

## Catalytic active sites are dynamical and metastable

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The determination of the structure of heterogeneous catalytic systems is a key aspect for a detailed understanding of the nature of active sites and for the rational design of efficient catalysts. However, the situation for the catalytic active sites is complicated and the determination of their structure is not straightforward. Indeed, catalysts are not static but dynamic, fluxional, metastable and they strongly evolve under reaction conditions, creating new active sites, not present for the as prepared catalysts. The best active sites are not found on the most stable structure of the catalysts, but require first its isomerization to a highly active metastable structure. The lecture will present several examples, based on quantum chemical calculations.

The first part will focus on the modelling of small Pt cluster ( $\text{Pt}_7$  to  $\text{Pt}_{13}$ ) under hydrogen pressure and on their reactivity for alkane dehydrogenation [1,2]. The approach combines Density Functional Theory, high-dimensional Neural Networks and evolutionary techniques. It also includes grand canonical global optimization to study variable amount of adsorbed hydrogen and novel constrained global optimization methods to determine the structure of the active site that makes the reaction easiest. The approach will be extended to  $\text{Cu}_4\text{O}_x$  clusters on amorphous alumina, showing that the irregular nature of the support is another parameter to generate diverse sets of supported clusters, and hence diverse catalytic reactivity. The second part will deal with single-atom catalysts, that are widely investigated heterogeneous catalysts. We will consider Rh single atoms on  $\text{TiO}_2$  as a generic example, investigating the optimal structure of the single atoms under  $\text{H}_2$  reduction, CO adsorption and its reactivity for reverse water gas shift (RWGS) reaction. The combination of theoretical and experimental studies clearly demonstrates that Rh single atoms change their structure and adapt their catalytic site under reaction conditions [3].

### References

1. G. Sun, P. Sautet, Metastable Structures in Cluster Catalysis from First-Principles: Structural Ensemble in Reaction Conditions and Metastability Triggered Reactivity, *J. Am. Chem. Soc.* **2018**, *140*,
2. W. Zhao, C. Chizallet, P. Sautet, P. Raybaud, Dehydrogenation mechanisms of methyl-cyclohexane on  $\gamma\text{-Al}_2\text{O}_3$  supported  $\text{Pt}_{13}$ : Impact of cluster ductility, *Journal of Catalysis* 370 (2019) 118–129
3. Y. Tang, C. Asokan, M. Xu, G. W. Graham, X. Pan, P. Christopher, J. Li, P. Sautet, Rh single atoms on  $\text{TiO}_2$  dynamically respond to reaction conditions by adapting their site, *Nature Communications*, 2019 in press