

# Computational study of rare-earth oxide catalysts

## Understanding the catalytic performance of rare-earth oxides: Toward a knowledge-driven design of catalysts from first-principles calculations

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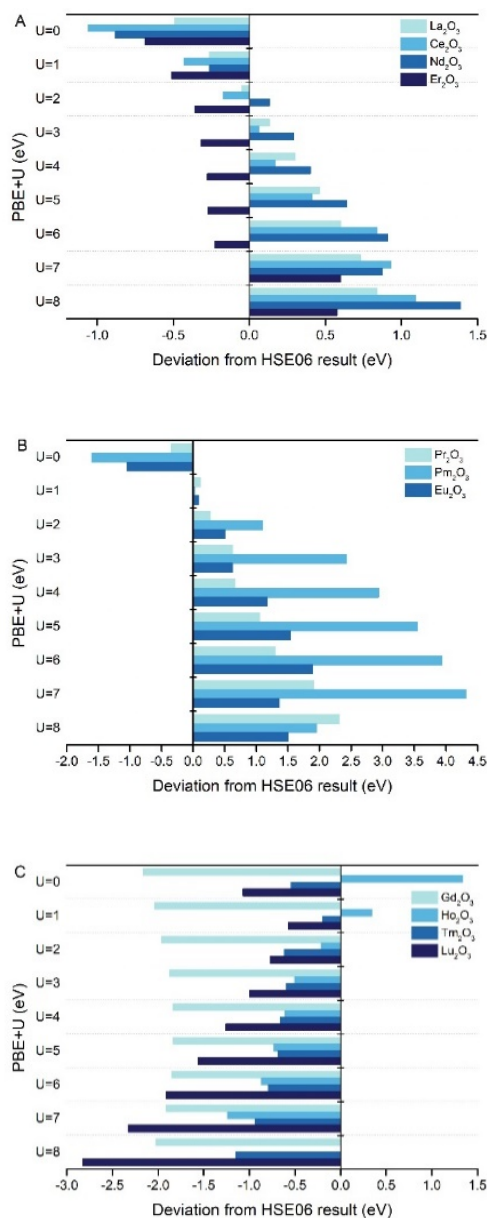
of lattice parameters small U values (1-3 eV) should be a safe choice for the PBE+U calculations of lanthanide sesquioxides.

### In Short

- Rare earth oxides (REOs) are promising catalysts
- Quantum-chemical treatment of REOs requires advanced electronic-structure methods and significant computing power
- Theoretical elucidation of reaction mechanisms on REO surfaces
- Design of reactivity descriptors

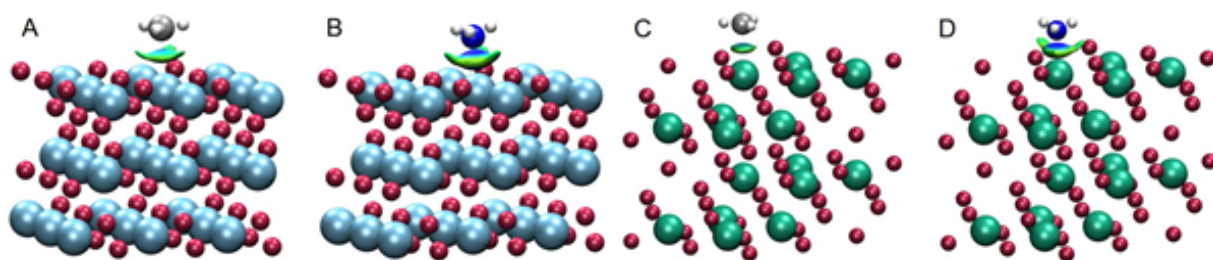
The full potential of rare earth oxides as versatile catalysts for various chemical transformations with great economic promise is still quite underexplored mainly because a detailed fundamental understanding of the catalytic properties of the REO series is lacking. The goal of the project is two-fold: (i) rationalize different catalytic function of the whole REO series through their first systematic quantum-chemical modelling at an atomic scale and (ii) use this knowledge to help design new catalysts for the oxidative coupling of methane (OCM), an economically highly attractive but not yet implemented in practice process for conversion of natural gas into value-added commodity chemicals [1]. Computational studies of REOs require the use of advanced electronic-structure methods and significant computing power [2]. In view of the difficult handling of f-electrons in rare earth elements by conventional DFT, PBE+U approach has been chosen and systematically compared to the results achieved with a hybrid functional HSE06. In doing that, a range of U values of PBE+U has been employed to find the best fit to HSE06 results. For the first half of the Ln series from La to Eu, and also for Lu the best agreement between PBE+U and HSE06 results in terms of the optimized cell parameters of  $\text{La}_2\text{O}_3$  could be achieved with the U values of 1-3 eV. For  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$  and  $\text{Er}_2\text{O}_3$  the best agreement between PBE+U and HSE06 was achieved using  $U = 8$  eV but with the U value of 3 eV the overestimation of the lattice volumes was under 1.8%.

The lattice parameters of  $\text{Ho}_2\text{O}_3$  and  $\text{Tm}_2\text{O}_3$  can be also accurately calculated using the PBE+U method with the U parameter of 3-4 eV, overestimating the cell volume by only 0.2% and 0.3%, respectively. We conclude that with respect to optimization



**Figure 1:** The relative reference reaction energies of A-type  $\text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Pm}, \text{Eu}, \text{Gd}, \text{Ho}, \text{Er}, \text{Tm}$ ) calculated by PBE+U with respect to HSE06 method. Reference reaction:  $2\text{LnF}_3 + 3\text{H}_2\text{O} \rightarrow \text{Ln}_2\text{O}_3 + 6\text{HF}$ .

To assess the performance of PBE+U with respect to energetic properties and to recommend the



**Figure 2:** Equilibrium adsorption geometries of  $\text{NH}_3$  molecule (left) and  $\text{CH}_3$  radical (middle) on the  $\text{CeO}_2(111)$  surface, and  $\text{NH}_3$  on the  $\text{Nd}_2\text{O}_3(0001)$  surface (right) calculated by PBE+U at  $U = 3$  eV. Color coding: O, dark red; H, white; N, dark blue; C, silver; Ce, light blue; Nd, dark green. Noncovalent interactions analysis. The isosurface of  $\delta_9^{\text{inter}(\rho)} = 0.01$  a.u. is shown for in the adsorption complex. A blue-green-red color scale represents the values of  $\text{sign}(\lambda_2)\rho$  ranging from -0.05 to 0.05 a.u. on the isosurface.

optimal U parameters for a given Ln sesquioxide, we have taken the following imaginary reaction as reference:  $2\text{LnF}_3 + 3\text{H}_2\text{O} \rightarrow \text{Ln}_2\text{O}_3 + 6\text{HF}$ . The deviations between the PBE+U energies and HSE06 energies are plotted as a function of U in Fig. 1. For all studied Ln elements the reaction energies get more endothermic with the increasing U. For most of the studied Ln elements, the best agreement with the HSE06 results was found with the small U values ( $U = 1\text{-}3$  eV), which is lower than the optimal U range derived on the basis of the band gap or other electronic structure properties.

On the basis of the obtained U values, we will be able to use a significantly less expensive than the hybrid functional but relatively accurate method PBE+U for the complicated systems and problems, such as the adsorption and reaction mechanisms on REOs surfaces and nanoparticles etc.

In order to evaluate the transferability of the derived optimal parameter U for calculations of surface properties,  $\text{CeO}_2$  and  $\text{Nd}_2\text{O}_3$  were selected as representative oxides to construct the respective surface slabs and to calculate net ionic charges of Ce and Nd ions, the work function, and the adsorption energies of the  $\text{CH}_3$  radical and  $\text{NH}_3$  molecule. Work function reflects the ease of releasing an electron from the surfaces, and hence, the reactivity of the surfaces. It is almost independent of the parameter U for the  $\text{CeO}_2(111)$  surface, differently from the  $\text{Nd}_2\text{O}_3(0001)$  surface, for which the work function increases with the increasing U value. The deviation of the PBE+U work function from the HSE06 result is up to 1.2 eV for the  $\text{CeO}_2(111)$  surface, indicating that the description of the process of electron emission from the surface by PBE+U is not satisfactory. For the  $\text{Nd}_2\text{O}_3(0001)$  surface, PBE+U with U values ranging within 5-8 eV could predict work function values close to the HSE06 result.

Both the  $\text{CH}_3$  radical and  $\text{NH}_3$  molecule adsorb on top of the surface cerium atoms of the  $\text{CeO}_2(111)$  surface which act as Lewis acid centers. The adsorption energies of the  $\text{CH}_3$  radical and  $\text{NH}_3$  molecule

on the  $\text{CeO}_2(111)$  surface almost remain constant with respect to the parameter U. Different from the adsorption on the  $\text{CeO}_2(111)$  surface,  $\text{NH}_3$  adsorption energy on the  $\text{Nd}_2\text{O}_3(0001)$  surface keeps a positive linear relationship to the parameter U. Moreover,  $\text{NH}_3$  adsorbs on top of the surface oxygen atom of  $\text{Nd}_2\text{O}_3(0001)$  surface via the hydrogen atom instead of nitrogen atom as illustrated in Fig. 2. The next phase of the project will aim at the acidity-basicity properties of doped or undoped reducible  $\text{CeO}_2$  surface and the migration of oxygen vacancy on this surface.

#### More Information

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#### Funding

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