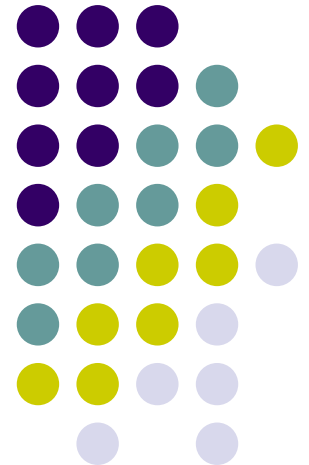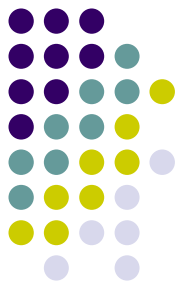# From Diffusion Research to Industrial Processes

Dechema, Frankfurt, *Oct26th2006*

Douglas M.Ruthven, University of Maine,
Orono, ME04469, U.S.A.

From Diffusion Research to Industrial Processes

Kinetic vs Equilibrium Separations:

Most adsorption Separations – Selectivity depends on equilibrium differences.

A few important separations depend on differences in kinetics.

Examples: Linear/Branched paraffins

Air Separation for N_2

Olefin/Paraffin separation

N_2/CH_4 Separation (Natural Gas)

Olefin/Paraffin Separations

High demand for light olefins (for polyethylene/polypropylene production).

Recovery of olefins from cat-cracker off-gas is preferred route.

Requires C_2H_4/C_2H_6 and C_3H_6/C_3H_8 separation.

C_3H_6 separation is especially important.

Processes for Olefin/Paraffin Separation

Cryogenic Distillation: Relative volatility is small so process is energy intensive.

Extractive Distillation.

Adsorption offers promising alternative.

Cationic zeolites show equilibrium selectivity for olefins (~12 on 5A).

Olex process (UOP) uses simulated counter-current flow to achieve a pure product with limited selectivity.

Traditional 8-Ring Zeolites for Olefin/Paraffin Separation (5A)

Equilibrium and Kinetic Data at 323K

	K	K_{ratio}	$D(cm^2s^{-1})$	D_{ratio}
C_2H_4	5100		$\sim 10^{-6}$	
		} 15	}	1.0
C_2H_6	340		$\sim 10^{-6}$	
C_3H_6	8.3×10^4		1.4×10^{-8}	
		} 12	}	2
C_3H_8	6800		7×10^{-9}	

Traditional 8-Ring Zeolites for Olefin/Paraffin Separation (4A)

Equilibrium and Kinetic Data at 323K

	K	K_{ratio}	D	D_{ratio}
C_2H_4	4600		1.5×10^{-11}	
		} 15		} 3
C_2H_6	300		5.5×10^{-12}	

C_3H_6/C_3H_8 Kinetics too slow on 4A

Olefin/Paraffin Separation by Adsorption

Olefins are preferentially adsorbed (stronger equilibrium **and** faster kinetics).

Recovery of preferentially adsorbed component at high purity is difficult – requires very high equilibrium selectivity or diffusivity ratio.

Traditional adsorbents (4A, 5A or 13X) do not give required product purity.
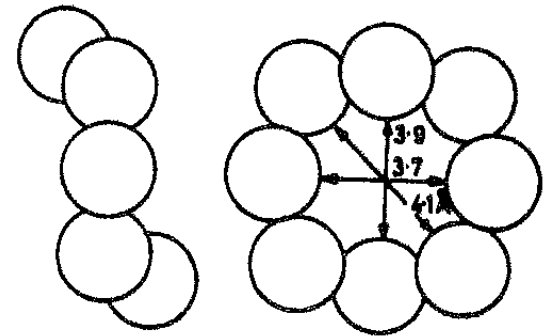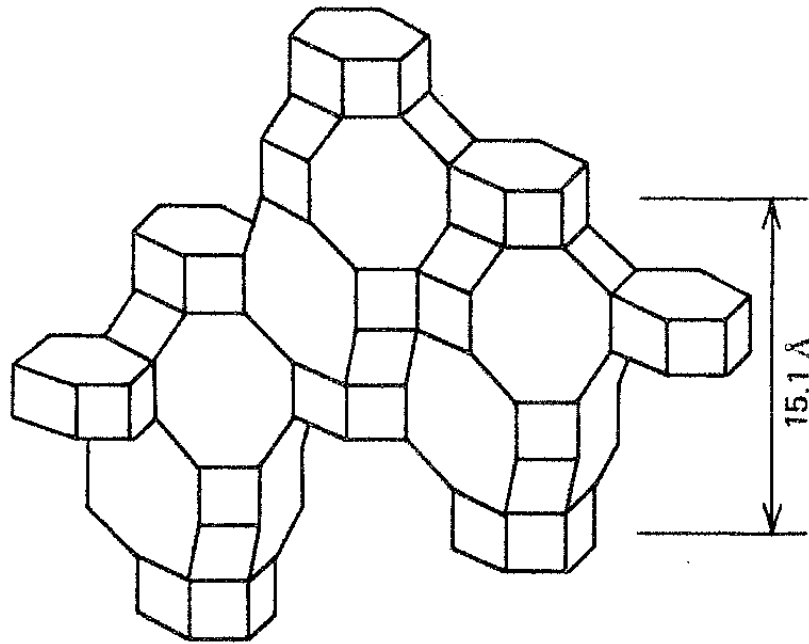
Look for adsorbents with high enough kinetic selectivity to give molecular sieve separation.

Structure of DDR3
8-ring silica framework: 2-dimensional channels (4.4x3.6A)

$[4^3 5^{12} 6^1 8^3]$

$[4^3 5^6 8^1]$

$[5^{12}]$
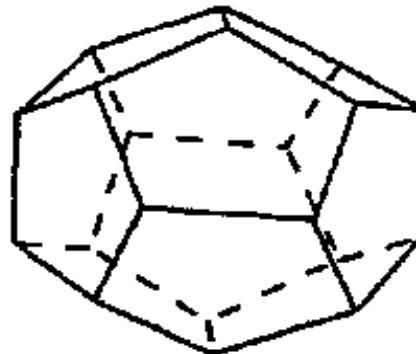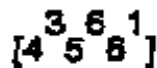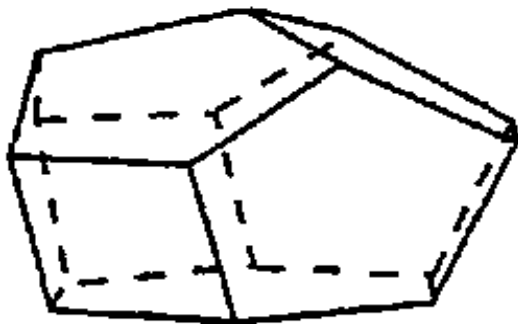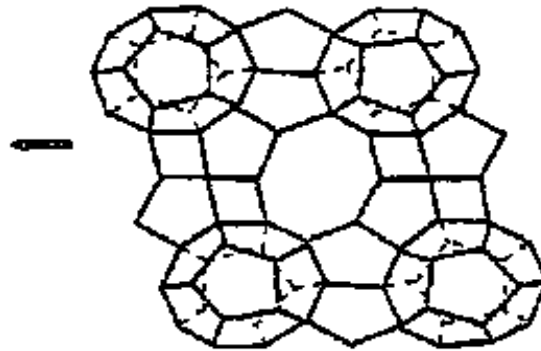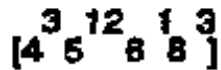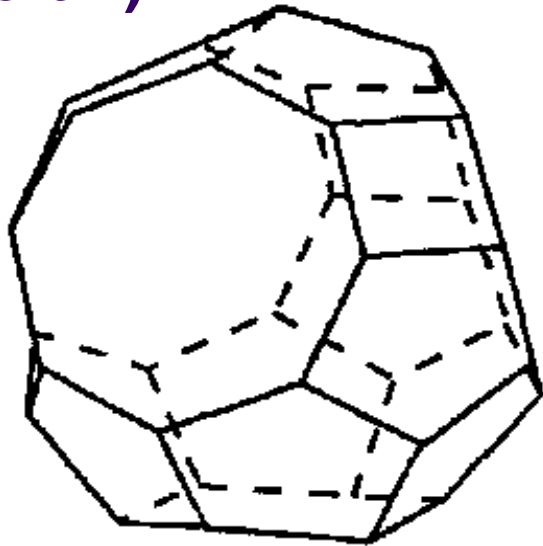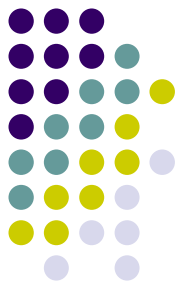
Chabazite Structure (CHA)

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
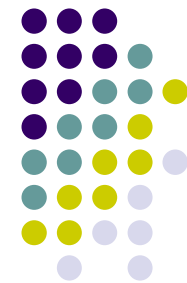
CHA Variants

Bond Lengths (Angstroms)

Al–O =1.75;

(1/2)(Al–O + P-O) =1.64

Si-O= 1.61

Reduction in unit cell volume and window dimensions with Si/Al Ratio:

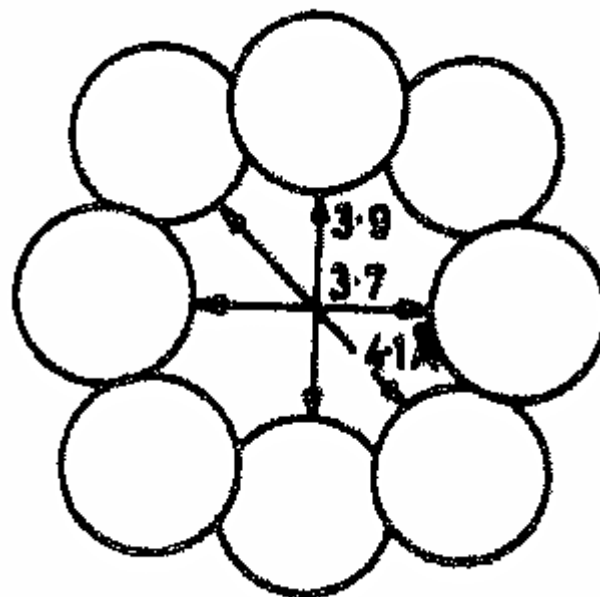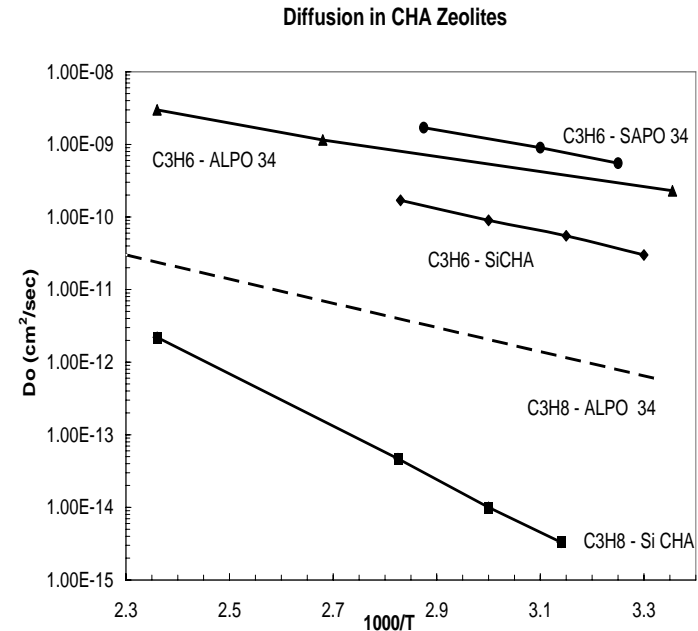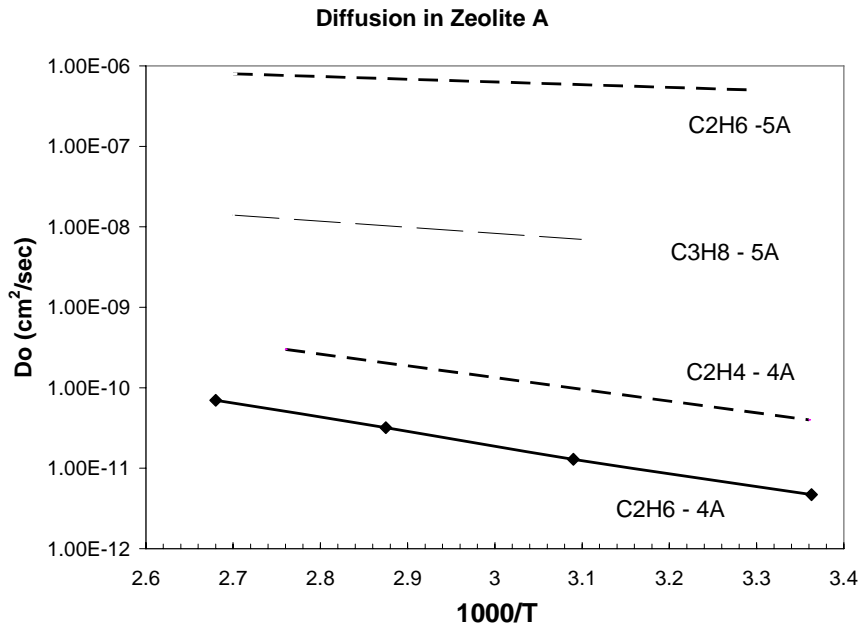CHA > SAPO34 > AlPO34 > SiCHA

Modified CHA Adsorbents

8-Ring Zeolites   (Angstroms)

4A	3.8x4.2
5A	4.2x4.2
CHA	3.9x4.1
SAPO34	3.8x4.3
AlPO34	3.7x4.5
SiCHA	3.65x4.3
DDR3	3.6x4.4 (not CHA)

Olefin/Paraffin Separation
Diffusion in Type A and CHA Zeolites

Diffusion in Zeolite A

- C2H6 -5A
- C3H8 - 5A
- C2H4 - 4A
- C2H6 - 4A

D_o (cm^2/sec)

1000/T

Diffusion in CHA Zeolites

- C3H6 - ALPO 34
- C3H6 - SAPO 34
- C3H6 - SiCHA
- C3H8 - ALPO 34
- C3H8 - Si CHA

D_o (cm^2/sec)

1000/T

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

Correlation of Diffusivity with Window Dimension

C3H6 at 323K

Minimum Diameter (Angstrom)
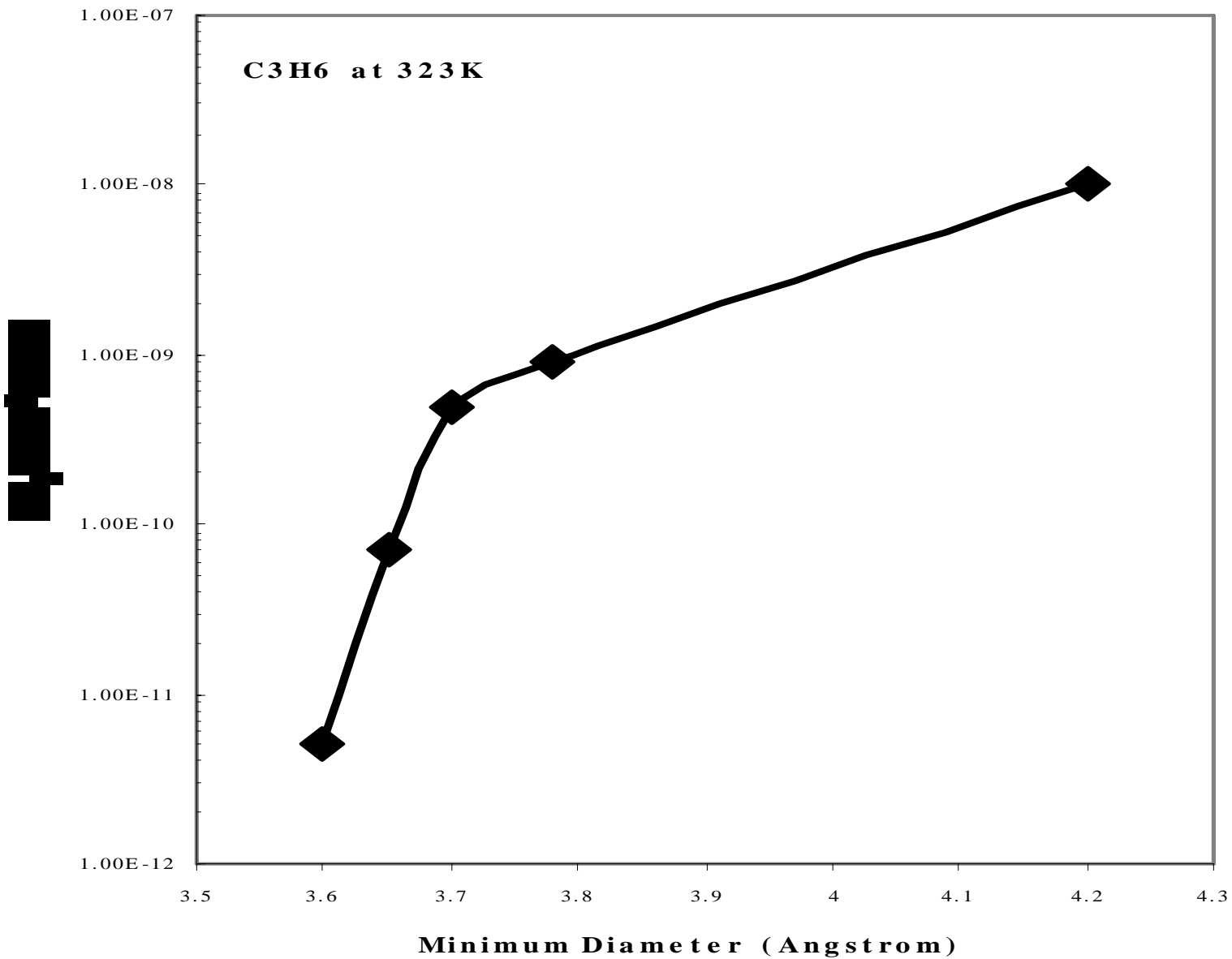
Olefin/Paraffin Separation

Variation of D and Kinetic Selectivity with Unit Cell Size

Diffusion of Propane and Propylene in CHA Zeolites
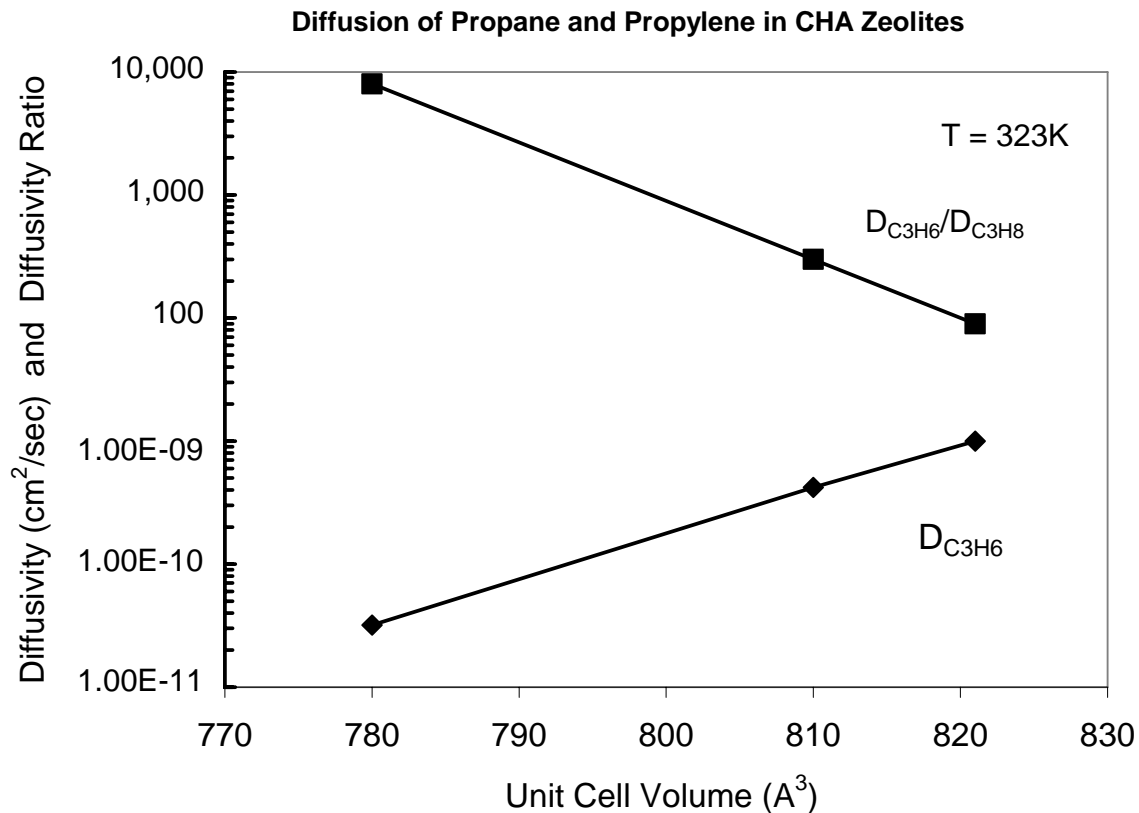
From Reyes et al. U.S. Patent 6,730,142 B2 May 4, 2004

Comparison of Activation Energies
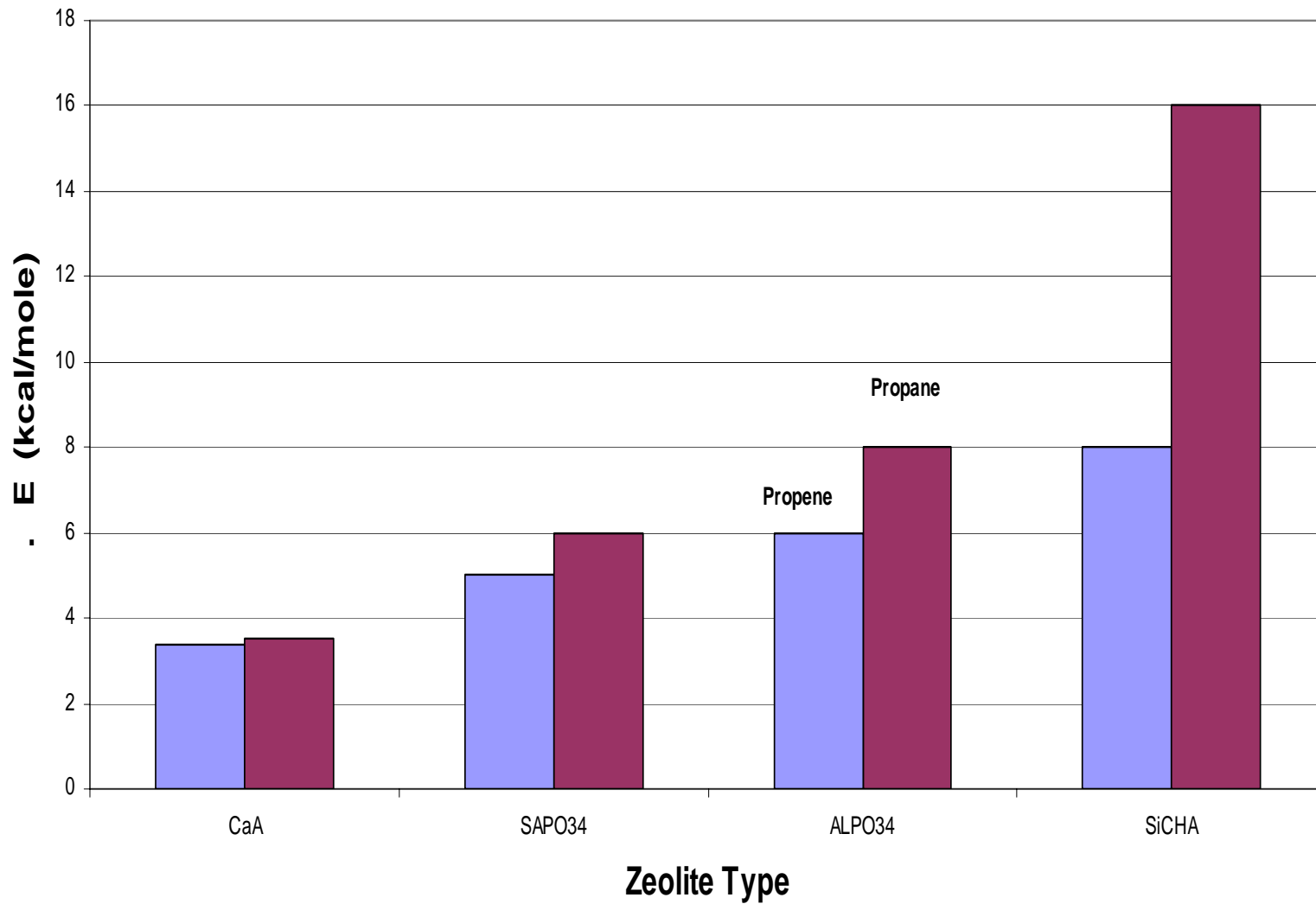
Preferred Adsorbents for C_3H_6 (323K)

	K	K_{ratio}	$D(cm^2s^{-1})$	D_{ratio}
SiCHA:				
C_3H_6	700		8×10^{-11}	
	}	0.8	}	11,500
C_3H_8	900		7×10^{-15}	
DD3R				
C_3H_6	1000		5×10^{-12}	
	}	1 ??	}	10,000
C_3H_8	No data		6×10^{-16}	

Olefin/Paraffin Separation

Comparative Uptake Rates for C_3H_6 and C_3H_8 in SiCHA at 80°C
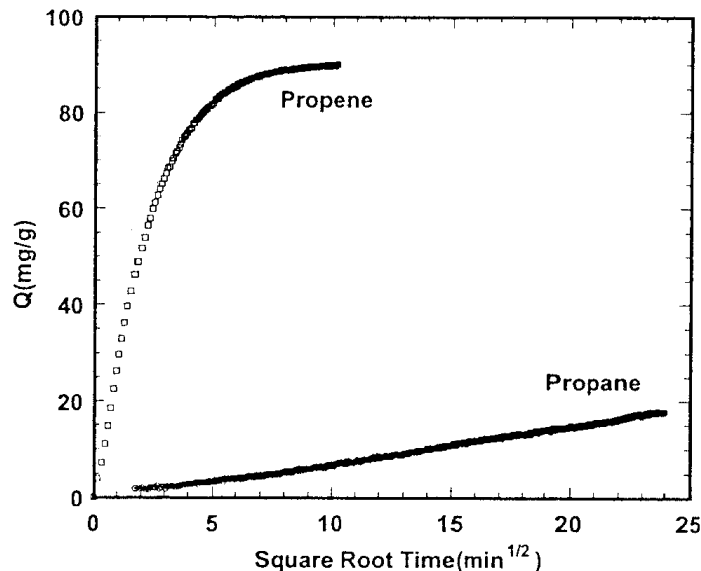
From Olson et al. *Microporous and Mesoporous Mats.* **67,** 27-33 (2004)

N_2/CH_4 Separation

Pipeline specifications for natural gas limit N_2 content to < 3%.

Many gas reservoirs contain higher N_2 %.

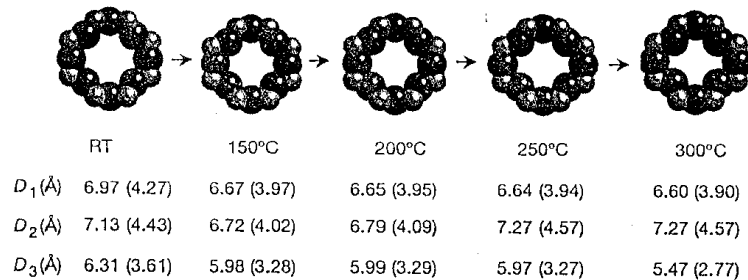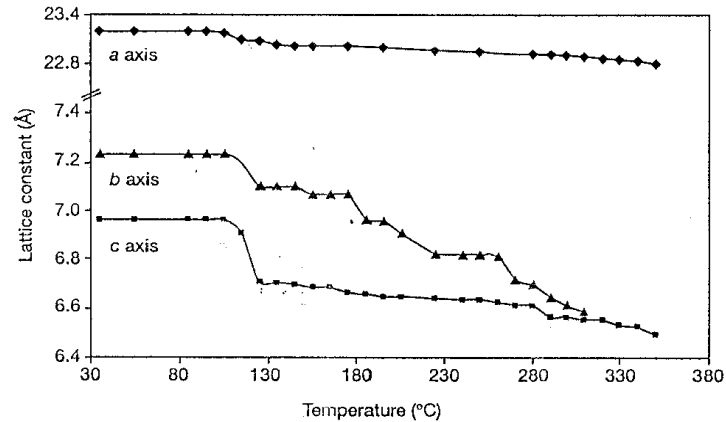On non-polar adsorbents CH_4 is adsorbed more strongly.

On polar adsorbents N_2 and CH_4 are adsorbed at similar rates and with similar equilibria.

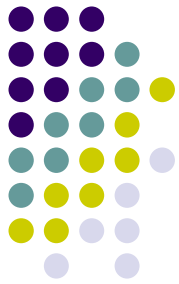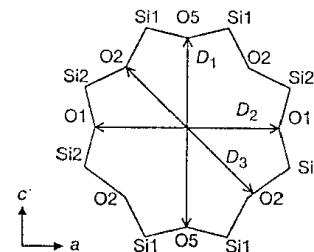For an efficient separation adsorbent should adsorb N_2 preferentially

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)
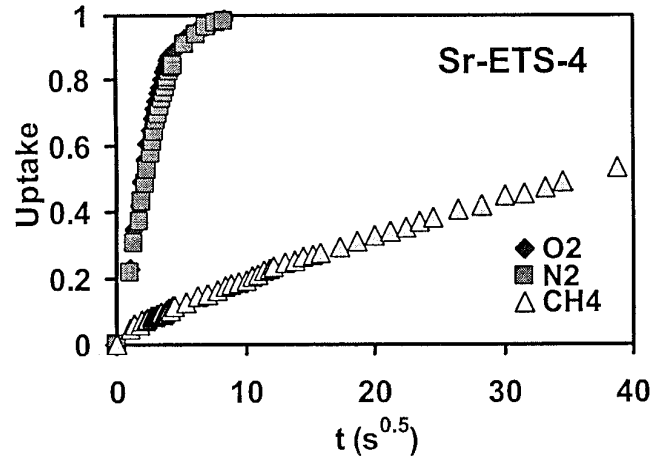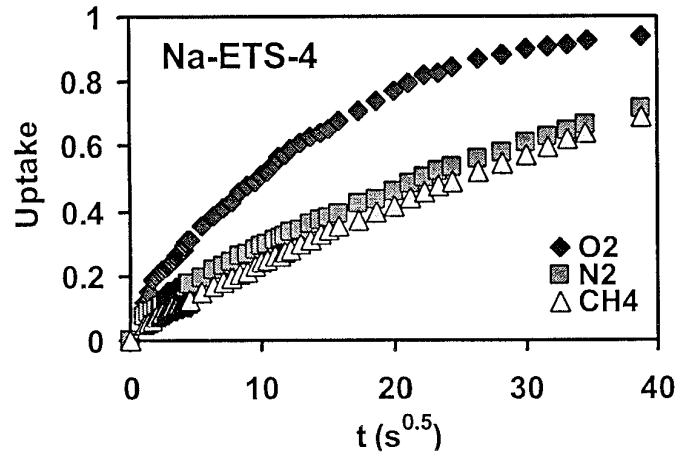
Sr-ETS-4; High kinetic selectivity N_2/CH_4 (Farooq)

N$_2$ – CH$_4$ Separation

Little difference in either kinetics or equilibrium on most adsorbents.

Sr–ETS4 offers good kinetic selectivity with

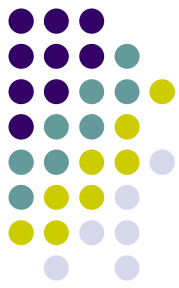N$_2$ (minor component) as the preferred species.

PSA Process with periodic thermal regeneration to remove higher hydrocarbons.

Conclusions
Olefin/Paraffin Separation

- Small differences in T – O distances lead to changes in free aperture of 8-rings.

- This has a large impact on the diffusional activation energy (and hence on D) for critically sized molecules.

- SiCHA andDDR3 have high kinetic selectivity for C_3H_6/C_3H_8 ($D_{ratio} > 10^4$).

- Under properly selected operating conditions (PSA or TSA) propylene can be recovered at high purity and high yield.

Conclusions (contd.)

Purification of N_2 containing Natural Gas

- CH_4 and N_2 are adsorbed at similar rates and similar strength on most polar adsorbents.

- SrETS-4 dehydrated at 270DegC shows high kinetic selectivity for N_2/CH_4, so N_2 is preferentially adsorbed, yielding a pure CH_4 product.

- Traces of higher hydrocarbons are slowly adsorbed necessitating periodic regeneration at elevated temperature.

Further Details

D.M.Ruthven and S.C.Reyes

"Adsorptive Separation of Light Olefins from Paraffins"   *Microporous and Mesoporous Materials* – in press.

D.H.Olson

U.S.Patent 6,488,741 (Dec3, 2002)

D.H.Olson et al.

Micro and Mesoporous Mats. **67,**27 (2004)

S.C.Reyes et al. *Ibid.* – in press (2006)

S.C.Reyes et al.

U.S.Patent 6,730,142 (May 4, 2004)