

Laboratoire de Chimie – UMR CNRS 5182

Thèse

Modélisation de la synthèse photo-assistée de nanoparticules métalliques sur TiO₂

PhD thesis

Modeling the photo-assisted synthesis of metallic nanoparticles on TiO₂

Supervision

Dr. Carine Michel

carine.michel@ens-lyon.fr

Context and aims:

The growth of supported metallic nanoparticles (NPs) is central to the synthesis of bespoke catalysts but also of chemical and bio-sensors, etc. However, there is a lack of clear causality relations between the synthesis and the resulting structure of the supported NPs. This is rooted in the challenge to investigate the steps involved, starting from the adsorption of a metal precursor at the support/water interface up to the reduction and growth of the NPs. In this PhD thesis, we will focus on the photo-assisted synthesis where the impregnation of the support by a metallic-salt solution is followed by a controlled light-directed support-mediated reduction. This synthesis provides an excellent control over the size and dispersion of metallic Ru NPs on a TiO₂ support¹ that can be used to upgrade biomass.² Combining our simulations with the experimental investigations operated by Nicolas Keller at ICPEES, Strasbourg, we aim at rationalizing the choice of the metal salts and the type of TiO₂ to understand and control the preparation of supported nanoparticles, including bimetallic nanoparticles. This project will also benefit from the IRP ELINE that aims at developing better approaches to model reactions at electrified interfaces.

Project:

The photo-assisted synthesis of metallic nanoparticles can be decomposed into two steps, both occurring at the interface between water and a semi-conductor: (i) impregnation of the metallic salt; (ii) photo-reduction and growth of the metallic nanoparticle. Modelling the adsorption of metal cations and the growth of NPs at the TiO₂/water interface is highly challenging.

First, solvation effects at the TiO₂/water interface need to be efficiently described. This can be achieved today using MMSolv,³ a hybrid scheme developed by C. Michel & S. Steinmann, which was proven to be in agreement with experimental estimates. Second, exploring the wide structural diversity of the seeds and the bi-metallic NPs can be tackled using global optimization tools such as the ones developed for supported metallic NPs. Coupling MMSolv with those global optimization tools will give access to the possible structures of mono and bi-metallic clusters at the TiO₂/water interface.⁴ We will benefit here of the expertise in global optimization of the IRP ELINE consortium.

With this methodological development at hand, we aim at understanding the photodeposition of Ru NPs on TiO_2 that is already well-mastered by Nicolas Keller, our experimental partner. We will identify the adsorption site and the strength of adsorption of the Ru^{3+} cation at the TiO_2 /water interface using our hybrid scheme MMSolv to include the influence of solvation. We will assess the influence of the nature of the surface (rutile- $\text{TiO}_2(110)$, anatase- $\text{TiO}_2(101)$, presence of a oxygen vacancy, etc.), of the metallic precursor (RuCl_3 , $\text{Ru}(\text{acac})_3$, etc.) and of the scavenger (none, ethanol, formic acid, etc...). Moving to the photo-reduction, we will determine the formation energy of the reduced Ru_{10} seeds on TiO_2 including the possible dissociative adsorption of water but also of some scavengers that can be used during the photo-assisted growth. This step will highly beneficiate from the coupling of MMSolv with global optimization methods. Then, using those clusters as starting structures, determining the growth mechanisms can be achieved using *ab initio* metadynamics, as recently done for the coalescence of NPs.⁵

Using the accumulated understanding on Ru, we will address the photo-assisted synthesis of bimetallic catalysts. Here, the main question is how favoring the synthesis of alloying vs. segregated metals. We plan to investigate the effect of co-impregnation vs. successive impregnation but also the relative stability of small seeds of alloys vs. pure metals. Last, we will assess if alloying can limit the Ostwald ripening that can be responsible of the large NPs size usually observed for some metals such as Cu. The mechanism and barriers of detachment of atoms and small clusters will be explored using *ab initio* metadynamics.⁶

References

- ¹ J. Wojciechowska, M. Jędrzejczyk, J. Grams, N. Keller, A.M. Ruppert, *ChemSusChem*, **2019**, *12*, 639; J. Wojciechowska, E. Gitzhofer, J. Grams, A.M. Ruppert, N. Keller, *Catal. Today*, **2019**, *326*, 8-14 ; J. Wojciechowska, E. Gitzhofer, J. Grams, A.M. Ruppert, N. Keller, *Materials*, **2018**, *11*, 2329
- ² C. Michel and P. Gallezot, *ACS Catal.* **2015**, *5*, 4130-4132.
- ³ P. Clabaut, B. Schweitzer, A. W. Goetz, C. Michel, S. N. Steinmann, *J. Chem. Theo. Comp.* **2020**, *16*, 6539
- ⁴ H. Zhai, P. Sautet, A. N. Alexandrova, *ChemCatChem*, **2020**, *12*, 762.
- ⁵ L. M. Farigliano, M. A. Villarreal, E. P. M. Leiva, and S. A. Paz, *J. Phys. Chem. C* **2020**, *124*, 24009-24016
- ⁶ R. Réocreux, E. Girel, P. Clabaut, A. Tuel, M. Besson, A. Chaumonnot, A. Cabiac, P. Sautet, and C. Michel, *Nat. Comm.* **2019**, *10*, 3139.