⁷⁶ However, only the Mo center undergoes oxidation. In fact, the reactivity of the Mn_xMoO_y anion clusters with water depends on the oxidation state only of the molybdenum center. Once the Mo center reaches its highest oxidation state (VI),

reaction with additional water molecules ends.

Electronic Structures of Cerium Oxide Clusters

Figure 10: Valence molecular orbitals of quartet (left) and doublet (right) Ce_2O^-

Figure 10 shows the frontier molecular orbitals (MOs) of **A-2** and **A-4**. The MO diagram of **A-4** is comprised of three general manifolds: 4f orbitals, σ and σ^* , and 5d orbitals. The first frontier orbital group includes two singly occupied 4f orbitals localized on the cerium centers. The σ and σ^* orbitals are doubly occupied and are predominantly Ce 6s-based. Finally, the (α) highest occupied MO (HOMO) of quartet Ce_2O^- , is a 5d-based singly occupied orbital with the electron delocalized over the space spanning the two cerium centers. The shown doublet Ce_2O^- MOs include occupied 4f orbitals localized on the cerium centers and the doubly occupied σ orbital. The main difference between **A-2** and **A-4** MOs lies in the manifold of singly occupied orbitals. Unlike its quartet analogue, the doublet Ce_2O^- exhibits three singly occupied orbitals: one $5d_\pi$ α orbital; one σ^* β orbital; and one $5d_\sigma$ β orbital.

MO diagrams for **C-2** and **C-4** (shown in Fig. 11) exhibit more similarity to each other than **A-2** and **A-4**. Both spin states of structure **C** include the two singly occupied 4f orbitals

present in their respective starting **A** clusters. In addition, both doublet and quartet spin states have a doubly occupied 6s-based σ orbital and a singly occupied σ^* orbital. The only difference is the spin of the electron occupying the σ^* orbital. The quartet has an α electron in the σ^* orbital, while that same orbital is occupied by a β electron in the doublet **C-2**.

Figure 11: Valence molecular orbitals of quartet (left) and doublet (right) Ce_2O_2^-

The combined oxidation state of the two cerium centers is (+I) in Ce_2O^- and (+III) in Ce_2O_2^- . Figures 10 and 11 show that the frontier molecular orbitals of both Ce_2O^- and Ce_2O_2^- exhibit delocalization of electrons over the two cerium metals. In addition, as discussed in the previous sections, all Ce–O bonds are equivalent within the same molecule in both the Ce_2O^- and Ce_2O_2^- . For these reasons, the oxidation states of the cerium centers should also be equal. In addition, given the delocalized nature of the frontier orbitals over the two cerium centers, these species can be described by two resonance structures that have cerium centers with unequal oxidation states. For Ce_2O^- , the studied structure can be described by two resonance structures of Ce_2O^- , with each resonance form featuring one Ce(0) and one Ce(I) center. In a similar manner, the final Ce_2O_2^- structures are described by two Ce(I)/Ce(II) resonance structures.

While the cerium-based 6s orbitals have been previously determined to be the sites of electron detachments in various cerium and cerium suboxide clusters (including Ce_2O^- and Ce_2O_2^-), we notice here that both σ and σ^* orbitals retain all or most of their electron occupations as the reaction proceeds. This shows that σ and σ^* electrons are not the source

of metal facilitated reduction of water. Instead, the electron source in the studied reaction is the set of singly occupied 5d orbitals. This observation is consistent with the reported experimental result that reaction of Ce_2O_2^- with water yields H-radical rather than H_2 . The reaction of water with Ce_2O^- depletes the metal centers of their d electrons and prevents further H_2 production.¹⁷

Conclusions

This work studied the reaction of water with Ce_2O^- clusters to produce Ce_2O_2^- and H_2 . Density functional theory calculations have been used to map out the full reaction pathway for hydrogen production. A thorough search for candidate intermediates and transition structures has shown that a key point in the progression of the reaction is the formation of successive bridging bonds that place the two hydrogen atoms in close proximity and eventually facilitates the production of H_2 . We have also shown that it is energetically possible for both experimentally identified electronic states of Ce_2O^- to react with water and eliminate molecular hydrogen with low energy barriers relative to the starting materials. Finally, while the valence molecular orbitals of the studied cerium oxide clusters consist of 4f, 5d, and 6s metal-centered orbitals, an examination of the molecular orbitals of initial and final cerium oxide clusters clearly indicates that the metal 5d electrons provide the means for water reduction. This work provides new insight to the reactivity of small lanthanide-based clusters with water.

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