INSIGHT FROM *AB INITIO* CALCULATIONS INTO THE STRUCTURE AND REACTIVITY OF COMPLEX CATALYSTS: THE CASE OF PLATINUM-BASED SUBNANOMETRIC PARTICLES SUPPORTED ON ALUMINA

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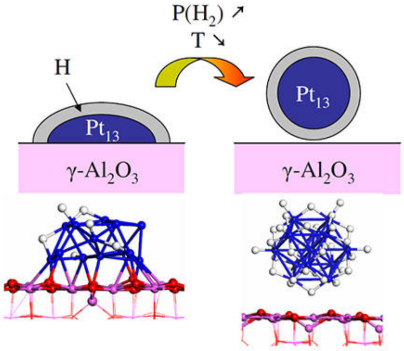
Most efficient heterogeneous catalysts used industrially are generally very complex systems. Computational chemistry is of great help to unravel their atomic-scale structures and understand their roles in the catalytic reaction. Very often however, simple structural models are proposed to understand catalytic reactions. In the present talk, we will show how Density Functional Theory (DFT) calculations were used to provide an original information about the structure for active sites of complex catalytic systems of industrial relevance, as a function of their environment, to assign spectroscopic observations and to quantify the kinetics of multi-step reactions they can catalyze.[1] The focus will be put on catalytic reforming heterogeneous catalysts. Catalytic reforming is a very important process in the refinery, at the core of the production of gasoline with high octane number, and also providing hydrogen. Catalysts are composed of sub-nanometric platinum particles dispersed on a gamma-alumina support. The nature of the active sites and their catalytic behavior remains a matter of debate. We will show the contribution of *ab initio* calculations to elucidate the physical-chemistry of these systems,[2] revealing original cluster morphologies in this size range (about 13 atoms),[3] which also depend on the level of hydroxylation,[4] possibly chlorination,[5] of the surface. The reactive environment-dependent (hydrogen and hydrocarbons) morphology of subnanometric platinum and platinum-tin clusters was also revealed,[6] and employed for a state-of-the-art assignment of XANES spectra.[7] The effect of platinum alloying with other metals is also addressed.[8] Finally, we show how these feature impact the reactivity of the particles for alkane dehydrogenation,[9] paving the way for the introduction of *ab initio* kinetic data in kinetic models, to access macroscopic predictions thanks to a multiscale approach.[10]



References

[1] C. Chizallet, P. Raybaud, *Catal. Sci. Technol*. **2014**, 4, 2797-2813.
[2] C. Chizallet, *L'Actualité Chimique* **2017**, 417, 34-39.
[3] C. H. Hu, C. Chizallet, H. Toulhoat, P. Raybaud, *Phys. Rev. B* **2009**, 79, 195416
[4] C. H. Hu, C. Chizallet, C. Mager-Maury, M. Corral Valero, P. Sautet, H. Toulhoat, P. Raybaud, *J. Catal.* **2010**, 274, 99-110.
[5] C. Mager-Maury, C. Chizallet, P. Sautet, P. Raybaud, *ACS Catalysis* **2012**, 2, 1346-1357.
[6] C. Mager-Maury, G. Bonnard, C. Chizallet, P. Sautet, P. Raybaud, *ChemCatChem* **2011**, 3, 200-207.
[7] A. Gorczyca, V. Moizan, C. Chizallet, O. Proux, W. Del Net, E. Lahera, J. L. Hazemann, P. Raybaud, Y. Joly, *Angew. Chem., Int. Ed* **2014**, 53, 12426 –12429.
[8] A. Jahel, V. Moizan-Baslé, C. Chizallet, P. Raybaud, J. Olivier-Fourcade, J. C. Jumas, P. Avenier, S. Lacombe, *J. Phys. Chem. C* **2012**, 116, 10073-10083.
[9] P. Raybaud, C. Chizallet, C. Mager-Maury, M. Digne, H. Toulhoat, P. Sautet, *J. Catal.* **2013**, 308, 328-340.
[10] W. Zhao, C. Chizallet, P. Sautet, P. Raybaud, *in preparation*.