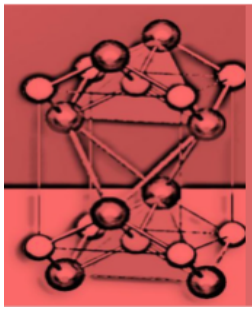

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# Assessment of Density Functional Approximations for correlated oxides surface chemistry: The case of CO bound to $CeO_2$ surfaces

M. Verónica Ganduglia-Pirovano [a], Pablo G. Lustemberg [a]

[a] *Instituto de Catálisis y Petroleoquímica-CSIC, Madrid, Spain.*

email:

This presentation comprehensively reviews the facet-dependent adsorption of CO on all three low-index oxidized and reduced $CeO_2$ surfaces. The primary focus is on investigating how CO coverage affects the IR vibrational modes and evaluating the performance of state-of-the-art quantum-mechanical methods in describing these phenomena.
To provide valuable insights, a meticulous comparison is made with a high-resolution IR spectroscopy study conducted on single crystal samples, which aids in assigning distinct CO vibrational bands observed on all three low-index ceria surfaces (see Figure). In contrast to the commonly applied DFT(PBE)+U method, our hybrid-DFT approach, employing the HSE06 functional and saturation coverage, exhibits excellent agreement and reliability in determining CO vibrational frequencies. We attribute the failure of conventional density-functional theory (DFT) to its inadequacy in accurately describing the facet- and configuration-specific donation and backdonation effects. The study convincingly demonstrates that the structure of cerium oxide surfaces and the presence of oxygen vacancies significantly influence CO behavior. The findings are pivotal in revealing the nature of the exposed facets of ceria nanoparticles.

[1]. P. G. Lustemberg, P. N. Plessow, Y. Wang, C. Yang, A. Nefedov, F. Studt, C. Wöll, M. V. Ganduglia-Pirovano, Phys. Rev. Lett. 125, 256101 (2020).

[2]. P. G. Lustemberg, C. Yang, Y. Wang, C. Yang, C. Wöll, M. V. Ganduglia-Pirovano, J. Chem. Phys. 159, 034704 (2023).