# Adsorption and diffusion of gold and copper atoms on stoichiometric and reduced rutile TiO2 (110) surfaces from DFT calculations

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In heterogeneous catalysis, various model studies aim to understand how complex catalytic systems effectively work *in operando* at the atomic scale. However, only a few experimental techniques truly allow the progress in the knowledge of this question. In numerous industrial processes, the catalytic system is composed of metallic particles supported on a large range of amorphous materials, with high partial pressure of reactants in a gaseous or a liquid environment. Since Haruta’s works at the end of the 80’s, the scientific interest conceded to catalysis by gold keeps on growing throughout the years. Recently, the nucleation, the growth and the morphology of gold nanoparticles deposited on rutile support have been studied by various techniques such as STM, UPS [1], HAADF STEM [2] and GISAXS [3]. In addition, the authors have investigated the carbon monoxide oxidation on this catalyst *in operando*. Interestingly, they have been able to probe the evolution of the particle morphology during the reaction. In spite of the accuracy of these methods, there are still open questions related to the interpretation of STM images, the mechanisms at the origin of the particle growth, the definition of the active site (the region where the reaction effectively occurs), the role of the oxide support (synergy with the metallic particle, presence of surface and subsurface oxygen vacancies).

In this experimental context, the role of atomic-scale theoretical modelling is essential to tackle those problems by a close comparison between atomistic models and state-of-the-art measurements. In the last decade, a large number of theoretical studies have reported on the adsorption properties of atomic gold and gold clusters at the subnano scale through Density Functional Theory (DFT) calculations. Although many efforts have been conceded to advance in the description of those systems, there are still controversies regarding the adsorption sites and bonding strength; due to the presence of oxygen vacancies in the support, and to the semi-empirical DFT+U methodology used to describe the strong electronic correlation in these delicate models. Moreover, modelling the adsorption and reactivity of a metallic particle supported on a reducible oxide at the nanoscale (2-3 nm) appears really challenging up to date. Similarly, almost no information is available for the case of Cu/TiO2 (110).

In our study, we propose DFT+U calculations for the adsorption and the diffusion of single gold and copper atoms on a rutile TiO2 (110) surface (stoichiometric and reduced supports). The most stable adsorption structures and diffusion activation barriers have been obtained by exploring the potential energy surface through bidimensional maps. This theoretical study opens perspectives for the understanding of the nucleation and the growth of gold and copper nanoparticles on this support, in particular for understanding the reactivity and the stability of those particles.

[1] Wahlström, Phys. Rev. Lett., 90 (2003) 026101

[2] Shibata, Phys. Rev. Lett., 102 (2009) 136105

[3] Saint-Lager, Faraday Discuss., 162 (2013) 179–190