

CO Adsorption and Activation on Supported Cu Nanoclusters

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Extended Abstract

Carbon monoxide is a reactant in many important industrial catalytic processes. CO dissociation that yields active carbon is a fundamental step in, e.g., the Fischer-Tropsch process for conversion of CO into hydrocarbons (Somorjai 1994). Another important reaction is CO oxidation in automobile catalytic converters. This has motivated investigations on the fundamental properties of CO adsorption and/or dissociation onto different catalytic surfaces using several surface science techniques in combination with highly predictive atomic-scale numerical investigations.

In the contest of developing efficient catalysts, metal nanoparticles are very interesting due to their high surface to volume ratio and the concentration of undercoordinated sites, edges and kinks, that make them very suitable for activating molecules for further reactions (Ferrando et al. 2008). In addition, finite-size effects may also play an important role. For applicative purposes, clusters are usually grown on a support, whose presence can both determine and modify the particles properties. The role of the template is also relevant in preventing sintering at high temperatures, thus yielding deactivation of the catalytic devices. Because of these and other reasons, the synthesis of ordered arrays of well-defined equally sized nanoparticles is the goal of many efforts. Ultrathin films of alumina onto the $\text{Ni}_3\text{Al}(111)$ substrate have been recently grown and characterized (Vesselli et al. 2010; Schmid et al. 2007). Depending on the bias voltage, the scanning tunneling microscopy gives different imaging of the periodic surface structure, and in particular the appearance of the so called “dot” structure has been related to the presence of holes in the alumina film down to the $\text{Ni}_3\text{Al}(111)$ support. This structure has been identified as a good template for the nucleation of metallic nanoclusters (Becker et al. 2002).

With a combined approach of highly accurate surface science experimental techniques and numerical simulations we have focused on Cu clusters grown onto $\text{Ni}_3\text{Al}(111)$ supported alumina ultrathin films. We have investigated the mechanism of their self-seeding, nucleation and anchoring on the holes of the alumina film, finding that adsorption inside the holes is much stronger than on the surface for the first stages of seeding, and diffusion at room temperature is feasible. Further nucleation proceeds with the formation of multi atomic seeds. At variance to what reported for other metals, up to 6 atoms can be accommodated inside the holes, in different thermodynamically stable configurations. By other hand, we have studied the reactivity of these supported nanoclusters for CO adsorption and breaking, discussing the influence of the support, finite size effects and coverage on different reaction paths (Olmos-Asar et al, in preparation). We propose that CO dissociation would

proceed via a disproportionation (Boudouard reaction) yielding carbon dioxide, and carbide poisoning the clusters.

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