09-Engineering and Computer Simulation of Inorganic Crystal Structures

MS-09.01.05 COMPUTER SIMULATION OF MICRO-POROUS SOLIDS by R.A.Jackson, Department of Chemistry, Keele University, Staffordshire, STS 5BG, UK

Computer Simulation is now well-established as a means of calculating the structural and other properties of microporous solids, including zeolites, ALPOs and germanates. The specific method that will be described is lattice energy minimisation (R.A.Jackson and C.R.A.Catlow, Mol Sim, 1988,1,207-224), which calculates equilibrium structures and lattice properties, and which has been applied to a wide range of materials from each of these categories. Crucial to the success of this technique is the availability of good quality interatomic potentials, and current progress in this area will be discussed. Applications will be described to the following problems: (i) framework modeling, (ii) relative stabilities of frameworks, and (iii) location of non-framework cations. Comparison with experimental data will be given where possible. Finally, future developments in the field will be discussed.

MS-09.01.06 FIRST-PRINCIPLES STUDIES OF PRESSURE-INDUCED PHASE TRANSFORMATIONS. By John S. Tse, Dennis D. Klug and Yvon Le Page, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

Recent advances in theoretical methodologies and improvement in computational technologies have enabled accurate prediction of the structure and properties of crystals from first principles methods. The emergence of molecular dynamics and of *ab-initio* total energy methods has greatly aided the fundamental understanding of the stability of crystal structures and has led to the development of new materials. Recently, known pressure-induced transformations in ice, α-quartz, α-berlinite and rutile have been successfully reproduced by our group, employing classical constant-pressure molecular dynamics calculations with realistic empirical potentials derived from quantum-mechanical calculations, or using *ab-initio* quantum total energy calculations. In particular, the theoretical results distinguish between the contrasting behaviour in isostructural α-quartz and α-berlinite under pressurization, and provide detailed mechanisms for the amorphization process and the memory effect. One of the advantages of first principles methods is the ability to study structures and properties of crystals under conditions not easily amenable to experimental studies. Novel high pressure (~ 100 GPa) structures for silica and rutile have been revealed from our studies. Since under extreme conditions, the empirical potentials may no longer be applicable, the electronic properties of the system must be treated in a self-consistent manner. Recent implementation of the Car-Parinnello techniques allows one to perform parameter-free molecular dynamics simulations. This method has now been applied to the study of the stability of the recently predicted high pressure phases of silica and rutile.

MS-09.01.07 PHYSICAL CHEMISTRY OF THE AGEING OF SILICAGEL by R.A. van Santen*, Schuit Institute of Catalysis, Eindhoven University of Technology, Department of Chemical Engineering, 5600 MB Eindhoven, The Netherlands

SAXS studies of silicagel formation enable the *in situ* study of aggregation and ageing processes. Aggregation can be analysed in terms of changes in elementary particle size, fractal dimension as well as radius of aggregation.
Cluster aggregation computer simulations can be applied to analyse the consequences of different aggregation and ageing models. Two ageing processes have been identified. At relatively high silica concentration initially gels of a fractal dimension 2.2 are formed. Ageing occurs by dissolution and non-uniform distribution of silicagel building units results. The fractal dimension decreases to 1.8.
At low concentrations initially a gel also of fractal dimension on 1.8 is formed. However, this gel has a uniform distribution of elementary particles. Ageing now occurs by internal reorientation processes of the silica particle chains resulting in a fractal dimension of 2.1. NMR relaxation spectroscopic studies as well as X-ray microsopic data will be shown to support the ageing mechanisms as deduced from computer simulated aggregation processes.

PS-09.01.08 ON THE USE OF FORCE CONSTANTS IN SIMULATED ANNEALING REFINEMENT D. TranQui

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Simulated annealing technique has shown to be an efficient procedure for refinement of protein and macromolecule crystal structure, specially in the case where the starting model is approximately known (Brunger, A.T., Kurian, J. and Karplus, M. ,1987, Science, 235. 458-460; Fujinaga, M., Gros, P. and Gunsteren W.F., 1989, J. Appl. Cryst. 22, 1-8).
In addition, due to its high convergence radius, this method is able to generate atomic-position shifts, up to 4Å and sometimes more, and/or large flipping moving the structure into the correct orientation: such large changes which necessarily involve jumpings over energy barrier are usually beyond the convergence radius of conventional standard least-squares procedure. It is also commonly recognized that simulated annealing refinement reduces substantially the need of human interventions during the structure refinement stage.

However, it is well known that simulated annealing refinement sometimes suffers serious drawbacks, even it was apparently applied following to the appropriate protocole. Thus, in the course of refinement of a ferredoxin from *Clostridium Acidurici*, (TranQui, D., Meyer J., Moulis J.M., Sieker, L and Jesior, J.L. to be published) a metalloprotein which harbours in its polypeptide chain two inorganic [4Fe-4S] clusters, we have obtained, whatever the starting points used, an unreasonable departure of the [4Fe-4S] geometry from the cubane-like structure. This is due to the fact that the minimizer tends to compensate the unproper force constant of covalent bond Fe-Sγ (Sγ of Cysteine) in tearing the internal bond lengths bond angles of [4Fe-4S] clusters. Finally, this unwanted effect was corrected in assigning two different constant values: $k_{0,1}$ and $k_{0,2}$ for

