

Palladium atoms and clusters at ceria nanoparticles: a DFT study

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CeO₂-based materials are well known by their catalytic activity in various industrial processes. Peculiar catalytic properties of ceria are attributed to the high mobility of its lattice oxygen. Transition metal atoms supported at ceria surface or incorporated in its framework can further enhance the redox performance and oxygen storage capacity of CeO₂. In turn, cerium oxide can affect the properties of adsorbed metal species, in particular, favors to dispersion of metal particles and suppresses their sintering at elevated temperatures. In line with experimental techniques, computational modelling is often utilized to investigate elementary processes occurred at ceria surface [1]. Present theoretical study is aimed at evaluating of oxygen vacancy formation energy – measure of lattice oxygen mobility – in dependence of the nature of adsorbed metal atom (Pd or Ag), size of the metal particle (atomic or tetrameric) and its position (intra- of extraframework). Denucleation of M₄ metal moieties at oxide surface is modelled as well.

Surface sites of the CeO₂ substrate were represented by a stoichiometric nanoparticle Ce₂₁O₄₂ exposing {100} and {111} nanofacets. A generalised-gradient corrected exchange-correlated functionals PW91 and PBE were utilised with the Hubbard-type on-site corrections U (U=4) for Ce4f states providing an improved description of Ce³⁺ ion formation in redox transitions [2].

As previously found for Ag particles [3], adsorption of Pd atom and Pd₂₋₄ clusters is about 2 times stronger at O₄-pocket of the {100} facet of Ce₂₁O₄₂ model than at its {111} facet. The adsorption energies of Pd and Pd₄ species at a partially reduced ceria nanoparticle Ce₂₁O₄₁ are by 1 eV smaller. Our calculations show that palladium clusters Pd₂-Pd₄ anchored at {100} facet are readily decomposed via migration of one atom to {111} facet. The activation barriers for such processes are low and stabilities of newly formed denucleated structures are high. Extraframework Pd moieties disfavors formation of O vacancies. This effect is more pronounced for single atoms and is reduced for Pd clusters. Opposite, intraframework Pd species results in spontaneous depletion of the first O atom and reduces formation of the second O vacancy.

[1] A. Bruix, K.M. Neyman, *Catal. Lett.* **2016**, *146*, pp. 2053-2080.

[2] V.A. Nasluzov, E.A. Ivanova-Shor, A.M. Shor, S.S. Laletina, K.M. Neyman, *Materials* **2021**, *14*, p. 6888.

[3] V.A. Nasluzov, E.A. Ivanova-Shor, A.M. Shor, K.M. Neyman, *Surf. Sci.* **2019**, *681*, pp. 38–46.