Diffusion Fundamentals
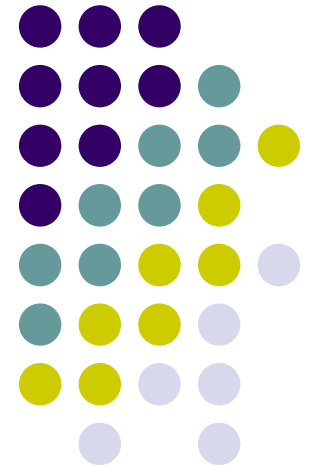**University of Leipzig, September 2005**

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)

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Outline
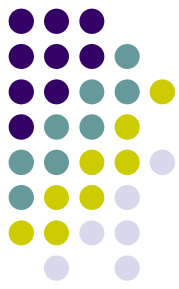
- Zeolite Structures
- Zeolite Membranes
  - Performance, Modelling, Mutual Diffusion Effects
- Olefin/Paraffin Separations
- Air Separation over CMS
- N_2/CH_4 Separation over ETS-4
  - A "tuneable" adsorbent
- Catalytic processes
  - Catalytic Cracking
  - Methanol to olefins (MTO)
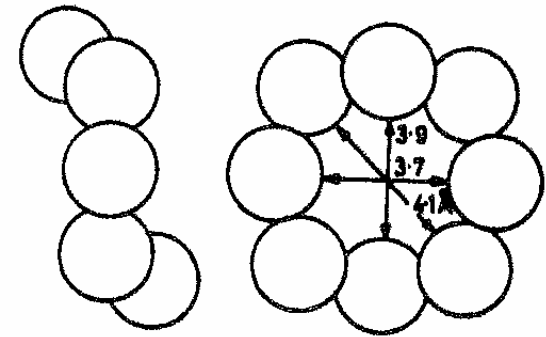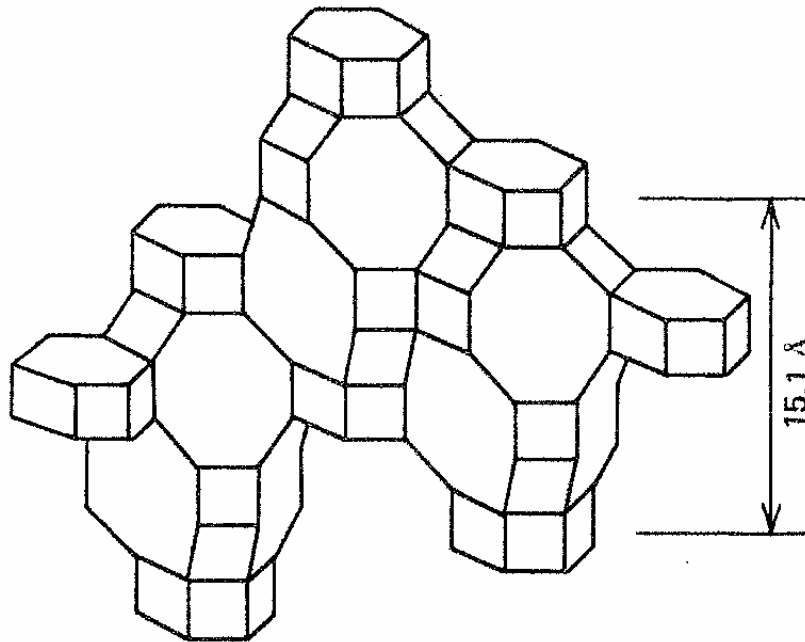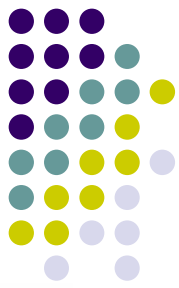- Measurement of transport rates in zeolites

Silicalite Pore Structure
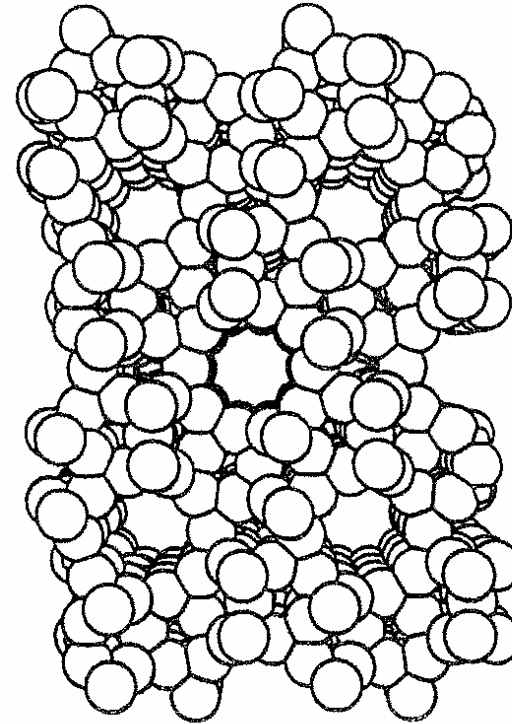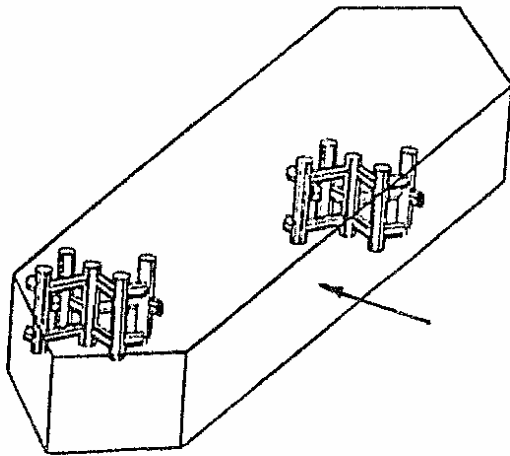
10-ring channels, ~6Å diameter

Intersecting straight and sinusoidal channels

Chabazite Structure (CHA)

Cages (free volume ~380Å^3) interconnected through tetrahedrally oriented 8-ring windows – free aperture 3.7 – 4.1 Å

SiCHA, SAPO-34:   cation free versions
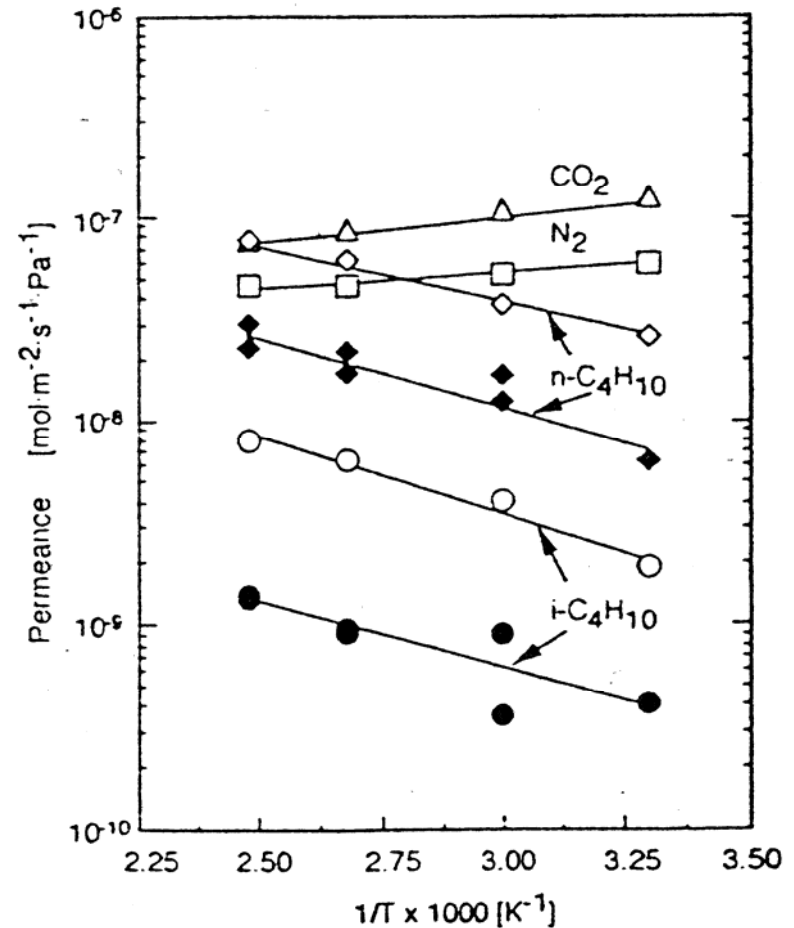
Zeolite Membranes
Single Component Permeation

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

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

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

$$(\text{may increase or decrease with } T)$$

Silicalite Membrane (Kusabe 1997)
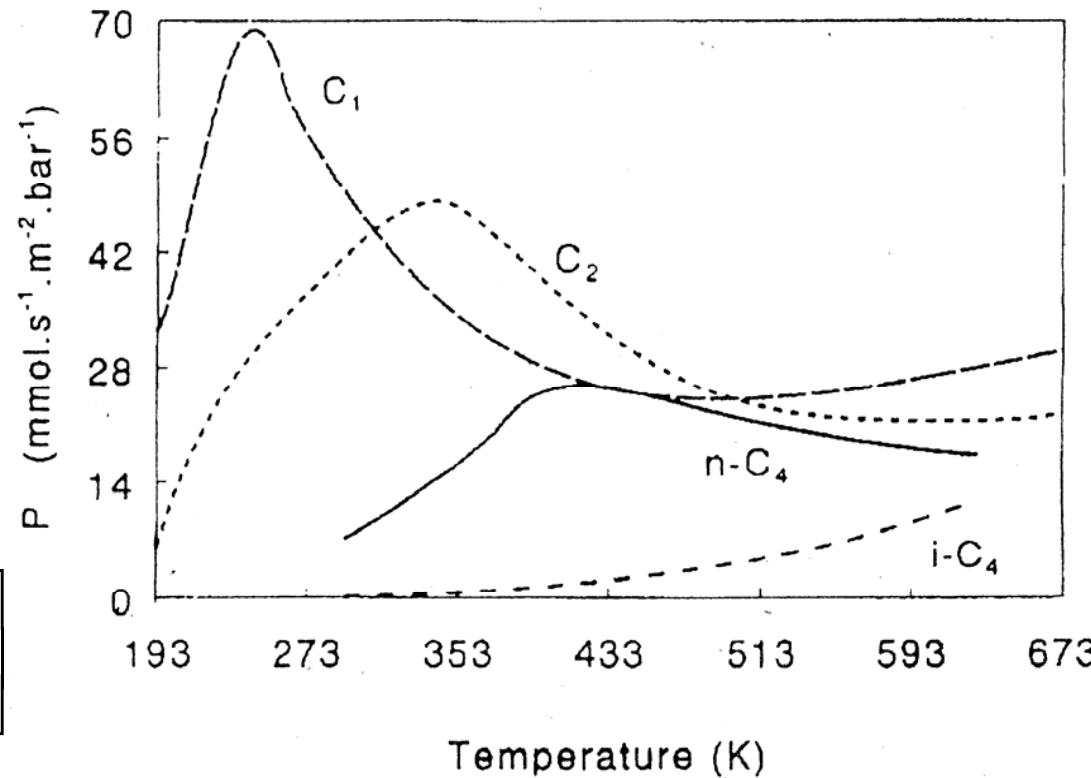
Zeolite Membranes
Non-Linear System

Langmuir Isotherm:

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

$$D_o = D\frac{d\ell nq^*}{d\ell np} = D(1 - q/q_s)$$

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

Permeance passes through a maximum with T

# Perm-Selective Separations
Size Exclusion/Single File Behavior

Table I Separation pattern of an $AlPO_4$-5-in-nickel-membrane foil at $91^\circ C$ and 1 bar pressure difference over the membrane. Feed: binary mixtures 1:1 of *n*-heptane and an aromatic compound. (From Caro et al[920]).

	n-heptane (single component)	*n*-heptane/ toluene	*n*-heptane/ mesitylen	*n*-heptane/ triethylbenzene	*n*-heptane/ triisopropylbenzene
Flux x 10^6/mole s$^-$ cm^2	3.9	0.85	0.43	1.82	0.94
Flux relative to pure *n*-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)
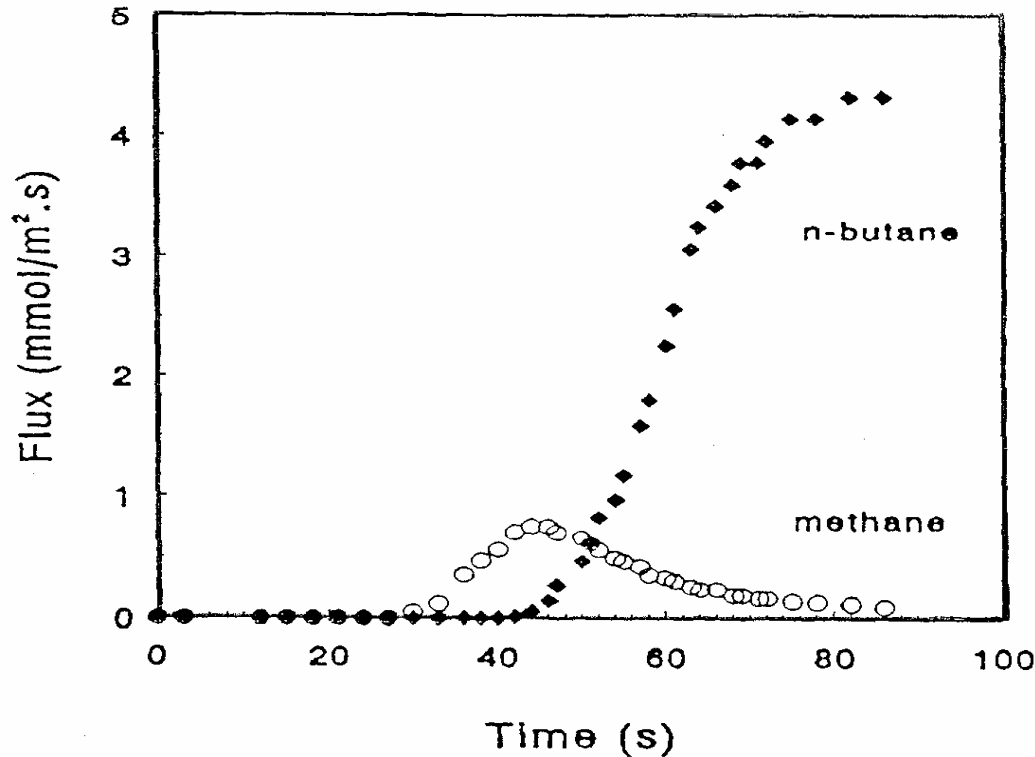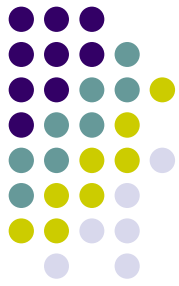
Variation of Flux and Selectivity with Loading
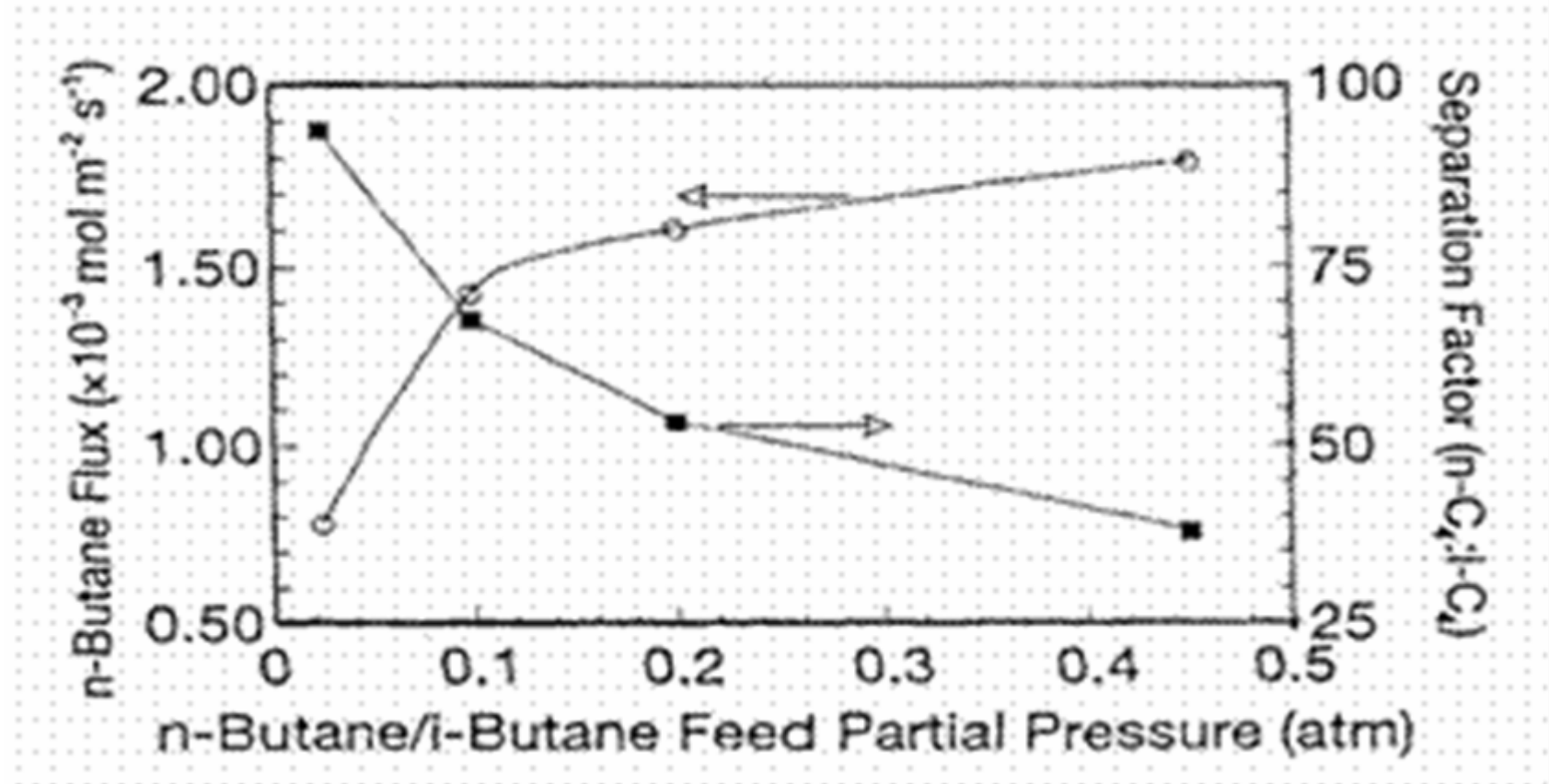
nC$_4$/iC$_4$ in silicalite
From Tsapatsis et al. *MRS Bull.* **1,** 30 (1999)

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

$$D_{CH_4} \gg D_{C_4H_{10}} \quad but \quad K_{CH_4} \ll K_{C_4H_{10}}$$

At steady state – high selectivity for nC_4H_{10}

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

Modeling Permeation in Binary Systems
Mutual Diffusion Effect

Maxwell-Stefan Model:

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

$$N_A = \frac{-q_s D_{OA}}{1-\theta_A-\theta_B}\cdot\frac{\left(1-\theta_B+\theta_A D_{OB}/Ð_{AB}\right)\dfrac{d\theta_A}{dz} + \left[\theta_A+\theta_A D_{OB}/Ð_{AB}\right]\dfrac{d\theta_B}{dz}}{1+\theta_A D_{OB}/Ð_{AB}+\theta_B D_{OA}/Ð_{AB}}$$
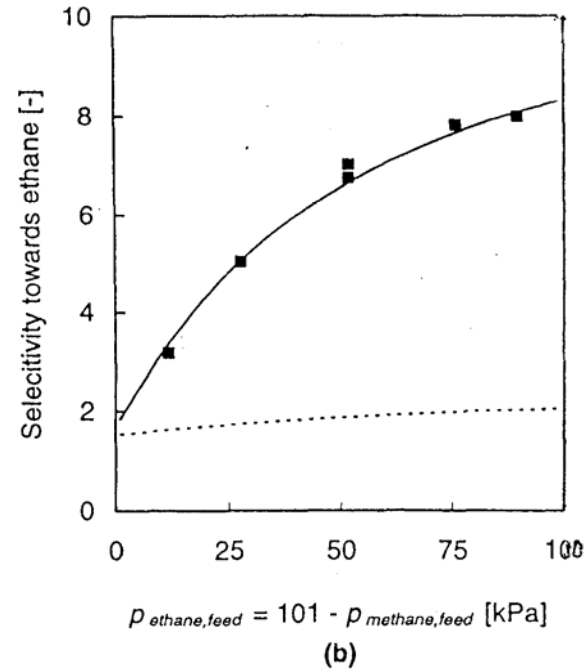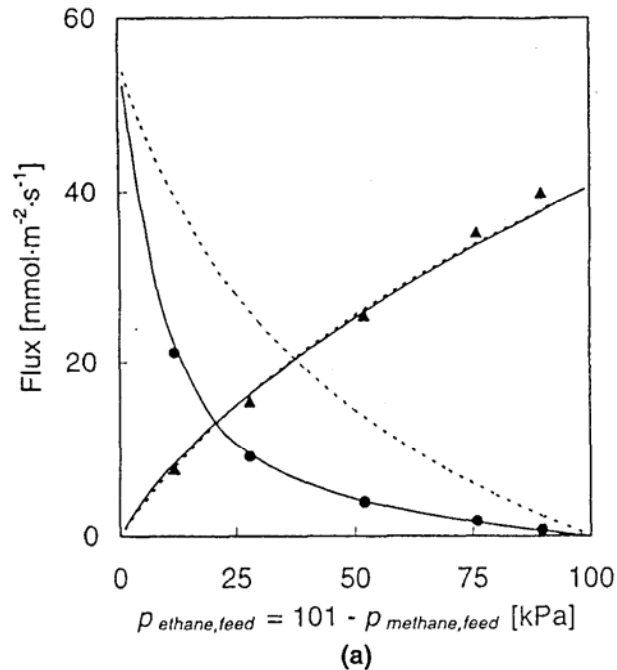
D_{oi} = Thermodynamically Corrected Diffusivity for Component i

$Ð_{ij}$ = 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
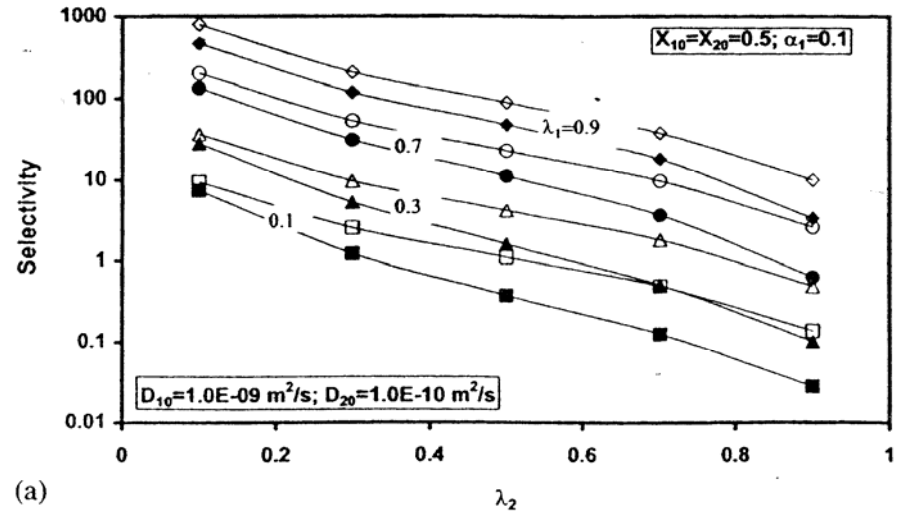

C$_2$H$_6$/CH$_4$ Permeation in a Silicalite Membrane

Neglect of mutual diffusion has a large effect on the flux for the faster species (CH$_4$); hence large errors in predicted selectivity
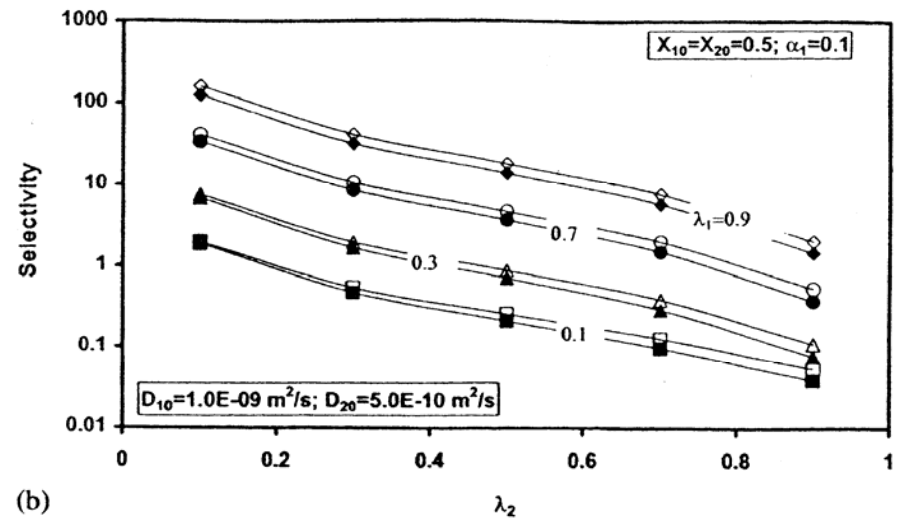
From de Graaf et al *AIChEJl.* **45**, 497 (1999)

Mutual Diffusion

**Effect is small
at low loadings
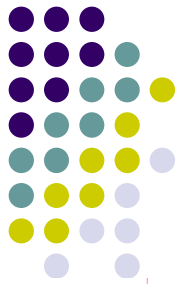but large at high loadings
if $Đ_A/Đ_B$ is large.**

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

Kinetic Separations
Olefin/Paraffin Separation

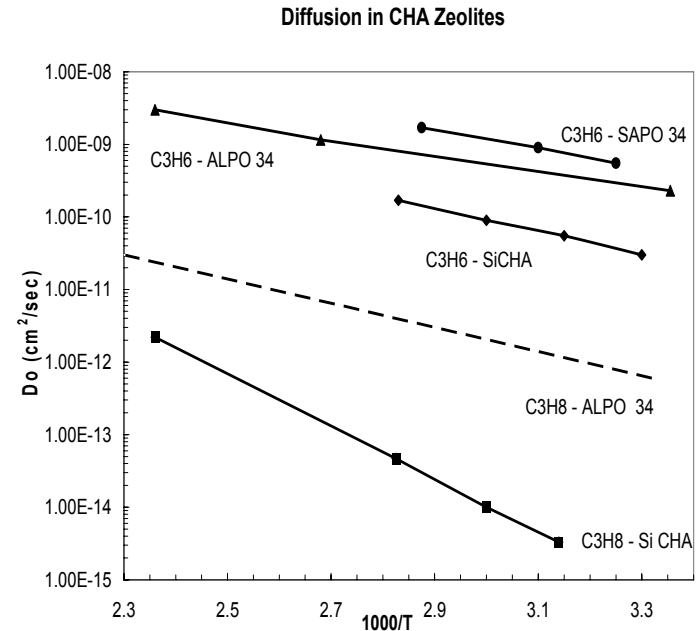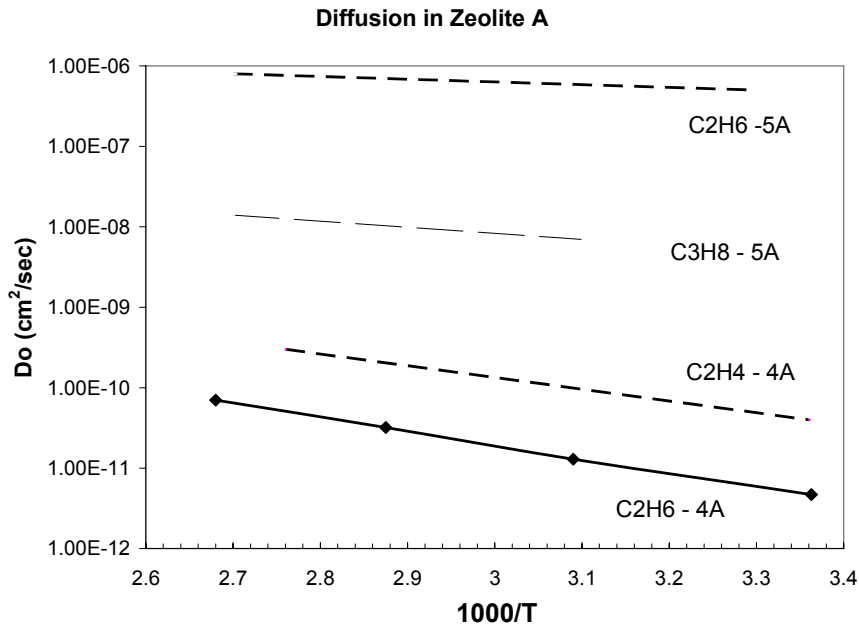Importance: Recovery of light olefins from cat-cracker off-gas

Equilibrium Selectivity (C_2H_4/C_2H_6)<<10

Kinetic Selectivity ~ 10 in 4A zeolite

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

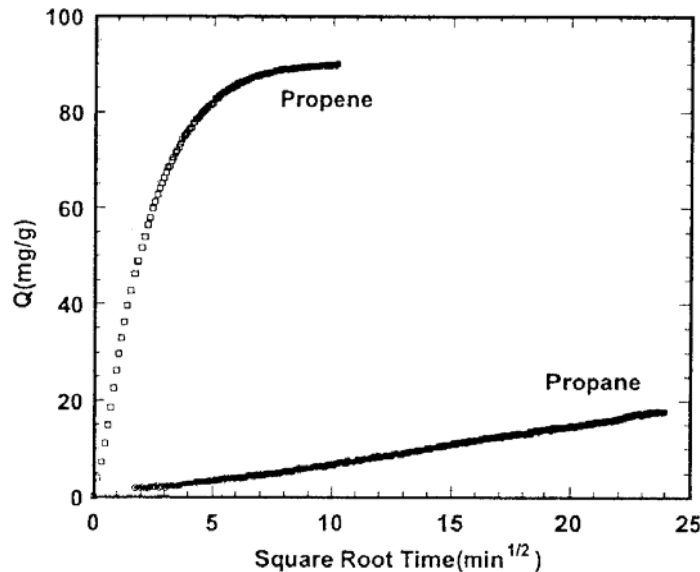# Olefin/Paraffin Separation
Diffusion in Type A and CHA Zeolites

Diffusion in Zeolite A

C2H6 -5A

C3H8 - 5A

C2H4 - 4A

C2H6 - 4A

Do (cm^2/sec)

1000/T

Diffusion in CHA Zeolites

C3H6 - SAPO 34

C3H6 - ALPO 34

C3H6 - SiCHA

C3H8 - ALPO 34

C3H8 - Si CHA

Do (cm^2/sec)

1000/T

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

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Olefin/Paraffin Separation

Comparative Uptake Rates for C_3H_6 and C_3H_8 in SiCHA at 80°C
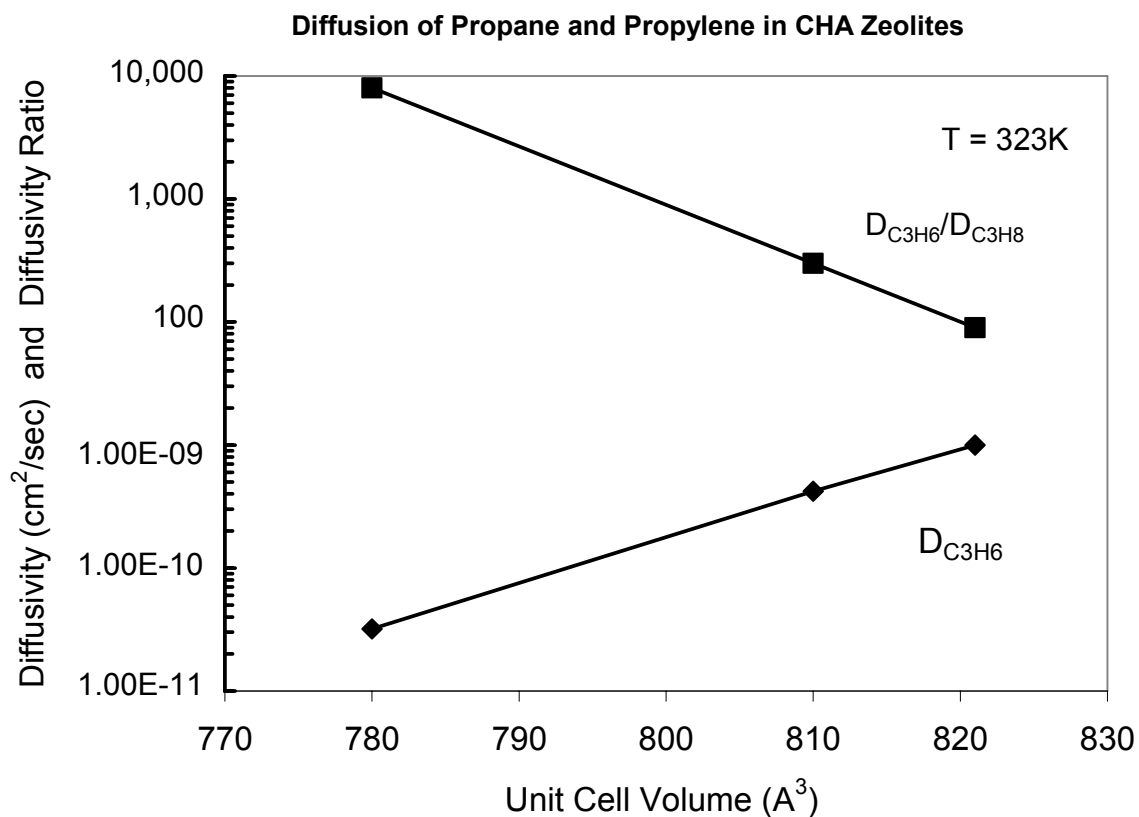

From Olson et al. *Microporous and Mesoporous Mats.* **67,** 27-33 (2004)
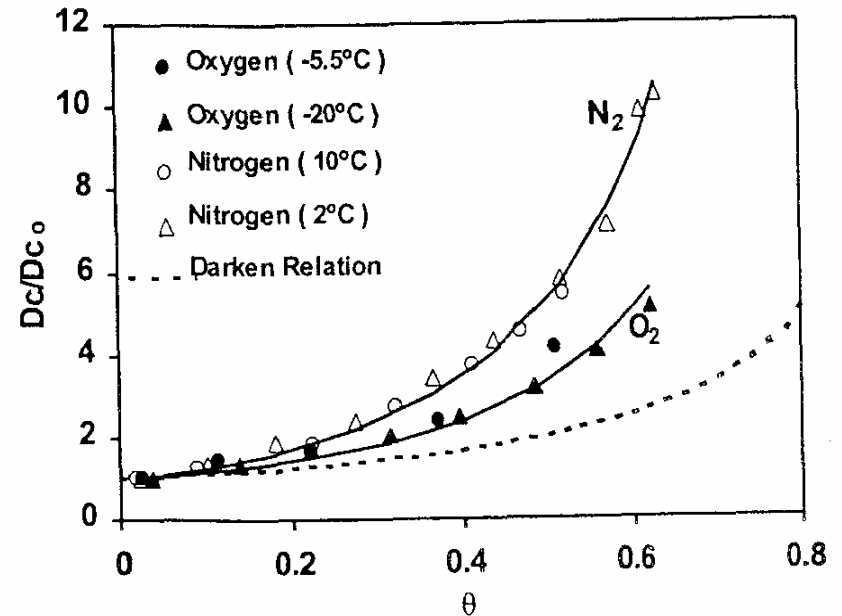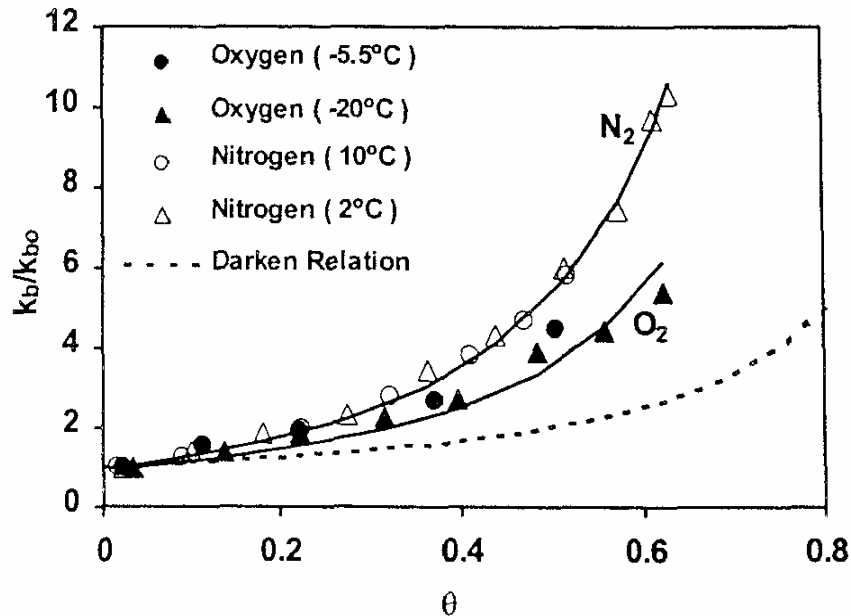
Olefin/Paraffin Separation

Variation of D and Kinetic Selectivity with Unit Cell Size

Diffusion of Propane and Propylene in CHA Zeolites

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

Kinetic Separation
N_2/O_2 Separation on CMS
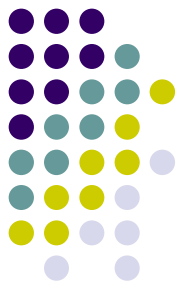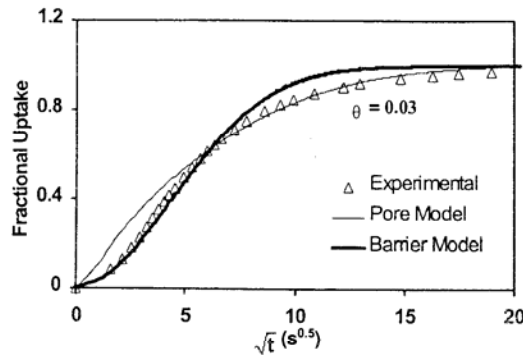

Strong concentration dependence of both k and D

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

Kinetic Separation
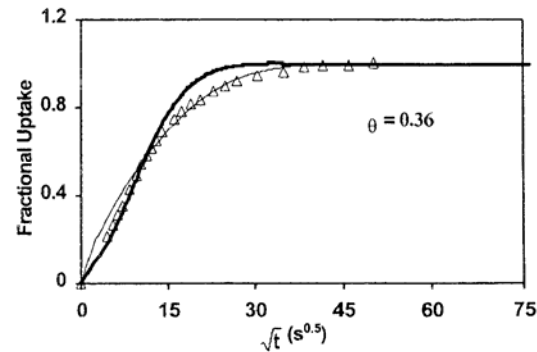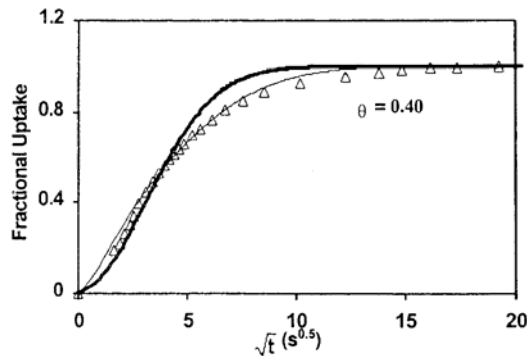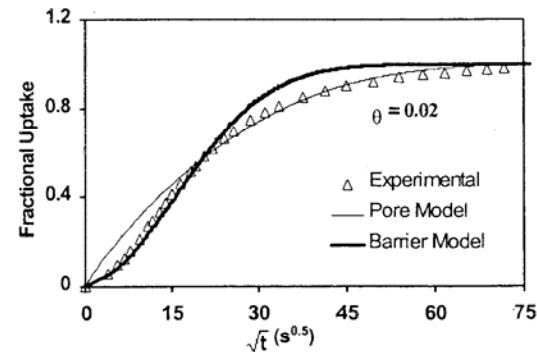## N_2/O_2 Separation over CMS

Nitrogen Uptake in BF CMS at 2°C

Oxygen Uptake in BF CMS at −20°C
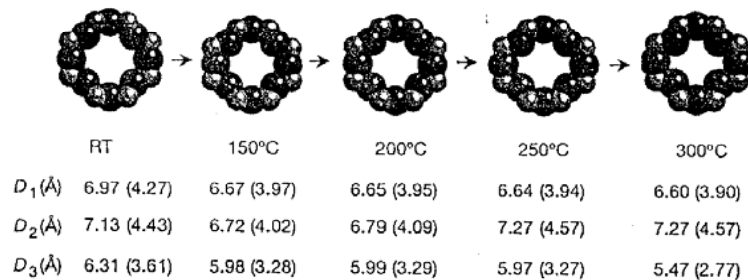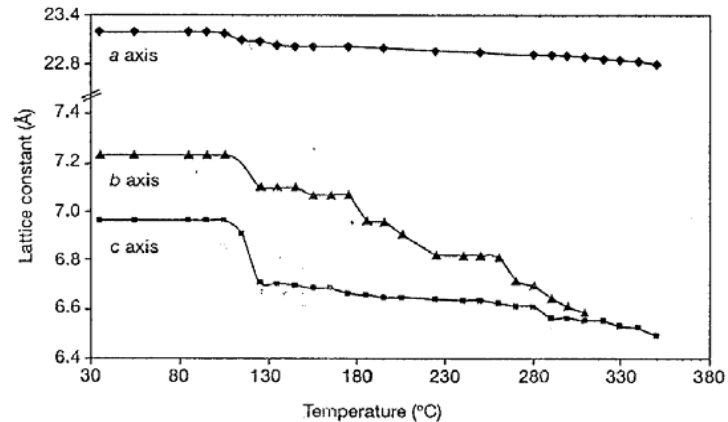
O_2 diffuses **much** faster than N_2.

Transition from Surface Resistance to Intracrystalline Control at longer times.

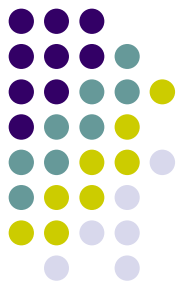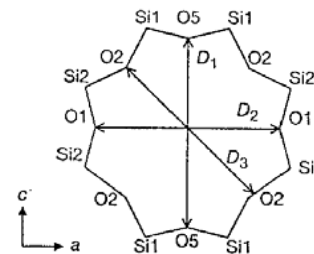From Sundaram et al. 7th Int. Conf. on *Fundamentals of Adsorption*. Nagasaki, May 2001.

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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)

	RT	150°C	200°C	250°C	300°C
D_1 (Å)	6.97 (4.27)	6.67 (3.97)	6.65 (3.95)	6.64 (3.94)	6.60 (3.90)
D_2 (Å)	7.13 (4.43)	6.72 (4.02)	6.79 (4.09)	7.27 (4.57)	7.27 (4.57)
D_3 (Å)	6.31 (3.61)	5.98 (3.28)	5.99 (3.29)	5.97 (3.27)	5.47 (2.77)

ETS-4 (270°C dehydration)
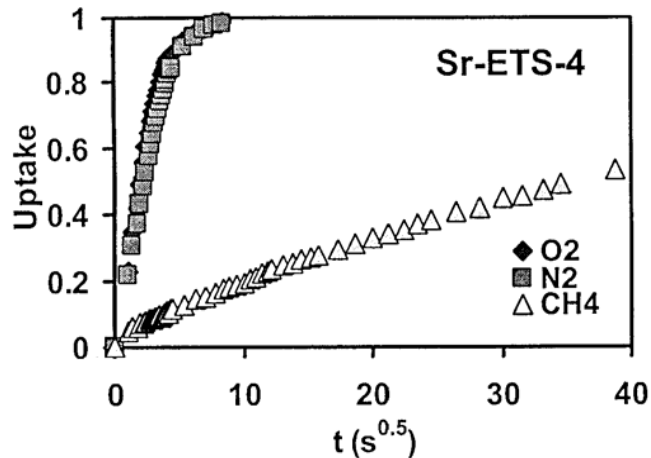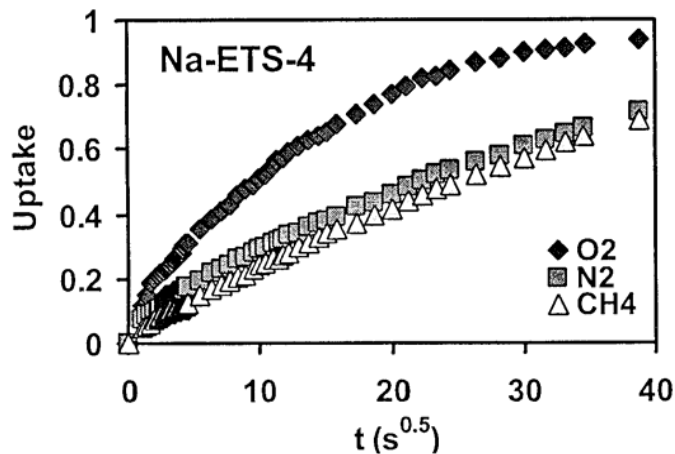
Sr-ETS-4; High kinetic selectivity N_2/CH_4 (Farooq)

Catalytic Reactions
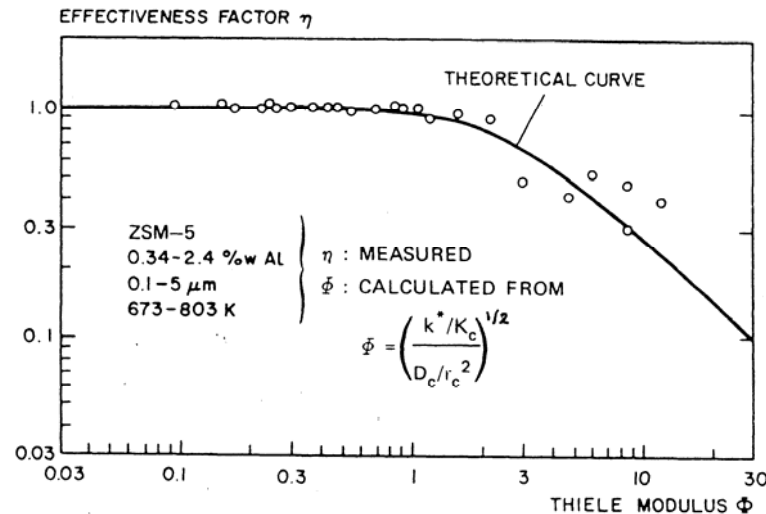## *Effect of Intraparticle Diffusion on Reaction Rate*

1st Order Rxn: $k_e = k\eta$

$$\eta = \frac{3}{\phi}\left[1 - \frac{1}{\text{Tanh}\phi}\right]$$

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

Isomerization of 2, 2 DMB on HZSM-5
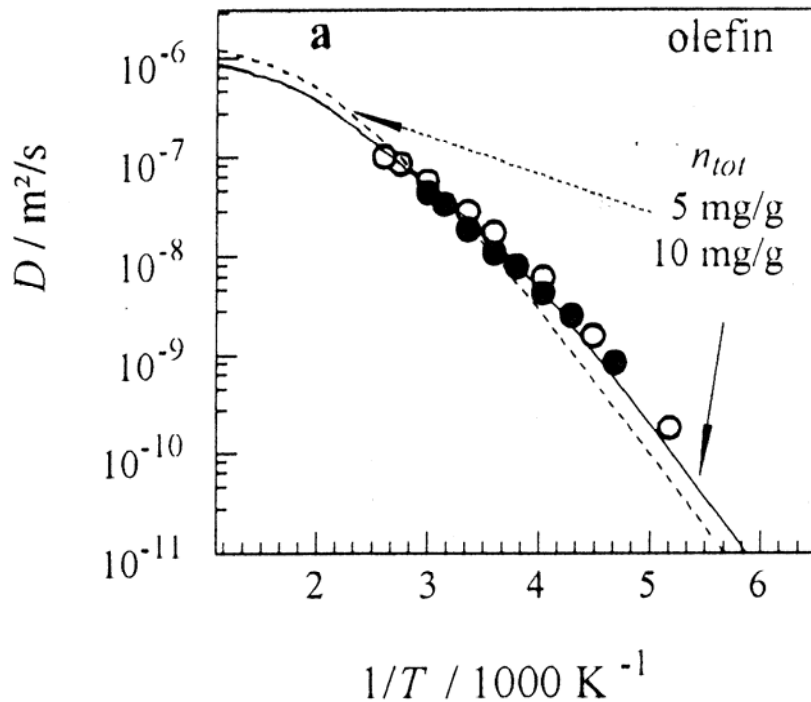
From Post et al. 6th Int. Zeolite Conf. Reno, 1984.

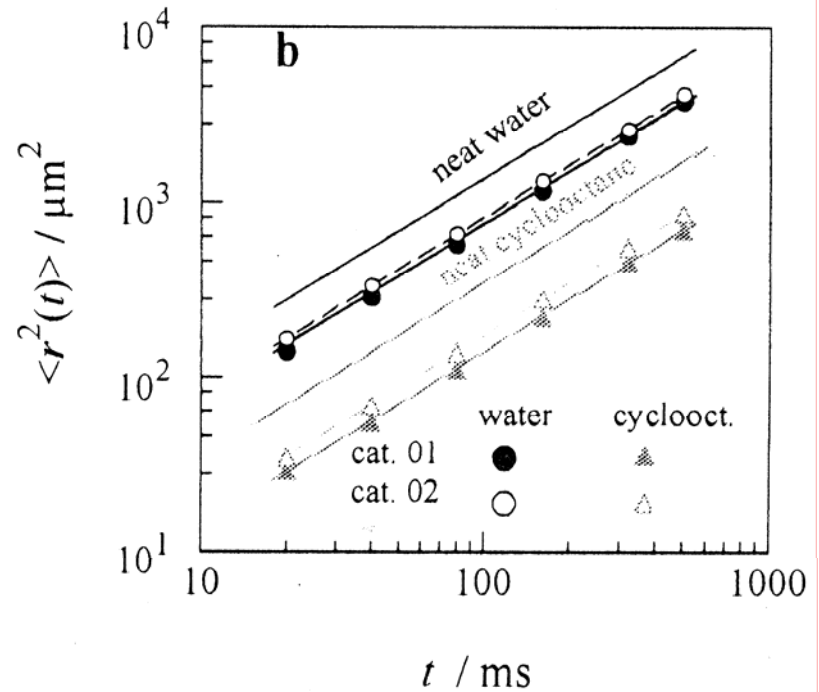# Macropore Diffusion in Catalyst Particles
Measurement by PFG NMR

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

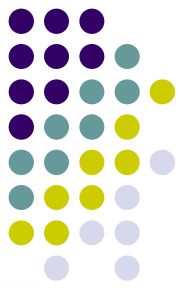Measured and Predicted D_{eff}

Determination of Tortuosity (τ)

Stallmach and Crowe – this conference

Catalytic Cracking (1)

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

(particles ~100μm)

$D_{intracrystalline}$ in micropores of zeolite

$D_{intraparticle}$

D_{inter} in mesopores of "matrix"
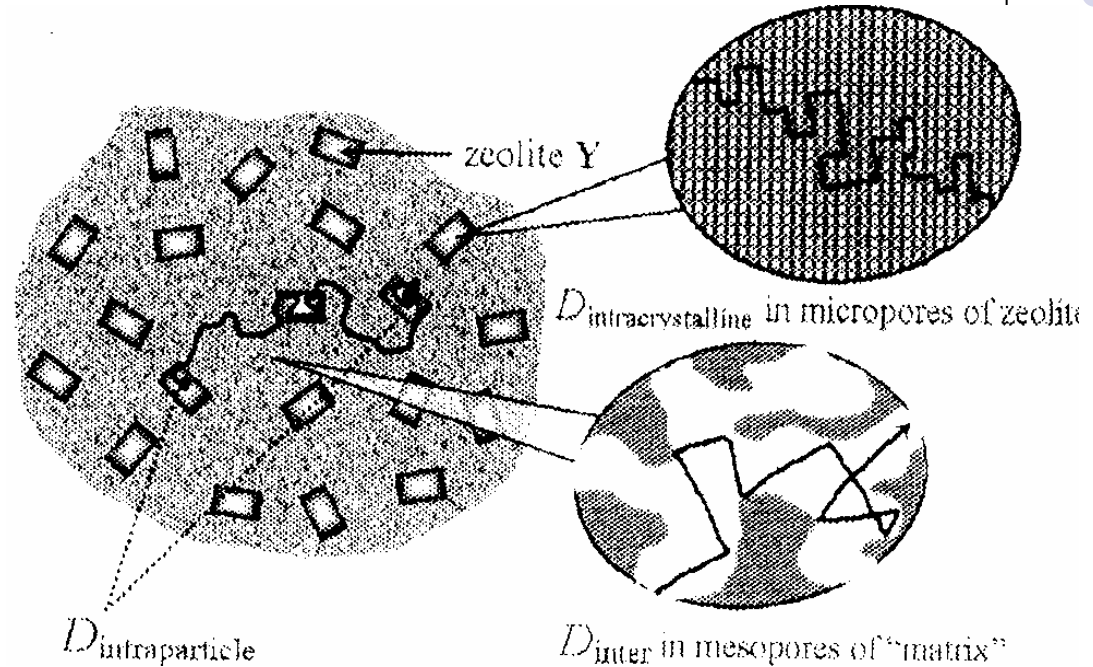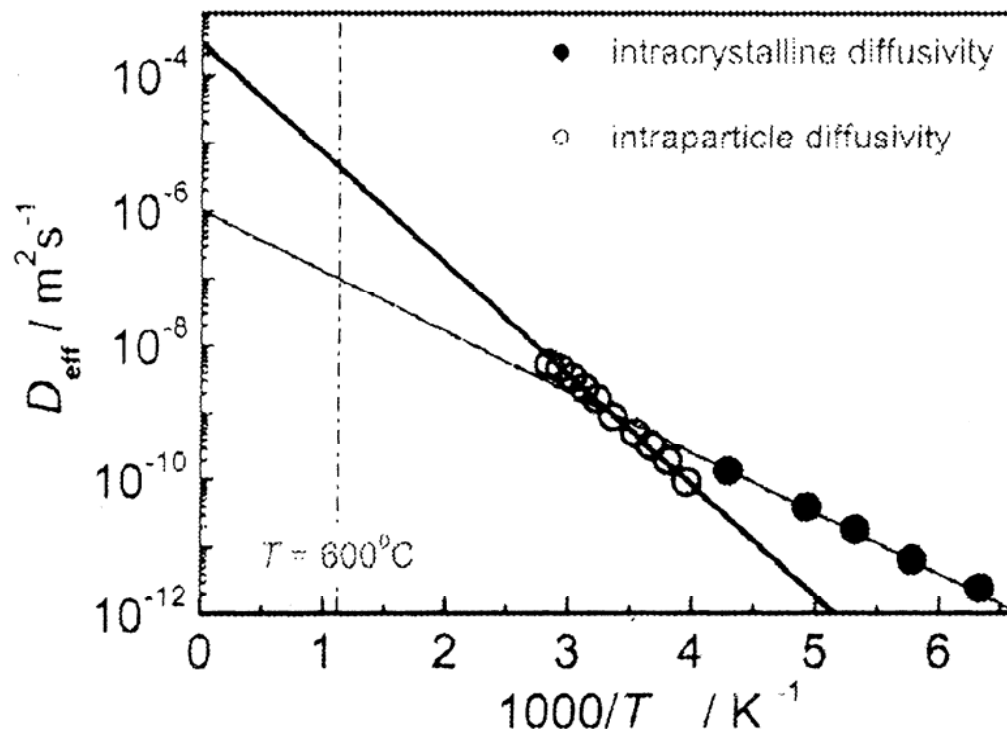
Which resistance is dominant?

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

Kortunov et al – this conference

Catalytic Cracking (2)

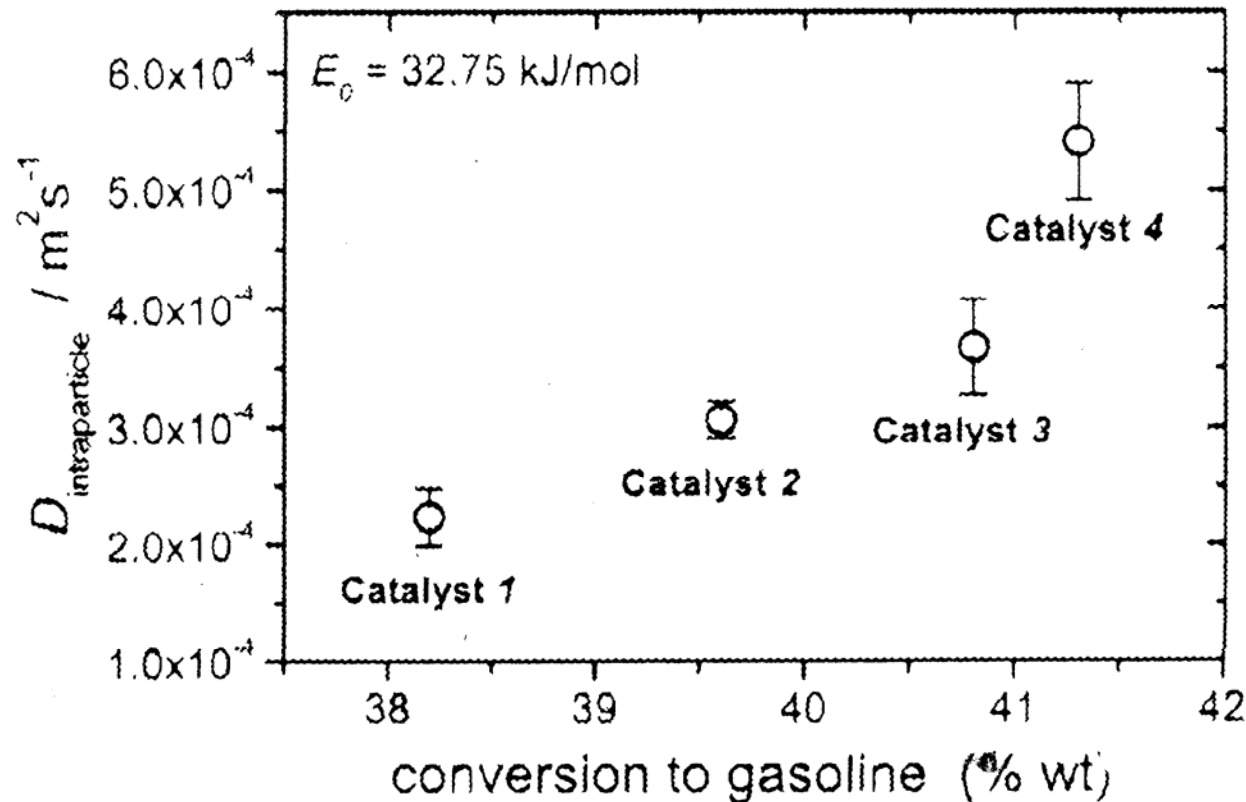**PFG NMR**: $D_{macro}/D_{micro} \sim 10$ (at 600°C)

$t_{micro}/t_{macro} \sim 10^{-3}$ Macro diffusion controls
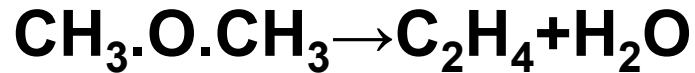
From Kortunov et al – this conference

Catalytic Cracking (3)

Conversion correlates with D_{macro}/K

From Kortunov et al – this conference

Methanol to Olefins (MTO)

$$2\ CH_3OH \rightarrow CH_3.O.CH_3 + H_2O$$
$$CH_3.O.CH_3 \rightarrow C_2H_4 + H_2O$$
$$1.5\ C_2H_4 \rightarrow C_3H_6$$

Slow polymerization to higher Mol.Wt.species

Diffusion and Reaction of Methanol in SAPO 34

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)
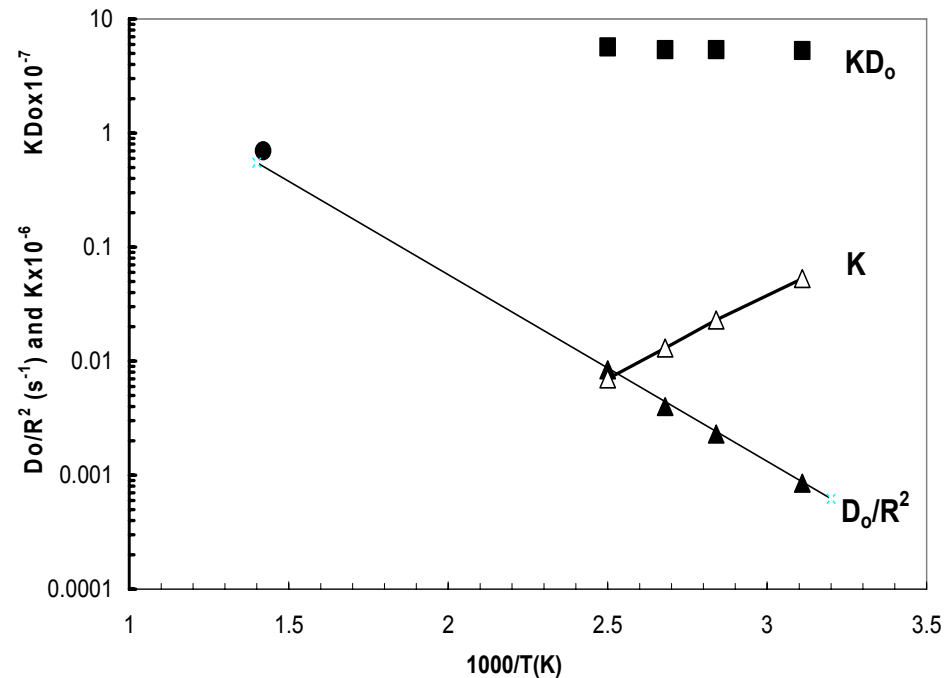
MTO Reaction (2)
Effect of Diffusion on Yield
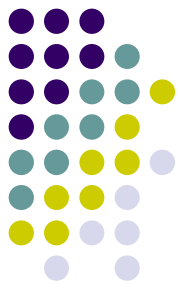
For high yield of C$_2$" and C$_3$" $\dfrac{\phi_2}{\phi_1} = \left(\dfrac{k_2 D_{MeOH}}{k_1 D_{DME}} \right)^{\frac{1}{2}} \gg 1$

(DME formed in Rxn1 must remain within zeolite crystal for long enough to achieve high conversion)
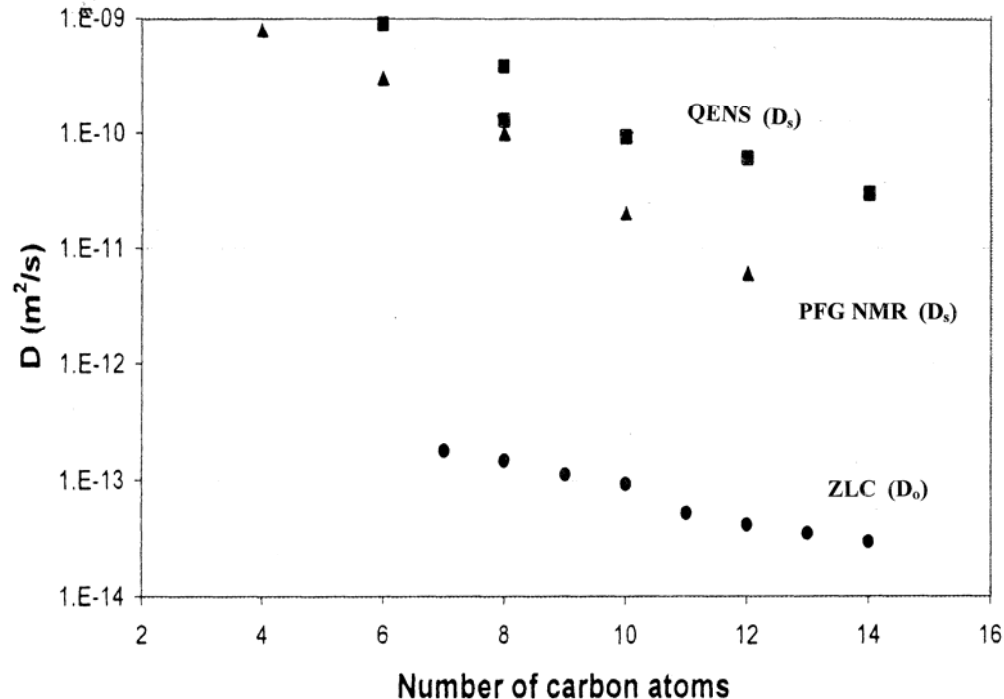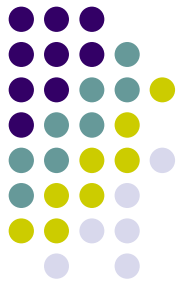
As catalyst ages coke build-up reduces D$_{DME}$ more than D$_{MEOH}$; C$_2$H$_4$ yield increases

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

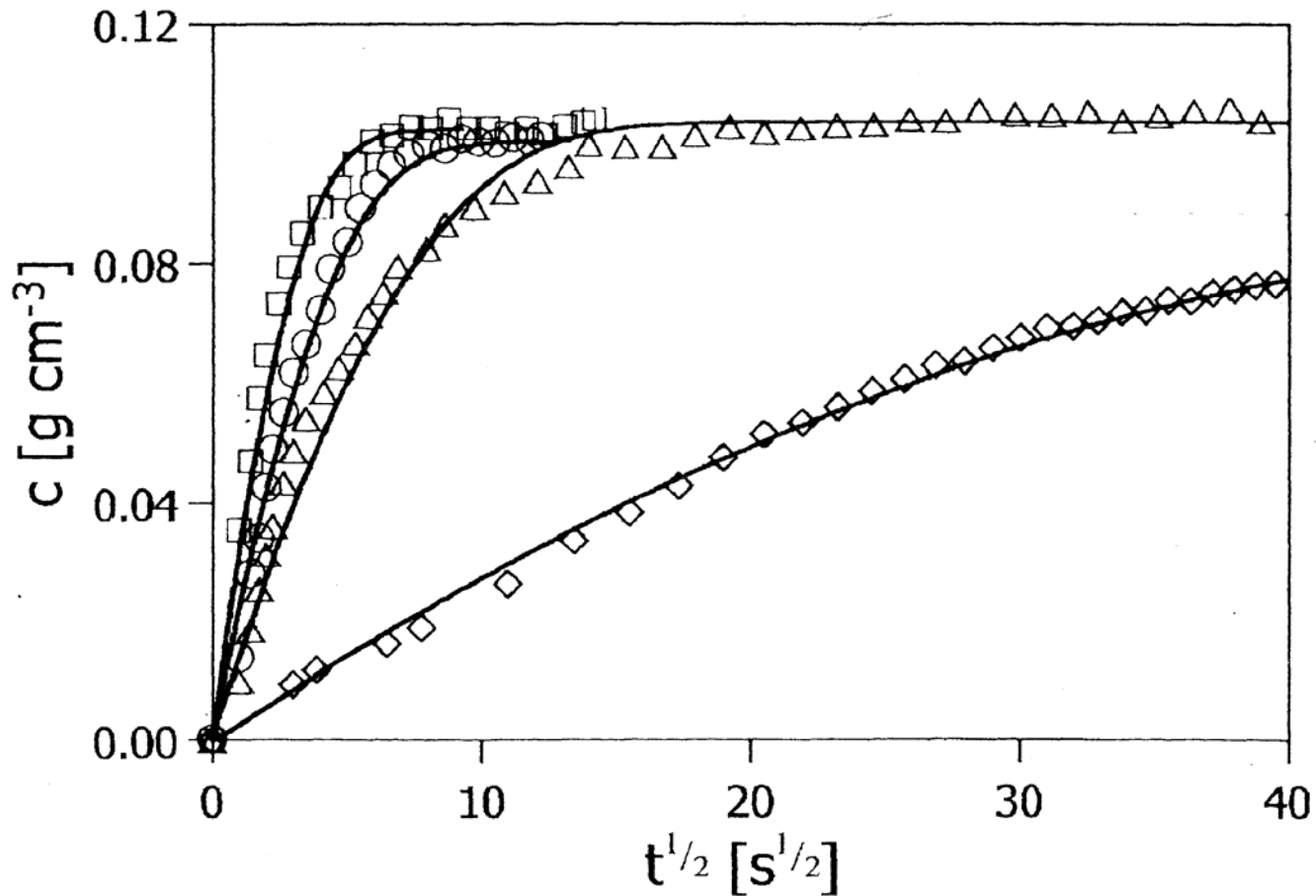Comparison of experimental results at 423K.

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

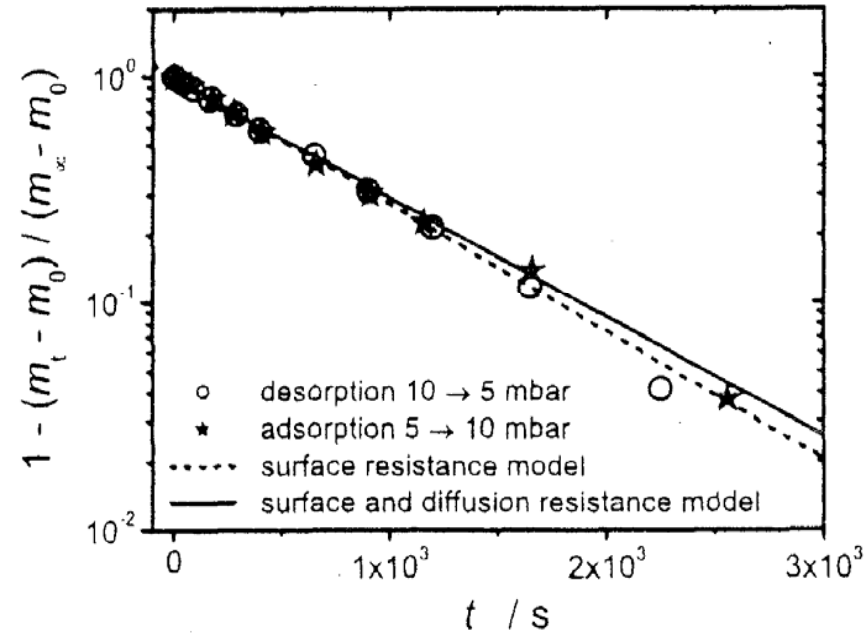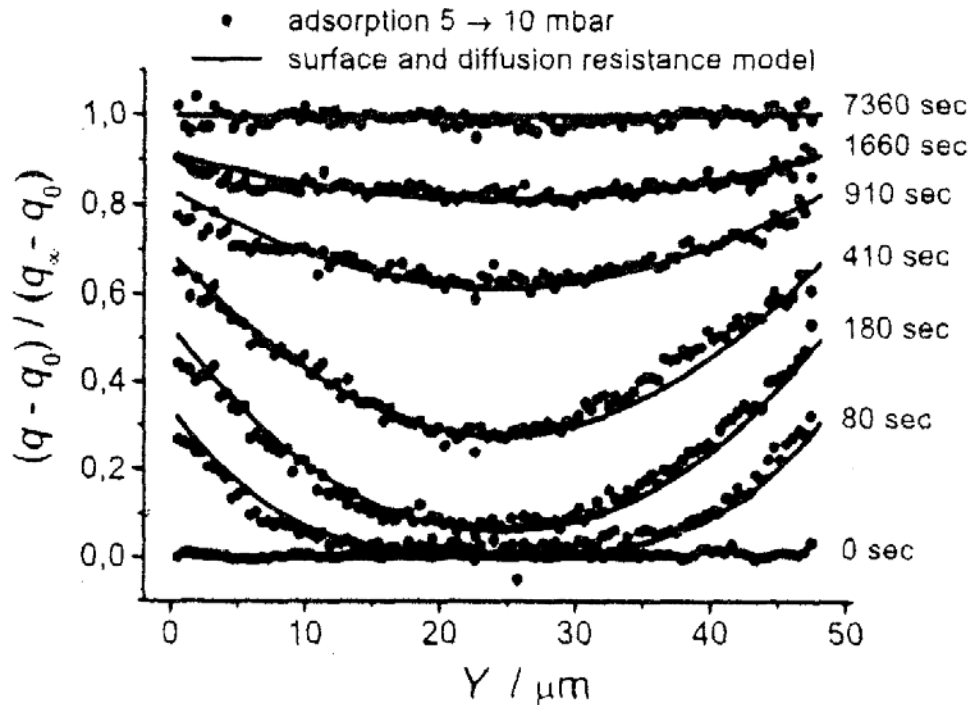# Evidence of Surface Barrier Control
n-Hexane – Silicalite at 298K

Uptake rate in HF etched sample is increased by ~300

From Wloch, *Microporous and Mesoporous Mats. (2004)*
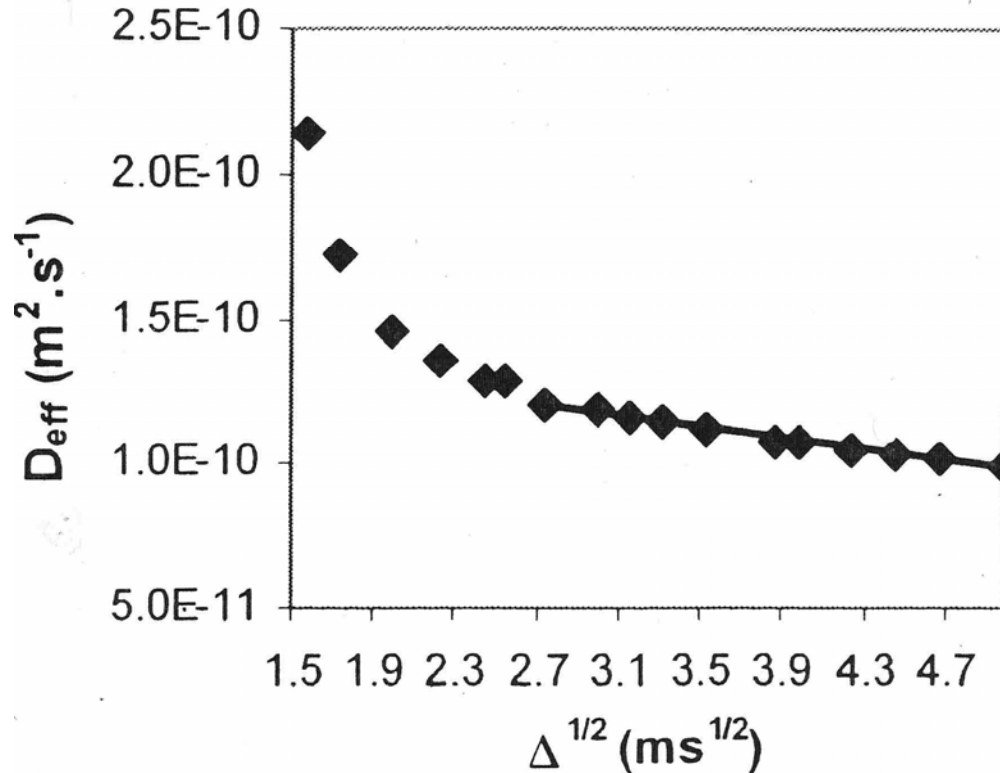
Evidence for Surface Resistance + Internal Diffusion
Methanol in Ferrierite

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