Atomistic Simulations of the influence of Aluminium and solvent on structure and stability of mezoporous surfaces

W. GREŃ AND S.C. PARKER

Department of Chemistry, University of Bath, BA2 7AY, UK (w.gren@bath.ac.uk)

In this work we used atomistic simulations to study surface structure and stability of zeolite A (LTA) and its interaction with water. The interactions were described according to the Born model of solids. The atom polarisability was taken into account by the means of the shell model.

We focused on alumino-silicate type of LTA with Al Si ratio of 1:1 and Na^+ counter ions (Na-A). Initially, using static lattice minimisation (code METADISE [1]), we found the slabs with the most stable surfaces. Then we introduced water into system and ran molecular dynamics (MD) simulations (code DL_POLY [2]).

We found that the most stable surfaces are {100} and {111}, which is analogous to siliceous LTA. The surface terminations have also the same structure as in siliceous case: single and double 4-rings for {100} and {111} respectively. We found that increased Al content changes the relative energies of these surfaces, making {100} more stable and {111} less stable. The surfaces were then immersed in water and we performed MD simulations in NVT ensemble and 300K for over 3 ns. Similar to the siliceous LTA, the density of water around Na-A slab revealed layering. However inside the pores the water density is localised, forming distinct crystallographic sites. Unlike siliceous LTA, there are no hydrophobic areas inside Na-A slabs. Furthermore the presence of water affects the distribution of Na^+. We found that sodiums initially sitting at the surface sites are leaching to the solution. Moreover simulations revealed that the bulk Na^+ ions are highly mobile with sodium ions, initially situated on external side of the 6-ring (S6R), readily enter the β-cage.

Our studies showed that atomistic simulations can provide useful, complementary insight into understanding of processes at the mineral-water interface. The simulations allowed us to investigate the effects which would be difficult to tackle by the experimental method.

[1] G. Watson, E. Kelsey, N. de Leeuw, D. Harris & S. Parker (1996) *Journal of the Chemical Society, Faraday Transactions* **92**, 433–438. [2] Smith & Forester (1996) *J. Mol. Graph.* **14**, 136-141.

Internally consistent thermodynamic data for magnesium sulfate hydrates

K.-D. GREVEL[1]* AND J. MAJZLAN[2]

[1]Institute of Mineralogy and Geochemistry, Albert-Ludwig-University, Freiburg, Germany
(*correspondence: Klaus-Dieter.Grevel@rub.de)
[2]Institute of Geosciences, Friedrich-Schiller University, Jena, Germany

Magnesium sulfate hydrates, especially epsomite ($MgSO_4 \cdot 7H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$), and kieserite ($MgSO_4 \cdot H_2O$) are important constituents of marine evaporite deposits. Results from the most recent Mars missions support the assumption that significant quantities of Mg-sulfate hydrates are also present on this planet (cf. [1]). Experimental studies on the stability of several Mg-sulfate hydrates including epsomite, hexahydrite, starkeyite ($MgSO_4 \cdot 4H_2O$), and kieserite as a function of temperature and relative humidity [1,2,3] are in poor agreement with calculations based on thermodynamic properties of these substances taken from the literature [4.5]. Therefore, we measured enthalpies of formation of four different hydrates by solution calorimetry at $T = 298.15$ K. The resulting enthalpies of formation from the elements are:

$\Delta_f H^0_{298}$ (epsomite) $= -3387.7 \pm 1.3$ kJmol^{-1}
$\Delta_f H^0_{298}$ (hexahydrite) $= -3088.1 \pm 1.1$ kJmol^{-1}
$\Delta_f H^0_{298}$ (sanderite, $MgSO_4 \cdot 2H_2O$) $= -1894.9 \pm 1.3$ kJmol^{-1}
$\Delta_f H^0_{298}$ (kieserite) $= -1612.4 \pm 1.3$ kJmol^{-1}

Using mathematical programming techniques [6] standard values consistent both with our calorimetric data and humidity brackets could be derived:

Epsomite: $\Delta_f H^0_{298} = -3388.7$ kJmol^{-1}, $S^0_{298} = 371.1$ Jmol^{-1}K^{-1}
Hexahydr.: $\Delta_f H^0_{298} = -3087.2$ kJmol^{-1}, $S^0_{298} = 348.4$ Jmol^{-1}K^{-1}
Starkeyite: $\Delta_f H^0_{298} = -2496.1$ kJmol^{-1}, $S^0_{298} = 259.9$ Jmol^{-1}K^{-1}
Kieserite: $\Delta_f H^0_{298} = -1612.4$ kJmol^{-1}, $S^0_{298} = 126.4$ Jmol^{-1}K^{-1}

[1] Chipera & Vaniman (2007) *Geochim. Cosmochim. Acta* **71**, 241–250. [2] Chou & Seal II (2003) *Astrobiology* **3**, 619–630. [2] Chou & Seal II (2007) *J. Geophys. Res. – Planets* **112**, E11004 10p. [4] DeKock (1986) *U.S. Bur. Mines Inf. Circ.* **9081**, 59p. [5] Wagman *et al.* (1982) *J. Phys. Chem. Ref. Data* **11**, Suppl. 2, 371p. [6] Grevel (2004) Habil.-Thesis, Univ. Bochum 113p.