Seeding, nucleation and reactivity of alumina/Ni_3Al(111) supported metallic nanoclusters: an ab-initio investigation

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Abstract

We investigate the mechanisms of seeding and nucleation of metallic nanoclusters onto an ultrathin alumina template supported on Ni_3Al(111) (Figure 1a,b) by means of *ab-initio density functional theory* calculations. Many atoms (Fe, Co, Ni, Cu, Pd, Ag and Au) show preferential occupation of the defective sites of the ordered so-called *"dot"* structure of the oxide film (Figure 1c), where the adsorption is stronger than in the *"network"* or any other surface site. The relative strength varies with the atomic species, going from the large values of Pd and Ni to the low value of Ag. These results rationalize the experimental evidence showing that some metals such as Pd and Ni create highly ordered patterns of seeds and further nucleation of nanoclusters (Figure 2), whereas others, such as Ag, give rise to less ordered superstructures at room temperature [1].
We study then the interaction of carbon monoxide with a self-seeded ordered array of Cu nanoclusters, comparing simulations with in situ X-Ray Photoelectron Spectroscopy measurements. Adsorption and dissociation of carbon monoxide occur at the copper clusters. The involved mechanisms are investigated at the atomic level, unveiling the effects of cluster finite size, reconstruction, support, and of local CO coverage. It is found that the high coverage of CO at the cluster surface, which considerably exceeds that achievable on single crystal surfaces, facilitates the metal restructuring and the reaction, yielding carbon incorporation into the bulk of the particles (Figure 3) [2,3].

References

[1] J. A. Olmos-Asar, E. Vesselli, A. Baldereschi and M. Peressi, in preparation

[2] J. A. Olmos-Asar, E. Vesselli, A. Baldereschi, and M. Peressi, *Self-seeded nucleation of Cu nanoclusters on Al2O3/Ni3Al(111): an ab-initio investigation,* Physical Chemistry Chemical Physics **16** (2014) 23134-23142.

[3] J. A. Olmos-Asar, E. Monachino, C. Dri, A. Peronio, C. Africh, P. Lacovig, G. Comelli, A. Baldereschi, M. Peressi, and E. Vesselli, *CO on supported Cu nanoclusters: coverage and finite size contribu- tions to the formation of carbide via the Boudouard process*, submitted

Figures

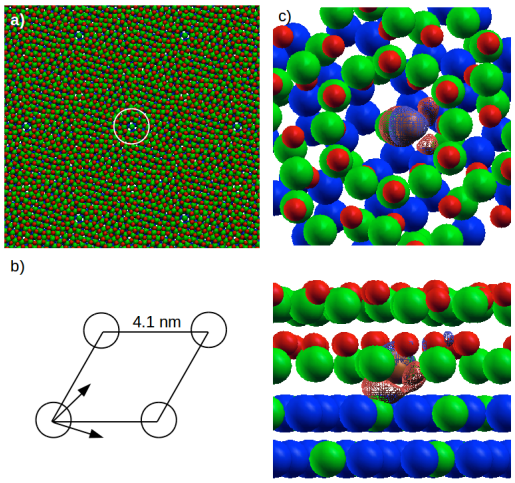

Fig. 1: a) Top view of the structural model of the Al_2O_3/Ni_3Al(111) (O: red; Al: green; Ni: blue); the white circle around the "dot" defect highlights a reduced model considered for calculations. b) The periodically repeated unit cell. c) Top and side view of the equilibrium configurations for a monoatomic Cu seed in the "dot" defect.

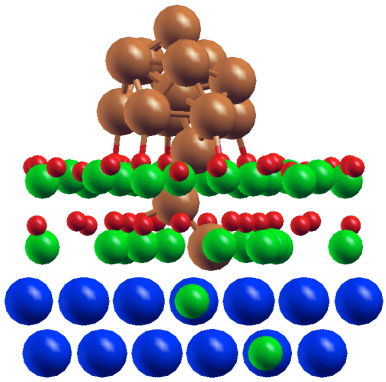

Fig. 2: Side view of the equilibrium configurations for a 15-atom Cu nanocluster nucleated in the “dot” defect of alumina/Ni_3Al film.

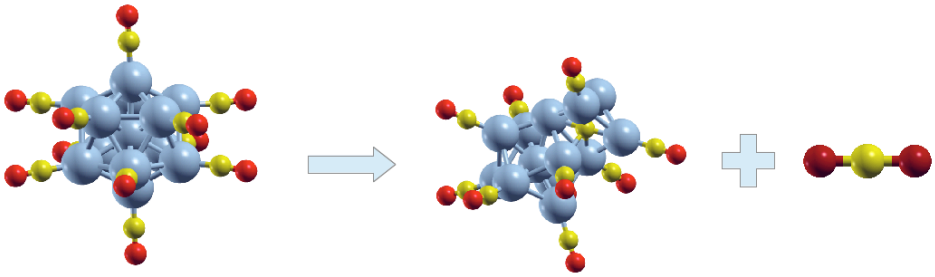

Fig. 3: A small Cu unsupported nanocluster covered by CO molecules and a possible resulting configuration after reaction of two molecules