ELSEVIER

Catalysis Today 23 (1995) 325–332

CATALYSIS TODAY

A multi-faceted approach to modeling heterogeneous catalysts

J.M. Newsam *, Y.S. Li

Biosym Technologies Inc., 9685 Scranton Road, San Diego, CA 92121, USA

Abstract

Modeling and simulation can contribute to several aspects of heterogeneous catalyst research and development (R and D). Different modeling approaches provide benefit at different stages in the R and D cycle. The value of a multi-faceted view of heterogeneous catalyst modeling is demonstrated by examples cited from the areas of: (1) structure determination, analytical data simulation and analysis, (2) molecular interactions, physisorptive phenomena and computation of thermodynamic parameters, and (3) electronic structure, chemical reactivity and kinetics. Heterogeneous catalysts are complex and substantial new methodology developments have been needed in each of these areas. Further progress in theory, implementation and computational performance is desirable. However, the growing number of industrial applications indicates a steadily increasing acceptance of modeling and simulation as valuable contributors to practical catalyst R and D.

1. Background

The commercial implementation of any new heterogeneous catalyst technology represents the successful culmination of a series of stages in which the fundamental aspects of catalyst and process research represent an important, but only partial component. An initially promising lead must pass muster at, for example, scale up, economic, process and engineering levels (Fig. 1). Perhaps least predictable are the economic drivers; swings in commodity or process costs can dramatically affect the attractiveness of new process technology options. The economic implications of innovative developments at the fundamental level can, however, be large. Even percentage improvements in bulk processes such as fluid catalytic cracking (FCC) or ethylene epoxidation translate into major cost savings and hence industrial competitiveness.

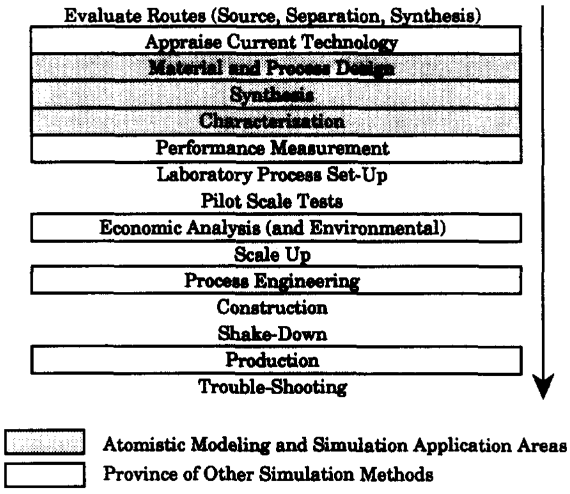

Fig. 1.

The industrial implementation of atomistic modeling and simulation is probably most mature in the life sciences sector, in the fields of macromolecular structure research and rational drug design. In drug development, however, even

---

* Corresponding author.

0920-5861/95/$09.50
SSDI 0920-5861(94)00145-6

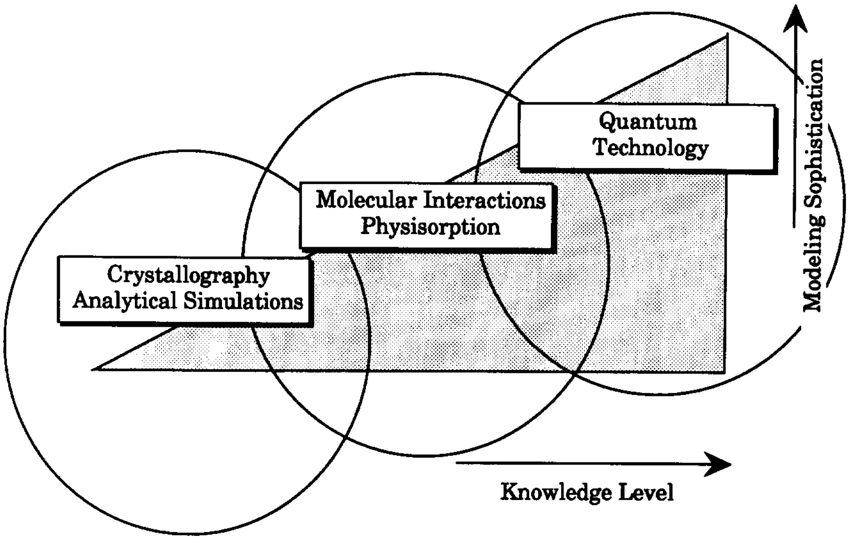

Fig. 2.

where modeling does shorten the initial exploratory or lead identification stage, several years of clinical trials are necessary before ultimate economic benefit from the original fundamental advance can be gained. In heterogeneous catalysis, however, new fundamental improvements, step-out or incremental, can often be translated rapidly into revenue-generating industrial application.

Traditional catalyst development has been largely Edisonian in nature. This does not imply exhaustive trial and error; rather, scoping experiments have been pursued in domains guided by individual intuition, chemical insight and, perhaps in part analogous to the steepest descent optimization procedure, by the trail of most promising results revealed in successive sets of experiments.

One possible implementation of modeling and simulation is to provide a structured framework for this insight. An R and D program that is founded on a fundamental understanding will, almost certainly, be better positioned than one suggested simply by empiricism.

We illustrate here the application of a range of different modeling techniques, principally through citations of recent work in this area. This is an individual perspective, not a review, with the examples taken subjectively from the authors' immediate experience. These examples serve simply as a means of illustrating the interplay between some of the various techniques that can be applied to heterogeneous catalyst problems and the reader is referred to the original works for appropriate citation of the related literature.

2. A spectrum of methods

Most practical heterogeneous catalysts are complex. Although this complexity has traditionally hampered the application of atomistic modeling and simulation methods, it also provides an incentive for the development of new methods and approaches. Our knowledge of the critical structural characteristics of heterogeneous catalysts ranges from quite detailed through to, at best, sketchy. With reasonable correlation, the kinds of development questions that are posed also vary widely.

Modeling and simulation can complement experimental data at differing levels, and can aid substantially in improving our knowledge of fundamentally important characteristics. As our detailed understanding of a particular system grows, the degree of modeling sophistication can grow in consort (Fig. 2). Analogously with experiment, it is usually inefficient to apply demanding or expensive methods until the characteristics of

Meso-Micro Scale	**Light Scattering** **Microtomography, NMR imaging**
Long Range Structure	**Powder Diffraction (X-ray, Neutron, Electron)** **Single Crystal Diffraction** **Fibre, Film Diffraction** **Wide-angle X-ray, Neutron Scattering** **High Resolution Lattice Images (Electron Microscopy)** **Scanning Electron Microscopy (SEM) micrographs**
Structure Dynamics	**IR, Raman Spectroscopy** **Inelastic, Quasielastic Neutron Scattering**
Surface Structure	**Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM)** **Grazing Incidence X-ray Diffraction** **LEED, RHEED**
Local Structure	**Extended X-ray Absorption Fine Structure (EXAFS)** **Solid State NMR** **Electron Spin Resonance (ESR)** **Electron Spin Echo Spectrometry**
Electronic Structure	**UV-Vis Spectra** **X-ray Photoemission**

Fig. 3.

the system and the key questions to be addressed have been clearly identified and given priority in importance. We wish to answer the question posed, at the level required, and by the correspondingly simplest and most straightforward approach, without introducing unnecessary detail or complexity.

3. Modeling and simulation in catalyst characterization

Atomic-level structural characterization is not yet a prerequisite for obtaining a composition of matter patent on a new heterogeneous catalyst. However, a knowledge of structure is almost universally desirable, be it of the acid sites in a zeolite, of surface defects in a partial oxidation catalyst, or of metal clusters dispersed on a microporous carbon support. Structural data can: (1) confirm and enrich definition of the active components in the system, potentially strengthening a patent position, (2) serve as a basis for assessing and quantifying differences between different preparations or formulations, (3) yield a first-level understanding of catalyst activity, and of structure–activity or structure–selectivity relationships, and (4) be an essential foundation for more detailed investigations using modeling and simulation in conjunction with experiment.

Improvements in experimentation have contributed to substantial advances in our ability to characterize the atomic structures of even quite complex materials. In parallel, developments in hardware and numerical methods have, indeed, led to computer modeling approaches becoming a key complement to experiment in the extraction and exploitation of this atomic-level structural knowledge.

Modeling aids in several ways. A computational environment is the preferred mains of collating analytical data for a particular sample so that all needed data are available. The usefulness of a piece of analytical information is often governed by the immediacy of its accessibility. Analytical data of diverse types can be simulated based on an appropriate model (Fig. 3) and these types of data can then contribute discretely or in combination to catalyst characterization.

Many heterogeneous catalysts are based on crystalline materials. Solid state modeling encompasses crystallographic concepts that allow the rapid development and evaluation of new or derivative structural models. These methods include symmetry manipulations and displays, techniques for aggregating structural constituents such as cages, polyhedra or layers, and the automatic determination of unit cells and space group symmetries from atomic models. Recent characterization work on synthetic and natural ferrierites provides an illustrative example [1]. Synthetic ferrierites are being commercialized for the isomerization of butene to isobutene, a precursor to methyl *tert.*-butyl ether (MTBE). Ferrierites are known to be susceptible to planar faulting; geometrical modeling methods were used to develop models for structure variants obtained via seven different faulting operations. Comparing the powder X-ray diffraction profiles simulated for each of these faulting models, as a function of faulting probability, against experimental data allowed identification of the common mode of faulting in the real materials, and provided a basis on which the extent of faulting in a given material could be estimated [1]. The octahedral molecular sieves OMS-2 [2], zeolites constructed from 6-ring building units stacked in various ways [3,4] and the titanosilicate ETS-10 [5] are related examples. Crystallographic modeling was used to develop models for a number of members of the ETS-10 structural family [6], based on crystallographic data for one end-member structure [7]. The US patent for ECR-35 [8], a material related structurally to zeolite Y and faujasite, is another example of the value of detailed structural characterization at the atomic level [9].

In the ferrierite example, the parent structural model was well known. To aid determination of unknown structures, simulated annealing has been implemented as a direct space approach to structure solutions from powder diffraction data. This approach has clear applicability to close-packed and framework inorganics, as well as organic or organometallic molecular solids [10–12]. The structure of a new sodium zinc arsenate was solved by this approach [13] and several related studies are in progress. This structure solution method is a good example of a new approach to a traditionally challenging problem that has become viable through combined developments in algorithms and hardware performance. After an initial structural model has been derived, modeling can also aid structure completion, the location of any structural components missing from the initial model, and structure refinement, the optimization of structural and experimental parameters so as to minimize the discrepancy between observed and simulated data. In addition to applying docking techniques to locate guest molecules within a host matrix [14,15], molecular dynamics techniques have been used, in conjunction with Rietveld full profile analysis, to probe preferred guest locations and to sample dynamical disorder [16].

Methods for handling certain of the material complexities typically present in heterogeneous catalyst samples, such as disorder, local ordering and planar faulting have proven to be quite important, as illustrated by the previously cited examples. Frequently, a single analytical technique is incapable alone of providing the required degree of structural definition. Thus, recent examples illustrate the use of simulation to interpret infrared and Raman spectra of sodalites [17,18], models of more complex aluminosilicate zeolites, and the shapes of crystallites produced under high temperature [19] or hydrothermal conditions [20–22] as are measured by scanning electron microscopy (SEM). Other techniques such as EXAFS and solid state NMR (Fig. 3) are also being used in combination with simulation [23], and it is easy to envisage combining the perspectives from several different analytical tools into self-consistent structural models within a modeling environment.

4. Molecular interactions and physisorptive phenomena

Molecule–solid interactions can be explored at a variety of levels. The graphical, geometrical or steric level [24–26] is perhaps most widely applied and has, as a result, perhaps had the most visibility. However, techniques that rely on evaluation, at an appropriate level of theory, of the guest–host interactions are now also being applied broadly.

The sites adopted by a guest molecule within a microporous host or on a surface can be examined using combined Monte Carlo and molecular dynamics methods [14]. This generalized technique has been used to study crystal growth modifiers, potential chromatographic column agents [27], sites preferred by sorbates in molecular sieves [28], and, in a rational approach to zeolite synthesis, the interactions between hypothetical and actual template molecules and zeolite framework structures [29–32]. The same approach was also applied by Santilli et al. [33] to compute relative di-methylbutane : n-hexane interaction strengths as a function of zeolite channel diameter for comparison against both experimental sorption data and measured hydrocracking selectivity patterns. This study led to the interesting concept of 'inverse shape selectivity' at intermediate channel diameters. Notably, this study also represents an early example of true simulation; the modeling methods were applied not only to models of known structure types for which experimental data could be measured, but also to hypothetical models with 9-, 11-, and 13-membered rings.

Thermodynamic parameters, such as sorption internal energies, are accessible via molecular dynamics or Monte Carlo methods (e.g. [34]). The reliability of the results is governed by the accuracy to which the interatomic interactions are described and substantial emphasis has been placed recently on validating and improving such potential functions, both based on first principles calculations and by experimental data fitting. A sophisticated potential for siliceous [35,36] and aluminosilicate zeolites has been developed via this ab initio approach; a somewhat simpler potential, calibrated based on experimental vibrational spectra [17,18] has already been used to probe breathing motion of zeolite pore windows [37]. Guest–host potentials are also subject to steady improvement and validation. In addition to isosteric heats accessible through Metropolis Monte Carlo sampling, full sorption uptake isotherms and isobars can be simulated by using the Grand Canonical Monte Carlo (GCMC) technique. Recent applications, such as to alkanes in microporous carbon [38], and hydro- and chlorofluorocarbons in faujasitic zeolites [39], have typically entailed potential validation or improvement as a significant component.

5. Catalyst reaction chemistry

Quantum technology has enjoyed a substantial history of application to problems in catalysis. Many topical systems have been studied. Recent applications of the DMol density functional code to Ziegler–Natta chemistry [40], nickel in zeolite Y [41], palladium clusters [42], ethylene epoxidation catalysts [43], NO dissociation on copper clusters [44], stimulated surface processes [45], titanium in ZSM-5 site models [46], Brønsted acid functions in zeolites [47] and copper carbohedrene clusters [48] are illustrative of but a few areas of application [49].

Electronic structure calculations were traditionally limited in applicability to rather simplistic models due to their intrinsic computational complexity and the adverse characteristics of their scaling with system size. Developments over the past 3–5 years are, however, now extending their impact into the practical domain. For example, hardware performance continues to improve at a dramatic pace, allowing for semi-empirical methods to be applied to quite large systems and for more routine application of first principles methods. Massively parallel computer architectures, after a relatively protracted gestation period, are now emerging as work-horse machines. DMol, for example, has been ported efficiently to distributed memory parallel architectures [50], with a goal of enabling study of larger models that are more representative of the complex active sites in real catalysts.

One other notable development, initially undertaken to address some of the specific challenges of simulating heterogeneous catalysts, has been the combination of quantum and classical mechanics [36,51,52]. By focusing the power of first principles, density functional or ab initio, techniques on the active site region, while simultaneously taking account of the site environment at a simpler level using an empirical forcefield, it is hoped to better model the structure and chemistry of practical catalytic materials. Quantum technology, in addition to being applicable more broadly in a chemical sense to structure optimizations, also provides access to all of the properties associated with the electronic structure. The transition states and reaction paths for a number of elementary conversions over model active sites in heterogeneous catalysts have already been determined. The characteristics of the reactant, product and transition states, and possibly of other points along the full reaction path can then be used to compute the rate constant for this given elementary reaction. Applying these methods in turn to each of the elementary steps in the full reaction scheme allows construction of a complete reaction kinetics model. Although the number of detailed studies of this type remains small and continued improvements in accuracy are needed, this area clearly has significant potential.

6. Links with process simulation methods

In many industrial organizations fundamental catalyst R and D and process development groups are separated, often geographically removed. There is, however, the potential for atomistic and process simulations to be coupled to a gradually increasing degree. Several of the system parameters provided by simulations at the atomic or electronic structural level, such as molecular diffusivities, thermodynamic parameters, heat capacities, reaction kinetics etc., are necessary input to process simulation models. Significant improvements in accuracy are needed, particularly for reaction kinetics, but tentative steps are already being taken to identify and evaluate appropriate linkages between the atomistic and process simulation sides.

7. Conclusion

Modeling and simulation at the atomistic or electronic structural level can clearly contribute at various levels to practical catalyst research and development programs. A multi-faceted approach to applying modeling will, in general, be of most value, given the various issues that arise in the practical implementation of any catalyst technology. Modeling is already being applied successfully, in instances, to catalyst structure determination, analytical data simulation and analysis, to probing molecular interactions and physisorptive phenomena, to computing thermodynamic parameters, and to calculating catalyst electronic structure, chemical reactivity and kinetics. Further progress in methodology is needed, but steady growth in the industrial implementation and application of modeling and simulation can be anticipated.

Acknowledgements

The Biosym Catalysis and Sorption Project is supported by a consortium of industrial, academic and government institutions. We also thank the various direct and indirect contributors to the capabilities mentioned in application here, including C.M. Freeman, A.M. Gorman, A. Ho, C.M. Kölmel, S.M. Levine, R.J. Lindsay, M. Muir, K.M. Roberts, R.F. Smith, M.A. van Daelen, B. Vessal, M.W. Deem, D.H. Gay, M. Katagiri, G. Ricchiardi, S. Veliah, A.K. Cheetham, N.J. Henson, J. Sauer, K.-P. Schröder, C.R.A. Catlow, A. Rohl, R.G. Bell and R.A. van Santen, T.V. Harris,

A. Nakanishi, M. Perrin, B. Toby, S.W. Carr and H. Phala.

References

[1] S.B. Rice, M.M.J. Treacy and J.M. Newsam, Zeolites, 14 (1994) 335–343.

[2] R.N. DeGuzman, Y.-F. Shen, E.J. Neth, S.L. Suib, C.-L. O'Young, S. Levine and J.M. Newsam, Chem. Mater., 6 (1994) 815–821.

[3] K.P. Lillerud and D.M. Akporiaye, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Editors), Zeolites and Related Microporous Materials: State of the Art 1994 (Stud. Surf. Sci. Catal., Vol. 84, Part A), Elsevier, Amsterdam, 1994, pp. 543–550.

[4] R. Szostak and K.P. Lillerud, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Editors), Zeolites and Related Microporous Materials: State of the Art 1994 (Stud. Surf. Sci. Catal., Vol. 84, Part A), Elsevier, Amsterdam, 1994, pp. 535–542.

[5] S.M. Kuznicki, K.A. Thrush, F.M. Allen, S.M. Levine, M.M. Hamil, D.T. Hayhurst and M. Mansour, in M.L. Occelli and H.E. Robson (Editors), Synthesis of Microporous Materials. Volume I: Molecular Sieves, Van Nostrand–Reinhold, New York, 1992, pp. 427–453.

[6] J.M. Newsam, S.M. Levine and F. von Trentini, (1994) unpublished.

[7] M.W. Anderson, O. Terasaki, T. Ohsuna, A. Philippou, S.P. Mackay, A. Ferriera, A. Rocha and S. Lidin, Nature, 367 (1994) 347–351.

[8] D.E.W. Vaughan, K.G. Strohmaier, M.M.J. Treacy and J.M. Newsam, US Patent No. 5, 116 590 (1992).

[9] M.M.J. Treacy, D.E.W. Vaughan, K.G. Strohmaier and J.M. Newsam, (1994) submitted.

[10] M.W. Deem and J.M. Newsam, J. Am. Chem. Soc., 114 (1992) 7189–7198.

[11] J.M. Newsam, M.W. Deem and C.M. Freeman, in E. Prince and J.K. Stalick (Editors), Accuracy in Powder Diffraction II (NIST Special Publication No. 846), National Institute of Standards and Technology, Bethesda, MD, 1992, pp. 80–91.

[12] C.M. Freeman, J.M. Newsam, S.M. Levine and C.R.A. Catlow, J. Mater. Chem., 3 (1993) 531–535.

[13] T.M. Nenoff, W.T.A. Harrison, G.D. Stucky, J.M. Nicol and J.M. Newsam, Zeolites, 13 (1993) 506–510.

[14] C.M. Freeman, C.R.A. Catlow, J.M. Thomas and S. Brode, Chem. Phys. Lett., 186 (1991) 137–142.

[15] M. Hochgräfe and H. Gies, Extended Abstracts, Proc. German Crystallographic Association Mtg., Bochum, Germany, (1992).

[16] Z.A. Kaszkur, R.H. Jones, D. Waller, C.R.A. Catlow and J.M. Thomas, J. Phys. Chem., 97 (1993) 426–431.

[17] J.A. Creighton, H.W. Deckman and J.M. Newsam, J. Phys. Chem., 95 (1991) 2099–2101.

[18] J.A. Creighton, H.W. Deckman and J.M. Newsam, J. Phys. Chem., 98 (1994) 448–459.

[19] S.C. Parker, P.J. Lawrence, C.M. Freeman, S.M. Levine and J.M. Newsam, Catal. Lett., 15 (1992) 123–131.

[20] N.L. Allan, A.L. Rohl, D.H. Gay, C.R.A. Catlow, R.J. Davey and W.C. Mackrodt, Faraday Discuss., 95 (1993) 273.

[21] J.O. Titiloye, S.C. Parker and S. Mann, J. Crystal Growth, 131 (1993) 533–545.

[22] S.D. Loades, S.W. Carr, D. Gay and A. Rohl, J. Chem. Soc., Chem. Comm., (1994) 1369–1370.

[23] J.M. Newsam, C.M. Freeman, S.M. Levine and M.W. Deem, in M. Doyama, J. Kihara, M. Tanaka and R. Yamamoto (Editors), Computer-Aided Innovation of New Materials II, Elsevier, Amsterdam, 1993, pp. 1077–1081.

[24] C.M. Freeman, S.M. Levine, J.M. Newsam, J. Sauer, S.M. Tomlinson, J. Brickmann and R.G. Bell, in C.R.A. Catlow (Editor), Modeling of Structure and Reactivity in Zeolites, Academic Press, New York, 1992, pp. 133–155.

[25] F. Blanco, G. Urbina-Villalba and M.M. Ramírez de Argudelo, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Editors), Zeolites and Related Microporous Materials: State of the Art 1994 (Stud. Surf. Sci. Catal., Vol. 84, Part C), Elsevier, Amsterdam, 1994, pp. 2155–2162.

[26] A. Corma, V. Fornés, H. García, M.A. Miranda, J. Primo and M.-J. Sabater, J. Am. Chem. Soc., 116 (1994) 2276–2280.

[27] F. Kobor, K. Angermund and G. Schomburg, High Res. Chromatogr., (1993) in press.

[28] N.J. Henson, A.K. Cheetham, A. Redondo, S.M. Levine and J.M. Newsam, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Editors), Zeolites and Related Microporous Materials: State of the Art 1994 (Stud. Surf. Sci. Catal., Vol. 84, Part C), Elsevier, Amsterdam, 1994, pp. 2059–2066.

[29] T.V. Harris and S.I. Zones, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Editors), Zeolites and Related Microporous Materials: State of the Art 1994 (Stud. Surf. Sci. Catal., Vol. 84, Part A), Elsevier, Amsterdam, 1994, pp. 29–36.

[30] D. Lewis, C.R.A. Catlow, J.M. Thomas and C.M. Freeman, (1994) in preparation.

[31] P.A. Cox, A.P. Stevens, L. Banting and A.M. Gorman, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Editors), Zeolites and Related Microporous Materials: State of the Art 1994 (Stud. Surf. Sci. Catal., Vol. 84, Part C), Elsevier, Amsterdam, 1994, pp. 2115–2122.

[32] C.M. Kölmel, Y.S. Li, C.M. Freeman, S.M. Levine, M.-J. Hwang, J. Maple and J.M. Newsam, J. Phys. Chem., (1994) submitted.

[33] D.S. Santilli, T.V. Harris and S.I. Zones, Microporous Materials, 1 (1993) 329–341.

[34] R.Q. Snurr, A.T. Bell and D.N. Theodorou, in R. von Ballmoos, J.B. Higgins and M.M.J. Treacy (Editors), Proceedings from the Ninth International Zeolite Conference, Vol. II, Butterworth–Heinemann, Stoneham, MA, 1993, pp. 71–78.

[35] J.-R. Hill and J. Sauer, J. Phys. Chem., 98 (1994) 1238–1244.

[36] J. Sauer, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Editors), Zeolites and Related Microporous Materials: State of the Art 1994 (Stud. Surf. Sci. Catal. Vol. 84, Part C), Elsevier, Amsterdam, 1994, pp. 2039–2057.

[37] M.W. Deem, J.M. Newsam and J.A. Creighton, J. Am. Chem. Soc., 114 (1992) 7198–7207.

[38] R.F. Cracknell, D. Nicholson and N. Quirke, Molecular Simulation, (1993) submitted.

[39] J.B. Parise, L. Abrams, J.C. Calabrese, D.R. Corbin, J.M. Newsam, S.M. Levine and C.M. Freeman, (1994) unpublished.

[40] F.U. Axe and J.M. Coffin, J. Phys. Chem., 98 (1994) 2567–2570.

[41] A.R. George, J.S. Sanderson and C.R.A. Catlow, J. Computer-Aided Mater. Design, 1 (1994) 169–176.

[42] Y.S. Li and J.M. Newsam, in J. Broughton, P. Bristowe and J. Newsam (Editors), Materials Theory and Modelling (Mat. Res. Symp. Proc. No. 291), Materials Research Society, Pittsburgh, PA, 1993, pp. 573–578.

[43] Y.S. Li and J.M. Newsam, in M. Doyama, J. Kihara, M. Tanaka and R. Yamamoto (Editors), Computer-Aided Innovation of New Materials II, Elsevier, Amsterdam, 1993, pp. 1043–1046.

[44] M.A. van Daelen, Y.S. Li, J.M. Newsam and R.A. van Santen, Chem. Phys. Lett., (1994) in press.

[45] A.R. Burns, D.R. Jennison, E.B. Stechel and Y.S. Li, Phys. Rev. Lett., 72 (1994) 3895–3898.

[46] R. Millini, G. Perego and K. Seiti, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Editors), Zeolites and Related Microporous Materials: State of the Art 1994 (Stud. Surf. Sci. Catal., Vol. 84, Part C), Elsevier, Amsterdam, 1994, pp. 2123–2129.

[47] M.S. Stave and J.B. Nicholas, J. Phys. Chem., 97 (1993) 9630–9641.

[48] I. Dance, J. Am. Chem. Soc., 115 (1994) in press.

[49] Y.S. Li, M.A. van Daelen, M. Wrinn, D. King-Smith, J.M. Newsam, B. Delley, E. Wimmer, T. Klitsner, M.P. Sears, G.A. Carlson, J.S. Nelson, D.C. Allan and M.P. Teter, J. Computer-Aided Mater. Design, 1 (1994) 199–214.

[50] Y.S. Li, M.C. Wrinn, J.M. Newsam and M.P. Sears, J. Comput. Chem., (1994) in press.

[51] C.M. Kölmel and C. Ewig, (1994) submitted.

[52] A. Kyrlidis, S.J. Cook, A.K. Chakraborty, A.T. Bell and D.N. Theodorou, this symposium (1994).