Insights into structure and morphology of zirconium oxide nanocrystals by HR TEM techniques combined with DFT molecular modelling and images simulations.

Joanna Grybos¹, Witold Piskorz¹, Rafal Dunin-Borkowski², Zbigniew Sojka¹,
¹Faculty of Chemistry, Jagiellonian University, Ingardena 3, Krakow
²Ernst Ruska-Centre, Forschungszentrum Jüllich GmbH, D-52425 Jüllich, Germany.
grybosjo@chemia.uj.edu.pl

Redox properties of oxide catalysts are determined by their structure and morphology. Nanostructured zirconium oxide catalysts are characterized by exposed facets, edges, corners and kinks that played crucial role their reactivity. In this contribution we combined HR TEM with DFT modelling to provide the morphological and structural description of monoclinic ZrO₂ surface at nano- and pico-scales. Equilibrium shape of the monoclinic zirconia nanocrystals with inclusions of entropy was predicted by means of plane wave periodic DFT/PW91 calculations combined with phonon structure calculations and Wulff construction. For modelling the VASP code and PHONON were applied. Atomic structure relaxation and reconstruction of the exposed zirconia planes were modeled and discussed in detail. The results were compared with HR TEM images (Fig. 1). The morphology predicted by the Wulff construction compares well with the experimental habit of the synthesized m-ZrO₂ nanocrystals. Small discrepancies in both shapes may be caused by the anisotropy in the rate of the crystal growth.

For experimental atomic-scale characterisation of the exposed planes, an aberration corrected HR TEM imaging at 300 keV was used. Quantitative measurements of the positions of the m-ZrO₂ atomic columns were performed by fitting the phase image areas to the two dimensional Gaussian function. To revealed the surface reconstruction, the space between the atomic planes was obtained by fitting the positions of the individual atomic columns to straight lines. The HR TEM images were simulated within the multislice approach, with inclusion of thermal vibrations of the crystal lattice, accounted for by the Debye-Waller factor. The calculated phonon structure of the bulk and the exposed facets of m-ZrO₂, helped to improve the accuracy of simulated images. The ab initio simulated images were validated against the experimental one. Furthermore the topographic irregularities of the exposed facets revealed by the picometric imaging were used to develop a complete picture of surface reconstruction.