A Reactive Global Optimization Approach to the Catalytic Reduction of CO_2 by Ni supported nanoclusters

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We discuss a predictive computational methodology that allows one to study the catalytic activity of small metal nanoclusters supported on oxide surfaces[1]. This methodology is based on two steps. In the first step, a reactive global minimization (RGO) search is conducted, in which first-principles (i.e., density-functional) methods are used to explore the potential energy surface of (both bare metal clusters and) combined supported-metal-cluster+reactant-molecules systems. In a second step, the results of the RGO search are combined with statistical mechanics techniques to simulate of the catalytic behavior of such systems. The computational models necessary to achieve the required compromise between accuracy and efficiency for supported particles are also discussed. The approach is first applied to exploring the structure of bare supported Ni clusters supported on MgO(100), where the MgO(100) surface is taken as an effective model of a simple ionic oxide substrate, along the lines of preliminary explorations[2]. By introducing hydrogen species into the RGO approach, a thermodynamic phase diagram for the hydrogenation of supported Ni particles is further derived. As the core of the work, the real catalytic process is finally tackled: both hydrogen and CO_2 species are simultaneously introduced as ligands of the Ni clusters, and CO_2 reduction by Ni nanoparticles is studied as a function of temperature and chemical potential of the involved species, at the same time illustrating the use of the basic concepts and the power of the approach. It is found that sub-nanometer Ni supported clusters in proper reaction conditions can act as affective catalysts for CO_2 reduction by H_2. Furthermore, the relevance of these developments to the general field of heterogeneous nanocatalysis (including photo- and electro-catalysis) is also discussed.

References:

[1] Fabio R. Negreiros, Daojian Cheng, Edoardo Aprà, Giovanni Barcaro, Luca Sementa, Stefabn Vajda, A. Fortunelli, Nanoscale, (submitted).

[2] A. Fortunelli and R. Ferrando, Theoretical Modelling of Oxide-Supported Metal Nanoclusters and Nanoalloys, in “Nanoparticles”, R. L. Johnston and J. Wilcoxon Eds. (Elsevier, Amsterdam, 2011, in press).