Mutiscale modelling and Computational spectroscopy

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ABSTRACT OF MY ABSTRACT

My presentation will deal with metal oxides with and without molecules "on top of them", and how we can use modelling of different flavours to acquire new knowledge where experiments need assistance. In particular I will mention multiscale modelling, simulated experiments (e.g. computational spectroscopy) and 'physics-based vs. data-driven' modelling.

METAL OXIDES AND MULTISCALE MODELLING

Metal oxide and their interfaces with molecules play crucial roles in technology, science, industry, and society. Metal-oxide-based catalysts, sensors and battery devices are just a few examples and finding the mechanisms that govern such functionalities is challenging. Here computer modelling can provide unique detail and insight.

Here I will describe some of our efforts to develop multiscale modelling protocols for metal oxide surfaces and nanoparticles (e.g. of CeO_2, ZnO and MgO). We combine a range of theoretical methods including DFT, tight-binding-DFT [1], and reactive force-field models [2]; cf **Fig. 1**. A key question is whether it is really possible to model redox-active metal oxides *without including the electrons*?

METAL OXIDES WITH MOLECULES

Cerium oxide (ceria) is a reducible metal oxide with intriguing chemical and physical properties. Experiments in the literature have shown that the oxygen storage capacity (OSC) of ceria at the nanoscale is strongly shape and size dependent [3,4]. An increased activity towards O_2 molecules has been observed for particles of exotic shapes (such as nanorods and nanocubes), and a increased OSC has been measured for very small nanoparticles (d < 5 nm). We combine density functional theory (DFT) calculations with micro-kinetic modelling (MKM) to simulate O_2 temperature programmed desorption (TPD) and H_2 temperature programmed reduction (TPR) spectra for ceria nanoparticles (Refs. [5] and unpublished work). The chemical origin of this enhancement has been amply discussed in the literature. dramatically.

The H_2O molecule deserves special attention as hydroxylation/hydration changes the stabillities and reactivities of metal oxides, often with far-reaching consequences. Furthermore, water and surface OH groups are central in many applications of metal oxides, either as key actors or because they are omnipresent under ambient conditions. Water is discussed in the next section.

WATER ADSORPTION, DATABASES AND COMPUTATIONAL MOLECULAR SPECTROSCOPY – PREDICTION OR INSIGHT?

Vibrational spectroscopy is one of the most sensitive methods to explore bound OH groups, although interface systems constitute a particular challenge also for such spectroscopies. Access to robust correlation curves is essential in order to decipher structural information from IR spectra. We generate such correlation curves from DFT and AIMD calculations followed by quantum vibrational calculations (=> anharmonicity).

We have recently [6, 7] created two databases (**Fig. 2**) of structures and properties of OH groups of water and hydroxides (i) on metal oxide surfaces, and (ii) within the crystalline state. We use these databases to find *fundamental scientific relations* as well as *structure-property models* for frequency predic-tion, and assess the prediction capabilities of a range of descriptors (features). Starting from a machine-learning geometrical descriptor we gradually include more physics/chemistry flavor in the descriptor and examine how the frequency prediction power (and "insight content") vary (cf. **Fig. 3**).

MUCH WATER: HYDROPHOBICITY OF CERIA

If time allows, I will mention some recent results on why ceria with a lot of water "on top" can be hydrophobic (an experimental fact!) while the direct ceria-water interaction is in fact hydrophilic. [8]

CONCLUSION

Molecular and materials modelling on metal oxide systems can deliver new and unique data and valuable relations/models which save time and energy.

ACKNOWLEDGMENT

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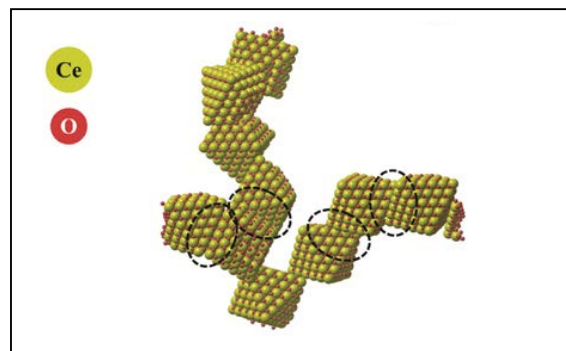
Fig. 1. Snapshot from a ReaxFF MD simulation of many $Ce_{132}O_{264}$ nanoparticles which agglomerate into a winding chain (remade from Ref. [2]].
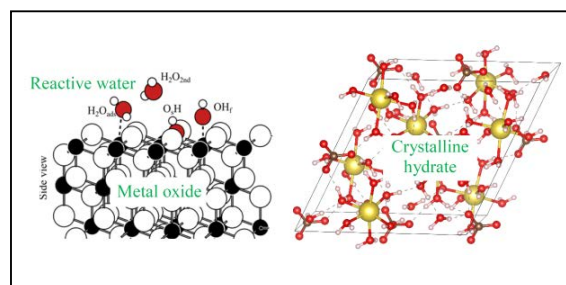

Fig. 2. We have created two databases of structures and properties of water and OH^- on metal oxide surfaces [6], and within crystalline hydrates and hydroxide [7]. From these we generate spectrscopic and other models/relations. All data were based on the same electronic structure (DFT) method.
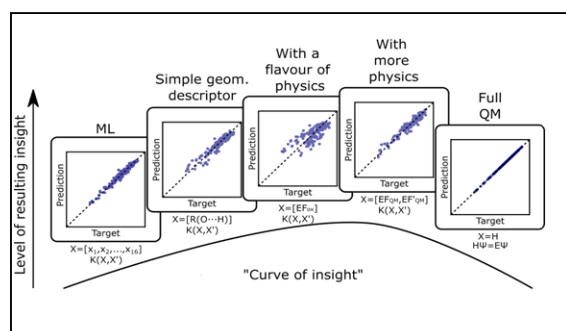

Fig. 3. Illustration of the progression of our descrip-tors in terms of the "amount" of physics coded into them and their respective level of insight. The scatter plots show the agreement between predictions and targeted reference values. (cf. Ref. 7).