Corinne Arrouvel
Department of Chemistry, University of Bath, UK

Email: C.Arrouvel@bath.ac.uk

Structure-property relationships of titania and alumina polymorphs: comparison between simulations and experiments.

We have undertaken a comparative investigation of these different TiO_2 and Al_2O_3 polymorphs using computational techniques bases on DFT/DFT+U (VASP) and interatomic potentials (METADISE and DL_POLY) to better understand the structural, chemical and electronic properties for various applications. By comparing the surfaces of lesser known phases of TiO_2 (brookite-TiO_2, TiO_2-B) with rutile and anatase phases, we find that brookite surfaces are more complex, with higher intrinsic activity of surface sites. We predict that this phase should be more suitable for (photo)catalytic applications as it is more acidic and more hydrophilic catalyst, whereas the anatase phase shows more interest for solar cells; and TiO_2-B is a candidate to replace the graphite anode in lithium battery materials. We have also compared γ^c-Al_2O_3 with the more ordered θ and α-Al_2O_3. The γ^c-Al_2O_3 phase can be made from the dehydration of boehmite (γ-AlOOH) and is already an industrial catalyst (i.e. support for MoS_2 active phase in hydrodesulphurisation).
We have extended the simulations under a range of working conditions (i.e. H_2O, H_2S, H_2 partial pressures and temperatures) to enable us to provide a detailed comparison with ongoing experiments, such as infrared spectroscopy (IR), temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS), which operate under different working conditions. For example, we can explain the controversy surrounding the hydroxylation of rutile, and show that OH coverage depends on temperature and pressure.
This work demonstrates that the close combination of experiments and simulations aids in increasing our understanding of nanoparticles or nanotubes and their reactivity. The comparison of TiO_2 and Al_2O_3 polymorphs highlights the characteristics of each phase and the importance to synthesise with a given morphology for a given application.