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GOALI: Multicomponent Molecular Transport in Nanoporous Materials

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Final Report for Period: 09/2010 - 08/2011**Submitted on:** 01/27/2012**Principal Investigator:** Ruthven, Douglas .**Award ID:** 0553861**Organization:** University of Maine**Submitted By:**

Ruthven, Douglas - Principal Investigator

Title:

GOALI: Multicomponent Molecular Transport in Nanoporous Materials

Project Participants**Senior Personnel****Name:** Ruthven, Douglas**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Sholl, David**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Chance, Ronald**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Nair, Sankar**Worked for more than 160 Hours:** Yes**Contribution to Project:****Post-doc****Graduate Student****Name:** Chen, Haiben**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Participated in molecular modelling calculations under supervision of David Sholl at CMU.

Name: Jee, Sang**Worked for more than 160 Hours:** Yes**Contribution to Project:**

PhD student working on molecular simulations under David Sholl's supervision.

Name: Condon, Jeremy**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Set up of ZLC system at UMaine under supervision of Douglas Ruthven

Name: Keskin, Seda**Worked for more than 160 Hours:** Yes**Contribution to Project:**

PhD student working on molecular simulations under David Sholl's supervision.

Name: Vidoni, Adam

Worked for more than 160 Hours: Yes

Contribution to Project:

PhD student working on diffusion measurement under supervision of Douglas Ruthven.

Name: Kassae, Mohamad

Worked for more than 160 Hours: Yes

Contribution to Project:

Theoretical modelling and simulation studies under direction of David Sholl (GA Tech).

Name: Awati, Rohan

Worked for more than 160 Hours: Yes

Contribution to Project:

Undergraduate Student

Name: Fisher, Christopher

Worked for more than 160 Hours: Yes

Contribution to Project:

Worked on summer lab project under Douglas Ruthven's supervision.

Technician, Programmer

Other Participant

Name: Kamakoti, Preeti

Worked for more than 160 Hours: Yes

Contribution to Project:

Carried out density functional theory calculations for 8-ring zeolite structures in collaboration with Ron Chance at ExxonMobil. No stipend from NSF funds.

Name: Reyes, Sebastian

Worked for more than 160 Hours: Yes

Contribution to Project:

Discussion and interaction with Douglas Ruthven and other participants. No funding from this project.

Name: Deckman, Harry

Worked for more than 160 Hours: Yes

Contribution to Project:

Measurement, analysis and modelling of permeance data for zeolite membranes. Financial support from ExxonMobil, not from project funds.

Name: Calabro, David

Worked for more than 160 Hours: Yes

Contribution to Project:

Supervision of Adam Vidoni during his stay at ExxonMobil research centre.

Name: Ravikovitch, Peter

Worked for more than 160 Hours: Yes

Contribution to Project:

Supervision of Adam Vidoni during his stay at ExxonMobil research centre. Analysis and interpretation of experimental data.

Research Experience for Undergraduates

Organizational Partners

Other Collaborators or Contacts

Sankar Nair

Activities and Findings

Research and Education Activities:

ANALYSIS OF EXPERIMENTAL DATA (2006 - 2007)

(a) Binary permeation through a polycrystalline Zeolite Membrane (Deckman, Ruthven, Condon)

An extensive set of permeance measurements for CO₂ - CH₄ mixtures in a DDR zeolite membrane has been accumulated (at the ExxonMobil Laboratory, Clinton, NJ). These data have been analyzed according to the generalized Maxwell - Stefan diffusion model. Initial analysis based on the multicomponent Langmuir equilibrium isotherm yielded results that are in approximate agreement with the predictions based on single component diffusivities but provide some evidence of a mutual diffusion effect. We are currently re-analyzing the data using the more accurate statistical isotherm in order to determine the mutual diffusivities with greater confidence and improve the match of the overall model to the experimental data.

(b) Single Crystal Permeation Measurements.

The 'time lag' method of determining the diffusivity from measurements of single component permeation through a membrane is well established but it depends on linear analysis and is therefore limited to systems operating within the Henry's Law regime. We have extended the analysis to a Langmuirian system with a concentration dependent diffusivity and succeeded in obtaining an analytic solution that provides a simple way to extract the diffusivity from the time lag. This method has been applied to re-analyze the data of Shah and Liou for diffusion of aromatic hydrocarbons through silicalite. The resulting D_0 values are in good agreement with those obtained by other methods such as ZLC thus resolving an anomaly in the published literature.

THEORETICAL AND MODELLING STUDIES (2006 - 2007)

(a) Density Functional Theory (Preeti Kamakoti at ExxonMobil)

Recent experimental studies have shown the potential of various 8-ring zeolites of the CHA family to provide kinetically selective adsorbents for the practically important separations of polyethylene/propane and carbon dioxide/methane. The adsorbents operate in the sterically hindered regime leading to very large differences in diffusivity for small changes in the window aperture and the critical diameter of the diffusing molecule. To provide greater insight into these materials and to explore the possibility of finding improved adsorbents for these and other important but difficult separations it was decided to investigate the ability of density functional theory to correctly predict the window dimensions in these 'puckered 8-ring' systems. DFT calculations for LTA, DDR, SAPO-34, AIPO-34 and SiCHA show excellent agreement with high resolution XRD measurements. In future studies we propose to use this approach to predict the effects of T atom substitution and to explore the possibility of tailoring kinetically selective adsorbents for a particular separation.

(b) Molecular Simulations (David Sholl + Students at CMU)

We have performed molecular simulations of CH₄ and CO₂ adsorption and diffusion in silica-DDR, a small pore zeolite of interest for CH₄/CO₂ separations. Our collaborators at ExxonMobil have fabricated and tested membranes from this material, so experimental information on the behavior of CH₄ and CO₂ as single-components in DDR is available. The main aim of our work is to provide detailed information on the properties of CH₄/CO₂ mixtures in this material. In our initial work, we used interatomic potentials that were adjusted to fit experimental single-component adsorption isotherms measured by our collaborators. With these potentials, we performed extensive simulations of binary adsorption, single-component self diffusion and transport diffusion, and mixture diffusion. This has provided some useful information into the behavior of adsorbed molecules in DDR, but our calculated results were in poor agreement with the single-component self-diffusion coefficients measurements that were recently completed by our collaborators. As a result, we have very recently reparameterized our interatomic potentials to match both the experimental single-component isotherms and the low loading self diffusion coefficients for CO₂ and CH₄ in DDR. These potentials are currently being used to examine adsorbed mixtures.

We have also performed exploratory modeling to understand whether framework substitution in small pore zeolites could be useful for increasing their selectivity for CH₄/CO₂ separations. Using lattice models for DDR with parameters derived from our molecular simulations, we have studied what selectivities would arise if a fraction of all 8 membered rings connecting cages in the material were blocked to CH₄

transport but not to CO₂ transport. This description places an upper bound on how effective this general approach could be. At the same time, we are combining molecular simulations and first-principles DFT calculations to estimate how effective pore blocking via framework substitution might be in zeolites with eight membered rings. Specifically, DFT calculations have been performed optimizing the structure of chabazite with and without framework substitutions, and we are currently performing molecular simulations using the structures derived from these DFT calculations.

THEORETICAL AND MODELLING STUDIES (2007 ? 2008)

Window Size Effects on Diffusion in 8-ring Zeolites

Small differences in window size and shape can have dramatic effects on molecular transport, especially when the window size and molecular size are comparable. As an example of such behavior we have studied the transport of methane in several 8-ring zeolites. Pulsed field gradient NMR experiments show that subtle differences in window dimensions of around 0.05-0.35 Å between siliceous LTA, CHA and DDR can cause room temperature methane self diffusivities to span two orders of magnitude, ranging from 1.42 × 10⁻⁶ cm²/s for LTA to 1.6 × 10⁻⁸ cm²/s for DDR. Currently, there is little understanding of the factors affecting window architecture, and no means identified for prediction of the significant structural variations that have been observed experimentally. To provide a better understanding of window architectures, we have performed Density Functional Theory (DFT) calculations on the same three siliceous zeolites LTA, CHA and DDR, wherein a complete relaxation of the cell volume, shape and atomic positions was performed. Results show that DFT is an excellent tool for quantitatively predicting structural information in siliceous zeolites. DFT is also surprisingly successful in capturing the subtle differences between window sizes and puckering in all three structures, those differences being critical to understanding molecular transport. The optimized structures obtained with DFT are used in conjunction with an atomistic model to simulate the adsorption and diffusion of CO₂ and CH₄.

We have used molecular simulations to examine the diffusion of CO₂ and CH₄ in DDR, CHA, and LTA, both as single components and as mixtures and performed a comparison with experimental results. These simulations give insight into the strong dependence of the observed diffusivity on zeolite structure and suggest opportunities for using the unusual properties of diffusing mixtures in some materials for practical applications.

Diffusion of CO₂ and CH₄ in DDR Zeolite

Because of the potential application of DDR (an 8-ring zeolite) for membrane based purification of CO₂ rich natural gas we have studied the adsorption and diffusion of CO₂ and CH₄ in this material in greater detail. We have used molecular simulation methods to probe the transport of mixtures of CO₂ and CH₄ in all-silica DDR. A key component in this effort has been the development of new interatomic potentials for CO₂/DDR and CH₄/DDR interactions. This was necessary because existing potentials from the literature gave molecular diffusivities at low loadings that were in poor agreement with detailed measurements carried out at ExxonMobil. The diffusion characteristics of CH₄ and CO₂ in this material are controlled by different aspects of the interatomic potentials. CH₄ diffusion in DDR is controlled by a large energy barrier that exists within the 8-ring. By adjusting the repulsive core of the CH₄/DDR potential while holding the attractive portion of the potential fixed, it was possible to develop a model that agrees with experimental adsorption and diffusion data.

An important implication of this result, however, is that CH₄ diffusion in DDR is too slow to be accurately simulated using standard Molecular Dynamics (MD) techniques. Transition State Theory (TST) was used to describe this slow diffusion. For CO₂ in DDR, molecules prefer to adsorb inside the 8MR, in contrast to CH₄. The activation energy for CO₂ diffusion is largely controlled by the electrostatic field of the zeolite, so minor adjustments were made in the charges on the framework atoms to define a model that gives adsorption and diffusion data in agreement with experimental observation. CO₂ diffuses considerably faster than CH₄ in DDR, so this diffusion can be effectively probed using MD simulations.

Using the new interatomic potentials we developed, we have probed mixture adsorption and diffusion of CO₂/CH₄ in DDR. An interesting observation from this study is that the usual Adsorbed Solution Theory (IAST) to DDR yields somewhat inaccurate results because of the difference between the preferred binding sites of the two species. We found, however, that a relatively simple correction to IAST that accounts for the two types of binding sites that exist for CO₂ in DDR can yield accurate predictions for the binary adsorption isotherm. MD simulations indicate that the presence of CH₄ does not greatly reduce the diffusion coefficient of CO₂, despite the very slow diffusion of CH₄. This counterintuitive result occurs because of the very different mechanisms of diffusion of the two molecules, and could be advantageous in membrane applications. We are currently developing a TST-based approach that can provide a detailed description of the impact of CO₂ on the slow diffusion of CH₄.

Zeolite Membranes

We have also applied molecular simulation techniques to two other scenarios involving crystalline nanoporous crystalline materials as membranes. We examined the modification of silica zeolite membranes using a thin amorphous silica layer on the zeolite's outer surface. These simulations suggest that this kind of surface modification may be an effective way to make zeolite membranes selective for small species such as H₂ without enormous reductions in flux compared to unmodified membranes. We also examined several issues associated with molecular diffusion in metal organic framework materials. Little is currently known about diffusion in these materials, and the results from our

calculations have made it possible for the first time to consider the application of these new materials as membranes for gas separations.

EXPERIMENTAL STUDIES (2007 - 2008)

Diffusion measurements have been carried out for several relevant systems by PFGNMR and frequency response methods at the ExxonMobil laboratory. Some of these data have been published (see publ. 3 and AIChE presentation in publication list).

The reconstruction of the ZLC system (at UMaine) has been seriously delayed by the departure of Jeremy Condon who abandoned his graduate studies in June 2007. A new student (Adam Vidoni) was recruited but he did not start his program until September 2007. During the academic year Adam was largely occupied with completing his course work so he had little time for laboratory work. He passed his qualifying exam (with excellent marks) in April 2008 and since then he has been working diligently on rebuilding the experimental system, which is now almost complete. Adam is scheduled to spend three months in the ExxonMobil laboratory starting June 2nd.

Research and Education Activities (2008 ? 2009)

Theoretical and Numerical Simulation Studies (Sholl Group ? GA Tech)

In our theoretical modeling studies, we have used molecular simulations to describe diffusion of CO₂ and CH₄ inside the pores of DDR zeolite. Our simulations introduce a new force field (a 6 ? 18 potential) which, for the first time, yields results that are consistent with experimental measurements of single component adsorption and diffusion. The diffusivities derived from previous simulations greatly overestimated the transport rates of CH₄, and to a lesser extent, CO₂. Since CH₄ diffuses extremely slowly in DDR, we applied a Transition State Theory-based Kinetic Monte Carlo scheme to accurately describe this diffusion.

The physical origins of this unusual behavior are explained by analyzing the adsorption sites and diffusion mechanism for each species. Our finding suggests DDR membranes are favorable for CO₂/CH₄ separations and that similar properties may exist for other 8MR zeolites. With the aim of identifying additional candidate materials for membrane applications we have therefore carried out preliminary calculations using our new force field for CO₂/CH₄ adsorption and diffusion in a variety of other zeolites that can be synthesized in pure silica form.

Modelling of Membrane Permeation (U Maine and ExxonMobil)

Extensive measurements of membrane permeation have been carried out for a range of different zeolite membranes at the ExxonMobil laboratory. For many systems the Maxwell-Stefan model provides a useful predictive correlation. However, this model does not provide a good prediction of the behavior of the CO₂ ? CH₄ mixtures in DDR membranes. The simulation results noted above provide a clear and convincing explanation for this behavior.

Experimental Studies (Sholl/Nair groups)

Experimental studies have been focused on functionalization of silanol defects inside MFI pores. Earlier work using alcohols to covalently attach alkyl chains to defect sites in MFI pores has been repeated and we are currently using a range of experimental methods to characterize molecular adsorption and diffusion in these internally modified materials. Simultaneously, we are developing chemical methods suitable for similar pore functionalization with amine-containing species. Some of the characterization studies are being carried out at U>Maine.

Experimental Studies (U>Maine/ ExxonMobil)

In accordance with our original plan Adam Vidoni spent four months in the ExxonMobil laboratory (June ? October 2008) working under the supervision of Harry Deckman, Peter Ravikovitch and David Calabro. During this time he made a detailed experimental study of adsorption of CO₂ on a range of different well characterized zeolite samples. In particular he studied the effect of hydroxyl content on the CO₂ isotherm. The results of these measurements yielded some surprising conclusions ? see below under 'Findings'.

Since he returned to Maine in October 2008 Adam has worked mainly on setting up and calibrating his experimental ZLC system for measurement of intracrystalline diffusion. The system is now operational and has been used to study some of the modified adsorbents prepared by the Sholl group at GA Tech. as well as to study (single component) diffusion of CO₂ and CH₄ in DDR. The extension of the ZLC method to measure the inhibition of CO₂ diffusion by the presence of CH₄ (in a binary system) has not yet been implemented but we hope to accomplish this shortly.

Research and Education Activities (2009-2010)

During the last year efforts have been directed in three main directions:

1. (U>Maine) Completing, calibrating and testing the experimental ZLC system.

2. (Georgia Tech) Preparation and characterization of modified zeolite adsorbents.
3. (U.Maine and GA Tech) Studying the adsorption and transport behavior of the modified adsorbents (by ZLC and gravimetric methods).

Previous work on functionalization of adsorbents has focused largely on mesoporous silica materials - see for example . S. Higgins, B.A. McCool, C.P. Tripp, D.M. Ruthven and W.J. DeSisto, 'Covalent attachment of monochlorosilanes to mesoporous silica membranes using supercritical fluid deposition', *Separation and Purification Technology*, 43, 4113 (2008).

Similar techniques can be used to functionalize microporous zeolite adsorbents. For this application silicalite (MFI) has proved particularly useful since the pore diameter (about 0.6 nm) is large enough to admit many functional groups and the presence of a significant number of surface hydroxyls provides sites for covalent attachment.

We have explored functionalization of the internal pores of MFI zeolites with aliphatic alcohols (1-butanol, 1-hexanol), aromatic alcohols (benzenemethanol), amino-alcohols (3-amino-1-propanol), and amines (1-propanamine, and 1,3-propanediamine). The mass loading of functional groups was established via TGA experiments, and determined to be between 0.72 to 0.93 mmol/SiO₂. Evidence that the functional groups are covalently attached to the internal pores comes from ¹³C cross-polarization magic angle spinning (CP-MAS) NMR and TGA/DSC results. ²⁹Si CP-MAS NMR studies indicate that the functional group loading is strongly dependent on the concentration of internal silanol defects in the original MFI crystals. Micropore volume, as characterized by N₂ physisorption, was found to decrease in the functionalized MFI crystals relative to parent MFI, as expected.

We have also explored functionalization of MFI membranes using knowledge from our functionalization studies of isolated crystals. The presence of internal functional groups inside MFI membranes has been confirmed using photoacoustic FTIR spectroscopy.

This work has considerably extended the range of functionalities that can be covalently attached to the internal pores of MFI, and creates a useful basis for future studies to optimize the properties of these functionalized materials for membrane-based chemical separations.

2010-2011

Equilibrium isotherms for the modified MFI samples have been measured both gravimetrically and by ZLC. Kinetic measurements have also been carried out by the ZLC technique in order to assess the extent to which the surface modification affects the sorption kinetics of guest molecules.

These studies have been carried out by direct collaboration between Mohamad Kassae (GA Tech) who prepared the samples and Adam Vidoni (U.Maine) who made the ZLC measurements.

Adam Vidoni has carried out an extensive series of measurements of the diffusion of methane, ethane, ethylene and propylene in DDR zeolite, as single components and also in the presence of CO₂, a common impurity in natural gas. A number of diffusion measurements have also been carried out by interference microscopy (in collaboration with Professor Kaerger at the University of Leipzig). These measurements provide useful insight concerning the diffusion mechanism for these systems.

Findings: (See PDF version submitted by PI at the end of the report)

Findings (2006-2007)

Density functional theory has been established as a useful approach for estimating the precise dimensions of 8- ring zeolite windows - see attached figure (Preeti Kamakoti).

The extreme sensitivity of the intracrystalline diffusivity for critically sized molecules in 8-ring zeolites has been demonstrated both experimentally and by molecular simulations. This provides a potentially useful way of tailoring an adsorbent for a particular separation.

Findings (2007-2008)

The anomalous behavior of CO₂ in DDR has been shown to arise from a segregation effect. The CO₂ molecules are located preferentially in the 8-rings leading to deviations from ideal adsorbed solution behavior and insensitivity of the CO₂ diffusivity to the presence of slower

diffusing CH₄. New interatomic potentials were developed to provide a satisfactory representation of the behavior of the CO₂-CH₄/DDR system.

Findings (2008 - 2009)

The simulation results (and comparisons with experimental data) show clearly that the standard 6-12 force field does not correctly predict diffusion in small pore systems where repulsive forces are dominant. However, a modified 6-18 potential does correctly predict the observed behavior.

The most important practical conclusion that can be drawn from these studies is that the characteristics of CO₂/CH₄ diffusion in DDR are very different from the usual situation in nanoporous materials, where the presence of a slowly diffusing species retards transport rates of a more rapidly diffusing species. Our results show that CO₂ diffusion rates in DDR are only weakly affected by the presence of CH₄, despite the very slow diffusion of the latter. The physical origin of this unusual behavior is explained by analyzing the adsorption sites and the diffusion mechanism for each species. Our finding suggests DDR membranes are favorable for CO₂/CH₄ separations and that similar properties may exist for other 8MR zeolites.

Permeation rates for CO₂-CH₄ in silicalite, SAPO-34 and DDR membranes show an interesting gradation. In the 10-ring pores of silicalite mutual diffusion effects are significant. In the smaller pores of SAPO-34 mutual diffusion effects are negligible and the behavior of the binary can be predicted from the pure component diffusivities (modified Habgood model). The behavior of the DDR membrane is more complex and cannot be correctly predicted by the Maxwell-Stefan model which does not capture the reduction of the methane diffusivity resulting from window blocking by CO₂.

The measurements of CO₂ isotherms in hydroxylated zeolites show that CO₂ uptake (at a given partial pressure) increases with the hydroxyl content. Surprisingly, however, this effect appears to be related mainly to an increase in saturation capacity rather than to any change in the Henry constant. It appears that at higher hydroxyl levels internal regions of the structure which in an ideal crystal are not accessible to CO₂ may become accessible.

Findings (2009 - 2010).

It has been shown that it is possible to functionalize the internal surface of MFI zeolites (pore size about 6 nm) using techniques similar to those that have been developed for functionalizing mesoporous silica materials. The measured equilibrium isotherms show that the affinities of the modified materials differ significantly from the parent MFI and, as a result, the adsorption selectivities for guest molecules show corresponding differences. Such effects are most pronounced at low loadings; at high loadings the isotherms for the modified and unmodified adsorbents tend to converge.

The Henry constants measured by ZLC appear to be consistent with the gravimetric isotherms thus enhancing our confidence in the validity of the ZLC measurements.

A limited series of kinetic measurements has also been carried out by the ZLC technique in order to assess the extent to which the transport behavior is affected by the surface modification. For the smaller molecules (ethane and methane) the kinetic measurements suggest that the diffusivities in the modified and unmodified adsorbents are quite similar. However, for larger probe molecules (propane and butane) the diffusion is significantly retarded (by a factor of two or three) compared with the parent MFI. Such a result is not unexpected since steric hindrance will be more pronounced for the larger probe molecules.

We are continuing these studies in order to confirm and refine the data in order to allow a more quantitative assessment of these effects.

Findings 2010 - 2011

Georgia Tech (Sholl, Nair, Kassaei)

Work at Georgia Tech during this period focused mainly on the experimental development of internally functionalized zeolites. We showed that the selective gas adsorption properties of pure-silica MFI zeolite crystals are significantly altered by modifying the internal pore structure with molecules such as aliphatic alcohols, aromatic alcohols, amino-alcohols, and amines. NMR and TGA/DSC characterization indicated that the functional groups are chemisorbed to the internal pores, and the organic molecule loading is strongly dependent on the concentration of internal silanol sites. Adsorption isotherms for CO₂ and CH₄ were measured for the functionalized samples from 0-400 kPa. In the low pressure region (1-10 kPa), the organic-modified materials showed gas adsorption behavior significantly different from that of the bare zeolite MFI, ranging from an enhancement in CO₂/CH₄ sorption selectivity in the amine-functionalized materials to an enhancement in CH₄ adsorption in the aromatic-functionalized material. The CO₂/N₂ sorption selectivity decreases for all the modified materials compared to bare zeolite MFI. This investigation of organic-modified MFI zeolites points toward the tuning of adsorption and molecular sieving behavior of zeolites through internal modification of the pores. Efforts were also made to adapt these functionalization routes from zeolite particles to use in

zeolite membranes. In this venue, there are challenges associated with achieving uniform functionalization throughout a zeolite film. Preliminary evidence, however, indicated that this challenge can be overcome and that internal functionalization appears to be a useful means to modify the properties of the micro-pores in zeolite membranes.

A small portion of the work at Georgia Tech used molecular modeling to describe the physisorption of H₂S inside zeolites. This effort involved testing the viability of intermolecular potentials available from other sources for predicting H₂S adsorption isotherms in several pure silica and cationic zeolites. The experimental data that is available to make comparisons is limited in scope, but initial comparisons indicate that molecular modeling based on current potentials is capable of making useful predictions about H₂S adsorption in zeolites.

U.Maine (Ruthven, Vidoni)

The equilibrium constants and diffusivities for methane - DDR derived from ZLC measurements are consistent with the values determined from frequency response and membrane permeation measurements carried out at the ExxonMobil laboratories as well as with the molecular simulations of Sholl and Jee. However, in contrast to the molecular simulations which suggest that in the presence of CO₂ the diffusion of methane is retarded, the experimental data show clearly that the methane diffusivity is increased! Furthermore the increase in the methane diffusivity is quantitatively consistent with what is to be expected for a competitive adsorption system thus calling into question the conclusion (from molecular modelling) that CO₂ molecules occupy preferentially the 'windows' while methane is adsorbed mainly within the cages.

The behavior of ethane and ethylene is strikingly different from methane and suggests that, for these species, adsorption of CO₂ is essentially non-competitive.

Some samples of DDR showed significant surface resistance to mass transfer (in addition to the intracrystalline diffusion resistance). A simple extension to the ZLC model was developed in order to determine both surface and internal resistances from a series of ZLC measurements at different flow rates.

Measurements with different DDR crystals showed significant differences in both diffusivity and diffusional activation energy, suggesting differences in the internal pore structure. This has been confirmed by interference microscopy measurements which show clearly that, in the faster DDR crystals, there is significant diffusion along the long axis of the crystal which is prohibited in the ideal DDR structure.

This result is consistent with recent CO₂ isotherm measurements that show large differences in the saturation capacity for the different samples. The lower capacities are consistent with the molecular modelling isotherms for an ideal DDR structure but the higher capacities can only be explained by structural defects that allow molecular access to the smaller cages within the structure.

Training and Development:

2007-2008

Students Chen, Jee and Keskin have learned the principles of molecular simulation and the modelling of binary membrane permeation.

Chris Fisher participated in a summer undergraduate lab. project but, unfortunately, he decided on graduation to take a job in industry rather than continuing on this project as a graduate student.

Adam Vidoni has passed his PhD qualifying exam and has gained some experience in setting up and commissioning an experimental system.

2008 - 2009

Adam Vidoni has gained valuable industrial research experience during a four month period working at the ExxonMobil research laboratory.

Mohamad Kassae, working with David Sholl, has learned the principles of molecular simulations.

2009 - 2010

Mohamad Kassae has learned and further developed the experimental techniques for surface modification of silicalite adsorbents as well as the associated characterization methods. During the past four months he and Adam Vidoni have been collaborating on the characterization of the new materials, including both kinetic and equilibrium measurements.

Sang Jee completed her PhD May 2010

2010-2011

Adam Vidoni (U.Maine) submitted his PhD thesis in September 2011 and successfully defended it at his oral examination in October 2011. He has now completed all requirements and will receive his degree in May 2012. Several publications based on his work have now been submitted and two further publications are in preparation.

Mohammad Kassae (GA Tech) is in the final stages of writing his thesis = should graduate in the Summer of 2012.

Outreach Activities:

Journal Publications

Haibin Chen and David Sholl, "Examining the Accuracy of Ideal Adsorbed Solution Theory without Curve-fitting Using Transition Matrix Monte Carlo Simulation", *Langmuir*, p. 6431, vol. 23, (2007). Published,

Ruthven,D.; Reyes,S., "Adsorptive Separation of Light Olefins from Paraffins", *Microporous and mesoporous Materials*, p. 59, vol. 104, (2007). Published,

Ruthven,D.M., "Transient Behavior of a Zeolite Membrane under Non-Linear Conditions", *Chemical Engineering Science*, p. 5745, vol. 62, (2007). Published,

Douglas M. Ruthven, "Diffusion of aromatic hydrocarbons in silicalite/HZSM-5", *Adsorption*, p. 225, vol. 13, (2007). Published,

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Sang E Jee, Alan J.H. McGaughey and David S.Sholl, "Molecular simulations of hydrogen and methane permeation through pore mouth modified zeolite membranes.", *Molecular Simulations*, p. , vol. , (2008). Accepted,

Seda Keskin, Jinchun Liu, J.Karl Johnson and David S. Sholl, "Testing the accuracy of correlations for multicomponent mass transport of adsorbed gases in metal organic frameworks: Diffusion of H₂/CH₄ mixtures in CuBTC.", *Langmuir*, p. , vol. , (2008). Accepted,

Sang Eun Jee and David Sholl, "Carbon dioxide and methane transport in DDR zeolite: Insights from molecular Simulations", *J.Am.Chem.Soc.*, p. 7896, vol. 131, (2009). Published,

Ruthven, Douglas M., "Diffusion in Zeolites: a Continuing Saga", *Adsorption*, p. , vol. , (2010). Accepted,

M.H.Kassee, D.S.Sholl and S.Nair, "Preparation and Gas Adsorption Characteristics of Zeolite MFI Crystals with Organic -Modified Interiors", *J., Phys.Chem C*, p. 19640, vol. 115, (2011). Published,

Douglas M.Ruthven and Adam Vidoni, "ZLC Measurements: Combined effect of Surface Resistance and Internal Diffusion", *Chem. Engg. Sci.*, p. , vol. , (2012). Accepted,

Adam Vidoni and Douglas M. Ruthven, "Diffusion of Methane in DDR Zeolite", *Microporous Mesoporous Materials*, p. , vol. , (2011). Submitted,

Adam Vidoni and Douglas M. Ruthven, "Diffusion of Ethane and Ethylene in DDR Zeolite", *Ind. Eng. Chem. Res.*, p. , vol. , (2012). Accepted,

Books or Other One-time Publications

Preeti Kamakoti, Sang E.Jee, Ronald R. Chance, Sebastian C. Reyes and David S.Sholl, "Computational Investigation of Window Size effects on Gas Transport in High Silica 8-ring Zeolites.", (2008). Presentation - AIChE Annual Meeting, Accepted
Bibliography: Oral Presentation - AIChE Annual Meeting, Nov 2008

Douglas Ruthven, "Diffusion through porous media:ultrafiltration,reverse osmosis and molecular sieving.", (2009). Book, Published
Editor(s): C.Chmelik, N.Kanellopoulos, J.Kaerger ans D.Theodorou
Collection: Diffusion Fundamentals III
Bibliography: Leipzig University Press,Leipzig (2009)

Douglas Ruthven, "Diffusion in Zeolites: a continuing saga.", (2008). Conference Presentation, Published
Bibliography: C.S.ChE Annu Conference, Ottawa, Ont. Canada, Oct 20 2008

Douglas Ruthven, "Molecular Sieve Separations", (2010). Conference Presentation, Published
Bibliography: Tutzing Symposium, "Delving into the Molecular Scale", June 13-15 2010, Tutzing, Germany.

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

New applications of Density Functional Theory to a practically important problem.
New insights on the behavior of zeolite membranes and the analysis and modelling of permeation data.
New insights on the transport behavior in 8-ring zeolites.
New information on segregation effects in DDR.
New insights on the mechanism of diffusion in DDR
New insights concerning the dramatic effect of minor structural defects in DDR on sorption kinetics and equilibria.
Direct measurement of transient concentration profiles in a DDR crystal

Contributions to Other Disciplines:

Contributions to Human Resource Development:

Training of research students.
S.E Jee PhD 2010
A.Vidoni PhD 2012
M.Kassaei PhD expected 2012

Contributions to Resources for Research and Education:

Undergraduate research experience for Chris Fisher

Contributions Beyond Science and Engineering:

Conference Proceedings

Categories for which nothing is reported:

Organizational Partners
Activities and Findings: Any Outreach Activities
Any Web/Internet Site
Any Product
Contributions: To Any Other Disciplines
Contributions: To Any Beyond Science and Engineering
Any Conference

GOALI (DFT)

Note that window dimensions predicted from density functional theory agree well with dimensions from high resolution X-ray diffraction.

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BENCHMARKING

