Exploring confined water on surfaces of metal-oxide nanoparticles with neutrons

NANCY L. ROSS[1]

[1]Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA (nross@vt.edu)

Surface water on metal-oxide nanomaterials has become a topic of great interest in geochemistry as the stability of metal oxide materials at the nanoscale is provided, in part, by the occurrence of water confined to their surfaces. These hydration layers have a pronounced impact on the morphology and polymorphism of the nanoparticles and can alter the oxidation-reduction equilibria as well as the relative phase stabilities of metal-oxide particles [1]. Inelastic neutron scattering (INS) provides key information about the structure and dynamics of the water species, namely molecular (H_2O) and dissociated water (OH, hydroxyl), confined to the oxide surfaces. INS spectra collected on TiO_2 (rutile and anatase), SnO_2, CoO, Co_3O_4, PdO, CeO_2, CuO and ZnO nanoparticles [2-5] support a 'core-shell' model for the structure of hydrated metal-oxide nanoparticles - a central core comprising the metal oxide particle surrounded by a multi-layered water shell. Translational motions of H_2O are strongly restricted on the nanoparticle surfaces, relative to those in ice-Ih, due to extensive H_2O–surface interactions. These interactions typically soften and distort the H-bond networks within the H_2O layers. The complexity inherent in the structure of the nanoparticle hydration layers is reflected in their phonon density of states (PDOS) determined from the INS spectra. Thermodynamic properties of the hydration layers calculated from the PDOS allow us to probe the effect of the confined water on the stability of the nanoparticle as a function of particle size, structure, and chemistry.

[1] A. Navrotsky *et al* (2010) *Science* **330** 199. [2] N.L. Ross *et al* (2011) *MRS Proceedings*, 1352. [3] E. C. Spencer *et al* (2011) *J. Phys.: Condens. Matt,* **23**, 205303. [4] E. C. Spencer *et al* (2012) *J. Chem. Thermodyn.*, **51**, 1034. [5] E. C. Spencer *et al* (2014) *Chemical Physics*, in press.