Structure predictions of technologically and environmentally relevant oxide nanoparticles

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Nanotechnology in recent years is playing a very important role in such diverse field as catalysis, electronics, optics, etc. The key role of the success of these classes of materials is the structure-property relationship. Moreover, several nanoparticles properties can be tuned by varying its size. There are several experimental techniques such as electron spectroscopies, that have been successfully applied to determine nanoparticles structure with high resolution. Nevertheless, theoretical structure predictions are still needed especially in an ultra small size regime (i.e. size ≤ 1nm) which usually is below the experimental resolution. At this size regime it is possible to predict the atomic structure of nanoparticles applying global optimization techniques such as Monte Carlo basin hopping (MCBH). This is a power tool that provide realistic models in order to elucidate the structure-property relationship.

We applied MCBH on titania (TiO_2) nanoclusters in order to predict the crystalline-to-amorphous crossover size[1]. At size of 2.0 – 2.5 nm we predict a crossover in energetic stability between photoactive anatase bulk-like (> 2.5 nm) and amorphous inactive TiO_2 nanoparticles (< 2.0). We studied as well titanosilicates systems which are industrial catalyst widely used for oxidation of organic molecules in mild conditions. These catalysts are based on crystalline zeolitic silica framework in which it is disperse a very low fraction of 4-coordinated titanium active centres. Only a very low fraction of titanium is included in the framework due to its low miscibility, however, at nanoscale we predicted a high miscibility between silica and titania at a wide range of compositions. Here we provide as well useful informations such as calculated harmonic IR spectra which contain "signatures" of mixed titanosilicates in order to help experimentalists characterize these structures[2]. Our next studies are focus on using MCBH on hydroxylated systems such as silica[3] and titania to better understand the influence of water on oxides clusters stability. Here, we are developing new strategies and methods to predict stable hydroxylated nanoparticles.

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[1] Lamiel-Garcia, O.; Cuko, A.; Calatayud, M.; Illas, F.; Bromley, S. Predicting Size-Dependent Emergence of Crystallinity in Nanomaterials: Titania Nanoclusters versus Nanocrystals. *Nanoscale* **2016**, *9*, 1049–1058.

[2] Cuko, A.; Calatayud, M.; Bromley, S. Size dependency of stability and structure in mixed-oxide titanosilicates: from nanocluster to bulk. In preparation

[3] Cuko, A.; Maciá, A.; Calatayud, M.; Bromley, S. Global Optimisation of Hydroxylated Silica Clusters: A Cascade Monte Carlo Basin Hopping Approach. *Comput Theor Chem* **2017**,1102, 38–43.