

Interactions of Hydrogen with CeO<sub>2</sub>Karl Sohlberg,<sup>\*,†,§</sup> Sokrates T. Pantelides,<sup>§,‡</sup> and Stephen J. Pennycook<sup>§,‡</sup>

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**Abstract:** The interactions of hydrogen with ceria have been the subject of several experimental studies, but whether hydrogen atoms enter the bulk or are merely chemisorbed on the surfaces is disputed. We combine first-principles calculations with thermodynamic arguments and conclude that the uptake of small amounts of hydrogen by ceria is spontaneous below 665 K. The calculations also predict that hydrogen atoms within the bulk form hydroxyl groups and slightly expand the lattice. The predicted hydrogen content, OH vibrational frequency, and ceria lattice expansion upon hydrogen uptake are consistent with available data.

## Introduction

Cerium oxide (ceria) is a critical and multifunctional component of automotive emissions catalysts.<sup>1</sup> One function of ceria is to act as an “oxygen storage” component. Ceria is capable of oxygen uptake during excursions of the air/fuel ratio into the net oxidizing regime and oxygen release during excursions into the reducing regime, thus facilitating the maintenance of the proper stoichiometric ratio for sustained CO and HC oxidation and simultaneous NO<sub>x</sub> reduction, that is, *three-way* catalysis (TWC).<sup>2</sup> Cerium oxide is also known to extend the lifetime of the noble metal component of the catalyst and to lower the effective activation barrier to CO oxidation, thus improving the catalyst performance at engine startup.<sup>2</sup>

Many of the key properties of ceria that contribute to its success in automotive catalysis are thought to arise from the fact that cerium has two stable oxidation states, Ce<sup>3+</sup> and Ce<sup>4+</sup>. As a consequence, cerium oxide may exist over a range of possible stoichiometries CeO<sub>(2-x)</sub> [0 ≤ x ≤ 0.5].<sup>3</sup> The deviation of ceria from its ideal CeO<sub>2</sub> composition has been extensively studied by temperature-programmed reduction (TPR) with hydrogen.<sup>4</sup> These studies have given rise to an important controversy: Is there hydrogen uptake by ceria upon reduction with hydrogen?

Fierro et al.<sup>5</sup> have reported nuclear magnetic resonance (NMR) spectra indicating the incorporation of hydrogen into cerium oxide when it is heated in a hydrogen atmosphere, and

electron spin resonance (ESR) and X-ray diffraction (XRD) data that are consistent with the incorporation of hydrogen as well. Bruce et al.<sup>6</sup> have reported the TPR of CeO<sub>2</sub> samples with a range of surface areas and conclude that there are two contributions to the hydrogen uptake, one due to hydroxylation of surface oxide and a second due to incorporation of hydrogen into the ceria lattice. Studies by Bernal et al.<sup>7</sup> employing TPR and mass spectrometry (TPD-MS), however, suggest that hydrogen interaction with ceria is strictly a surface process.

In this paper we report first-principles calculations of hydrogen in cerium oxide, the goals of which are to determine whether incorporation of hydrogen is thermodynamically favorable and, if so, its equilibrium concentration.

## Theoretical Methods

Structural calculations and unit cell optimizations were carried out on unit cells of an infinitely periodic bulk and were based on density functional theory (DFT).<sup>8</sup> The generalized gradient approximation (GGA) to the exchange-correlation energy ( $V_{xc}$ ) was used.<sup>9</sup> The electron-ion interactions were described with the ultrasoft pseudopotentials of Vanderbilt.<sup>10</sup> The valence electronic wave function was expanded in a basis of plane waves, truncated according to a cutoff energy  $E_c = 410$  eV, as determined by convergence studies. Integrations over the Brillouin zone employed a grid of k-points with a spacing of 0.1 Å<sup>-1</sup> chosen according to the Monkhorst–Pack scheme.<sup>11</sup> Unit cell optimizations were taken to be converged when the change between iterations was less than the following values: total energy 2.0 × 10<sup>-5</sup> eV/atom, rms displacement of atoms 1.0 × 10<sup>-3</sup> Å, RMS force on atoms 5.0 × 10<sup>-2</sup> eV·Å<sup>-1</sup>, and the rms of the stress tensor 1.0 × 10<sup>-1</sup> GPa. When determining the equilibrium structure for computing the numerical second derivatives of the potential, the above tolerances were decreased by ×10, ×10, ×5, and ×4, respectively. All structural calculations

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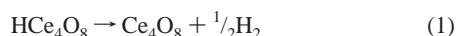
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and unit cell optimizations were carried out with the CASTEP suite of codes, reviewed by Payne.<sup>12</sup>

Vibrational frequencies for H were computed in the harmonic approximation by diagonalizing the mass-weighted Cartesian force constant matrix for the H atom.<sup>13</sup> The Cartesian force constants were approximated by computing divided-difference numerical second derivatives of the potential. The step size for the numerical differentiation was taken as 0.01 Å. Unfortunately, the same property that makes ceria so useful in automotive catalysis, the fact that cerium has two stable oxidation states, also renders it a very challenging (expensive) system to treat computationally. The challenge of computing vibrational frequencies for hydrogen in ceria with accurate first-principles methods was met by computing in parallel the individual total energy function evaluations required for computing the numerical second derivatives of the potential. Since 19 independent evaluations of the total energy are required, a parallel implementation results in a 19-fold decrease in the turn-around time for the calculation. The parallel implementation of the vibrational analysis scheme was first tested on a simpler problem, hydrogen vibrations in hydrogen-doped alumina, which had previously been carried out serially on a local workstation. The computed frequencies reproduced those of the original serial calculation,<sup>14</sup> which were in excellent agreement with experiments,<sup>15</sup> thus validating not only the methodology but also the parallel implementation.

To determine the affinity of ceria for hydrogen, we considered the reaction:



Here  $\text{Ce}_4\text{O}_8$  is used as the reference, instead of the empirical formula  $\text{CeO}_2$ , since the former is the formula for the primitive unit cell of cerium oxide. At any given temperature, the sign of  $\Delta G$  (free energy change) for the above reaction 1 determines the position of the equilibrium: for  $\Delta G < 0$ , products are favored, and for  $\Delta G > 0$ , reactants are favored. To determine  $\Delta G$ , we begin with the expression,

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

Given the total energy  $E_i$  for each of the species in reaction 1 from the DFT calculations,

$$\Delta H \approx \sum_i E_i^{\text{products}} - \sum_i E_i^{\text{reactants}} \quad (3)$$

The entropic contribution  $\Delta S$  is then similarly obtained from tabulated third-law entropies for the products and reactants. The third-law entropy for  $\text{H}_2$ ,  $S_{\text{H}_2}^{298\text{K}} = 130.59 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .<sup>16</sup> As suggested by the work of Wolverton and Hass,<sup>17</sup> we neglect the entropic contributions of the solid-state phases. Considering the reaction,



this approximation may be justified as follows: The third-law entropy for  $\text{Al}_2\text{O}_3$ , (which may also be written  $\text{Al}_2\text{O}_3\cdot 0(\text{H}_2\text{O})$ ),  $S_{\text{Al}_2\text{O}_3}^{298\text{K}} = 50.92 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .<sup>18</sup> The third-law entropy for boehmite, (boehmite has the formula  $\text{Al}_2\text{O}_3\cdot \text{H}_2\text{O}$ )  $S_{\text{boehmite}}^{298\text{K}} = 96.86 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .<sup>18</sup> Since  $\text{HAL}_5\text{O}_8$  is a transition species in the dehydration sequence that takes boehmite into  $\text{Al}_2\text{O}_3$  and since  $\text{HAL}_5\text{O}_8$  may also be written  $\text{Al}_2\text{O}_3\cdot\frac{1}{5}\text{H}_2\text{O}$ , we interpolate to find that  $S_{\text{HAL}_5\text{O}_8}^{298\text{K}} \approx 60.11 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The difference

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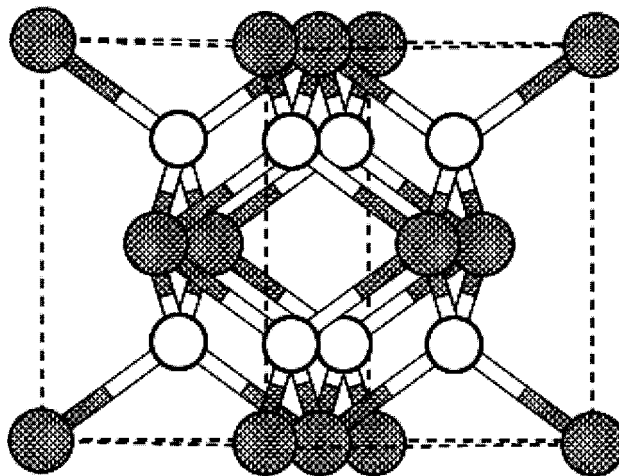


Figure 1. Structure of bulk  $\text{CeO}_2$ .

between  $S_{\text{Al}_2\text{O}_3}^{298\text{K}}$  and  $S_{\text{HAL}_5\text{O}_8}^{298\text{K}}$  is therefore less than  $10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , which is indeed very small in comparison to  $S_{\text{H}_2\text{O}}^{298\text{K}} = 188.83 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Noting that H represents a small perturbation in  $\text{HCe}_4\text{O}_8$  as it does in  $\text{HAL}_5\text{O}_8$ , we employ a similar approximation here and assume that only  $\text{H}_2$  contributes significantly to  $\Delta S$  in reaction 1. Given the similarity of the OH structures formed within the alumina and ceria bulks, the relatively small contribution of H to the composition in both cases, and the fact that the contribution of H to the composition is actually smaller in ceria, it seems reasonable to conclude that the approximation of neglecting the entropic contributions of the solid-state phases is *at least as good for ceria as for alumina*, where it has been demonstrated to be very reliable.

## Results and Discussion

Cerium oxide  $\text{CeO}_2$  crystallizes in the  $Fm\bar{3}m$  fluorite structure. The unit cell is  $\text{Ce}_4\text{O}_8$  with O filling tetrahedral sites among the cubic close packed Ce. The unit cell is shown in Figure 1. We have carried out a full structural relaxation of cerium oxide including unit cell optimization and find  $a_0 = 5.43 \text{ \AA}$ , in excellent agreement with the experimental value  $a_0^{\text{expt}} = 5.411 \text{ \AA}$ .<sup>18</sup>

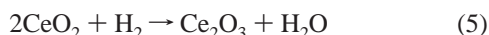
The unit cell of ceria has a very interesting “cube within a cube” structure. Note in Figure 1 that the unit cell is based on *ccp* cerium, but within the unit cell, the eight oxygens fill tetrahedral interstices in the *ccp* cerium lattice, forming the vertexes of a smaller cube. The interior of this small cube formed by oxygens is vacant. We have carried out structural relaxations including unit cell optimization with H placed within this cavity. We found that the H does not remain at the high-symmetry position in the center of the cavity but relaxes away and associates more closely with one of the eight neighboring oxygen atoms. What results is the formation of a hydroxyl structure within the cerium oxide bulk. Other trial structures, including a “hydride” form where the H is octahedrally coordinated by Ce, all resulted in relaxed structures that were energetically unstable with respect to dissociation into pure  $\text{CeO}_2$  and  $\text{H}_2$ , that is,  $\Delta H$  for reaction 1 as computed with eq 3 is negative, guaranteeing  $\Delta G < 0$ . Calculations also showed 2H within each oxygen cavity to be energetically unstable.

The presence of hydrogen in ceria has been probed by infrared spectroscopy (IR),<sup>19</sup> and a characteristic OH band has been identified at  $3510 \text{ cm}^{-1}$ . This band is not sensitive to benzene adsorption, indicating that it is not due to surface OH, but it is not known whether this band corresponds to OH within the

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cerium oxide bulk or on internal surfaces arising from defects. We have computed the harmonic vibrational frequency for H in its fully relaxed position within one of the oxygen cubes. The computed vibrational frequency is 3414 cm<sup>-1</sup>. Given that we are limited in accuracy by the harmonic approximation, the error of 2.7% is well within the expected reliability of the calculation (~5%). The calculation, therefore, suggests that the OH structure is a possible source of the observed 3510 cm<sup>-1</sup> vibrational band. As noted by Badri et al.,<sup>19</sup> however, it is also possible that this band arises from OH in pores within the ceria bulk. The expected accuracy of the calculation is not sufficient to make a definitive assignment.

On the basis of XRD experiments, Fierro et al.<sup>5</sup> conclude that the uptake of hydrogen leads to an increase in cell lattice parameters.<sup>5</sup> More recently, Lamonier et al.<sup>20</sup> have carried out a thermogravimetry and XRD study of the behavior of cerium oxide upon treatment with hydrogen and similarly report an increase in the cell lattice parameters, expanding by 0.6–2.1% depending on the temperature. We found for HCe<sub>4</sub>O<sub>8</sub>, after full structural relaxation, that  $a_0 = 4.51 \text{ \AA}$ , which is a 1.5% increase upon hydrogen uptake. The computed result falls within the observed range. Increases in lattice parameter of greater than the 1.5% that may be attributed to hydrogen uptake may result from the competing reduction process.<sup>6,20,22</sup>



not considered here. Large departures from the CeO<sub>2</sub> stoichiometry are well documented at high temperatures.<sup>5</sup>

To ascertain whether the uptake of hydrogen by ceria is spontaneous at a given temperature, we need to determine the value of  $\Delta G$  for reaction 1 at that temperature. The free-energy change was determined as outlined in the previous section, employing DFT total energies to determine  $\Delta H$  and tabulated third-law entropies to determine  $\Delta S$ . We find that for reaction 1,

$$\Delta G(T) = 0.45 - 6.768 \times 10^{-4}T \quad (6)$$

where the energies are given in eV/molecule. From eq 6 we find that below 665 K hydrogen uptake is spontaneous.

Using the above temperature dependence of  $\Delta G$ , and assuming equilibrium conditions, we can predict the fraction of unit cells containing H (in the hydroxyl configuration) as a function of temperature. The probability<sup>21</sup> is given by

$$\rho = \frac{\exp(-\Delta G(T)/kT)}{1 + \exp(-\Delta G(T)/kT)} \quad (7)$$

where  $k$  is the Boltzmann constant and  $\Delta G(T)$  is given by eq 6. Table 1 reports the predicted equilibrium concentration of H in ceria as a function of temperature along with experimental values. Given the uncertainty in the computed  $\Delta G$ , and the exponential dependence of H content on  $\Delta G$ , the agreement is remarkably good.

A possible source of error in the calculation is hydrogen uptake by vacancies in the structure, particularly those resulting from the competing reduction process (5), which could be

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**Table 1.** Comparison of Theoretical and Experimental Hydrogen Contents of Ceria at Various Temperatures. Reported Is  $x$  in H<sub>x</sub>Ce<sub>4</sub>O<sub>8</sub>

temp K	$x$ theo.	$x$ expt.	expt. ref
500	1	—	—
600	9.7	—	—
665	0.5	—	—
673	0.48	0.4	[5]
700	0.4	—	—
873	0.13	0.3	[6]
900	0.11	~0	[22]

important at high temperatures.<sup>22</sup> It is interesting to note the lack of experimental data at low temperature. While the uptake of small amounts of hydrogen by ceria bulk is thermodynamically favored at low temperatures, Yao and Yao<sup>23</sup> have reported that the rate of H<sub>2</sub> uptake is dependent on surface area below 500 °C, suggesting that surface processes heavily dominate.

Another possible source of error in the theoretical calculation is the neglect of the zero-point vibrational energy correction (ZPE) to the computed total energies. Given that the vibrational frequency for OH is somewhat higher than that of gas-phase H<sub>2</sub>, we expect ZPE to raise the energy of the reactants in reaction 1 slightly, relative to the products. In this case, the dehydrogenation reaction should become spontaneous at a somewhat lower temperature, and the predicted equilibrium H concentrations given in Table 1 should be slightly too high. We therefore expect the ZPE correction to improve the agreement with experimental results. A proper calculation of the phonon spectra is beyond the scope of our calculations, however.

## Conclusions

We have carried out first-principles calculations to study the possible uptake of hydrogen by ceria. The calculations suggest that the uptake of hydrogen by ceria to form HCe<sub>4</sub>O<sub>8</sub> becomes thermodynamically spontaneous below about 665 K. This uptake produces a lattice expansion of about 1.5%. The H taken up forms hydroxyl structures within the ceria bulk with a predicted vibrational frequency of 3414 cm<sup>-1</sup>. These results are in good agreement with experimental reports. Predicted equilibrium hydrogen content as a function of temperature also agrees relatively well with experimental reports and is expected to improve if quantum zero point vibrational energy corrections are incorporated. An experimental mapping of equilibrium H content over a wider temperature range would be of considerable value in guiding future theoretical investigations.

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