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Ab initio thermodynamic study of the oxidative dispersion of Pt nanoparticles on ceria

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Introduction

Platinum is an exceptional catalyst for a wide variety of industrial reactions, but it is susceptible to sintering, which compromises its catalytic activity,¹ and motivates the development of in situ protocols to achieve fine control over the dispersion and particle size. Oxidative treatments exposing Pt catalysts to 1.5 mbar of O₂ at ~500 °C have been shown to promote the dispersion of nanoparticles into smaller oxidized Pt species.² In particular, the ceria (CeO₂) support has been proposed for its strong interaction with Pt, enabling a more gradual evolution of particle size and morphology.

Nevertheless, many questions remain regarding the factors governing the dispersion process, such as the role of oxygen and the types of sites required for Pt trapping.³ Experimental characterization techniques such as TEM are limited by the weak contrast at small particle sizes.⁴ For this reason, theoretical studies constitute a promising avenue to shed light on this phenomenon. In this work, we provide atomic-level insight into the oxidative dispersion of Pt nanoparticles supported ceria, by performing a DFT study of the relative stability of Pt_xO_y as a function of size (x) and degree of oxidation (y/x). We integrate several approaches to generate models encompassing a wide range of particle sizes from single atoms to 1.5 nm of diameter.

Methods

DFT calculations were performed using VASP 6.2.1, with the PBE exchange-correlation functional and the D3(BJ) correction for long-range dispersion. The plane-wave energy cutoff was set to 400 eV, and core electrons were represented with the PAW method. Total energies were calculated with a numeric precision of 10⁻⁶ eV. The DFT+U approach was implemented to consider strong electronic correlation effects, with U_{eff} set to 4.5 eV for Ce(4f). The forces were converged to ±0.02 eV/Å. The Brillouin zone was sampled using a 2×2×1 k-point grid for (3×3) cells, and gamma-point for larger cells.

Results and Discussion

The most stable CeO₂(111) termination was chosen for thorough exploration, and subsequently selected systems were evaluated in the more reactive CeO₂(100) termination for comparison. The computational modeling of Pt/CeO₂ in a wide range of particle sizes requires the use of multiple approaches for the generation of the models, in order to achieve a balance between accuracy and computational cost. In this sense: PtO_y (atomically dispersed Pt) species were modeled using input from the literature, Pt₂O_y structures were screened using a grand canonical genetic algorithm (GCGA), Pt₁₃O_y morphologies were explored using annealing via ab initio molecular dynamics (AIMD) calculations at 800 K, and Pt₁₄₇O_y models were proposed via a heuristic approach, deriving them from the most stable high symmetry cluster of Pt₁₄₇ in gas-phase or from the PtO₂ bulk.

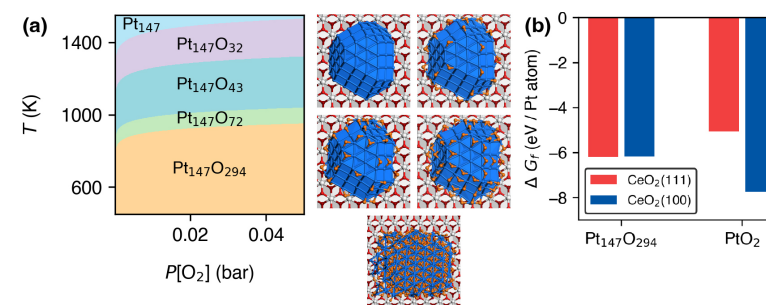


Figure 1. (a) Thermodynamic phase diagram of Pt₁₄₇O_y/CeO₂(111) under oxidizing conditions, and corresponding structures. The temperature and pressure ranges are 450–1550 K and 1.10⁻⁴–5.10⁻² bar, respectively. (b) Free energy of formation of PtO₂ and Pt₁₄₇O₂₉₄ at T=773.15 K and P[O₂] = 0.21 bar on CeO₂(111) and (100) surfaces.

To understand the effect of the oxidizing environment on the dispersion of Pt species supported on cerium oxide, we calculated the Gibbs free energy of formation per Pt atom (ΔG_f) for all the Pt/CeO₂ systems considered, with respect to the clean ceria surface, isolated Pt atoms, and a gas reservoir of O₂ at given temperature and pressure. Figure 1a illustrates this analysis for the case Pt₁₄₇O_y, showing the structure with the lowest ΔG_f as a function of temperature and pressure. A similar analysis can be done for each particle size separately, from which we observe that smaller Pt particles are more easily oxidized, and do not reach a O/Pt ratio of zero in the T,P range evaluated.

Furthermore, from the comparison between all systems, we conclude that single atoms are not accessible at 500 °C on the (111) surface, since for all O/Pt ratios, the large Pt₁₄₇O_y nanoparticle has a lower (more negative) ΔG_f. On the other hand, we find that oxidized atomically dispersed Pt could be stabilized on stronger adsorption sites such as the ones present in the CeO₂(100) surface termination, on which PtO₂ moieties are up to 2.7 eV more stable than Pt₁₄₇O₂₉₄ nanoparticles (Figure 1b).

Significance

Achieving fine control over platinum dispersion is key to improve its catalytic performance and make efficient use of the noble metal. In this work we present a comprehensive thermodynamic study of Pt dispersion showing the importance of the support's morphology.

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