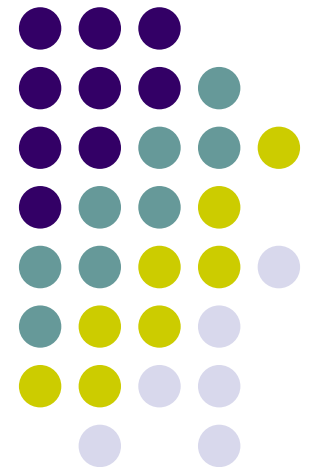


Diffusion Fundamentals
University of Leipzig, September 2005

**The Technological Impact of
Diffusion in Nanopores**

Douglas Ruthven
Department of Chemical Engineering
University of Maine,
Orono, ME, 04469, U.S.A.





Impact of Pore Diffusion

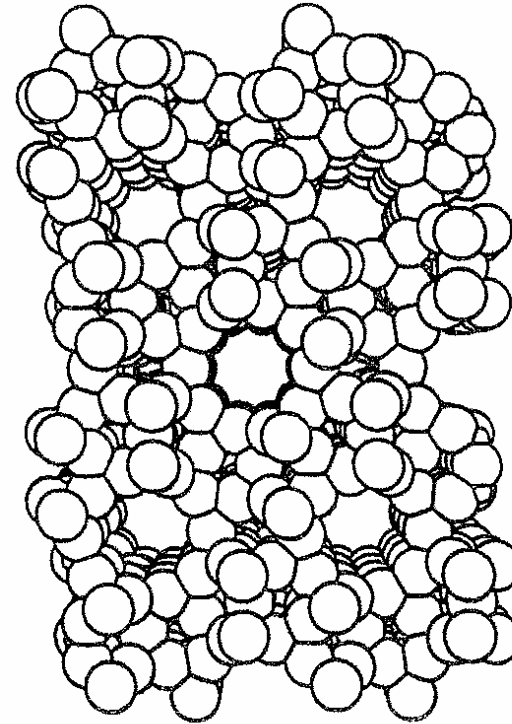
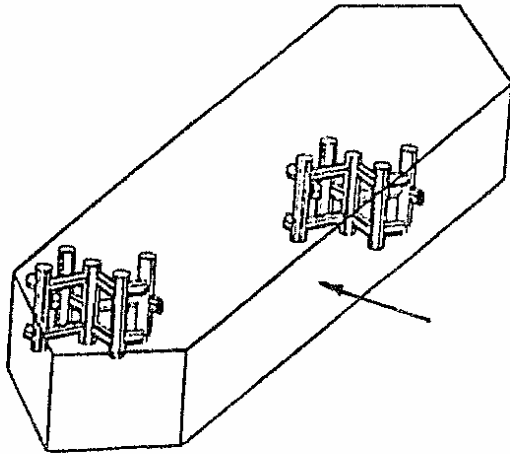
- Separation Processes
 - Cyclic Adsorption-Desorption Processes
 - Equilibrium Selectivity – negative impact
 - Kinetic Selectivity – positive impact
 - Nanoporous (Zeolite) Membranes
- Catalytic Processes
 - Diffusional resistance affects catalyst activity and selectivity. (Positive or negative effects are possible)

Outline



- Zeolite Structures
- Zeolite Membranes
 - Performance, Modelling, Mutual Diffusion Effects
- Olefin/Paraffin Separations
- Air Separation over CMS
- N₂/CH₄ Separation over ETS-4
 - A “tuneable” adsorbent
- Catalytic processes
 - Catalytic Cracking
 - Methanol to olefins (MTO)
- Measurement of transport rates in zeolites

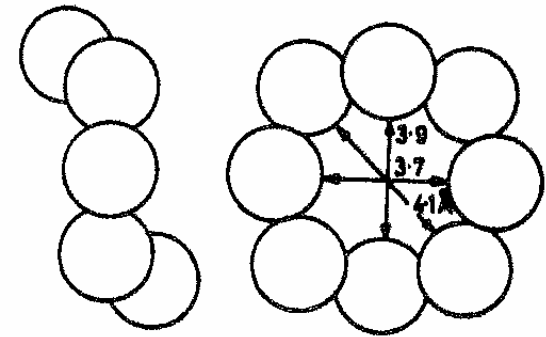
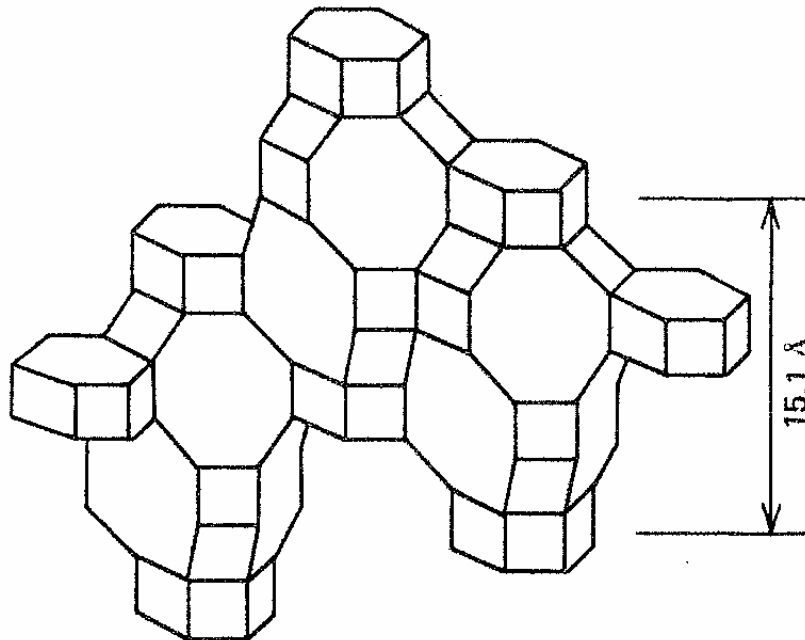
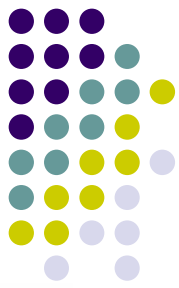
Silicalite Pore Structure



10-ring channels, $\sim 6\text{\AA}$ diameter

Intersecting straight and sinusoidal channels

Chabazite Structure (CHA)



Cages (free volume $\sim 380\text{\AA}^3$) interconnected through tetrahedrally oriented 8-ring windows – free aperture 3.7 – 4.1 Å

SiCHA, SAPO-34: cation free versions

Zeolite Membranes

Single Component Permeation

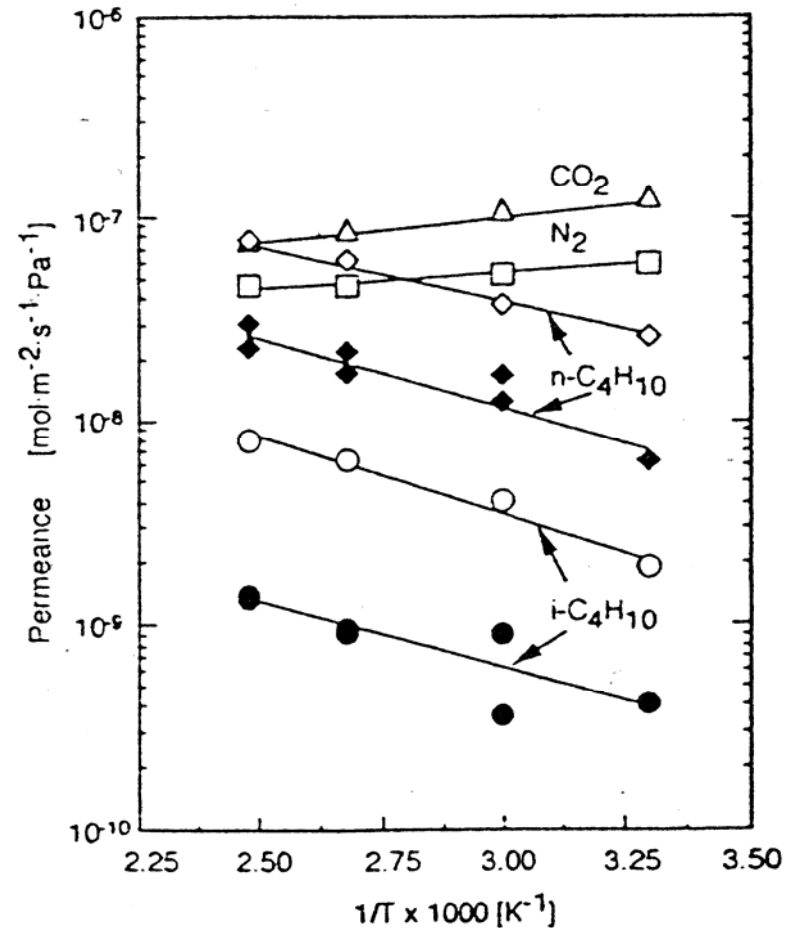


$$\text{Flux} \equiv -\Pi \frac{dp}{dz} = \frac{KD}{\ell} (p_H - p_L)$$

$$\text{Selectivity} \equiv K_A D_A / K_B D_B$$

$$KD \propto e^{-(E+\Delta H)/RT}$$

(may increase or decrease with T)



Silicalite Membrane (Kusabe 1997)

Zeolite Membranes

Non-Linear System

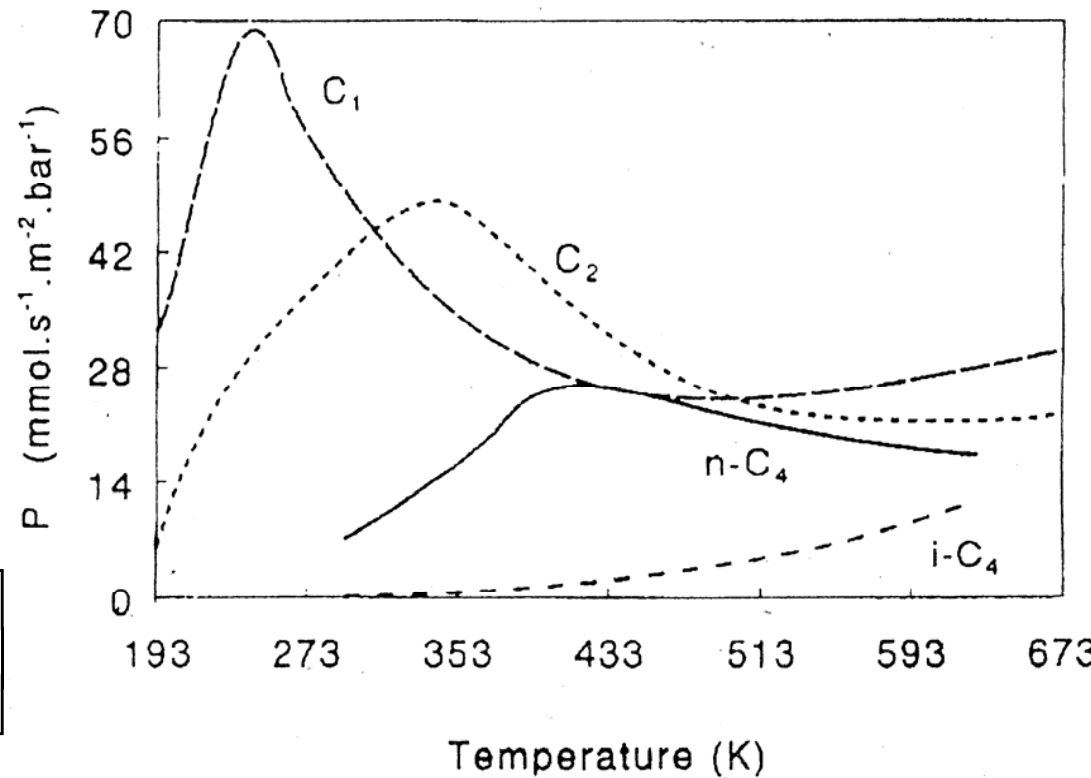


Langmuir Isotherm:

$$\frac{q}{q_s} = \frac{bp}{1+bp}$$

$$D_o = D \frac{d \ln q^*}{d \ln p} = D(1 - q/q_s)$$

$$\text{Flux} = \frac{D_o q_s}{l} \ln \left[\frac{1 + bp_H}{1 + bp_L} \right]$$



Permeance passes through a maximum with T

Perm-Selective Separations

Size Exclusion/Single File Behavior

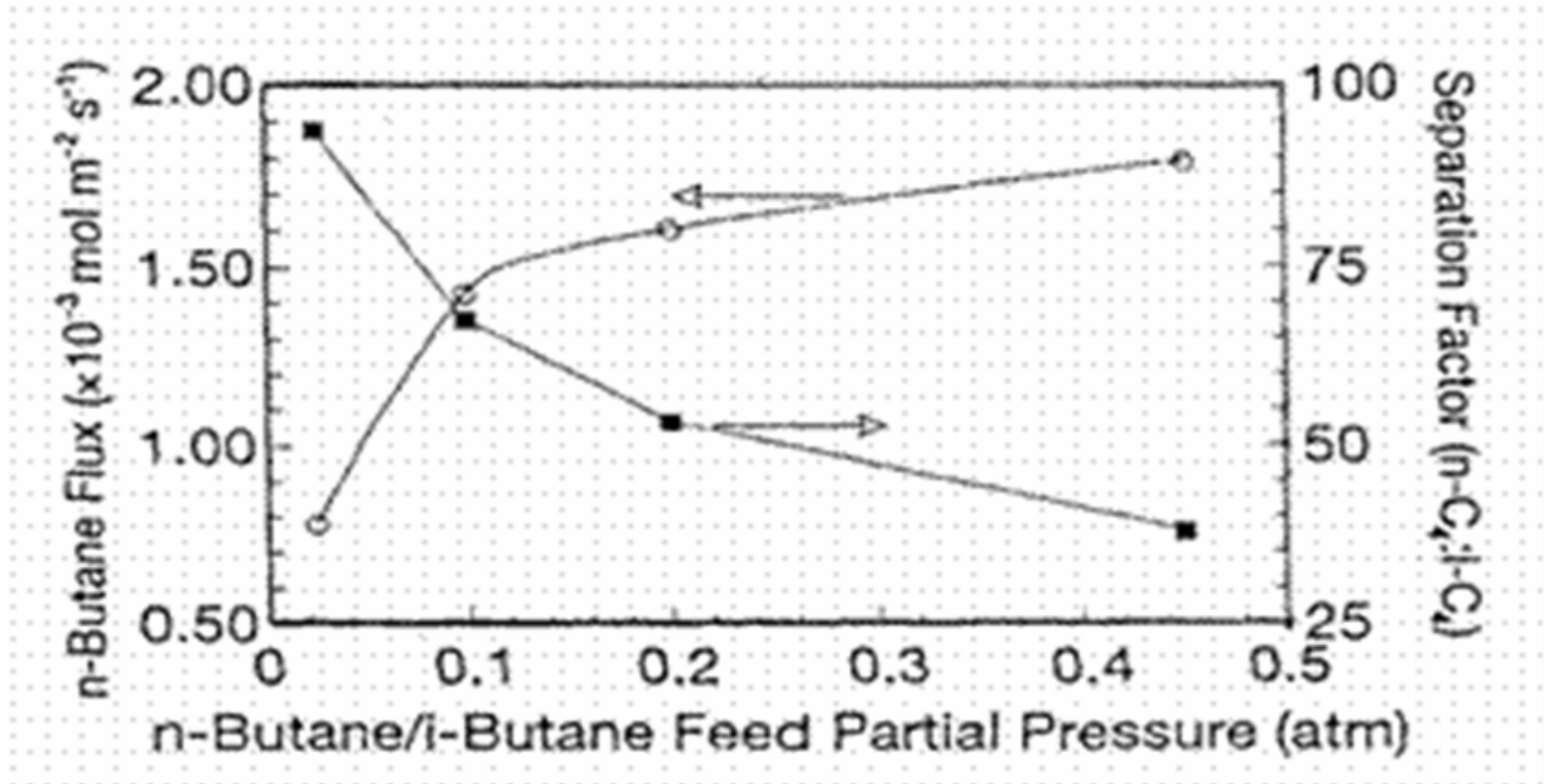


Table I Separation pattern of an $\text{AlPO}_4\text{-5}$ -in-nickel-membrane foil at 91°C and 1 bar pressure difference over the membrane. Feed: binary mixtures 1:1 of *n*-heptane and an aromatic compound. (From Caro et al⁹²⁰).

	<i>n</i> -heptane (single component)	<i>n</i> - heptane/ toluene	<i>n</i> - heptane/ mesitylen	<i>n</i> -heptane/ triethylbenzene	<i>n</i> -heptane/ triisopropylbenzene
Flux x $10^6/\text{mole s}^{-1}$ cm^2	3.9	0.85	0.43	1.82	0.94
Flux relative to pure <i>n</i> - heptane	100%	22%	11%	47%	24%
Selectivity	-	0.8	1.7	105	1220

From Caro *et al.* *Microporous and Mesoporous Mats.* **38**, 3-24 (2000)

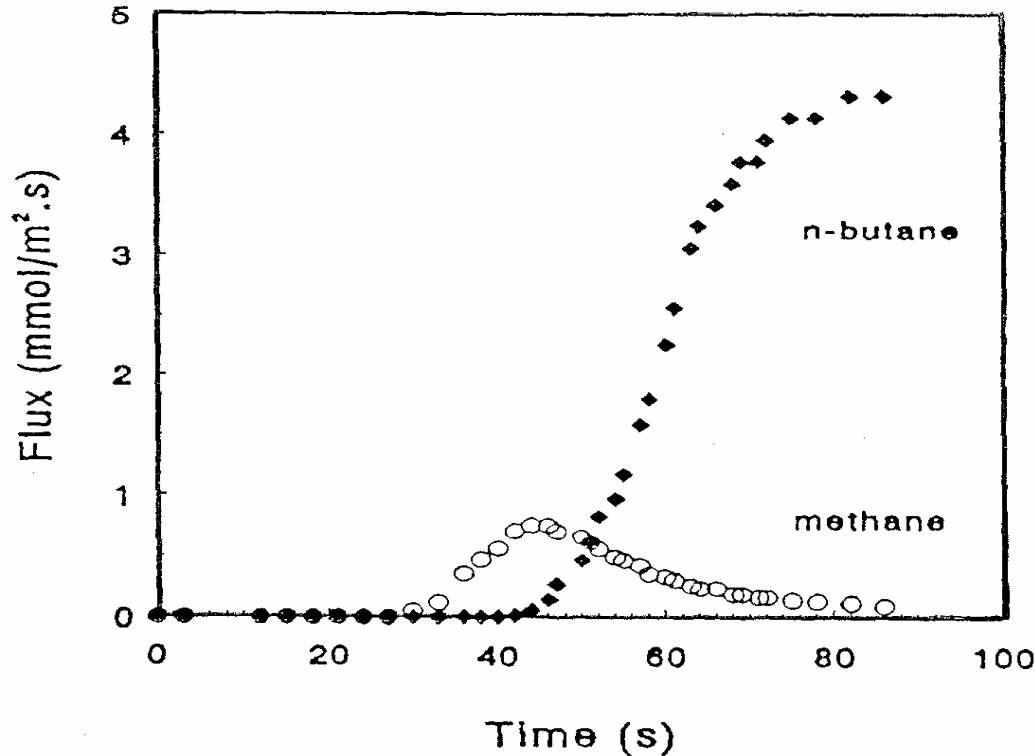
Variation of Flux and Selectivity with Loading



$n\text{C}_4/i\text{C}_4$ in silicalite

From Tzapatsis et al. *MRS Bull.* 1, 30 (1999)

Effects of Diffusion and Equilibrium *methane/n-butane/silicalite membrane*



$$D_{\text{CH}_4} \gg D_{\text{C}_4\text{H}_{10}} \quad \text{but} \quad K_{\text{CH}_4} \ll K_{\text{C}_4\text{H}_{10}}$$

At steady state – high selectivity for nC₄H₁₀

From Geus et al. *Microporous Mats.*, 1, 131 (1993)

Modeling Permeation in Binary Systems

Mutual Diffusion Effect



Maxwell-Stefan Model:

$$-\frac{q_i}{RT} \nabla \mu_i = \sum_{s=i}^n \frac{q_j N_i - q_i N_j}{q_s \mathfrak{D}_{ij}} + \frac{N_i}{D_{oi}}$$

$$N_A = \frac{-q_s D_{OA}}{1 - \theta_A - \theta_B} \cdot \frac{(1 - \theta_B + \theta_A D_{OB} / \mathfrak{D}_{AB}) \frac{d\theta_A}{dz} + [\theta_A + \theta_A D_{OB} / \mathfrak{D}_{AB}] \frac{d\theta_B}{dz}}{1 + \theta_A D_{OB} / \mathfrak{D}_{AB} + \theta_B D_{OA} / \mathfrak{D}_{AB}}$$

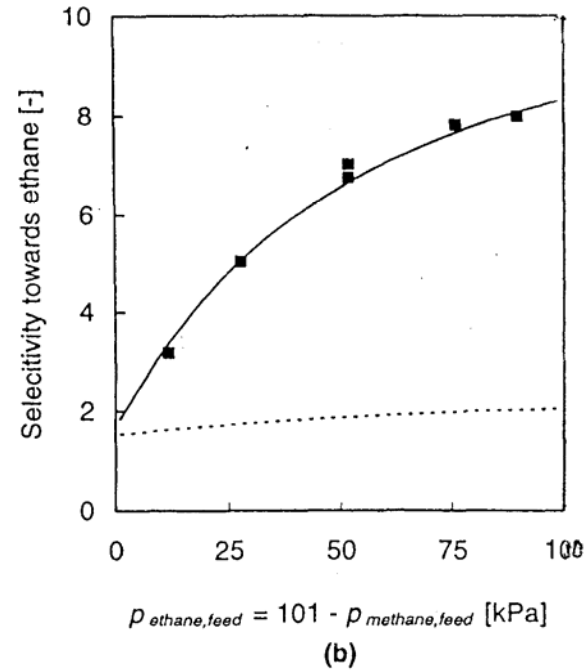
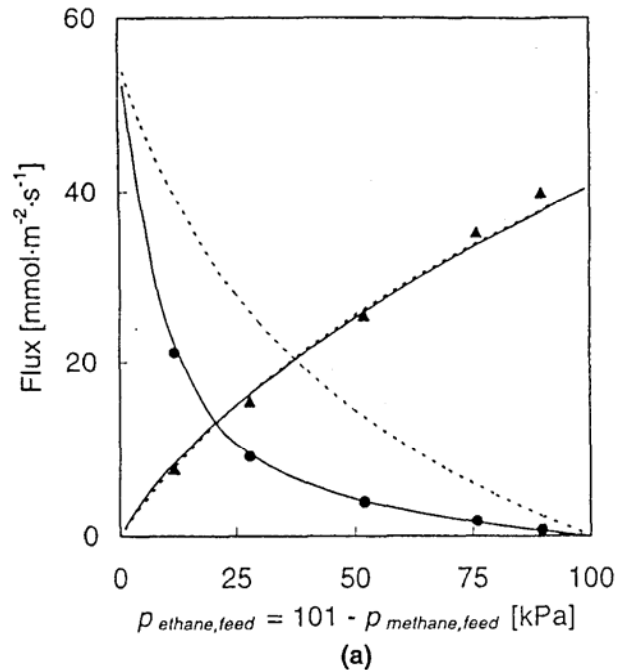
D_{oi} = Thermodynamically Corrected Diffusivity for Component i

\mathfrak{D}_{ij} = Mutual Diffusivity (estimated as geometric mean)

For single component permeation flux reduces to:

$$N_i = -\frac{D_{oi} q_i}{RT} \frac{d\mu_i}{dz}$$

Mutual Diffusion in a Binary System



C_2H_6/CH_4 Permeation in a Silicalite Membrane

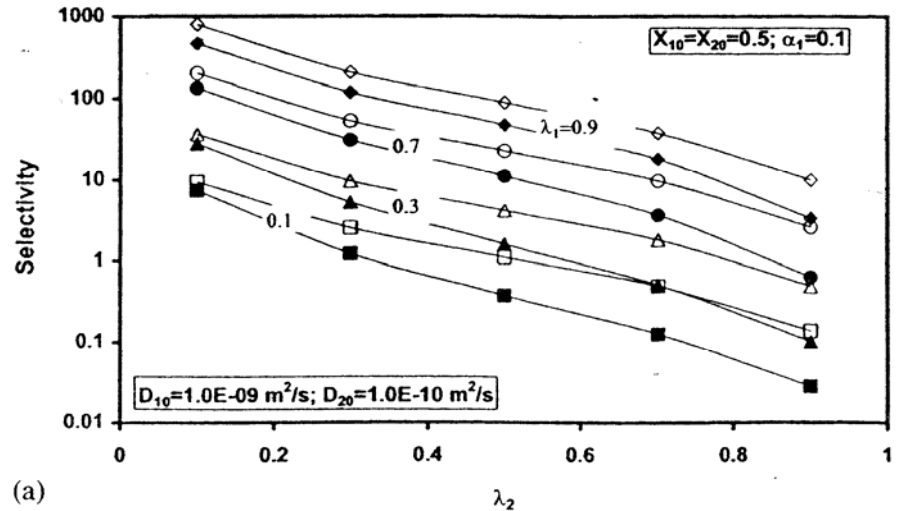
Neglect of mutual diffusion has a large effect on the flux for the faster species (CH_4); hence large errors in predicted selectivity

From de Graaf et al *AIChEJl.* **45**, 497 (1999)

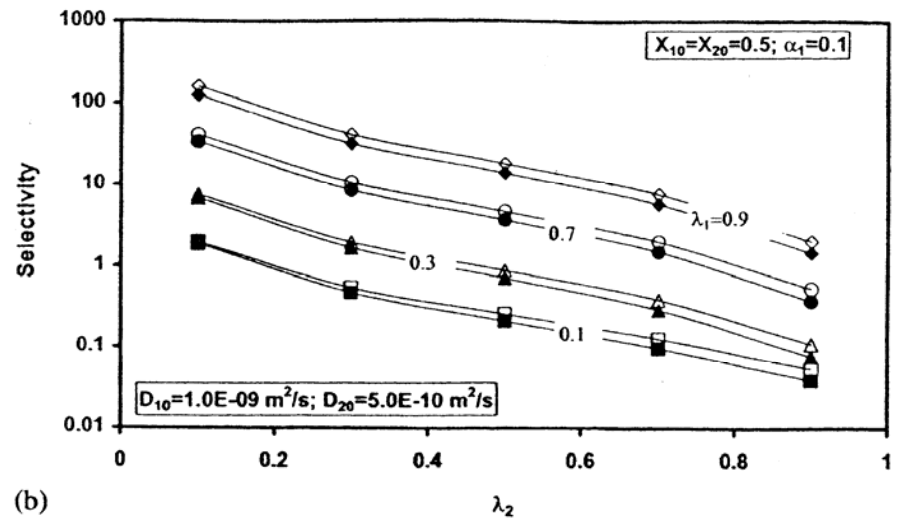
Mutual Diffusion

Effect is small
at low loadings
but large at high loadings
if D_A/D_B is large.

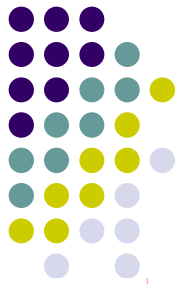
From Karimi and Farooq.
Chem.Eng.Sci., **55**, 3529 (2000)



(a)



(b)



Kinetic Separations

Olefin/Paraffin Separation



Importance: Recovery of light olefins from cat-cracker off-gas

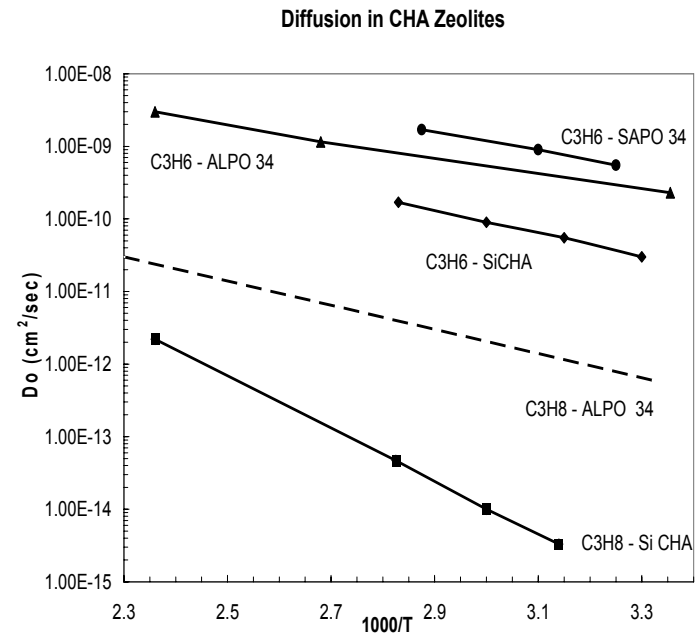
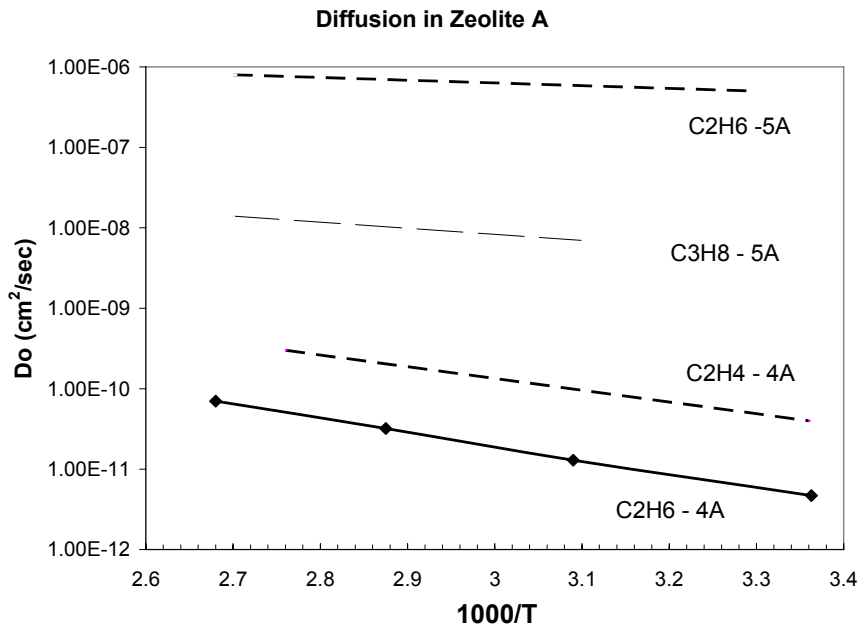
Equilibrium Selectivity (C_2H_4/C_2H_6) $\ll 10$

Kinetic Selectivity ~ 10 in 4A zeolite

Much higher Kinetic Selectivity in CHA zeolites such as SAPO-34

Olefin/Paraffin Separation

Diffusion in Type A and CHA Zeolites

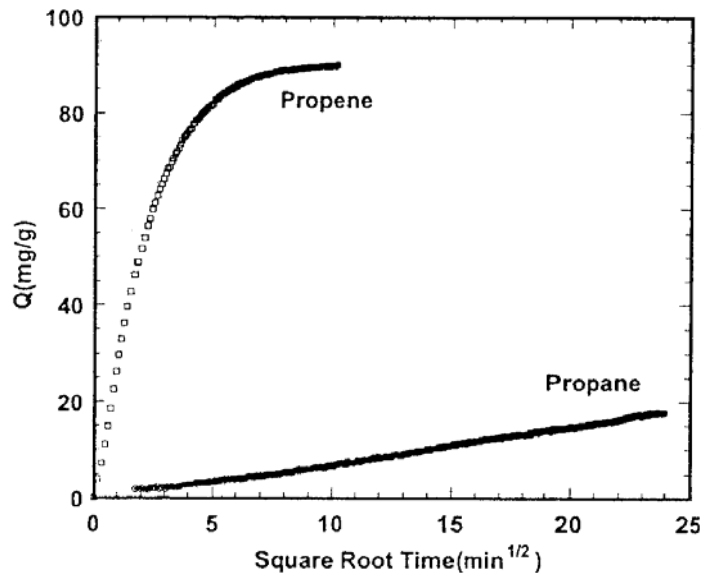


D and E are sensitive to subtle differences in T – O distance



Olefin/Paraffin Separation

Comparative Uptake Rates for C_3H_6 and C_3H_8 in SiCHA at $80^\circ C$

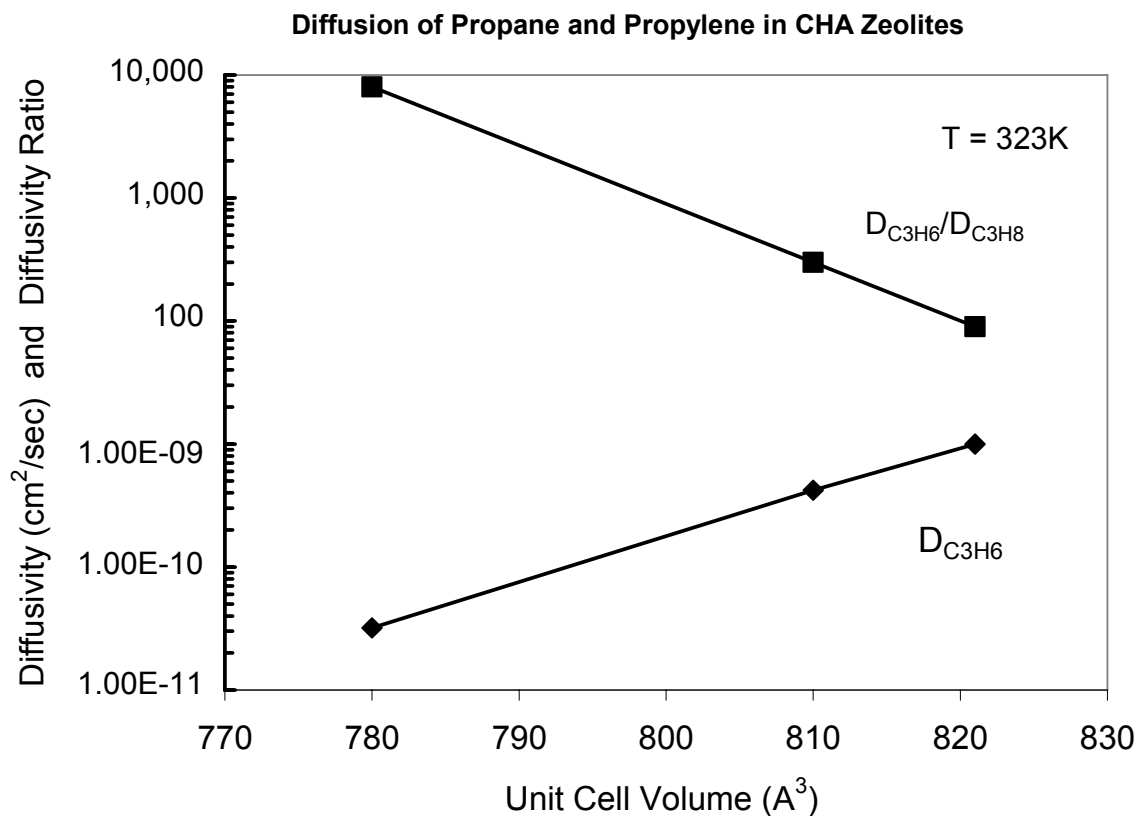


From Olson et al. *Microporous and Mesoporous Mats.* **67**, 27-33 (2004)



Olefin/Paraffin Separation

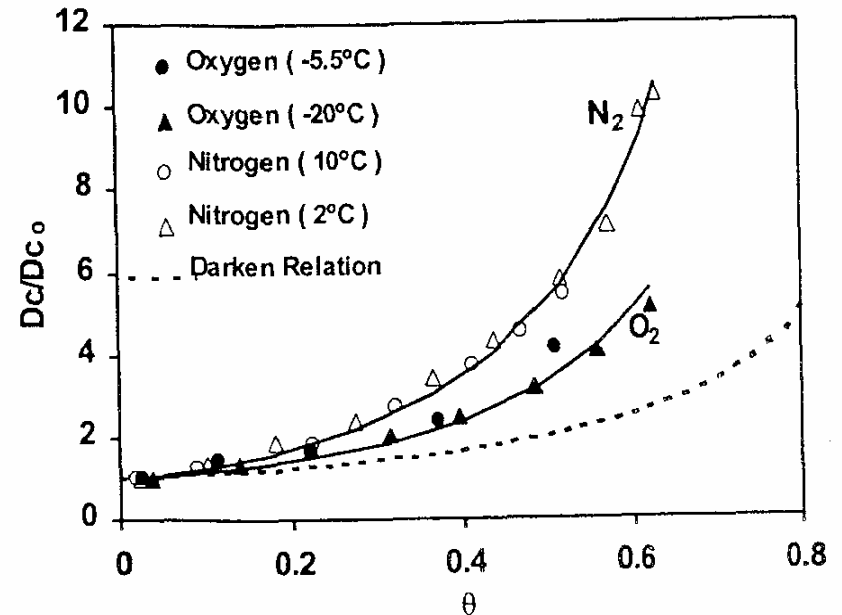
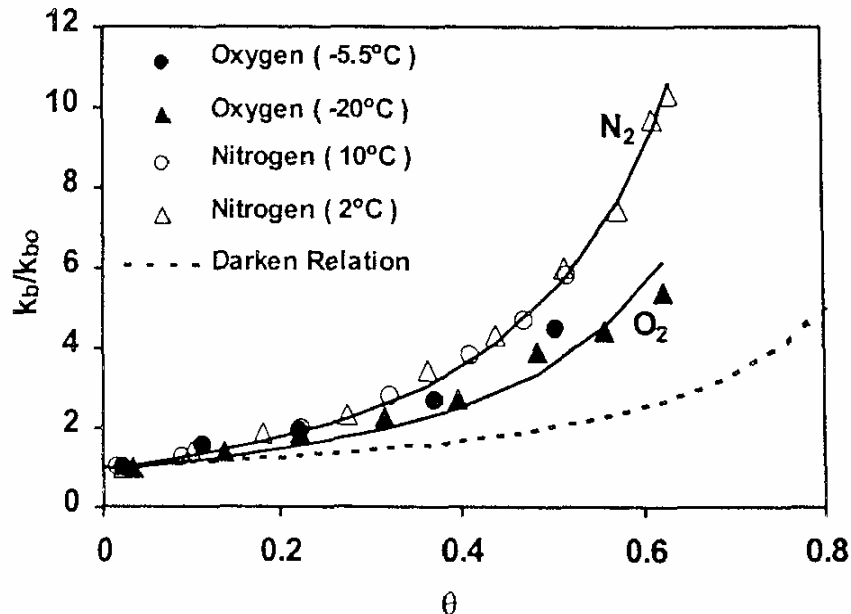
Variation of D and Kinetic Selectivity with Unit Cell Size



From Reyes et al. U.S. Patent 6,730,142 B2 May 4, 2004

Kinetic Separation

N_2/O_2 Separation on CMS



Strong concentration dependence of both k and D

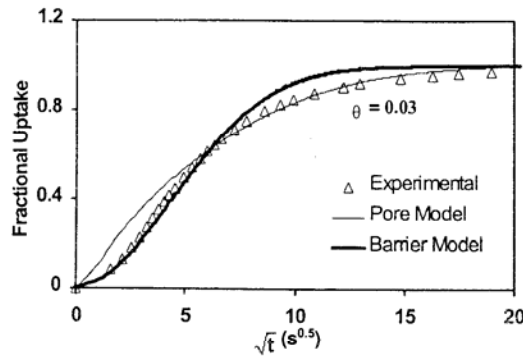
From Sundaram et al. 7th Int. Conf. on *Fundamentals of Adsorption*. Nagasaki, May 2001.

Kinetic Separation

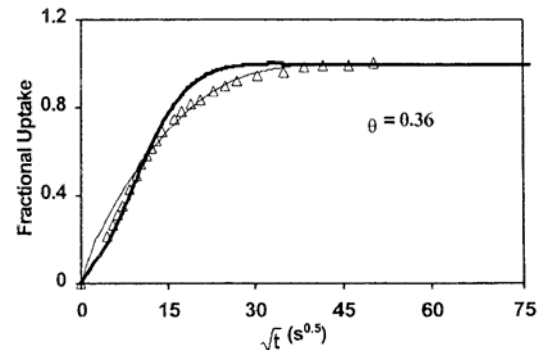
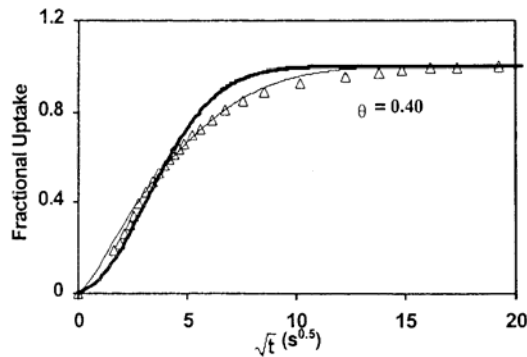
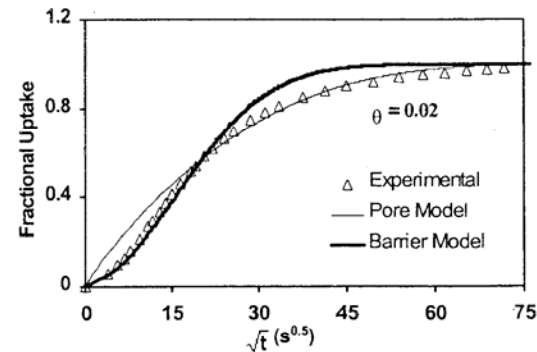
N_2/O_2 Separation over CMS



Nitrogen Uptake in BF CMS at 2°C



Oxygen Uptake in BF CMS at -20°C



O_2 diffuses **much** faster than N_2 .

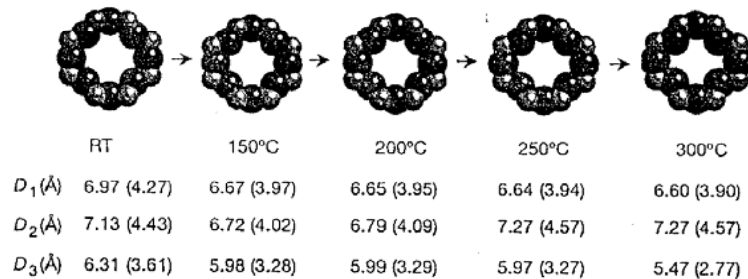
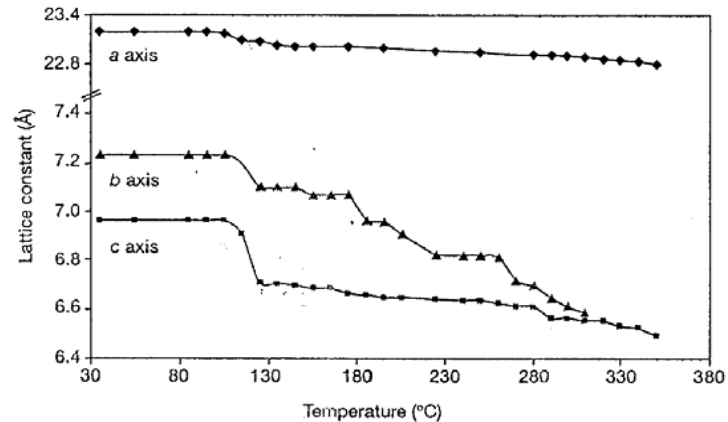
Transition from Surface Resistance to Intracrystalline Control at longer times.

From Sundaram et al. 7th Int. Conf. on *Fundamentals of Adsorption*.
Nagasaki, May 2001.

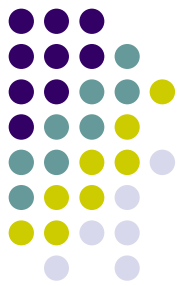
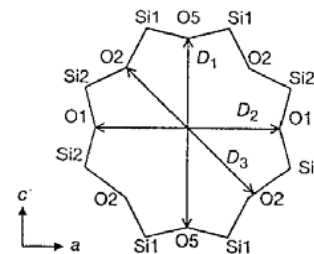
Titanosilicates – ETS-4

A “Tuneable” Adsorbent

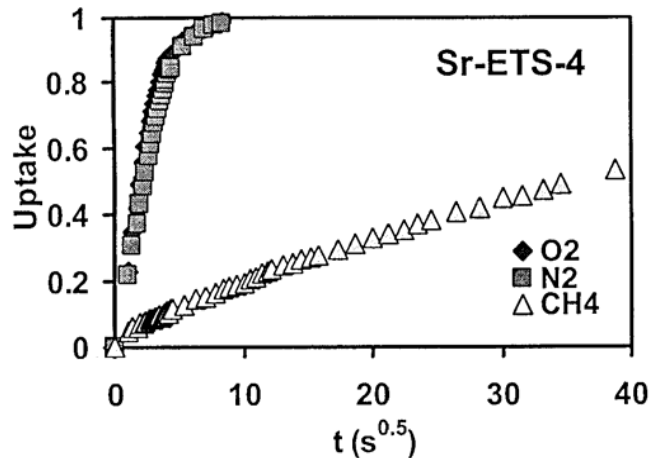
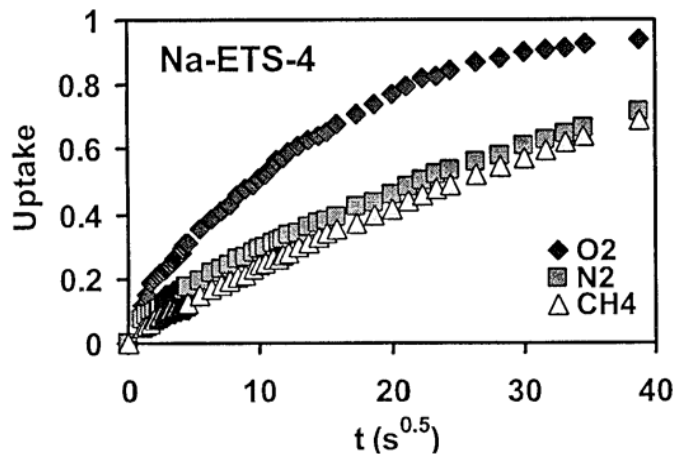
Dimensions of unit cell
(and 8-ring windows)
depend on dehydration
temperature



From Kuznicki et al.
Nature, **412**, 720 (2001)



ETS-4 (270°C dehydration)



Sr-ETS-4; High kinetic selectivity N₂/CH₄ (Farooq)

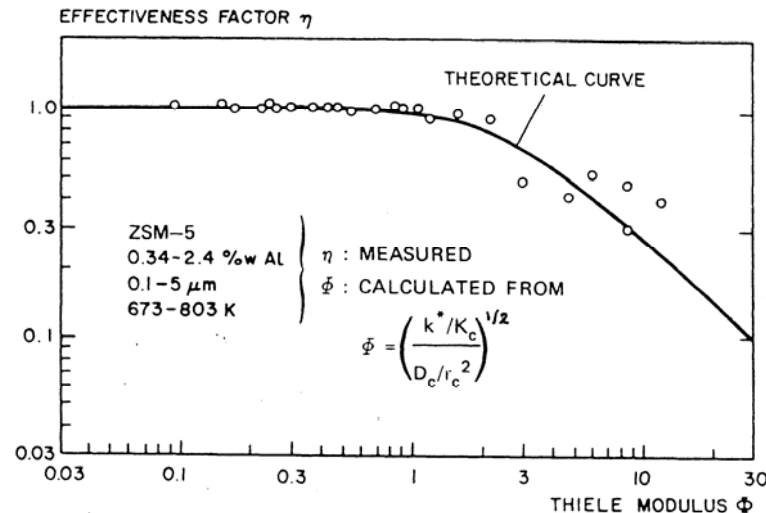
Catalytic Reactions

Effect of Intraparticle Diffusion on Reaction Rate



1st Order Rxn: $k_e = k\eta$ $\eta = \frac{3}{\phi} \left[1 - \frac{1}{\text{Tanh}\phi} \right]$

Macropore Diffusion: $\phi = R \sqrt{\frac{k}{D}}$ Micropore Diffusion: $\phi = r \sqrt{\frac{k}{KD}}$



Isomerization of 2, 2 DMB on HZSM-5

From Post et al. 6th Int. Zeolite Conf. Reno, 1984.

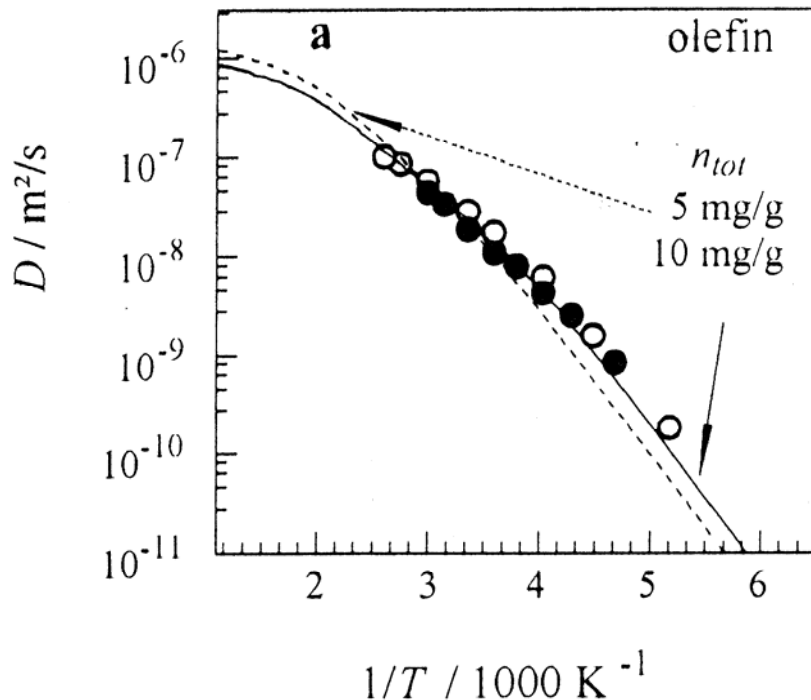
Macropore Diffusion in Catalyst Particles

Measurement by PFG NMR



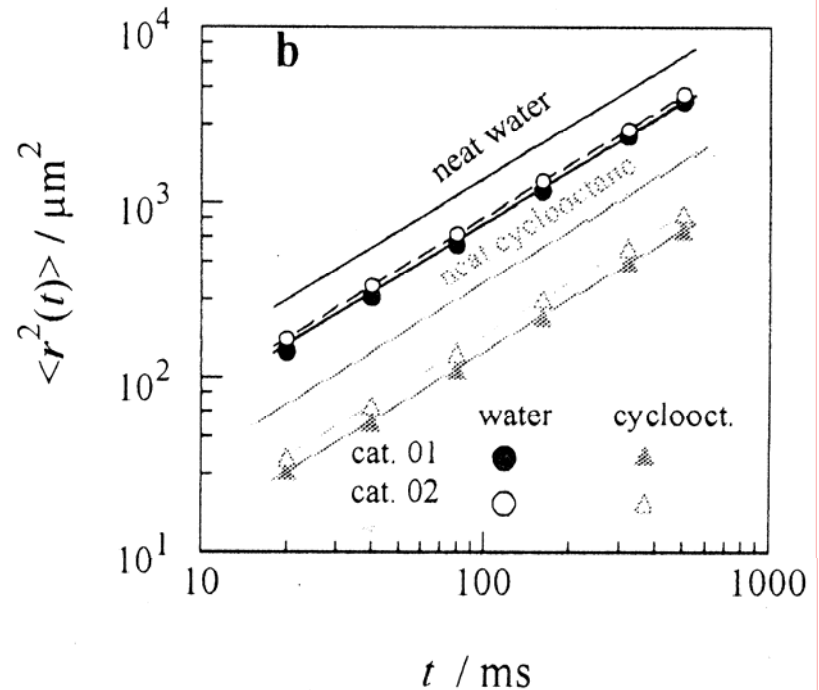
$$D_{\text{eff}} = \frac{n_{\text{pore}}}{n_{\text{pore}} + n_{\text{ads}}} \cdot \frac{D}{\tau}; \quad \frac{1}{D} = \frac{1}{D_K} + \frac{1}{D_M};$$

$$\frac{n_{\text{ads}}}{n_{\text{pore}}} = \frac{bq_s}{1 + bc}$$



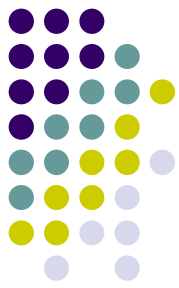
Measured and Predicted D_{eff}

Stallmach and Crowe – this conference

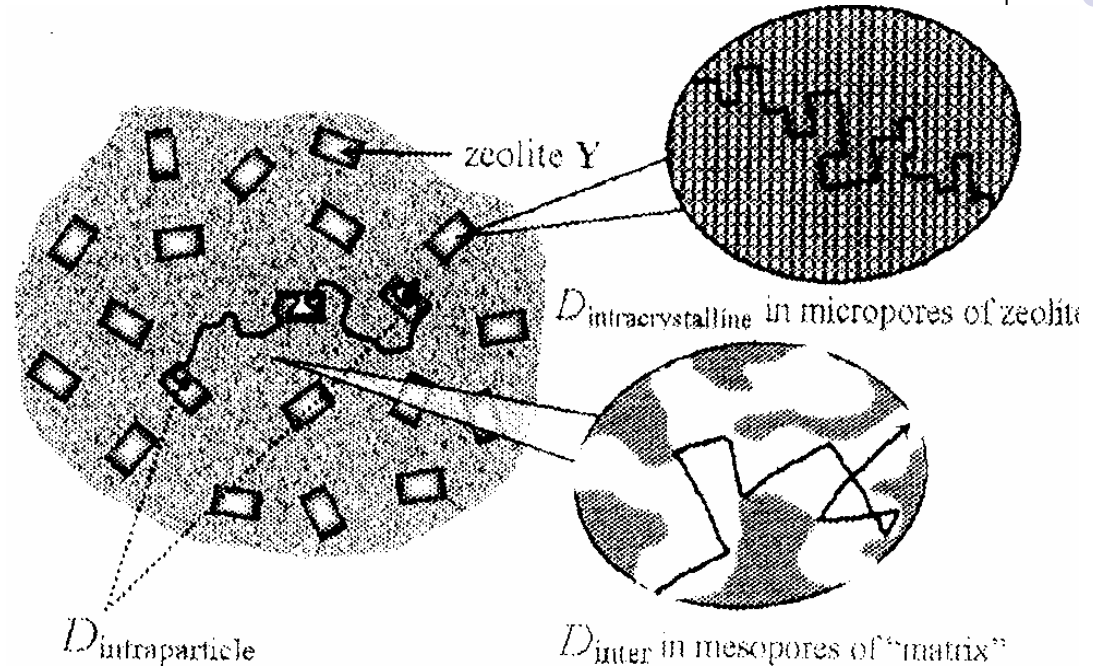


Determination of Tortuosity (τ)

Catalytic Cracking (1)



HY or REY (~1 μm crystals) in macroporous matrix
(particles ~100 μm)

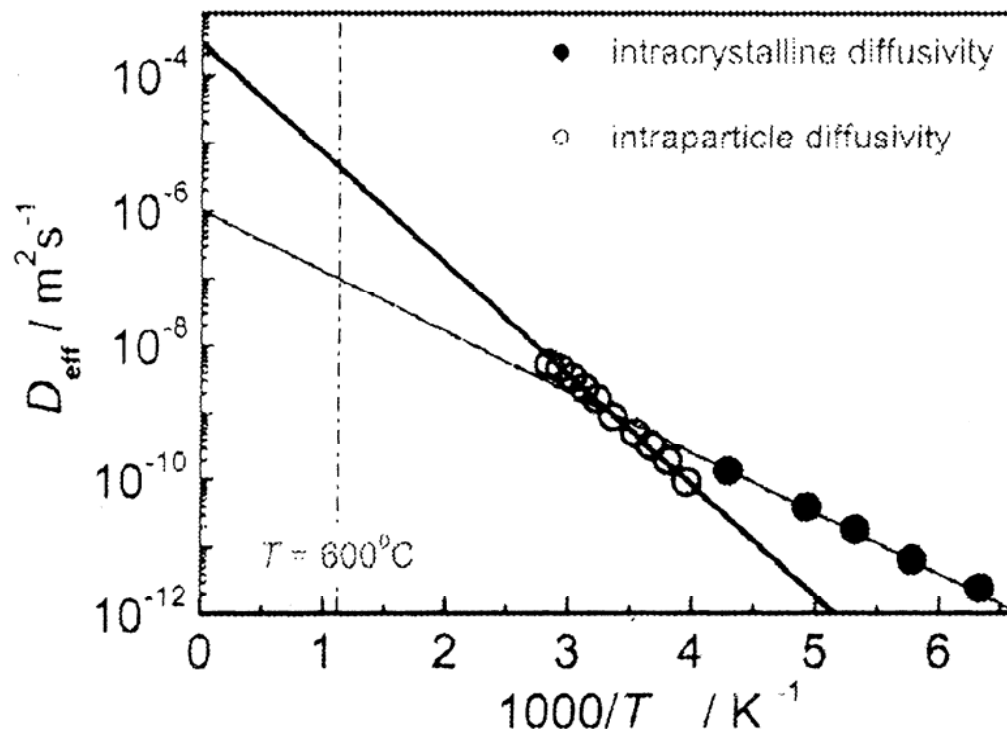


Which resistance is dominant?

$$\frac{t_{\text{micro}}}{t_{\text{macro}}} = \frac{D_{\text{macro}} / R^2}{D_{\text{micro}} / r^2} \approx 10^{-4} \frac{D_{\text{macro}}}{D_{\text{micro}}}$$

Kortunov et al – this conference

Catalytic Cracking (2)

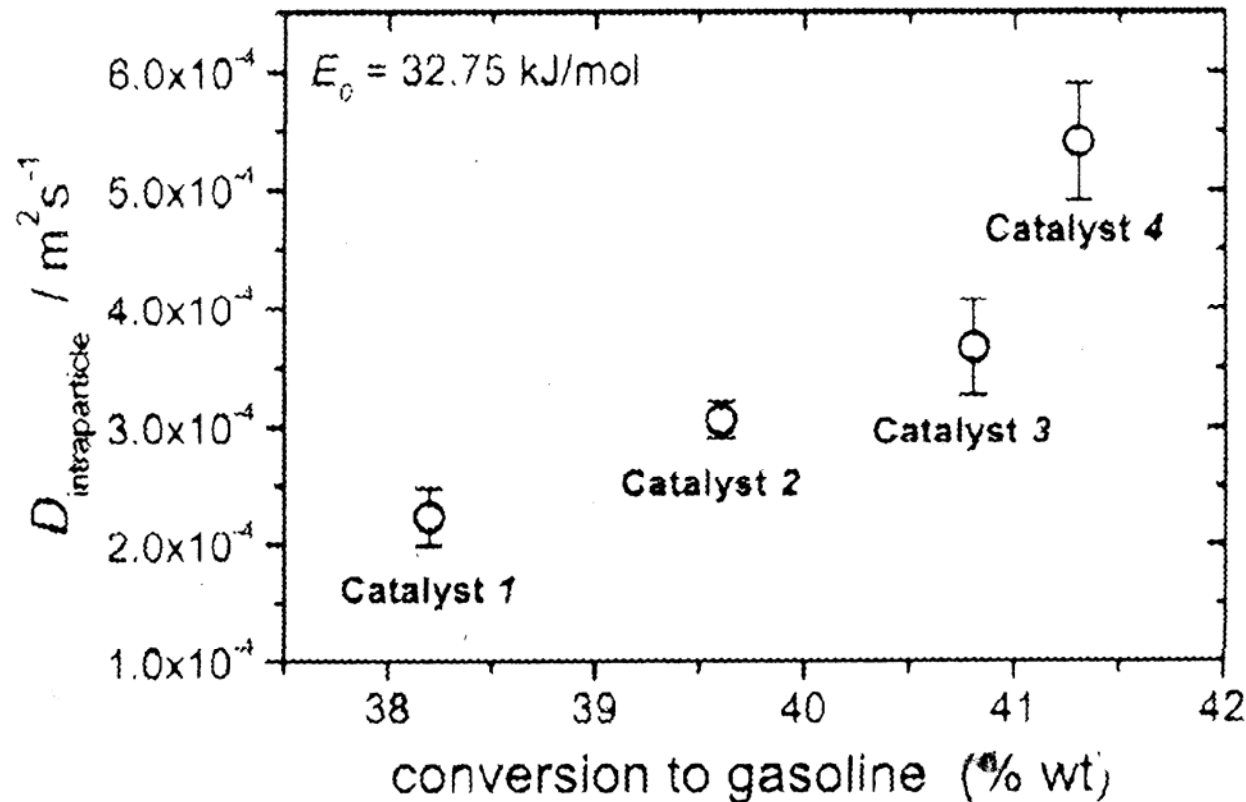


PFG NMR: $D_{\text{macro}}/D_{\text{micro}} \sim 10$ (at 600°C)

$t_{\text{micro}}/t_{\text{macro}} \sim 10^{-3}$ Macro diffusion controls

From Kortunov et al – this conference

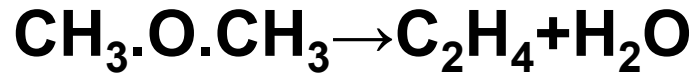
Catalytic Cracking (3)



Conversion correlates with D_{macro}/K

From Kortunov et al – this conference

Methanol to Olefins (MTO)

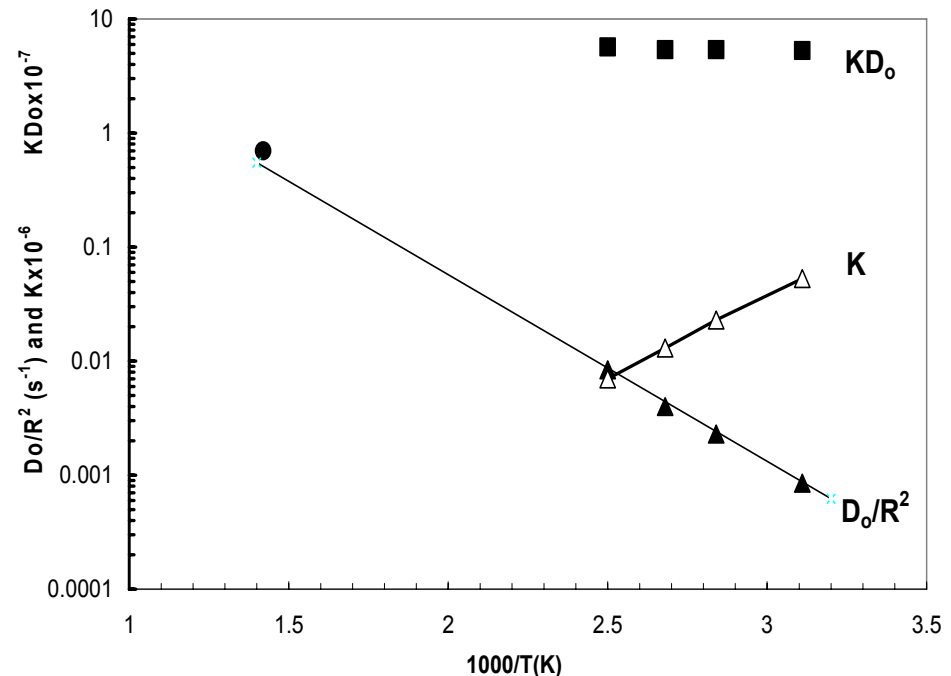


Slow polymerization to higher Mol.Wt.species

Measured D and K values consistent with reaction rate data (Thiele analysis)

From data of Chen et al. *Ind.Eng.Chem.Res.***38**, 4241 (1999)

Diffusion and Reaction of Methanol in SAPO 34



MTO Reaction (2)

Effect of Diffusion on Yield



For high yield of C_2 and C_3 $\frac{\phi_2}{\phi_1} = \left(\frac{k_2 D_{MeOH}}{k_1 D_{DME}} \right)^{\frac{1}{2}} \gg 1$

(DME formed in Rxn1 must remain within zeolite crystal for long enough to achieve high conversion)

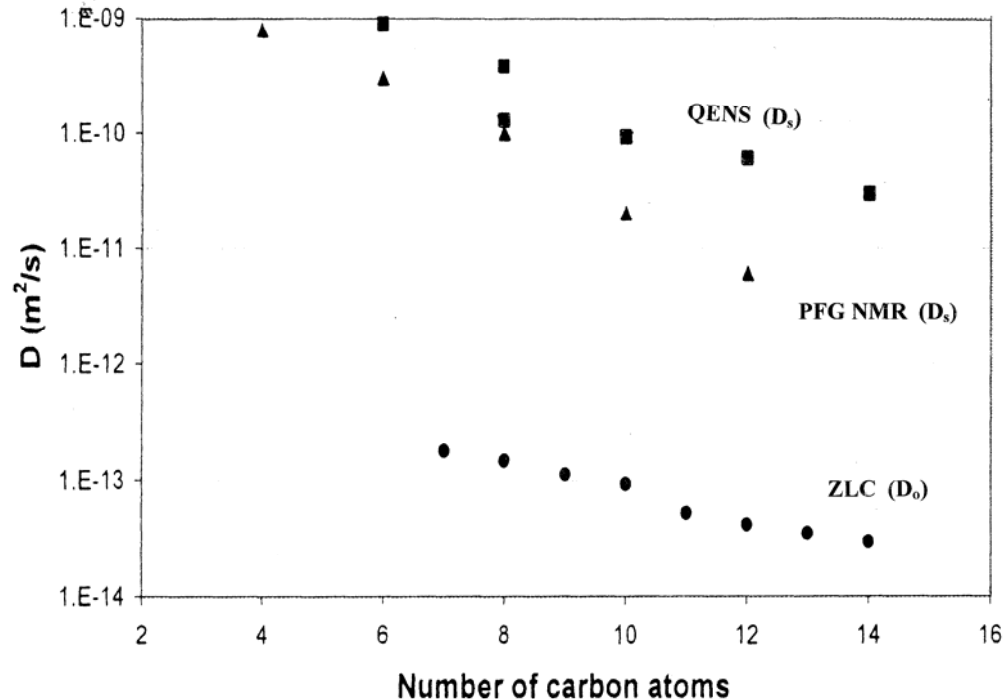
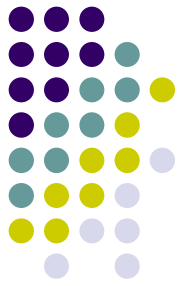
As catalyst ages coke build-up reduces D_{DME} more than D_{MeOH} ; C_2H_4 yield increases

Crystal size – no effect on yield (since ratio of Φ_2/Φ_1 is independent of r)

From Chen et al – various papers.

Measurement of Intracrystalline Diffusion in Zeolites

Light Alkanes in Silicalite



Comparison of experimental results at 423K.

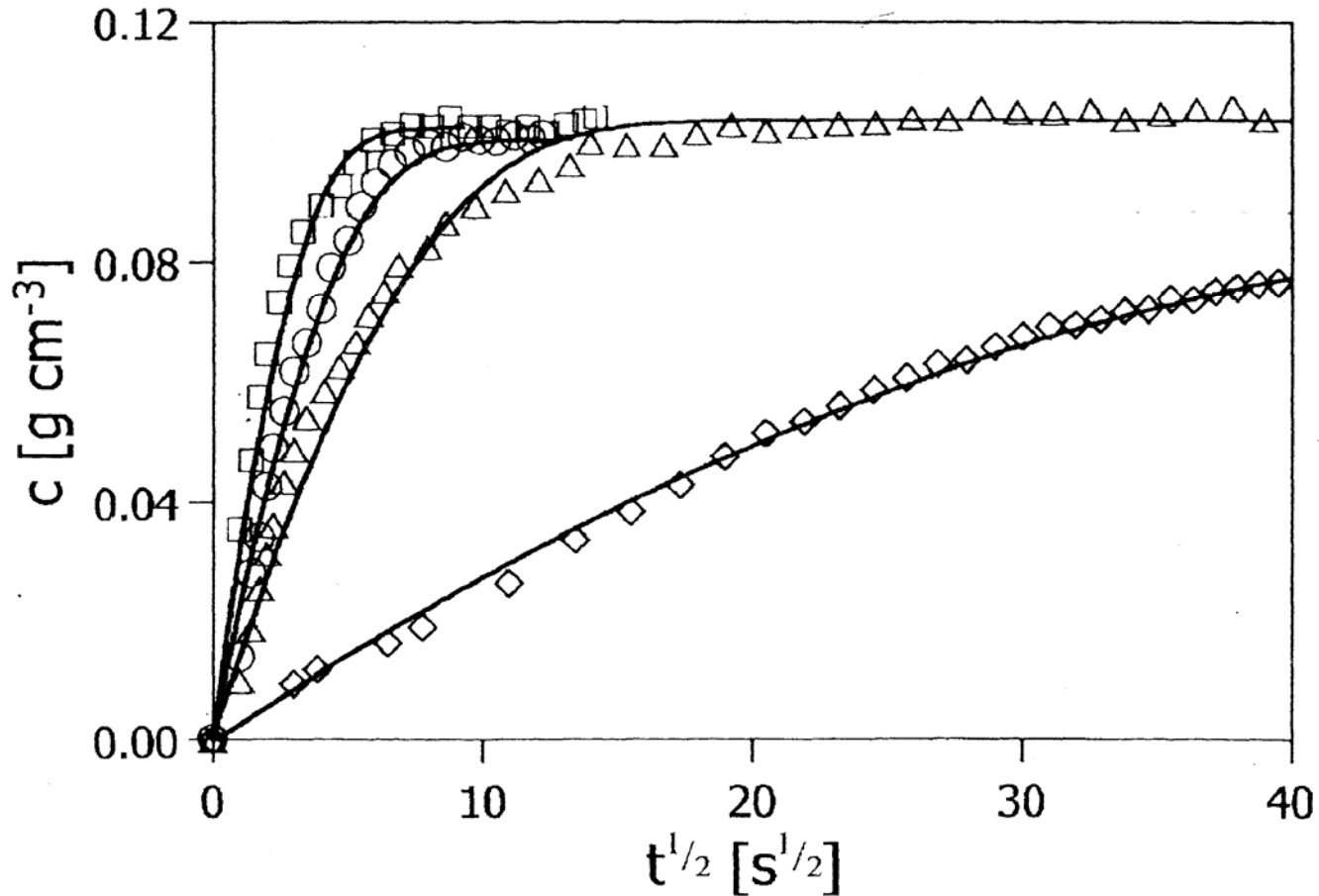
Diffusion of Linear Alkanes in Silicalite at 423K

Microscopic measurements (QENS and PFG NMR) yield much higher D values than macroscopic (ZLC) measurements

From Bourdin et al – this conference

Evidence of Surface Barrier Control

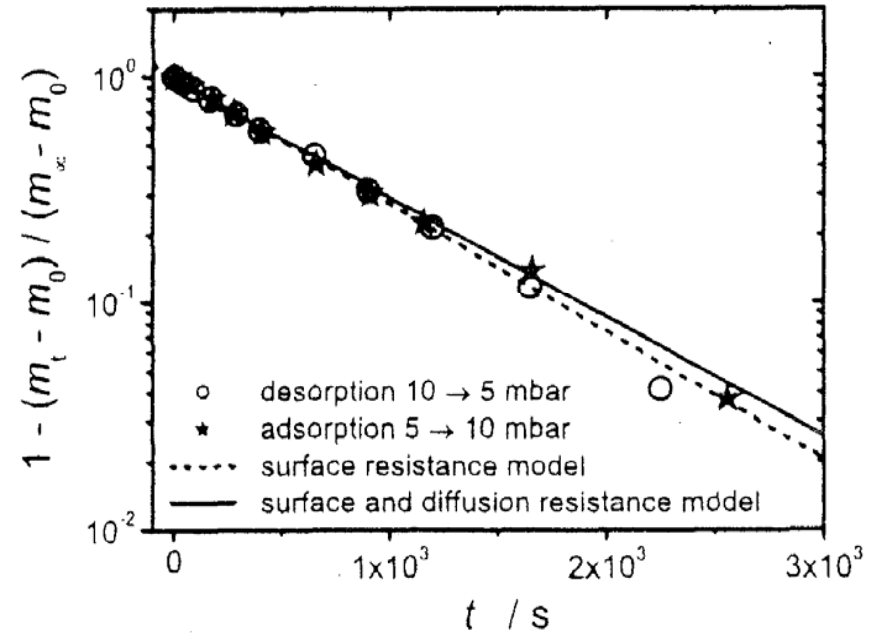
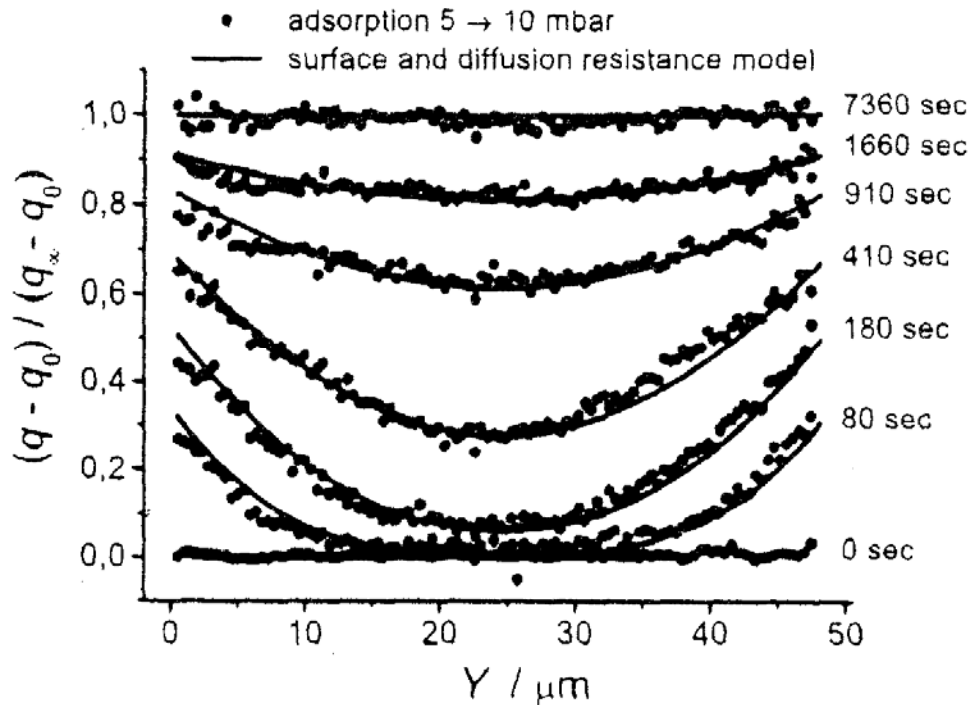
n-Hexane – Silicalite at 298K



Uptake rate in HF etched sample is increased by ~300

From Wloch, *Microporous and Mesoporous Mats.* (2004)

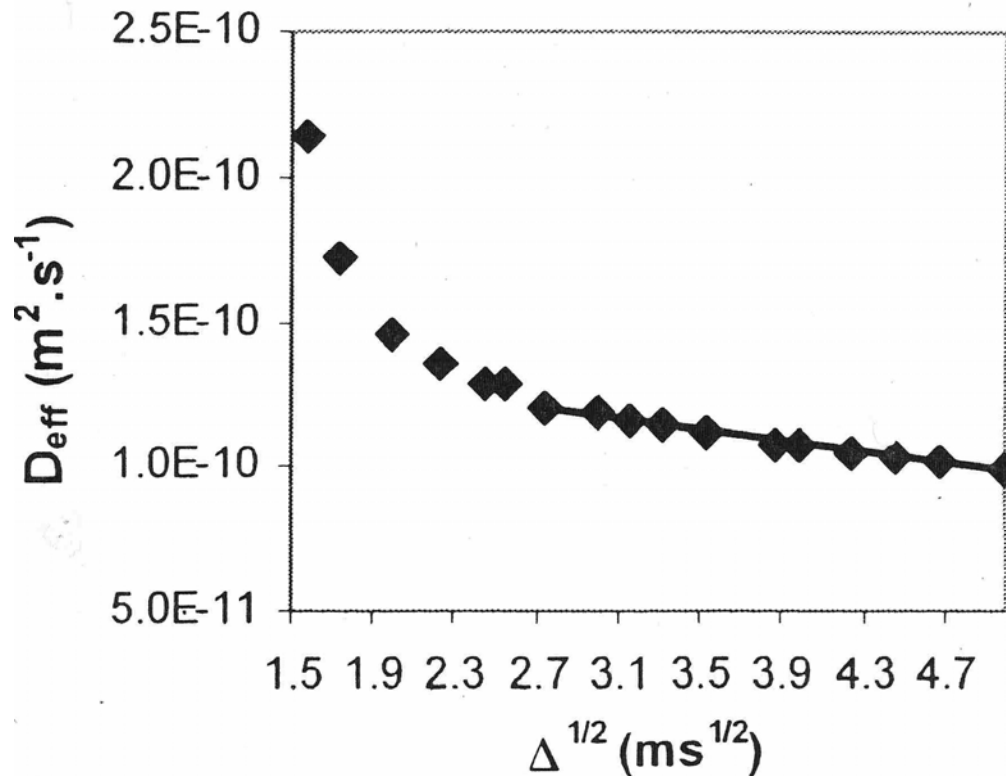
Evidence for Surface Resistance + Internal Diffusion Methanol in Ferrierite



From Kortunov et al – this conference

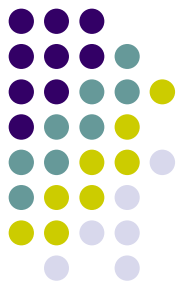
Evidence of Internal (non-framework) Barriers

Diffusion of n-Hexane in NaX at 293K



PFG NMR values of D_{eff} decrease with increasing scale of measurement – suggesting structural (non-framework) barriers.

From Adem et al – this conference



Conclusions (1)



- Diffusion at both nm (intracrystalline) and μm (intraparticle) scales has major impact on performance of both adsorption separation processes and catalytic processes
- Impact can be positive or negative
e.g. MTO Reaction: increased intracrystalline diffusion resistance improves performance
- Improved understanding of intracrystalline diffusion would lead to improved process design

Conclusions (2)



- Measurement of intracrystalline diffusion is not straightforward
- “Microscopic” (QENS, PFG NMR) diffusivities do not necessarily correlate with sorption rates or even long range internal diffusion
- “Macroscopic” diffusivities do not necessarily represent diffusion in an ideal zeolite framework
- The “Holy Grail” of predicting intracrystalline diffusivities in *real* catalysts and adsorbents remains elusive