Vrije Universiteit Brussel
Department of Chemical Engineering

Chabazite: A zeolite allowing selective adsorption of short chain alcohols

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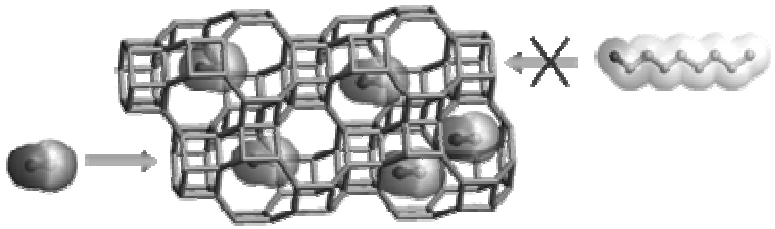
Gino V. Baron, Joeri F.M. Denayer

(* Dept. Chem. Eng., Monash University, AU)



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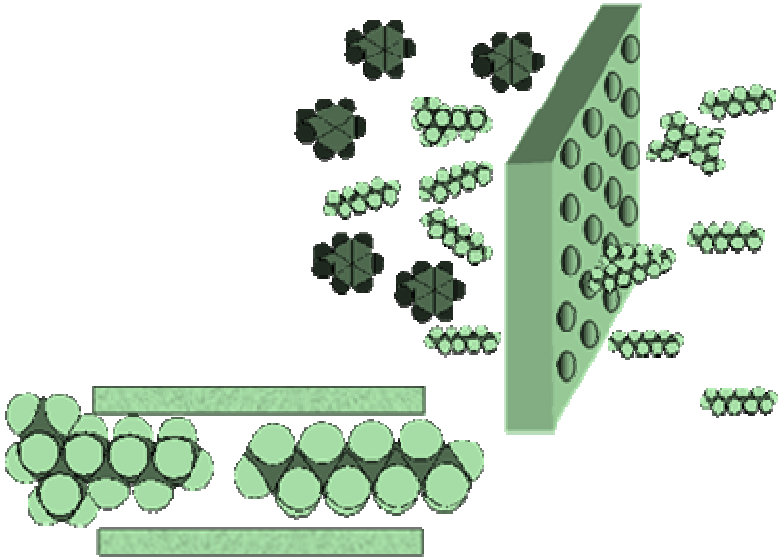
i-SUP 2008

Molecular sieving: Classical view

Small pore openings

- Large host-guest contact surface
- Classical shape and size selectivity
- Exclusion

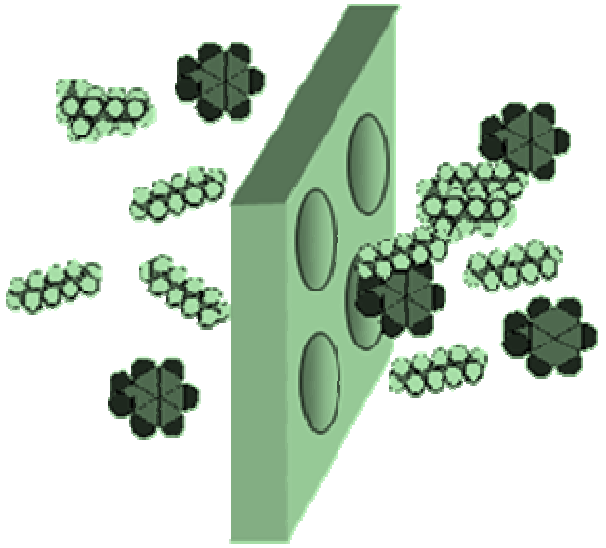
- Slow diffusion
- Larger molecules can not enter



Large pore openings

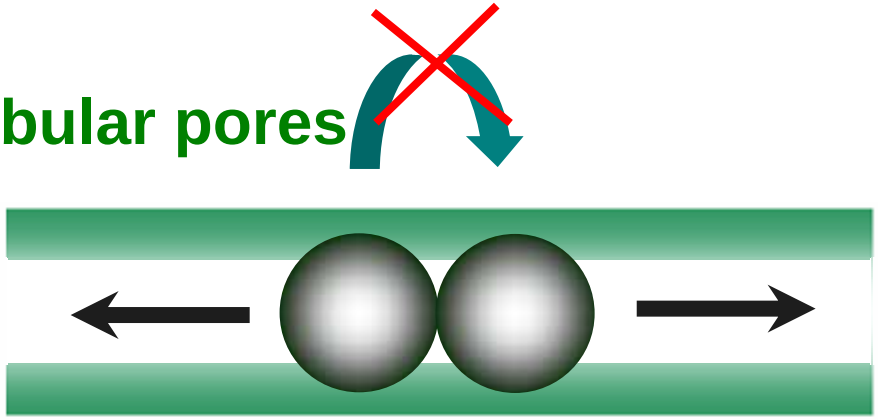
- Fast diffusion
- All molecules can enter

- No classical shape and size selectivity



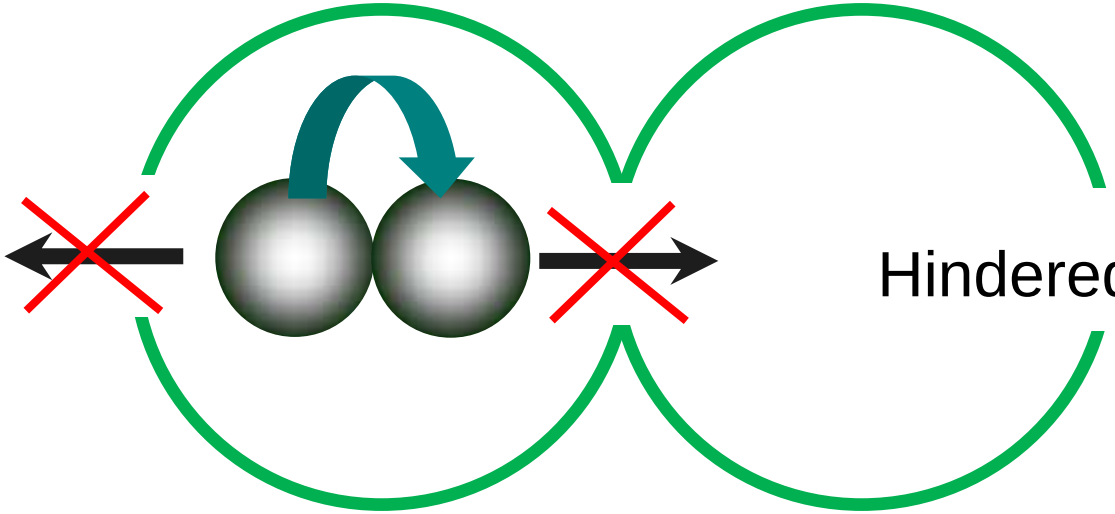
Zeolitic pore systems

Tubular pores



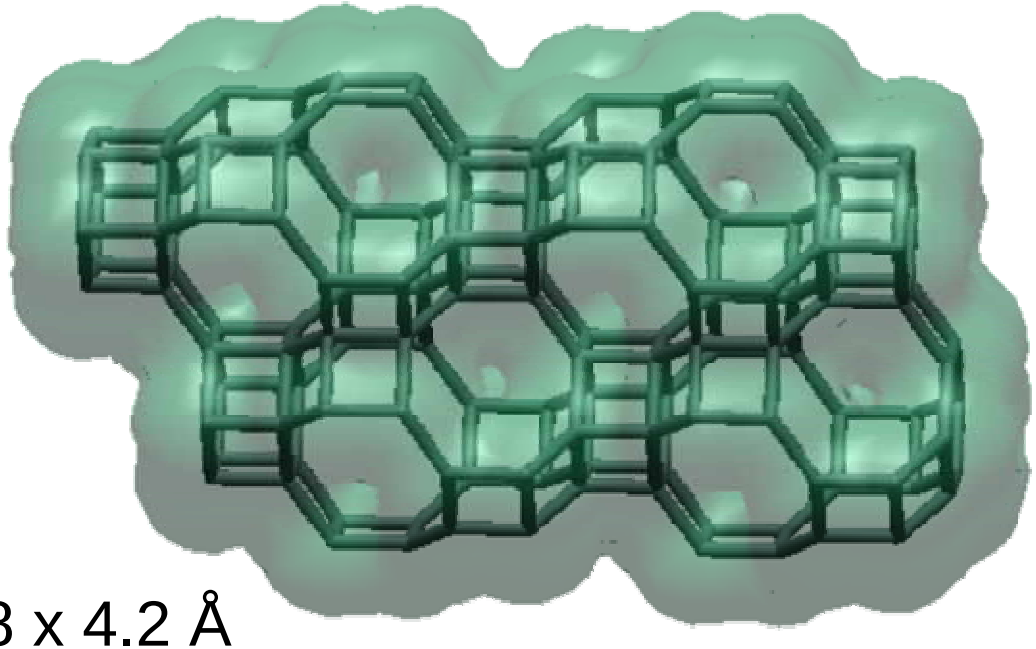
1D translation

Spherical pores: Cage and Window zeolites



Hindered intra-cage diffusion

Chabazite



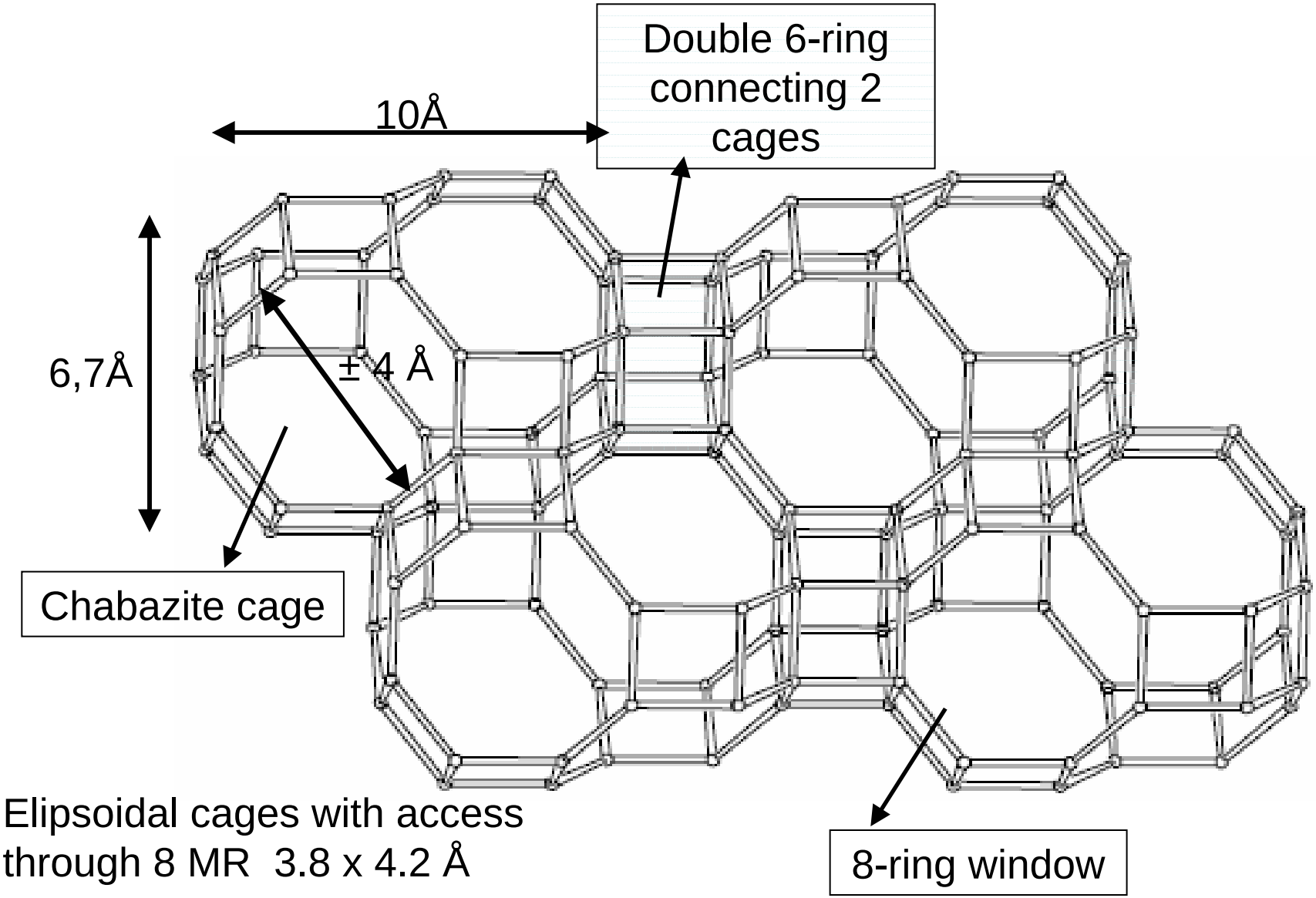
- Naturally occuring zeolite
- Elipsoidal cages connected

through 8 MR windows of 3.8 x 4.2 Å

- Separation of N_2 and O_2 from Ar
- Propane / propene separation
- Isostructural to SAPO-34: Methanol

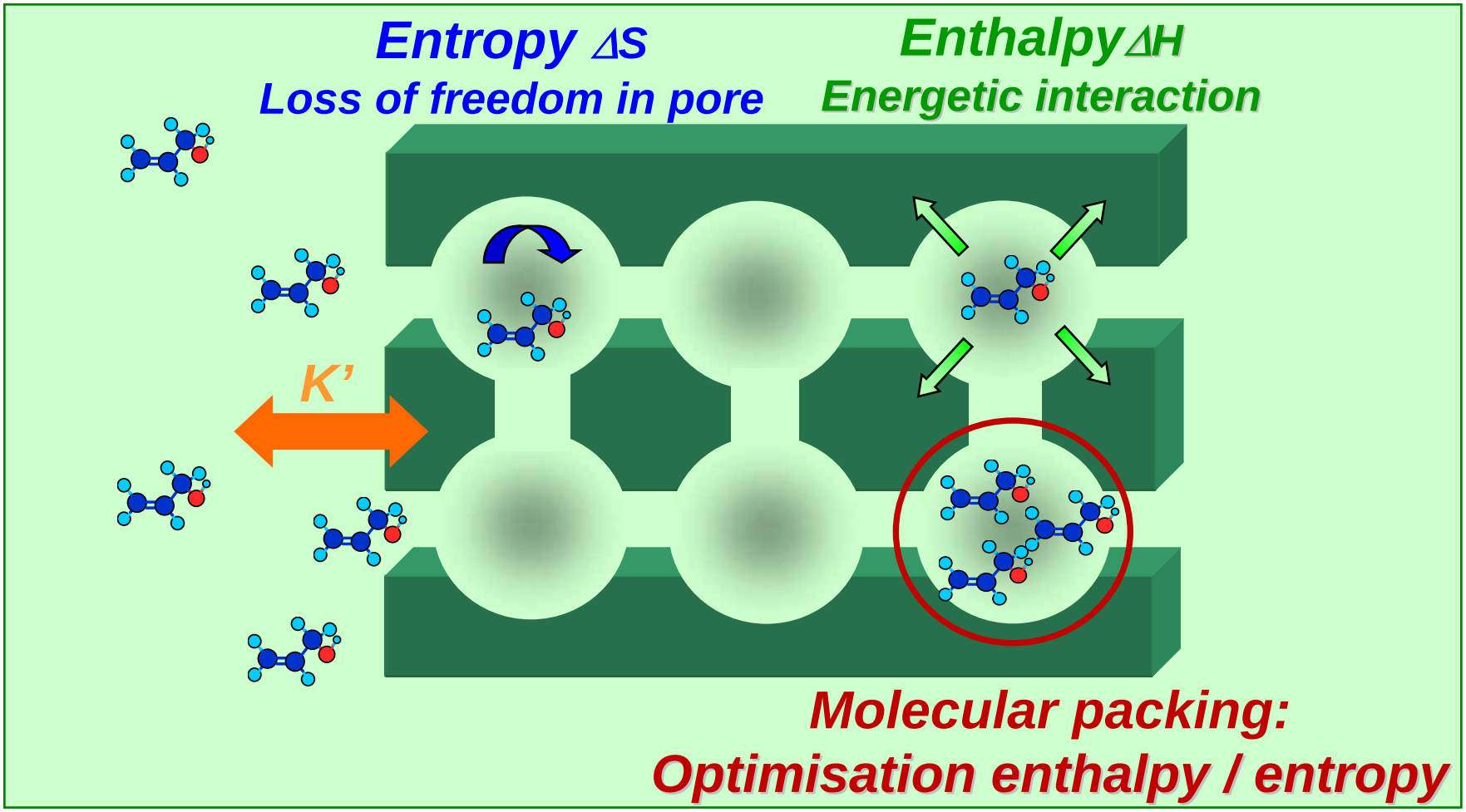
to Olefins (MTO) catalyst

Chabazite



Elipsoidal cages with access through 8 MR 3.8 x 4.2 Å

Molecular Assembling in Confined Spaces



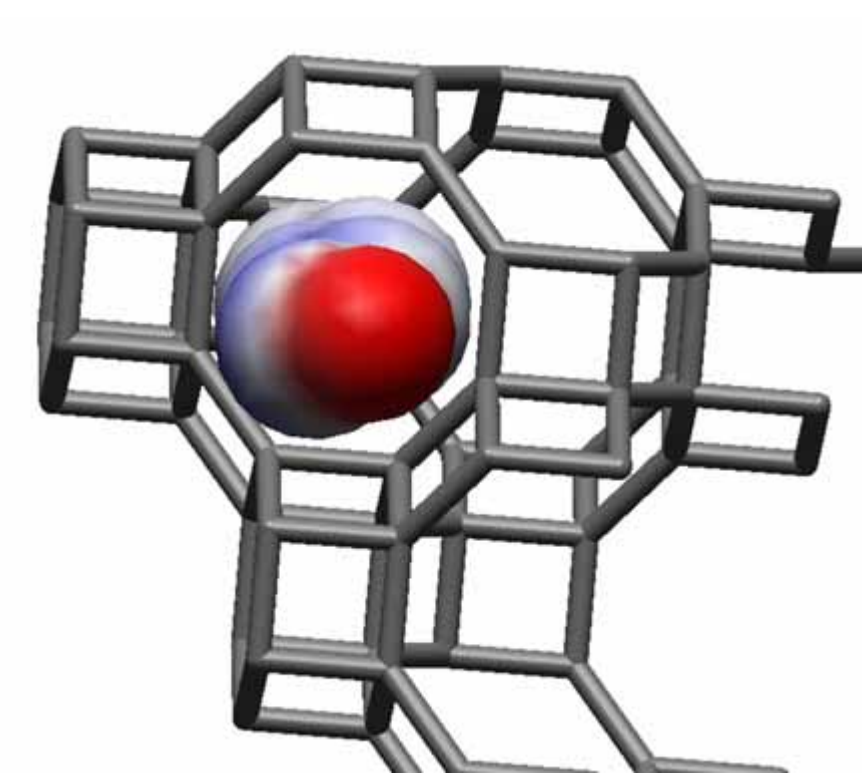
$$K' = K_0' \, e^{\frac{-\Delta H_0}{RT}} \qquad \Delta G_0 = -RT \ln(K' \rho_c RT)^* \qquad \Delta S_0 = \frac{\Delta H_0 - \Delta G_0}{T}$$

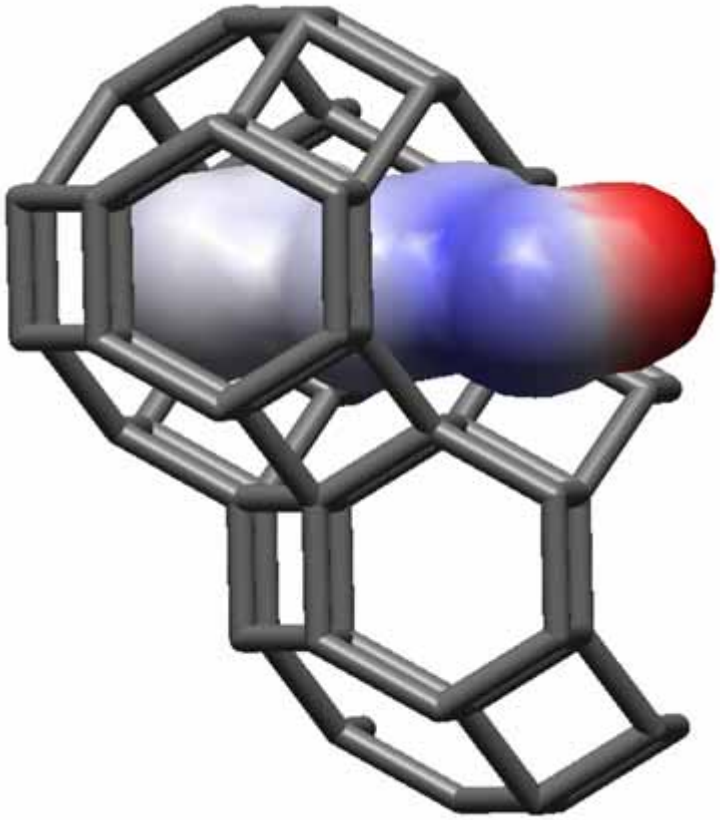
*Schenk M. et al, Journal of Catalysis, 214, 88-99, 2003

Chain length exclusion in CHA zeolite

Linear hydrocarbon chains
n-alkanes
alcohols
alkenes

Chain molecules in CHA

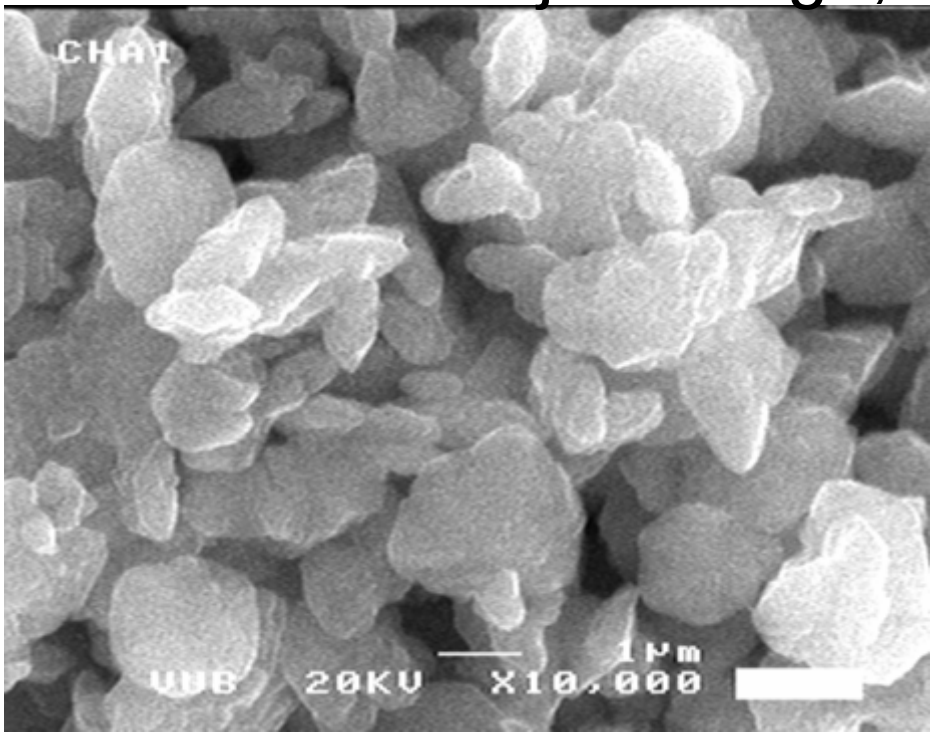


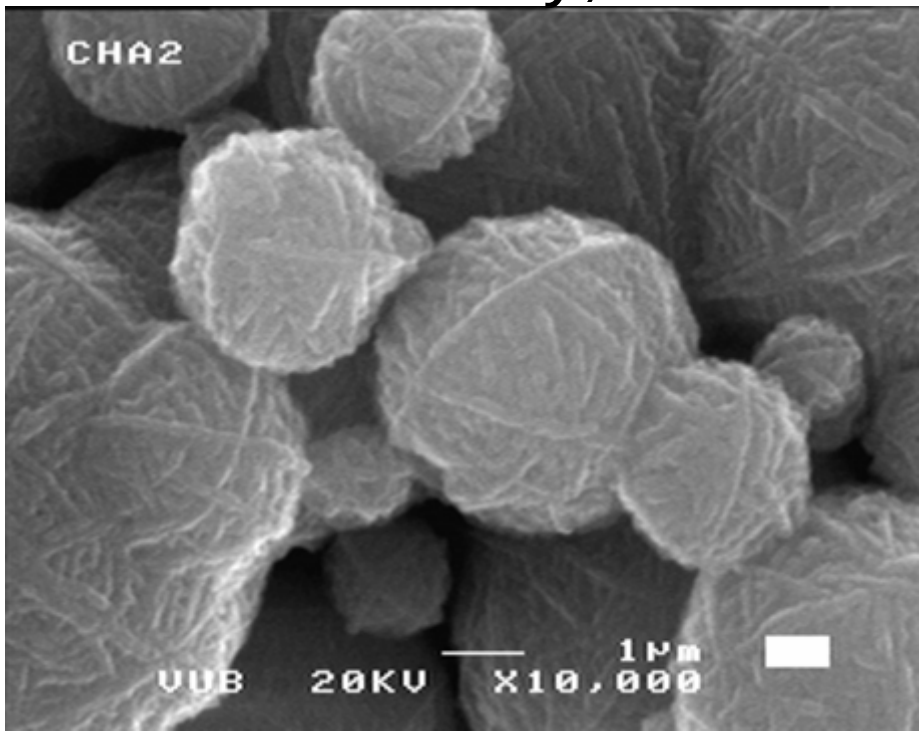


Linear hydrocarbon chains can diffuse through 10 MR

Synthetic CHA

Ranjeet Singh, Monash University, AU





M. Bourgogne, J.L. Guth, R. Wey, U.S. Patent 4503024, 1985

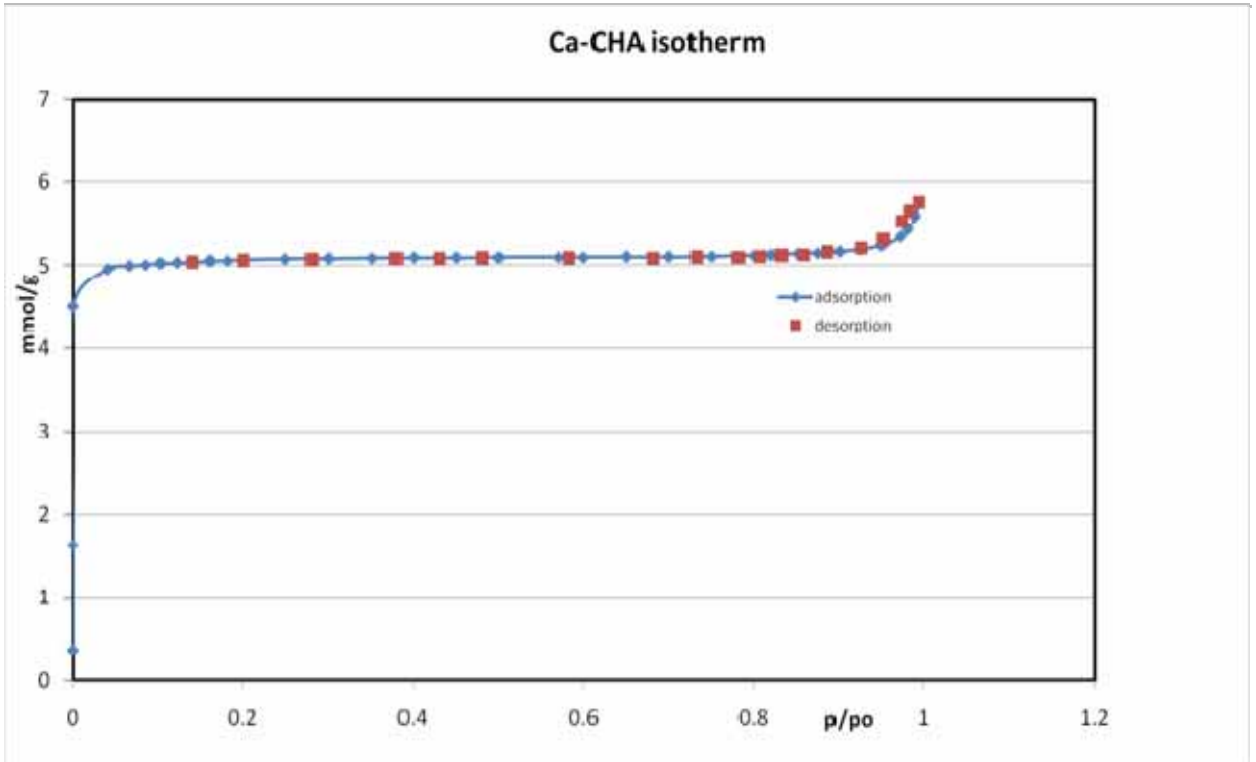
gel composition 0.17 Na_2O : 2.0 K_2O : 5.18 SiO_2 : Al_2O_3 : 224 H_2O **Si/Al ratio of 2.59**

UC: $Na_{0.8}K_{9.5}[Al_{10.3}Si_{25.7}O_{72}]$ N_2-porosimetry **0.17 ml/g** (486 m^2/g) , activated 350°C

Ion exchanged CHA

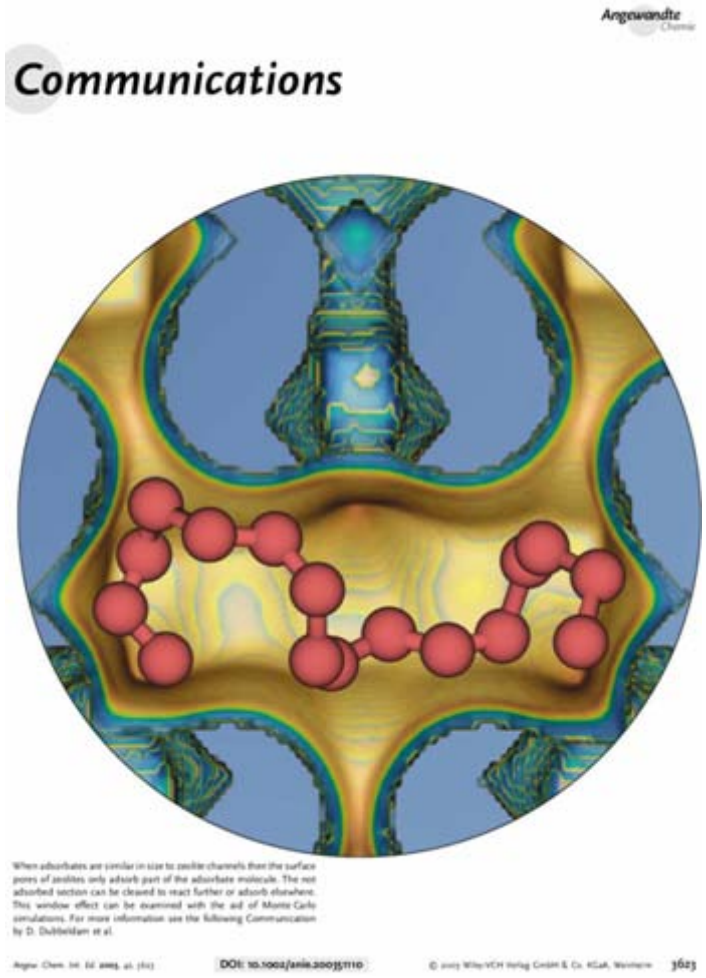
UC composition of exchanged Na-K-CHA

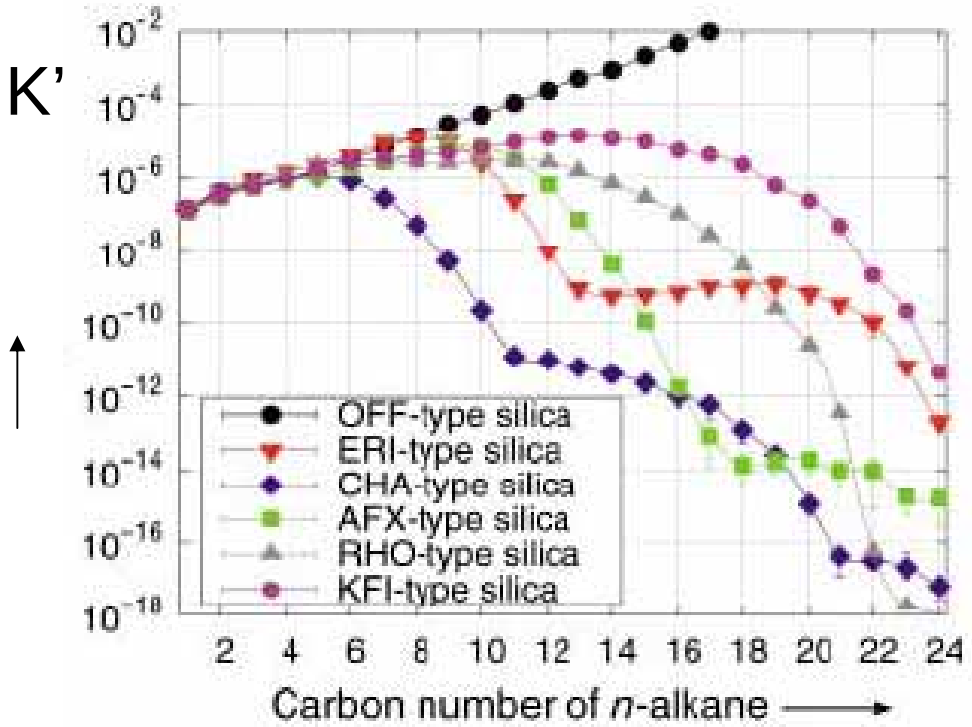
K-CHA	$K_{10.7}$ $[Al_{10.7}Si_{25.3}O_{72}]$	0.17 ml/g
Na-CHA	$Na_{9.5}K_{0.9}$ $[Al_{10.4}Si_{25.6}O_{72}]$	0.23 ml/g
Ca-Cha	$Ca_{4.7}K_{0.8}$ $[Al_{10.2}Si_{25.8}O_{72}]$	0.19 ml/g



Molecular Simulations

Monte Carlo simulations: deviations when molecule length approaches that of cage with small window



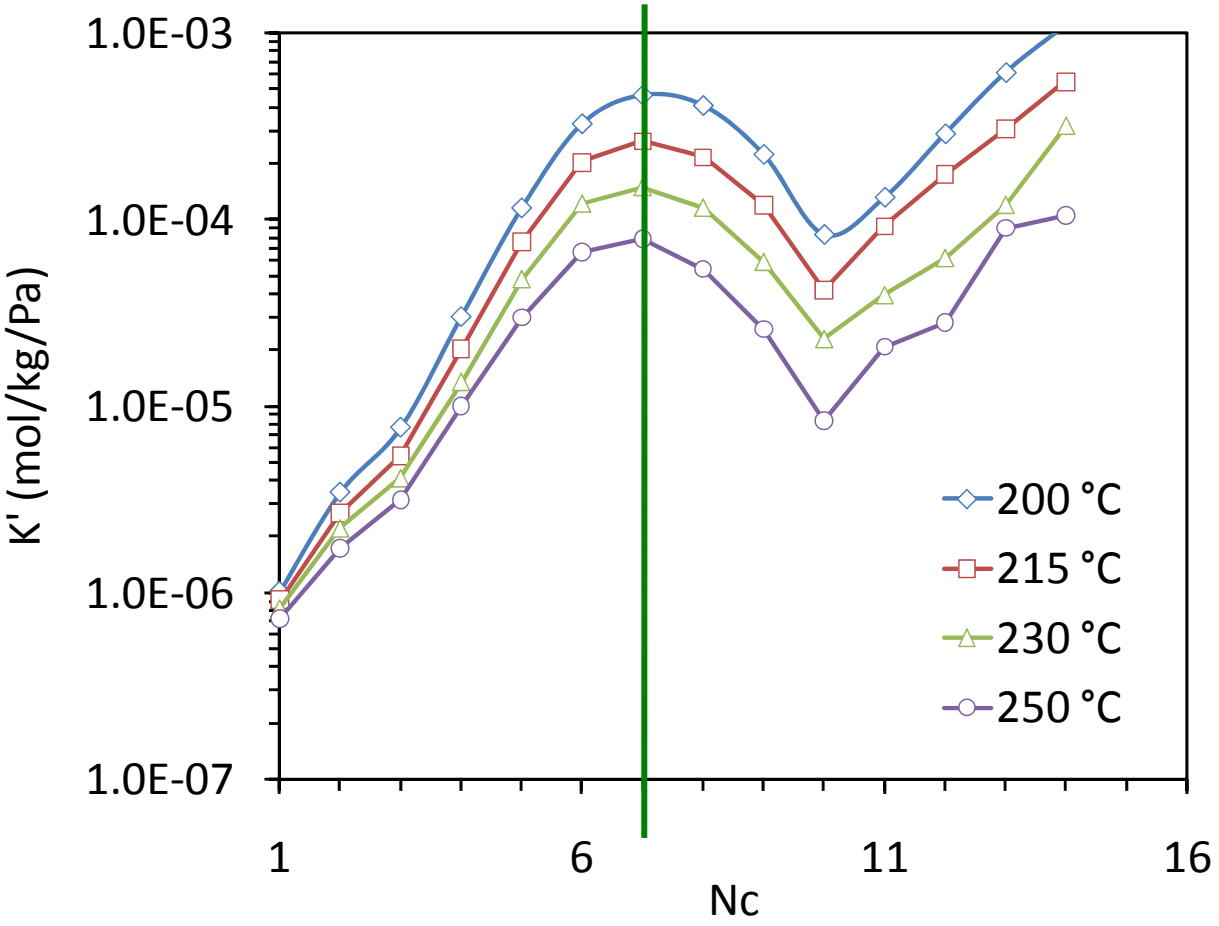


[1]David Dubbeldam et al., Understanding the window effect in zeolite catalysis,

Angew Chem Int Ed. 2003, 42, 3624-3626

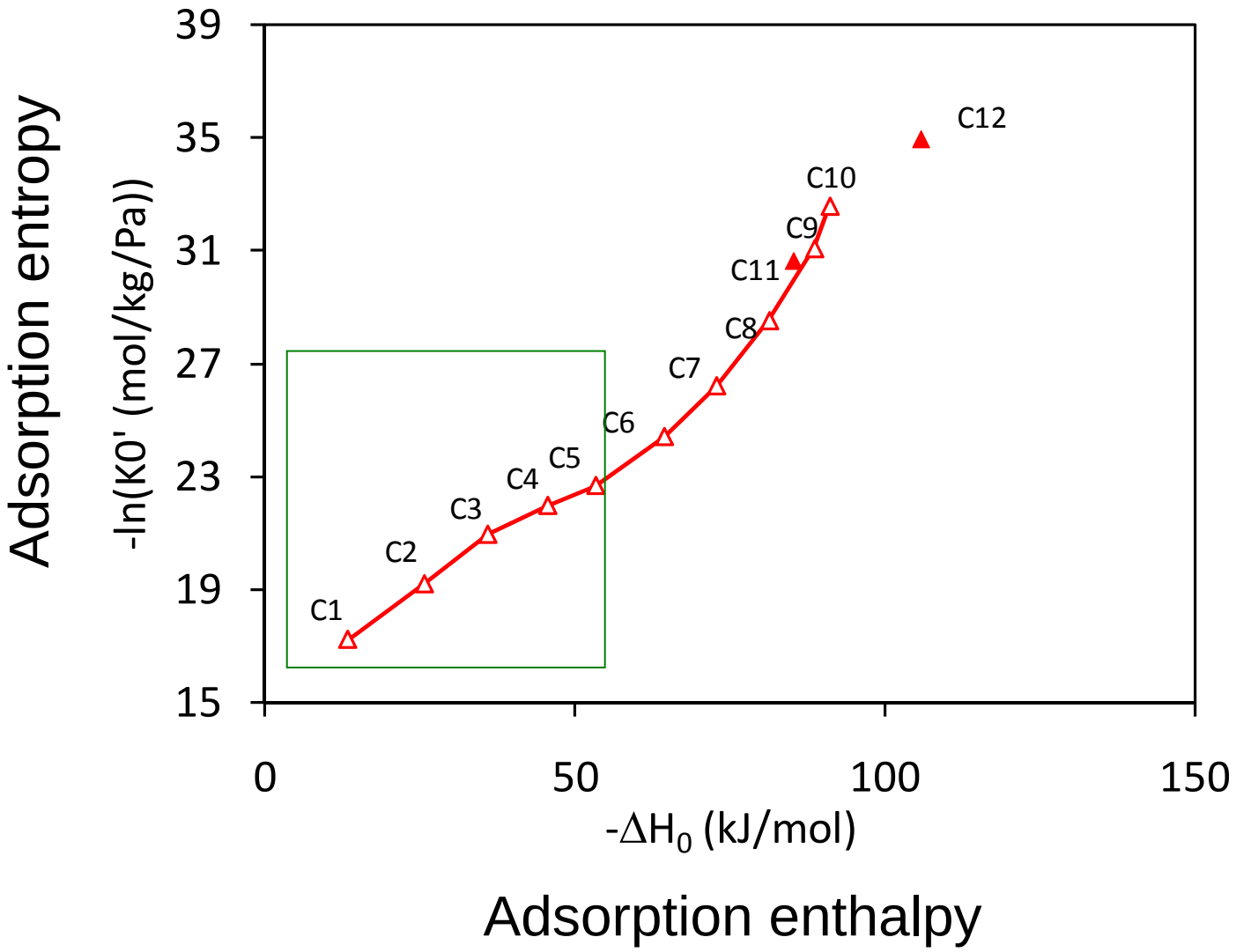
n-alkane Henry constants

Very low degree of pore filling



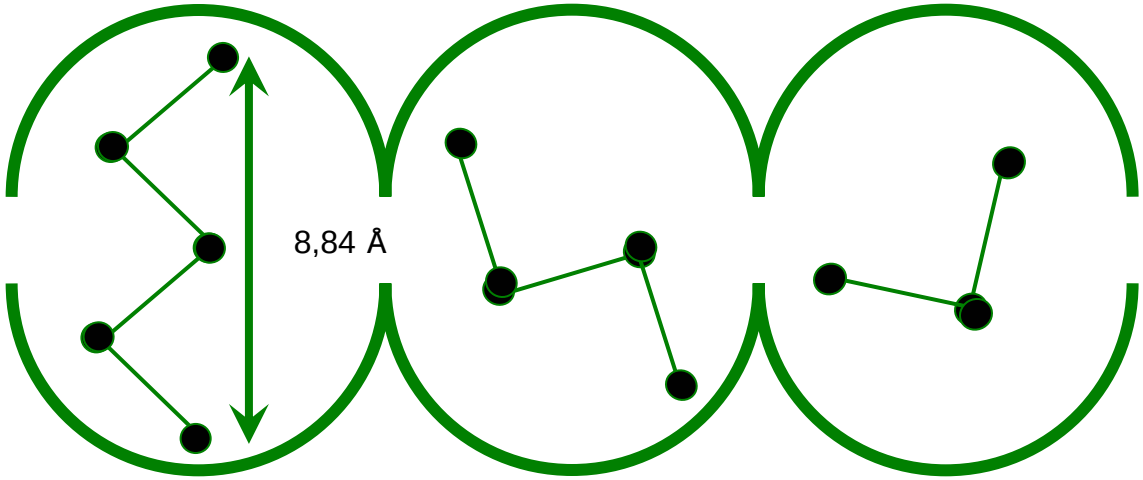
Steric constraints: n-hexane: 10.1 Å - CHA cage: 10 Å

Adsorption thermodynamics



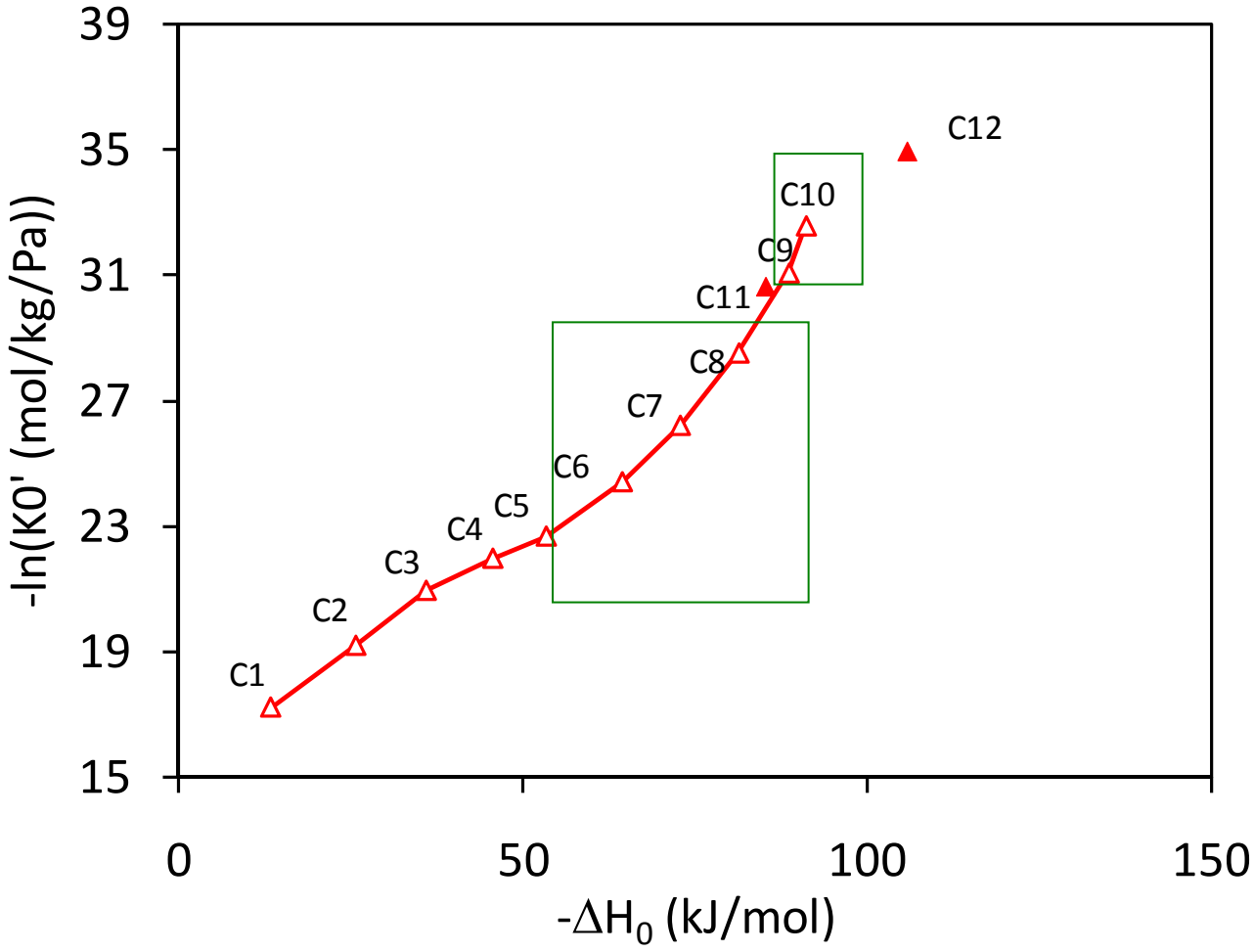
Adsorption mechanism

C_1 to C_5



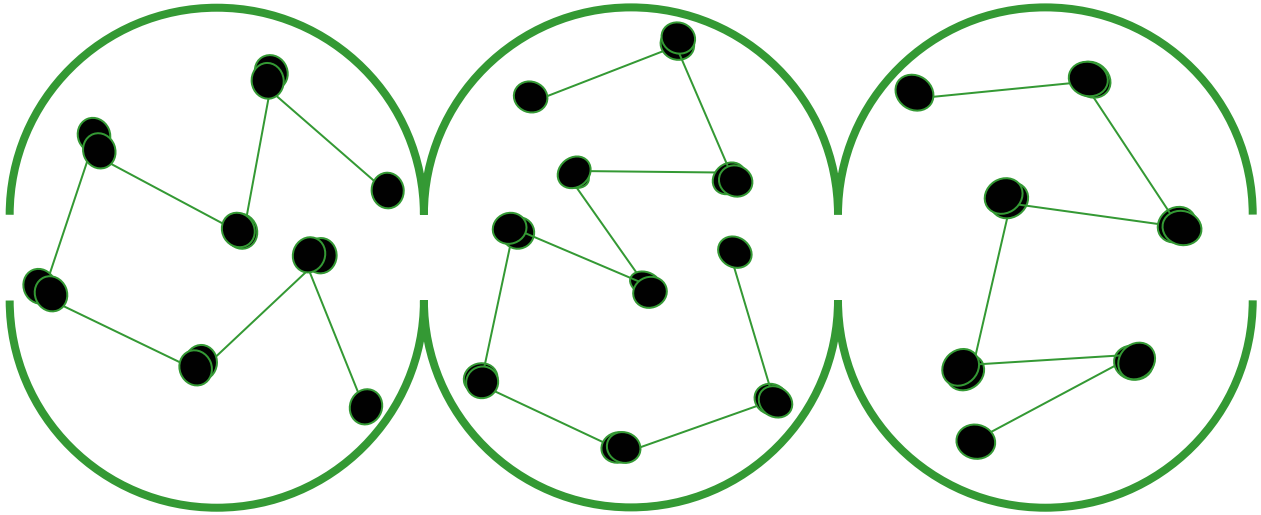
Alkanes to C_5 : stretched in cages

Adsorption thermodynamics



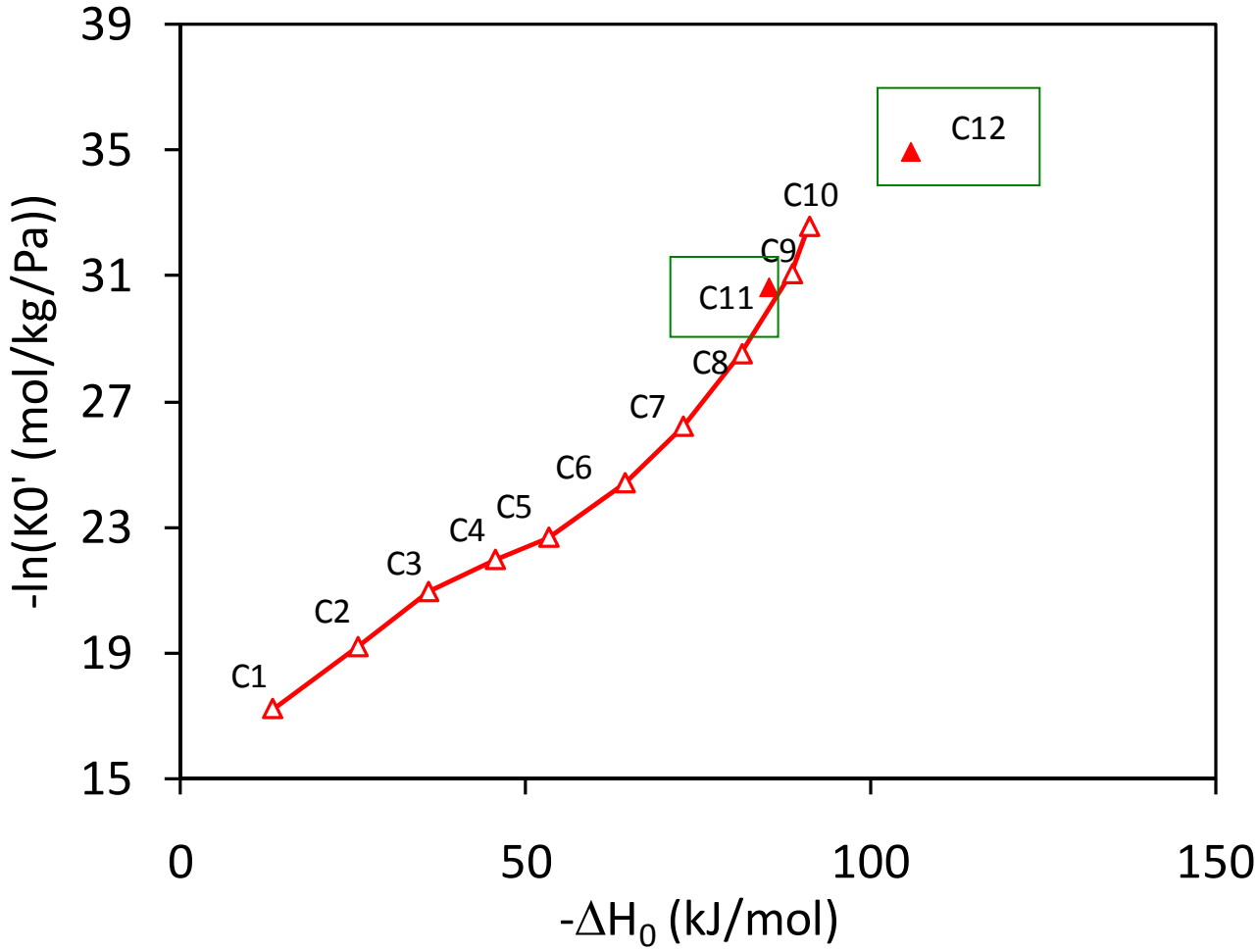
Adsorption mechanism

C_6 to C_{10}



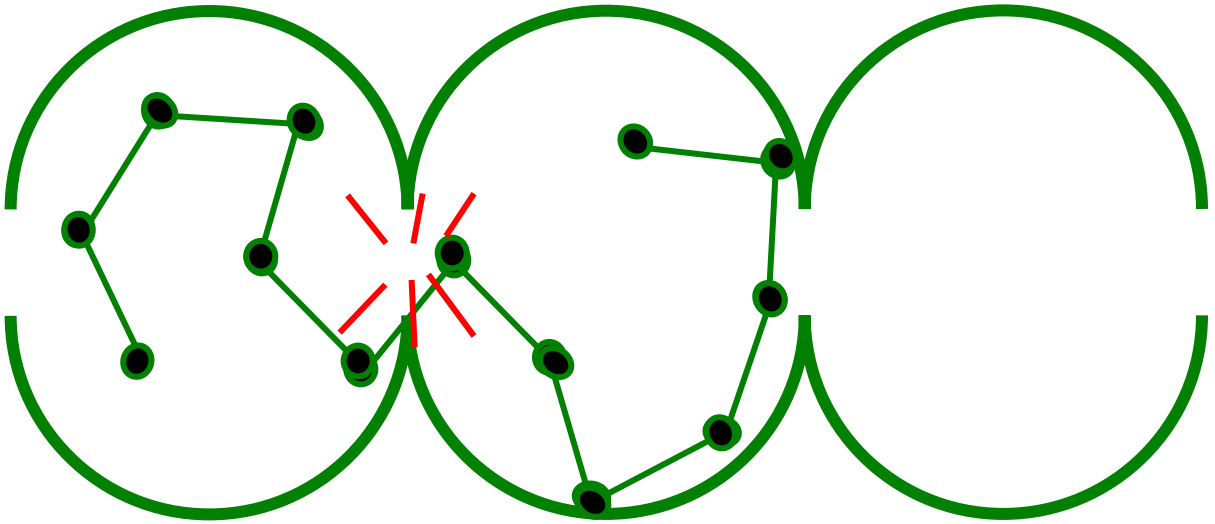
- C_6 to C_{10} alkanes : coiled configuration
- Maximally 10 CH_2 groups per cage

Adsorption thermodynamics



Adsorption mechanism

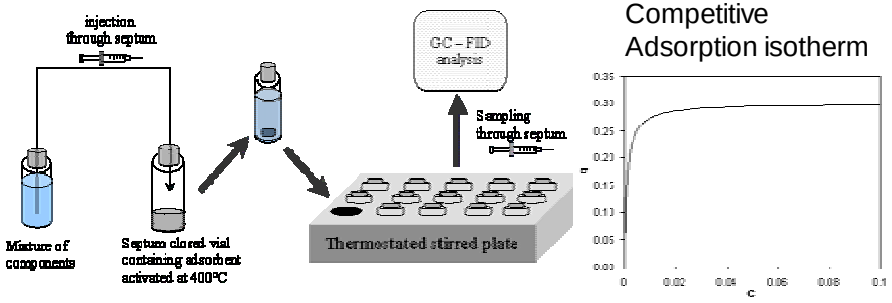
C_{11} and larger



Alkanes > C_{11} : stretched over adjacent cages

What happens in liquid phase, at high degree of pore filling ?

Batch isotherms



Competitive Adsorption isotherm

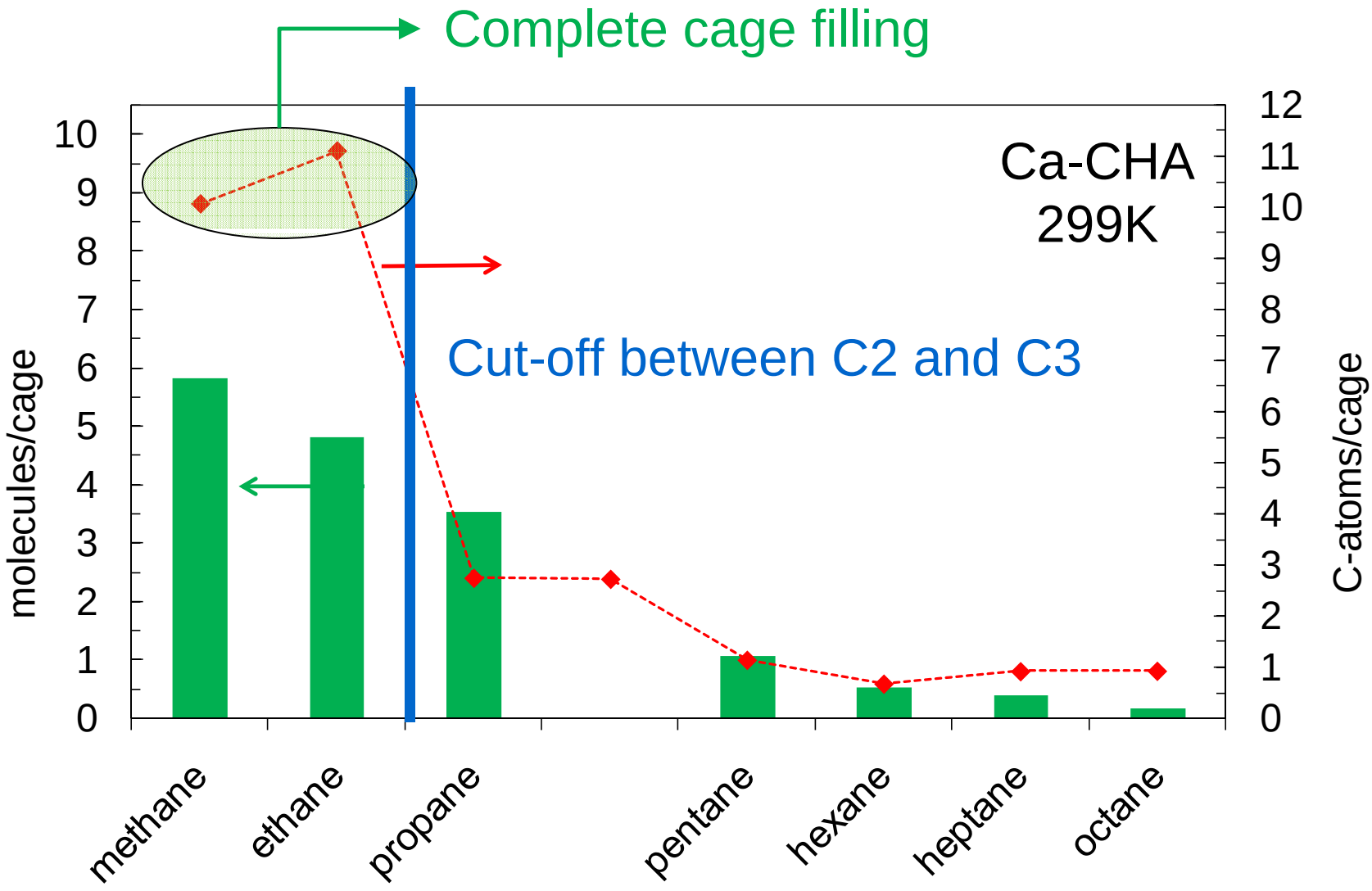
K' adsorption constant

q_s saturation capacity

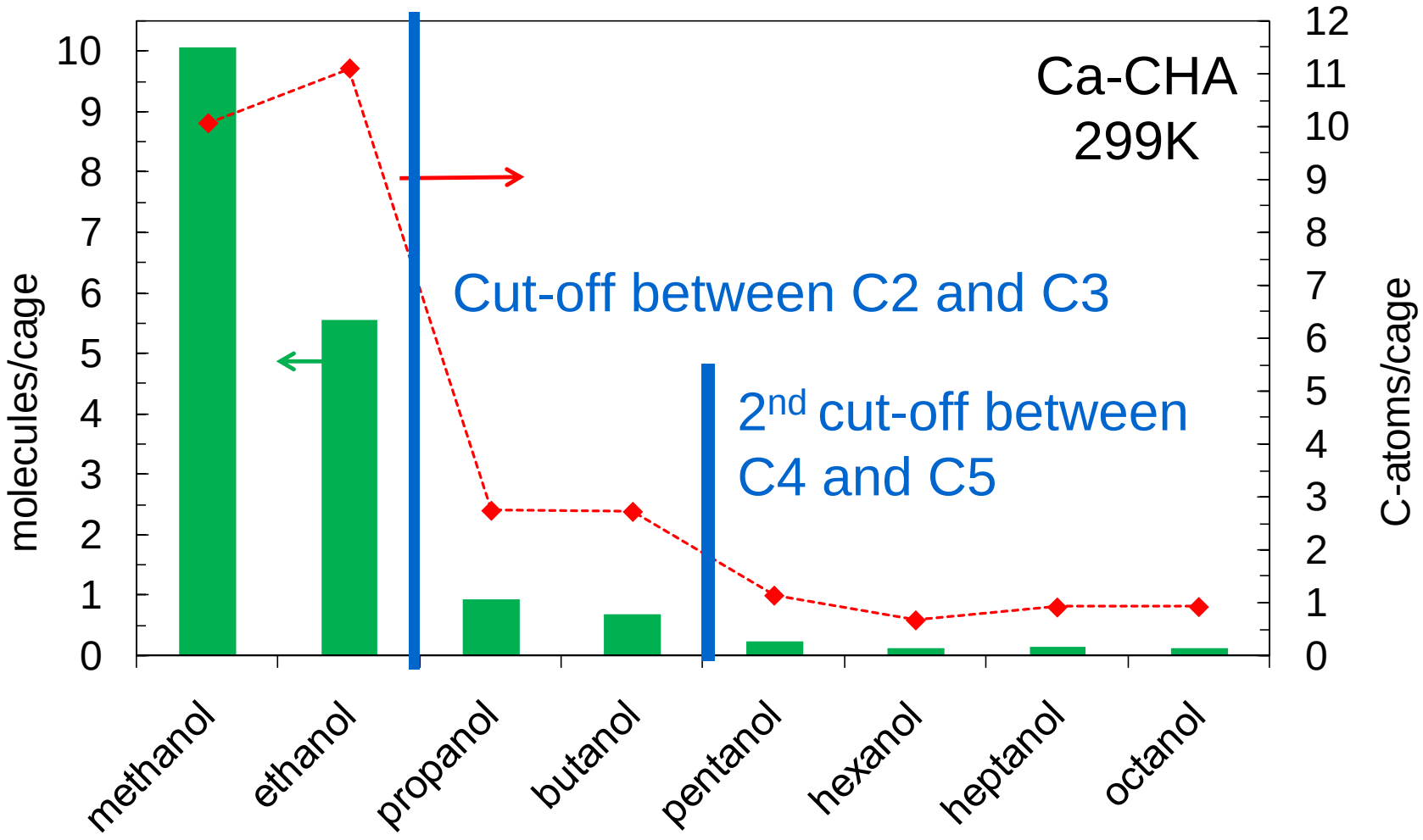
$$\frac{q}{q_s} = \frac{bC}{1+bC} \quad \text{and} \quad q = \frac{K'C}{1+bC}$$

Langmuir equation

n-alkanes on CHA in liquid phase

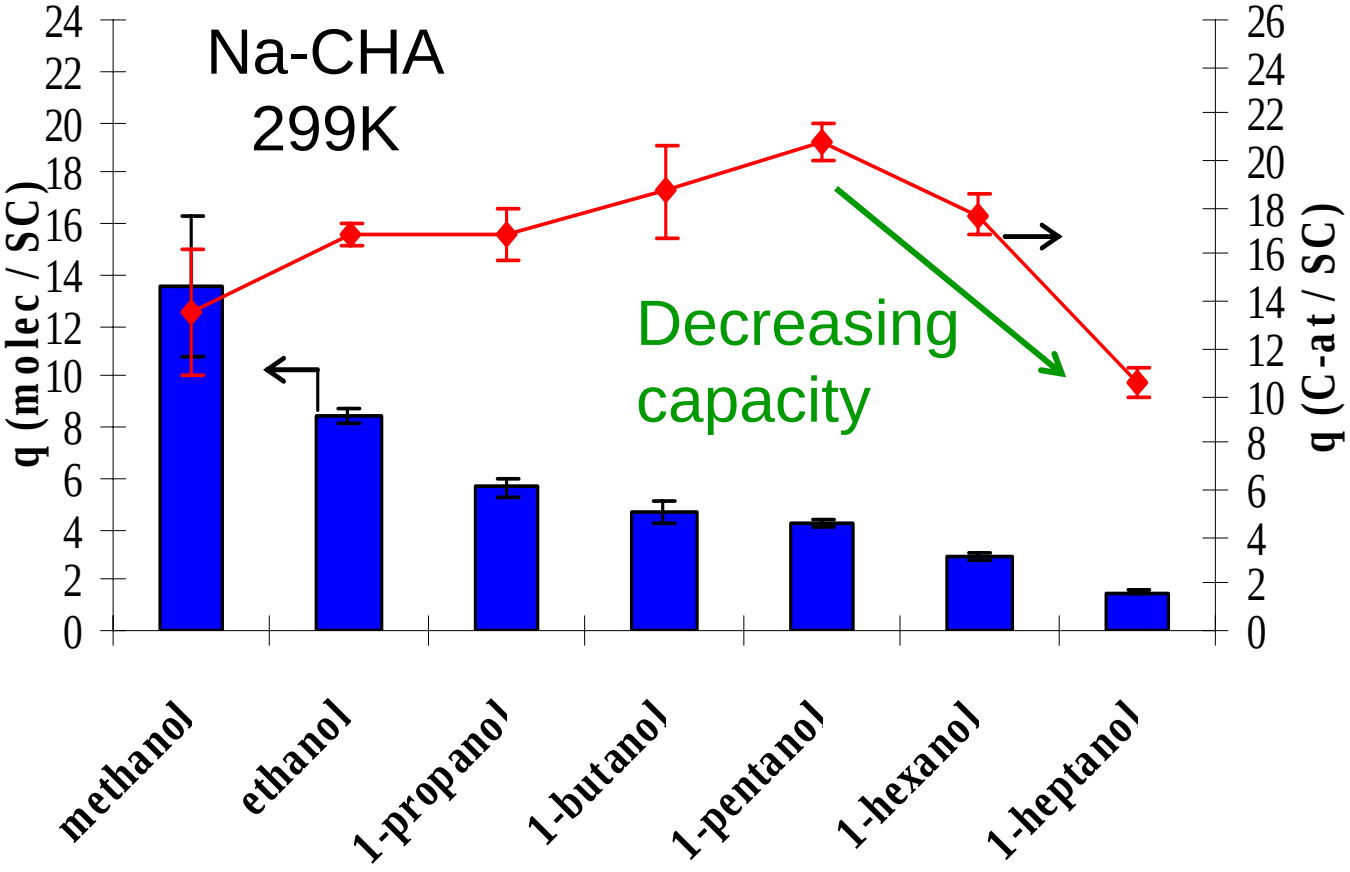


1-alcohols on CHA in liquid phase



1-alcohols on CHA in liquid phase

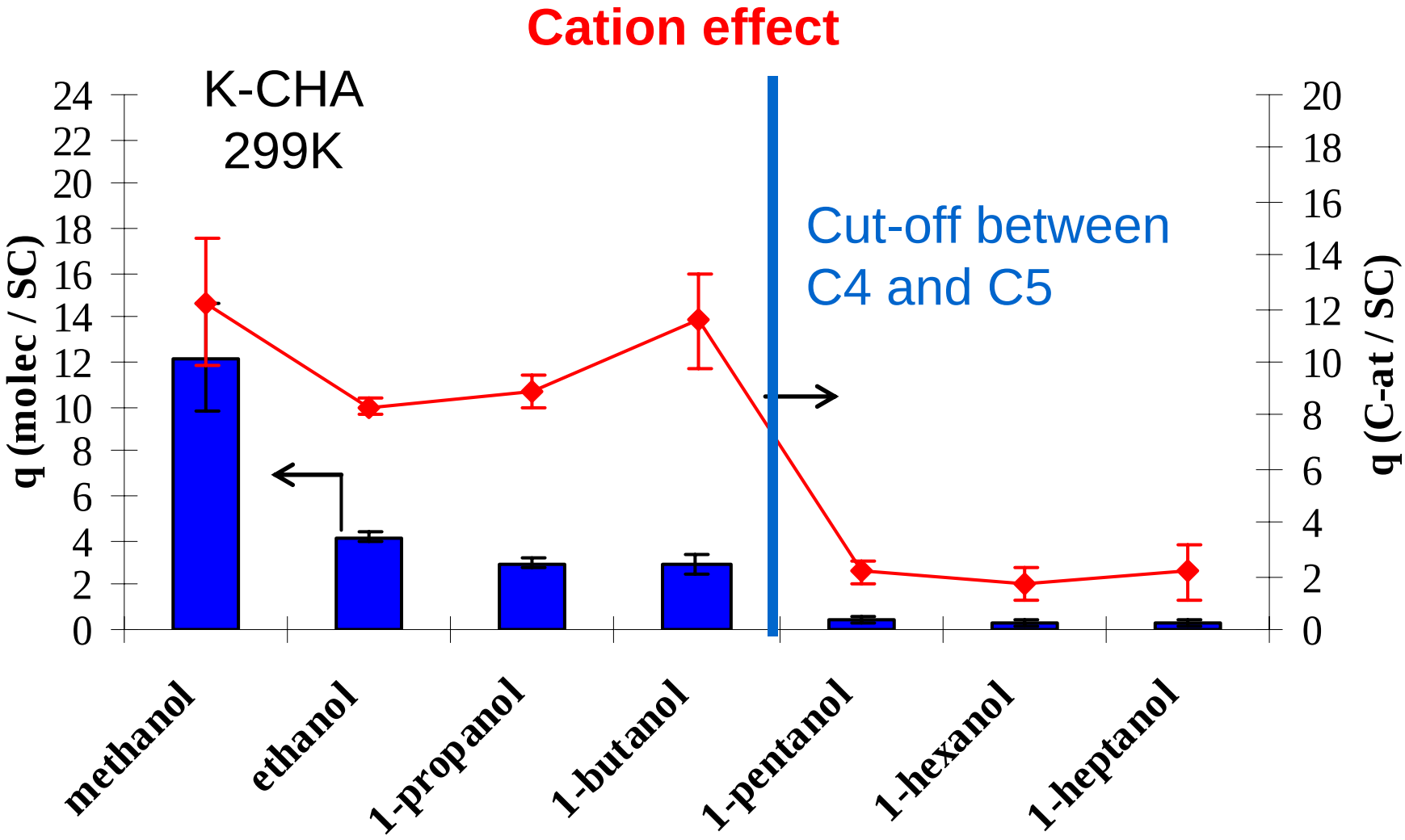
Cation effect



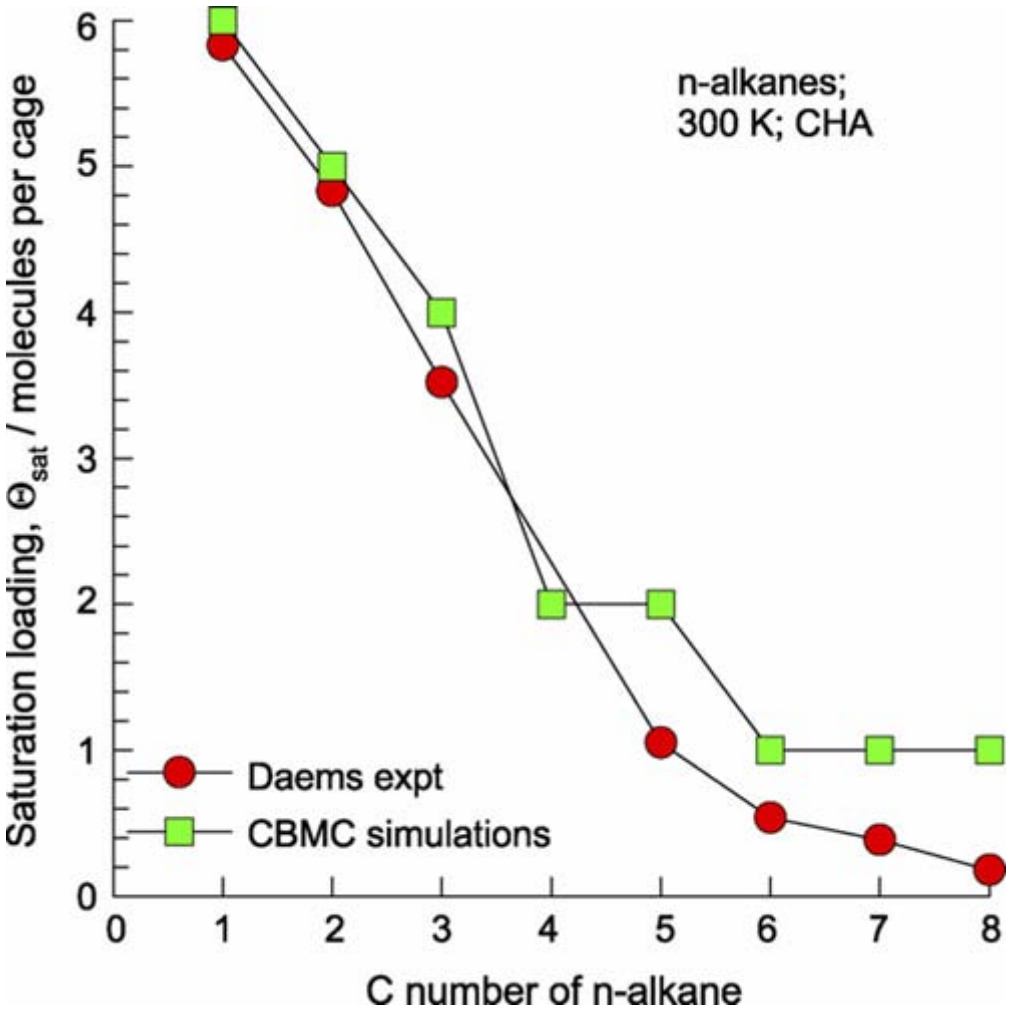
⇒ No clear cut-off

⇒ Cations affect adsorption mechanism

1-alcohols on CHA in liquid phase



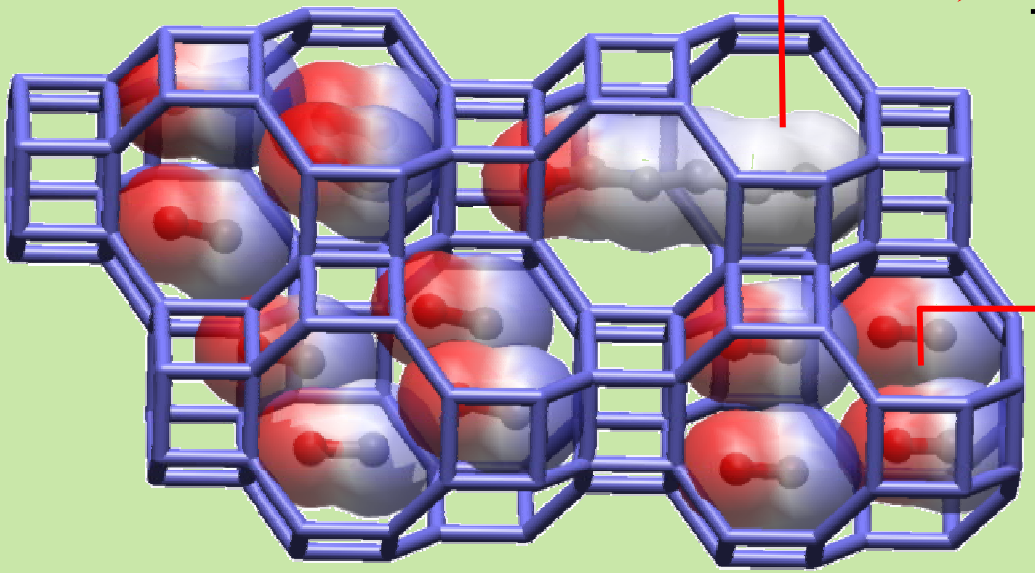
CBMC modelling



⇦ With cations!

R. Krishna, J.M. van Baten,, Sep. Purif. Technol. (2007), doi:10.1016/j.seppur.2007.09.008

Gas phase versus Liquid phase

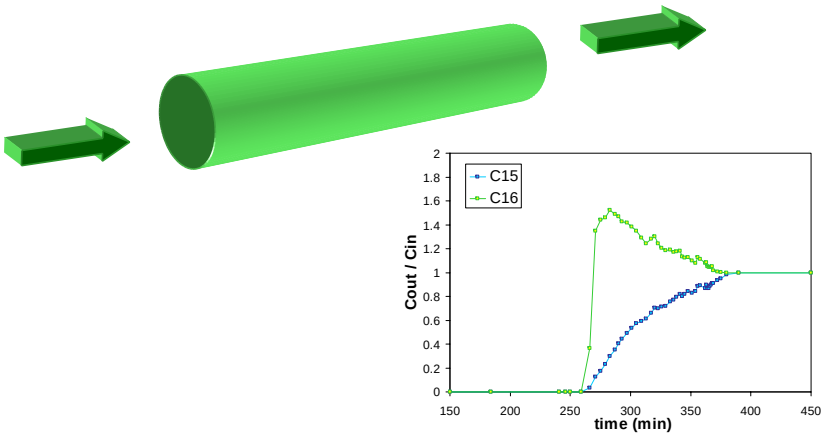


Liquid phase:

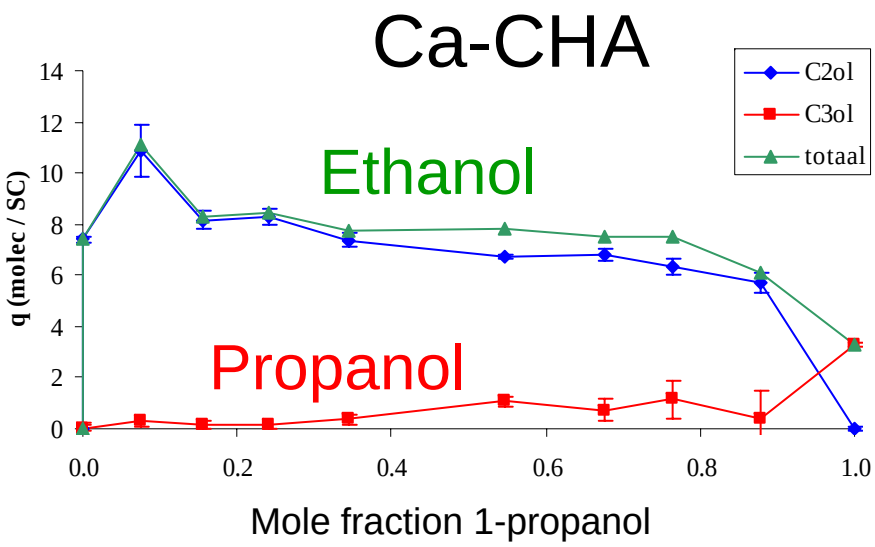
- High degree of pore filling
- Restricted motion from cage to cage
- Molecular packing becomes critical
- Small molecules pack better: configurational entropy advantage

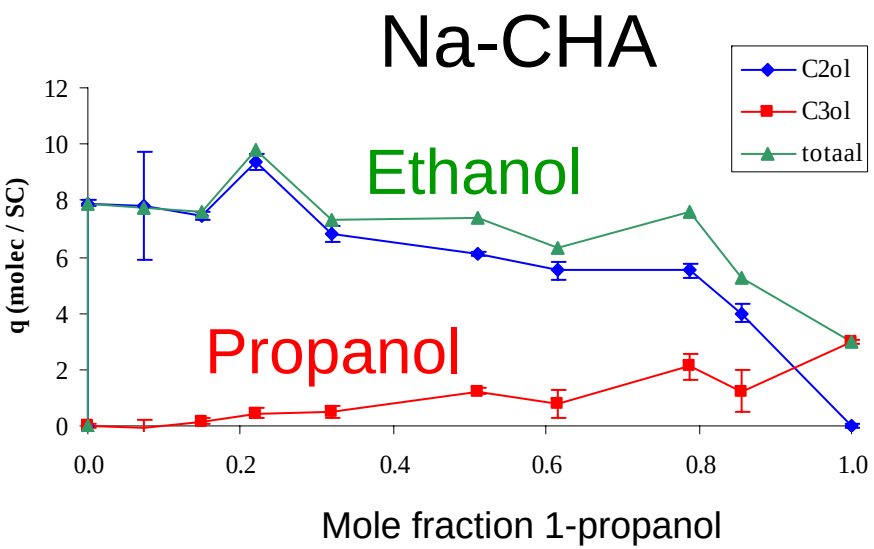
Liquid phase, mixtures?

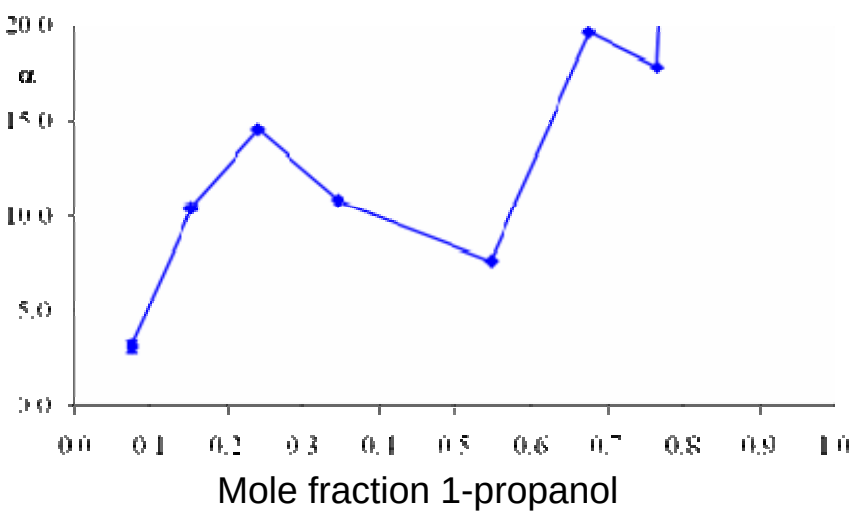
Column separation experiments

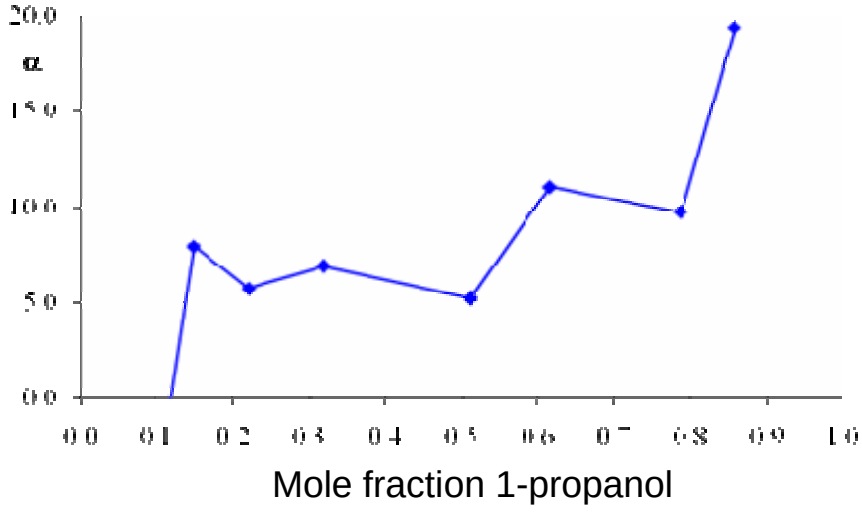


Ethanol / propanol mixture adsorption

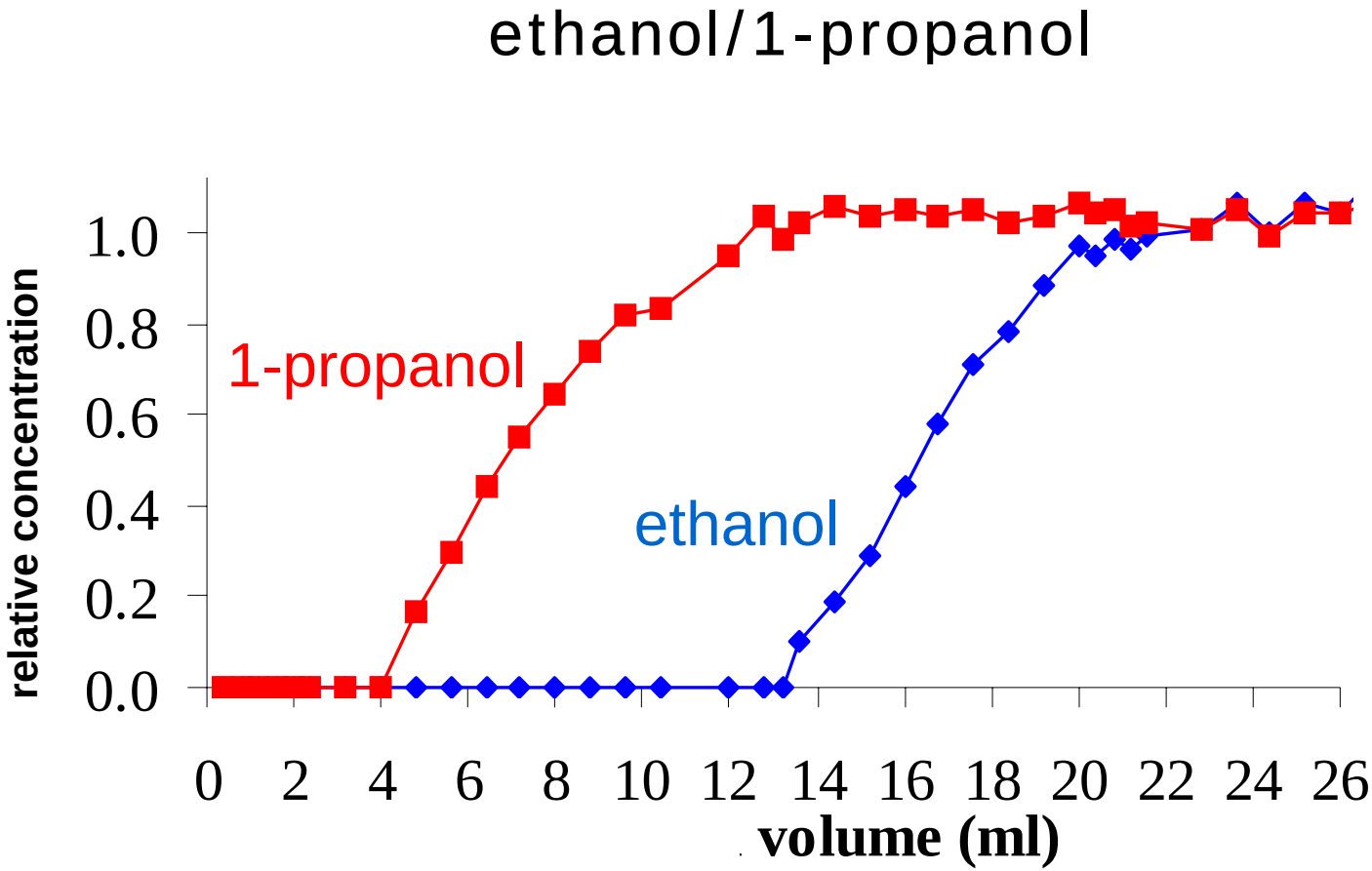








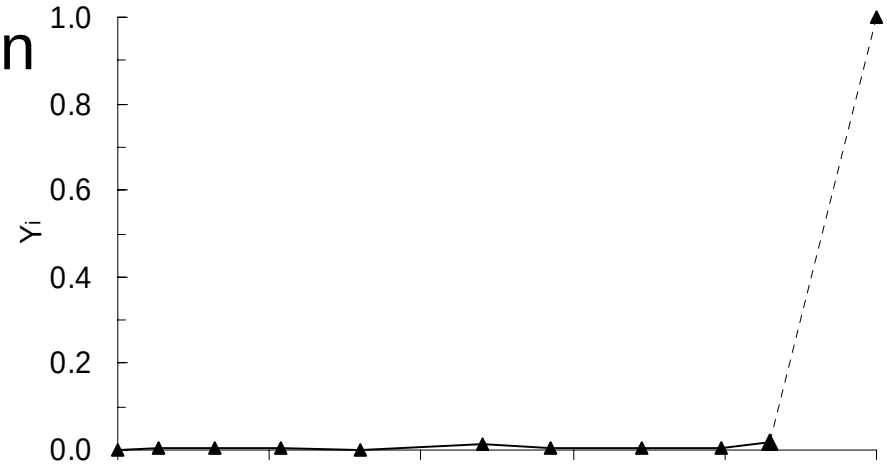
Breakthrough curves Ca-CHA



⇒ preferential adsorption of the shortest molecule ethanol

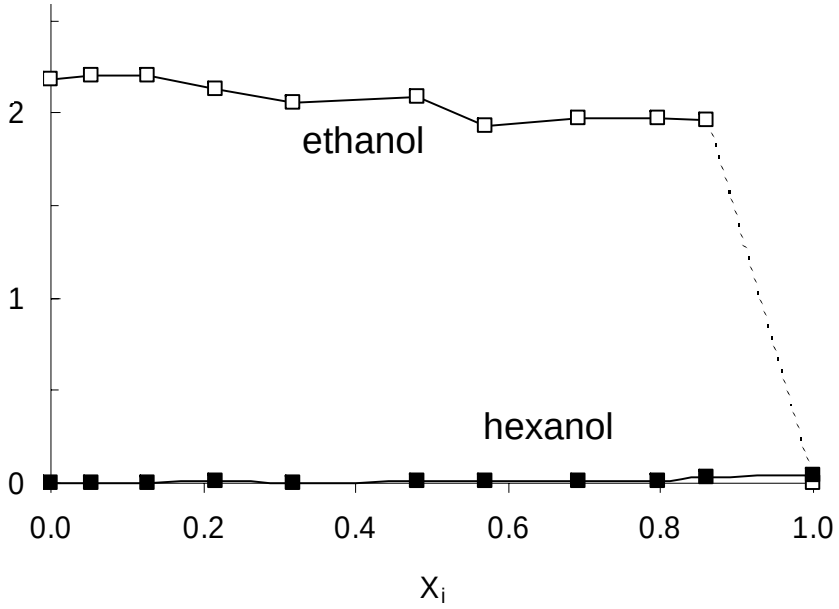
Ethanol – Hexanol binary equilibrium

Mole fraction C6-ol



Mole fraction C6-ol

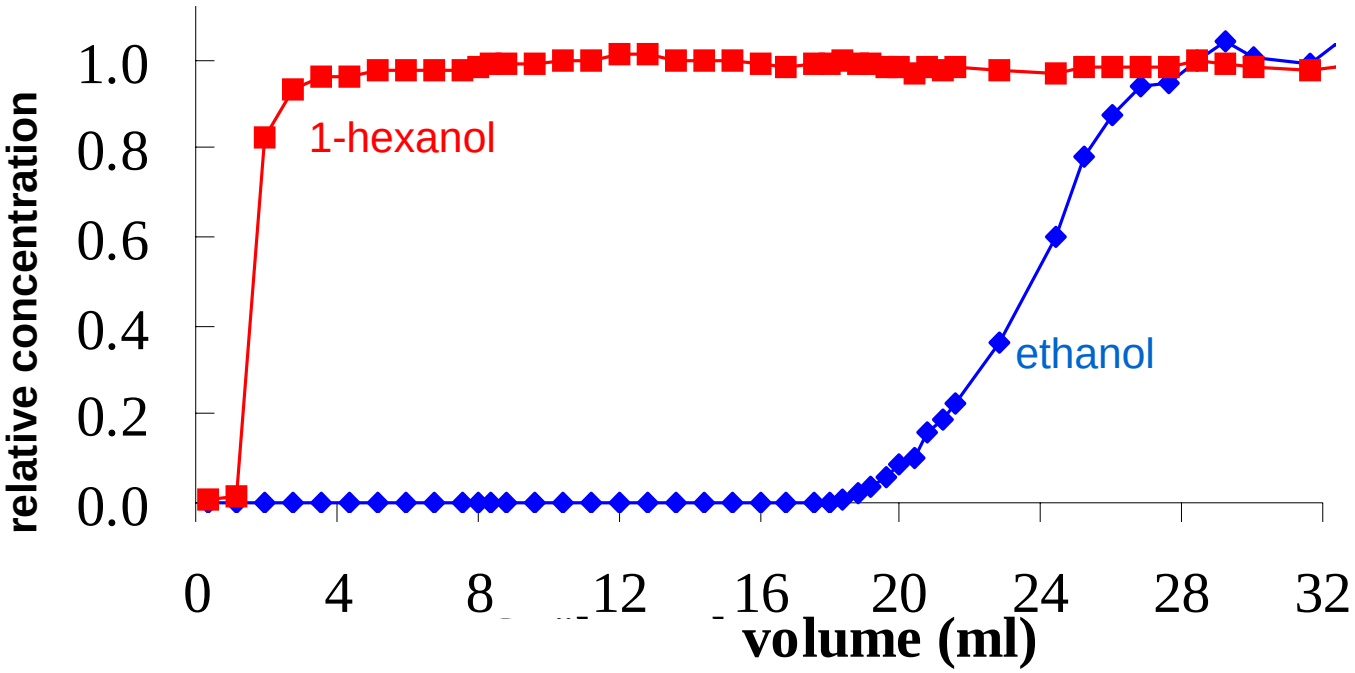
q (mmol /g)



Mole fraction C6-ol

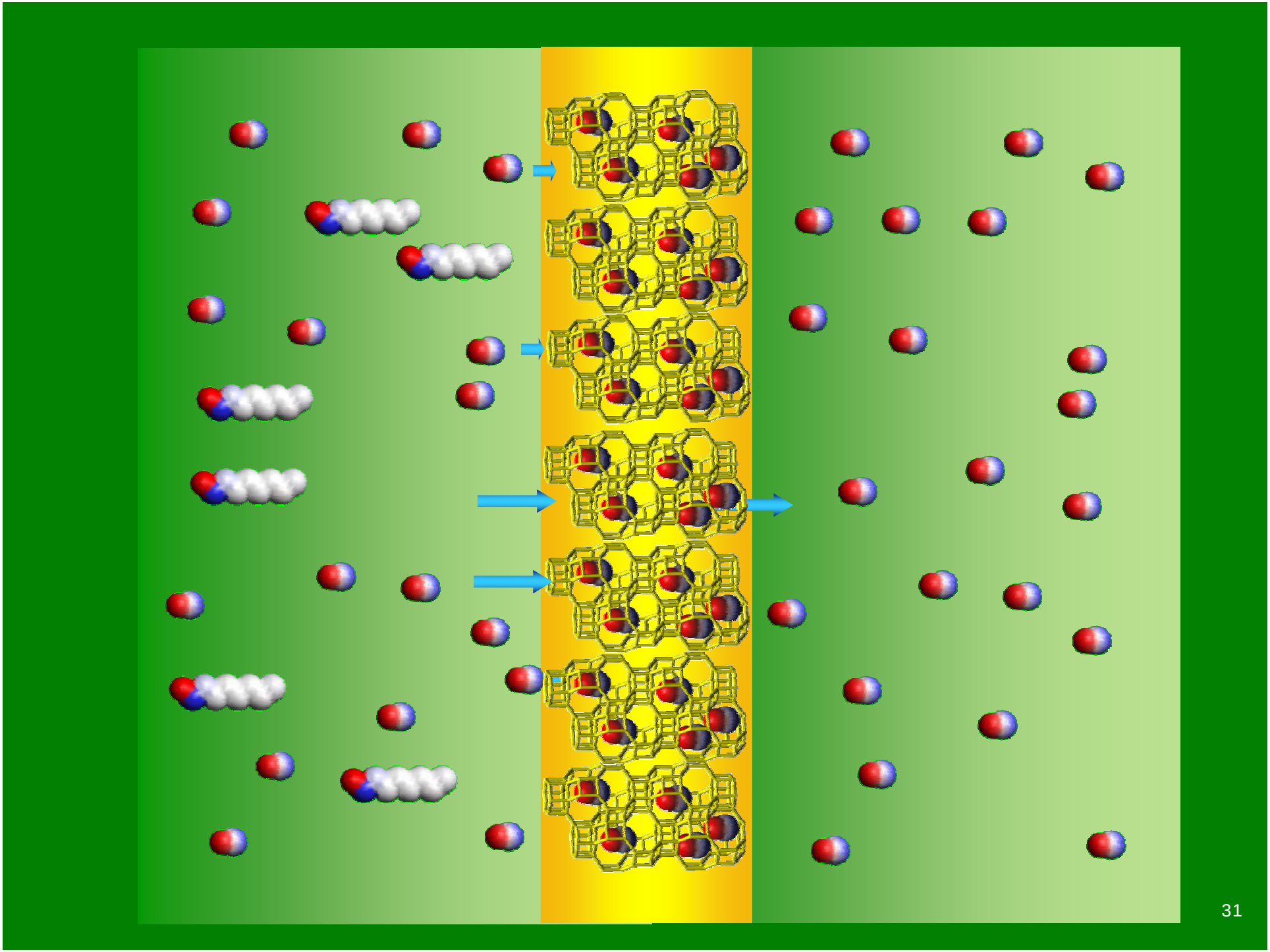
Breakthrough curves Ca-CHA

ethanol/1-hexanol

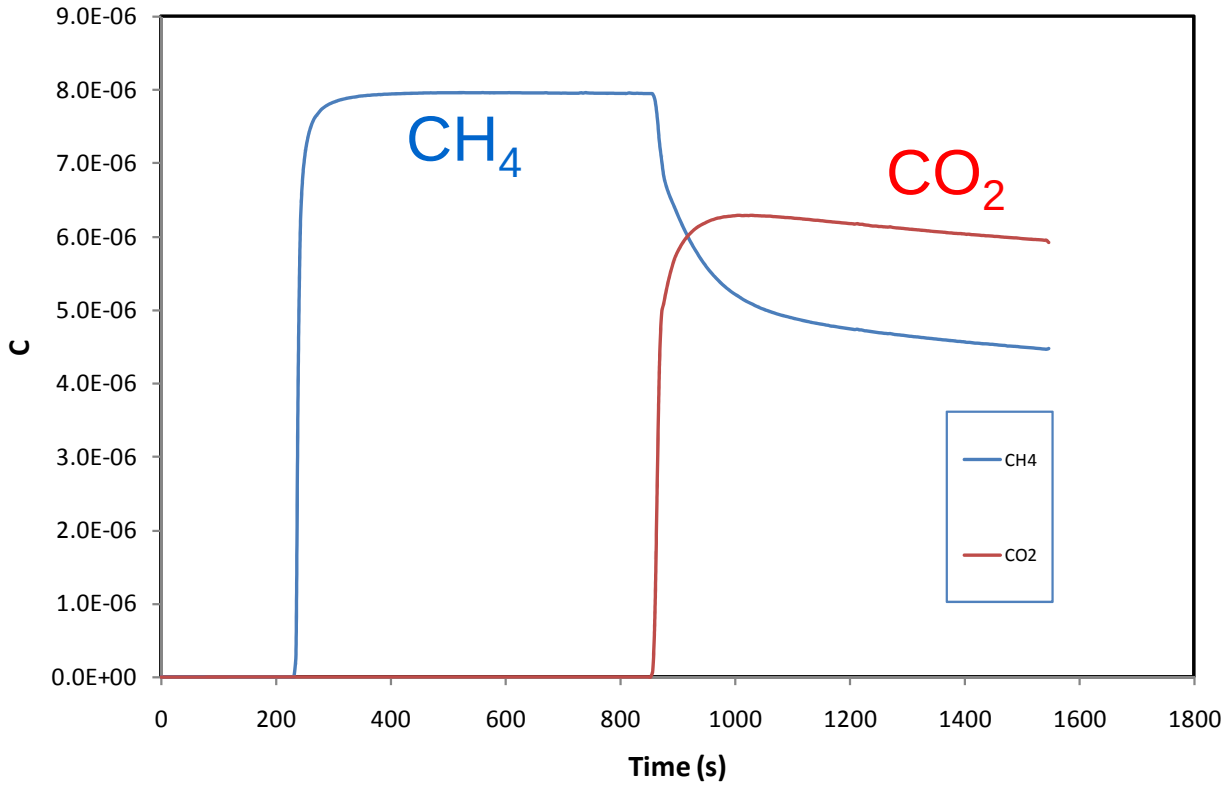


⇒ preferential adsorption of ethanol

⇒ exclusion of 1-hexanol



CO_2 / CH_4 separation



Conclusions

- CHA operates in the opposite way to most zeolites and excludes longer chains from adsorption.
- In zeolites with cages connected by narrow windows, molecules are preferably confined in the cage, not in the windows.
- Purification processes: remove traces of small molecules from mixtures of heavier components.
- Use in membrane processes?

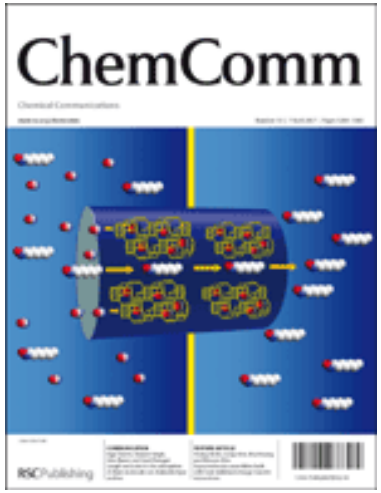
Acknowledgements

Ir. Els Leemans

IAP, IWT

FWO Vlaanderen

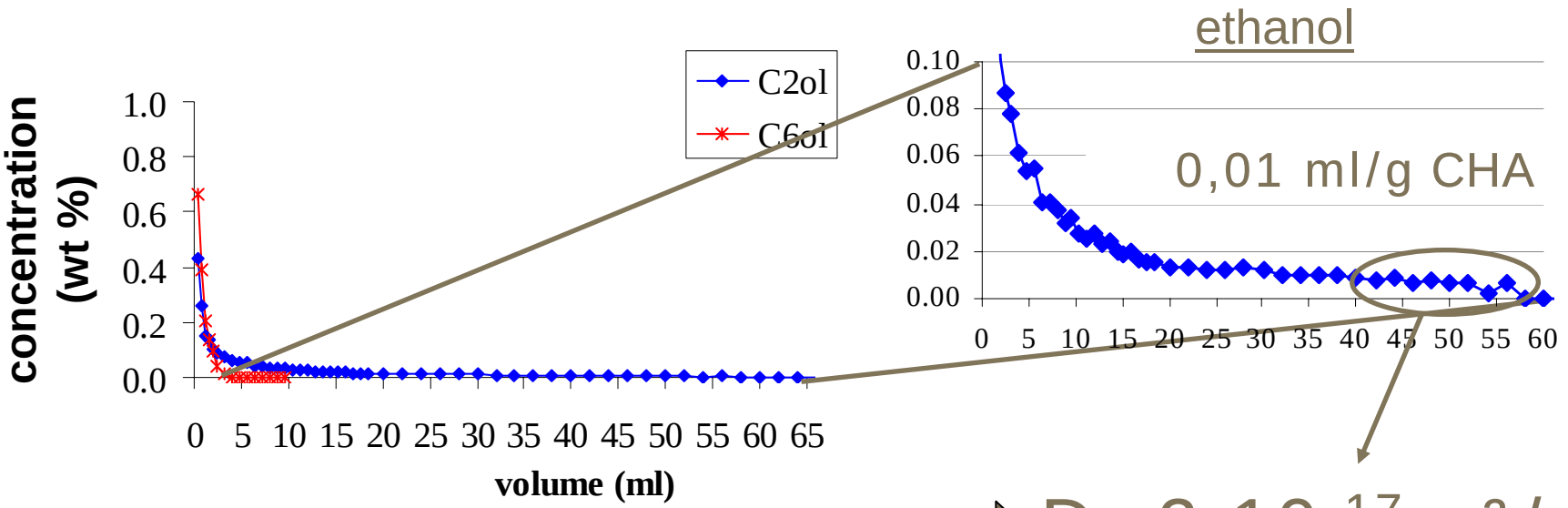
I. Daems, et.al, Chem. Comm. (2007) **13**, 1316–1318




Thank you!

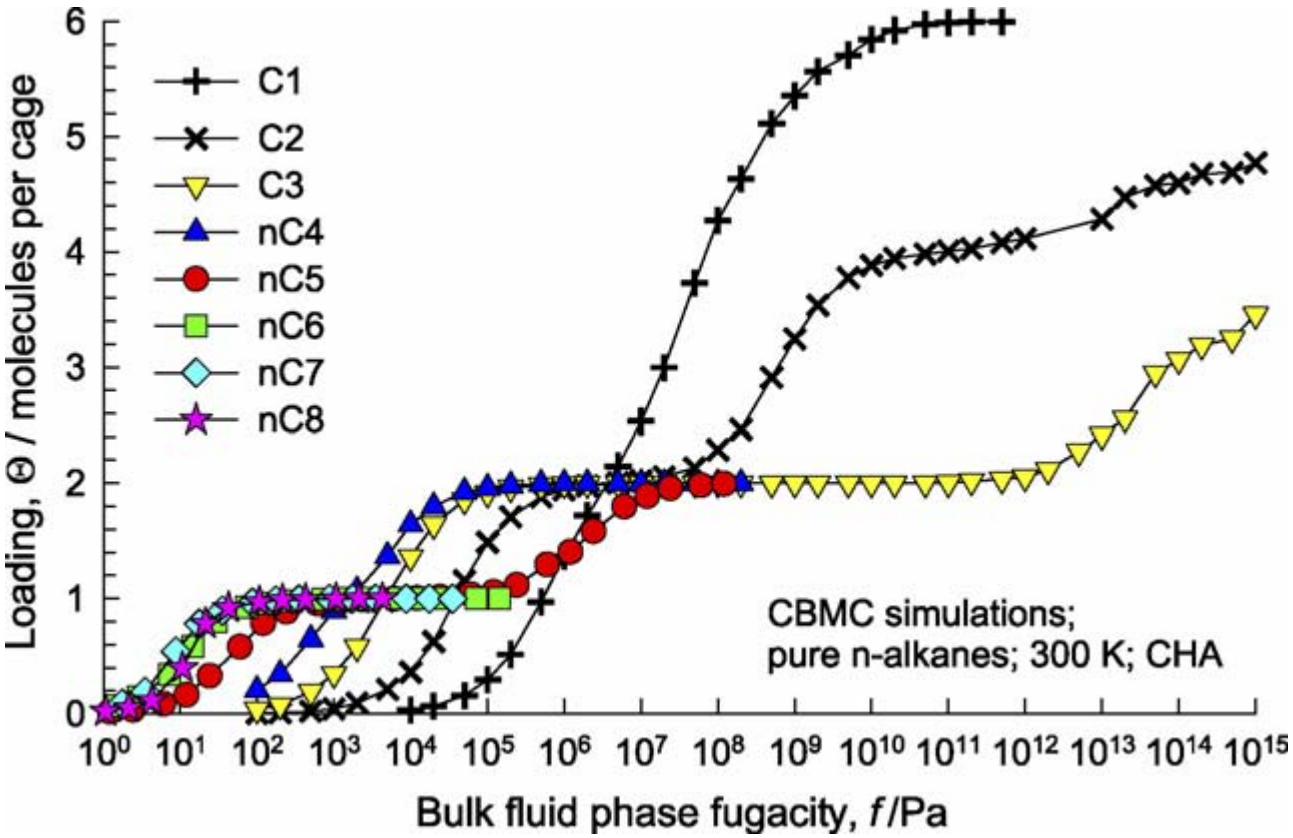
Very difficult, slow desorption

Ca CHA: Desorption with octane



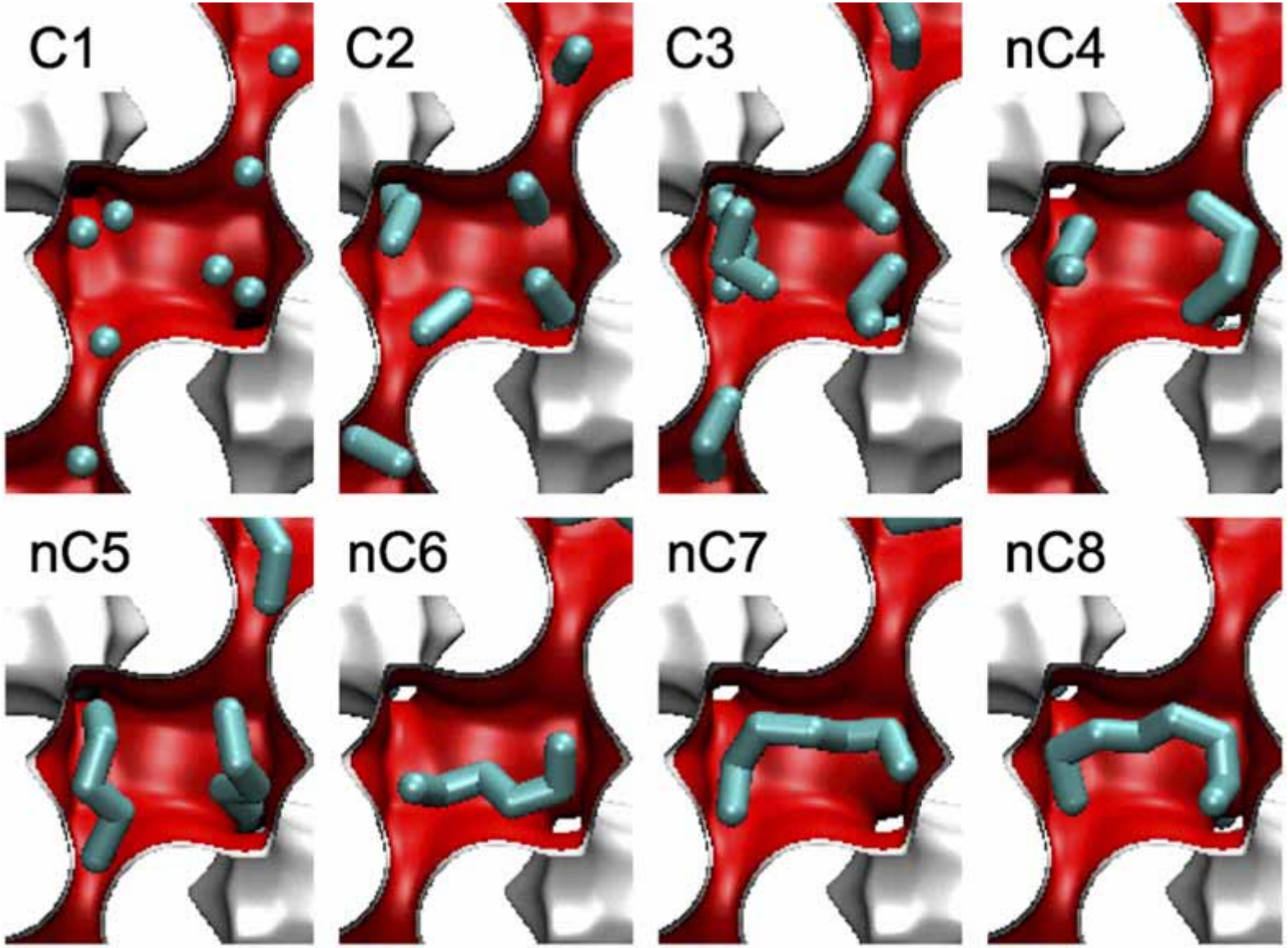
$D \sim 2.10^{-17} m^2/s$

CBMC pure component prediction

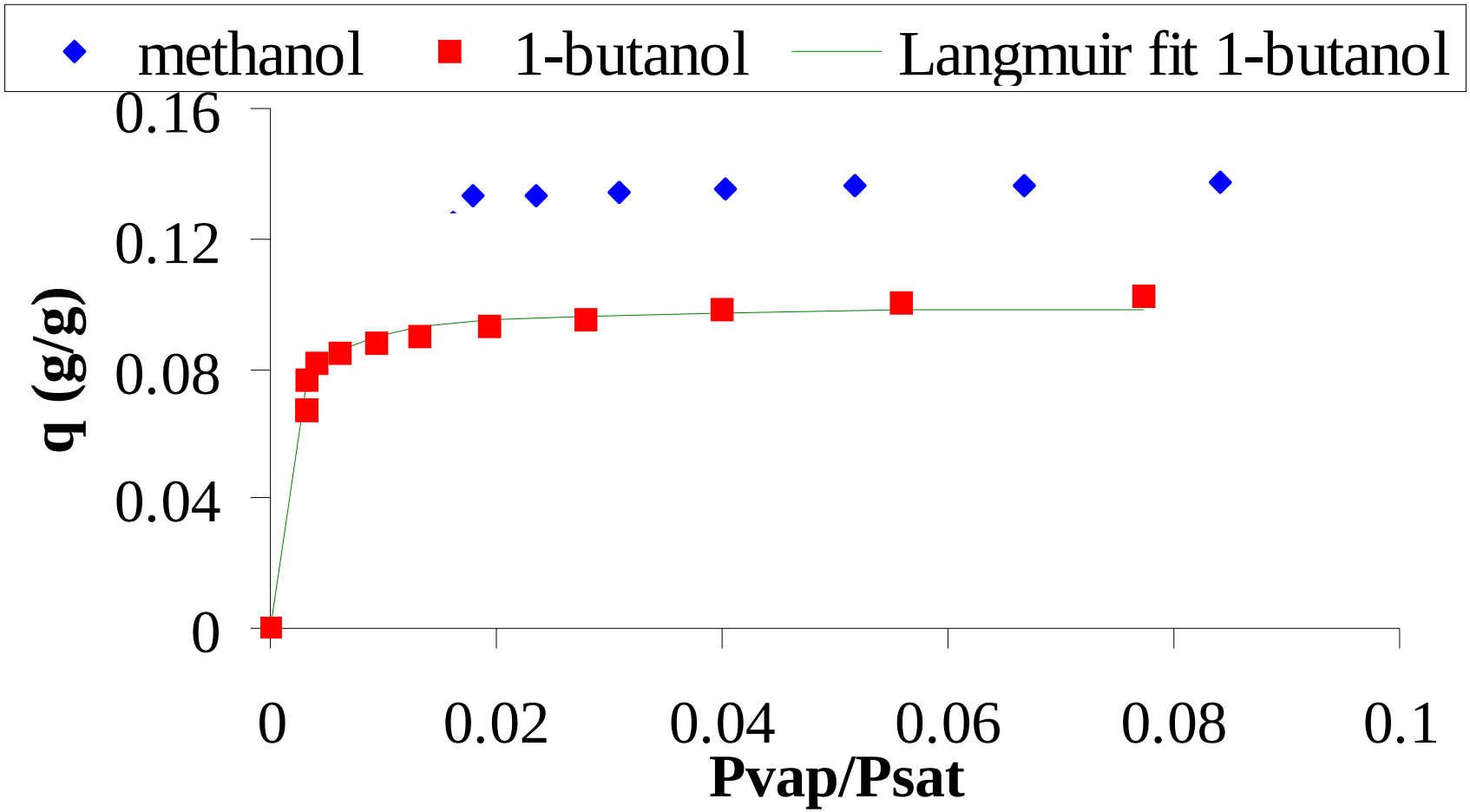


R. Krishna, J.M. van Baten, Separating *n-alkane mixtures by exploiting differences in the adsorption capacity within cages of CHA, AFX and ERI zeolites*, Sep. Purif. Technol. (2007), doi:10.1016/j.seppur.2007.09.008

Alkane conformations in CHA

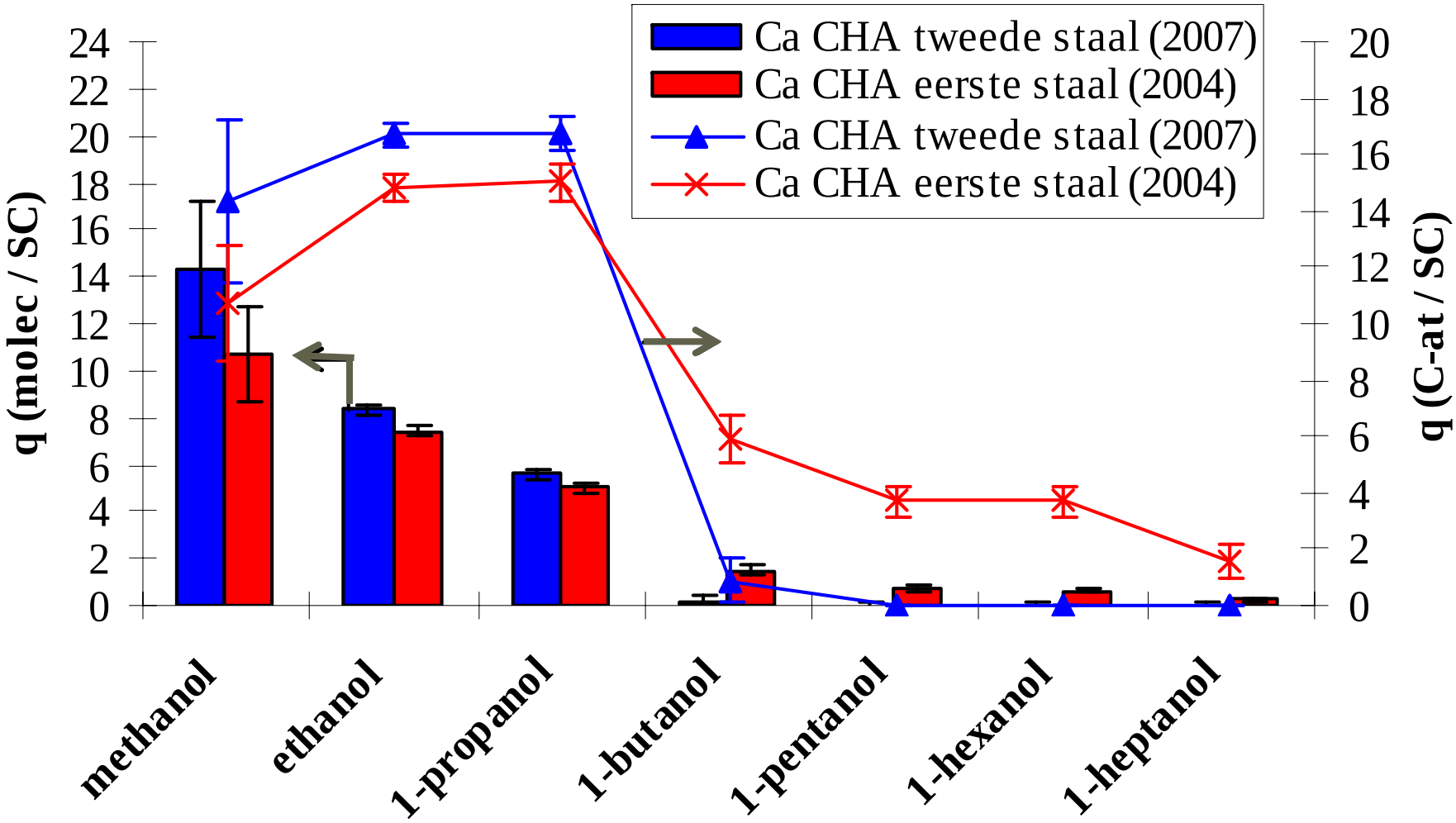


Vapor phase isotherms Ca-CHA 70°C

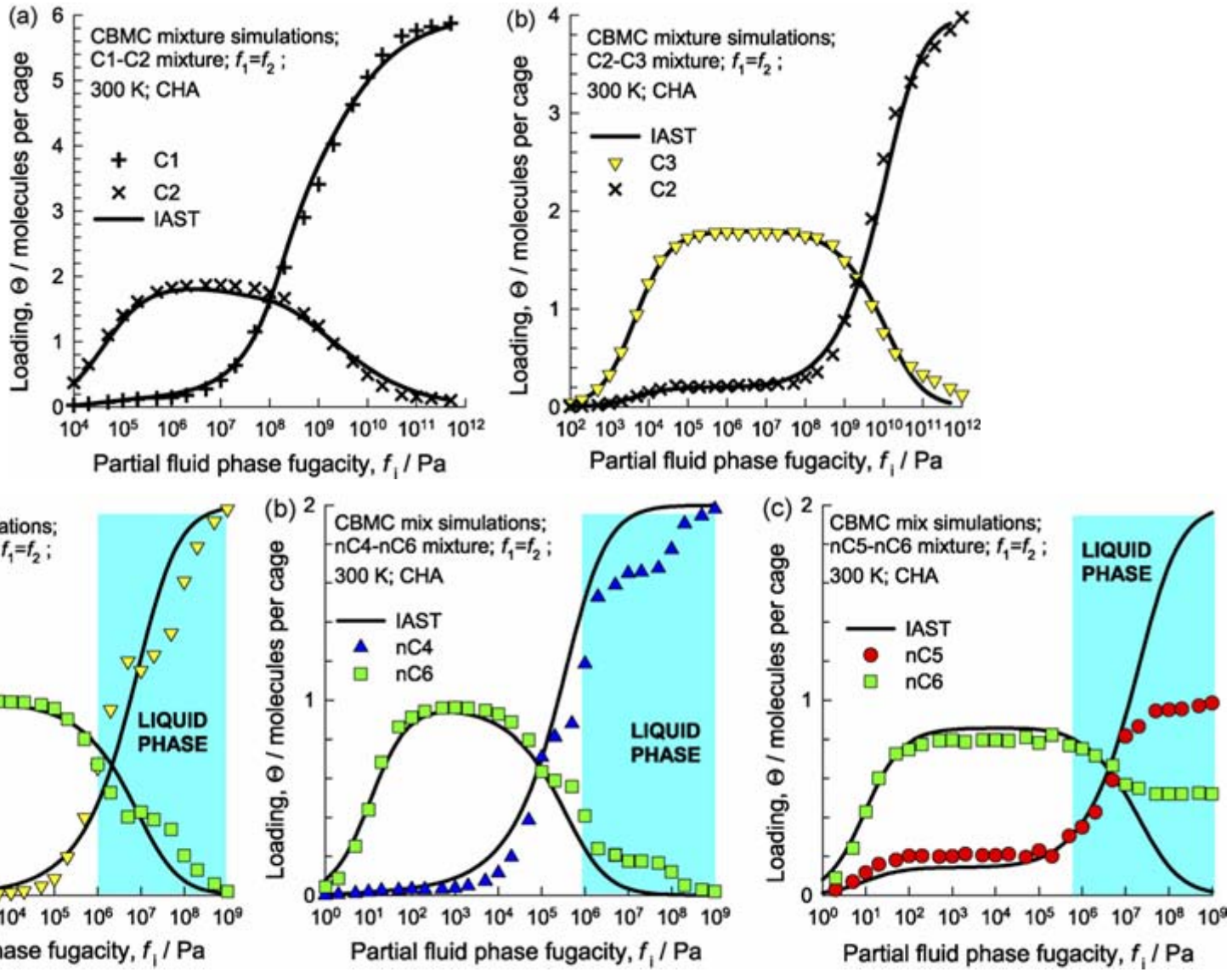


⟹ higher capacity for methanol

Liquid phase in iso-C8 on Ca-CHA

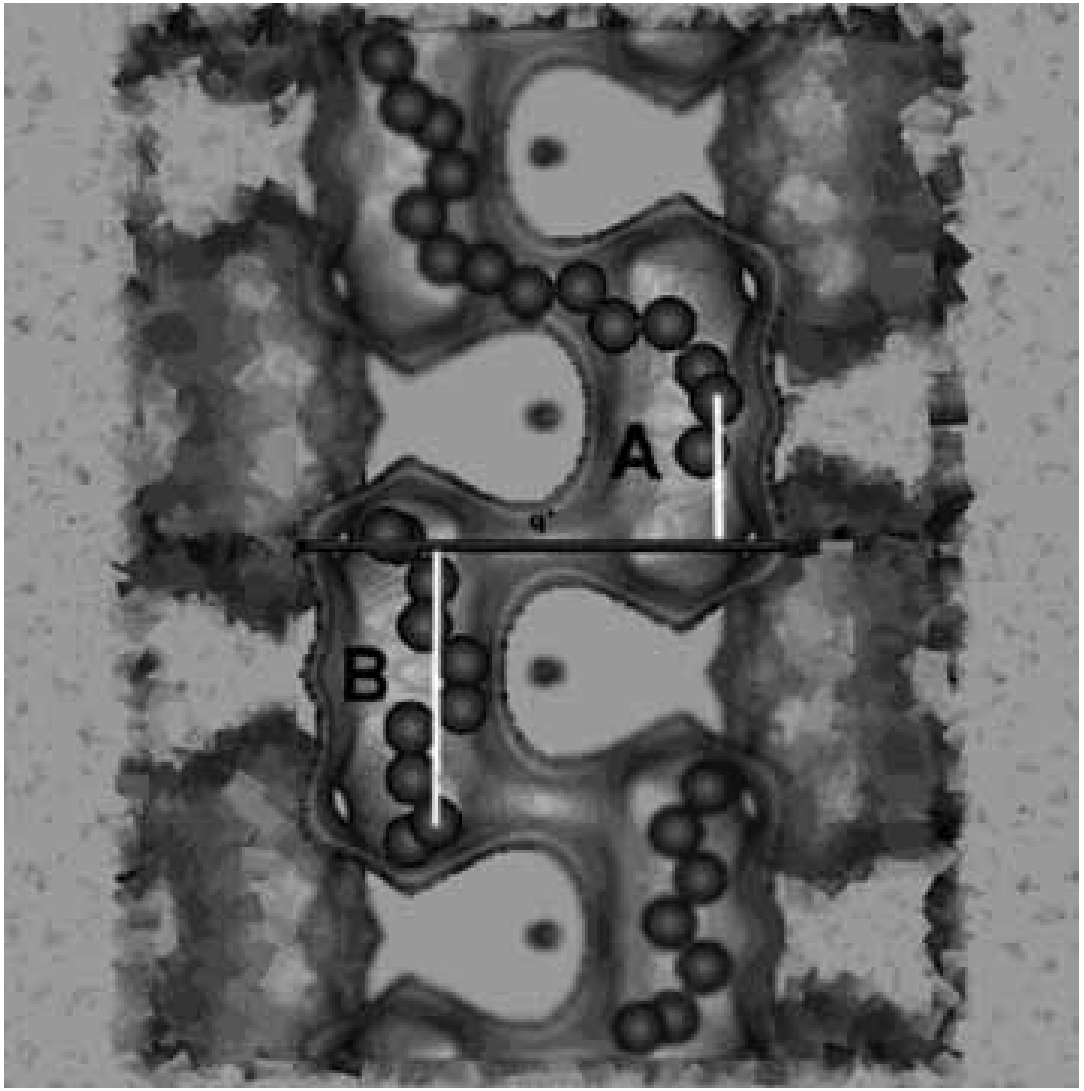


Equimolar mixture simulations



Window effect - Commensurate diffusion

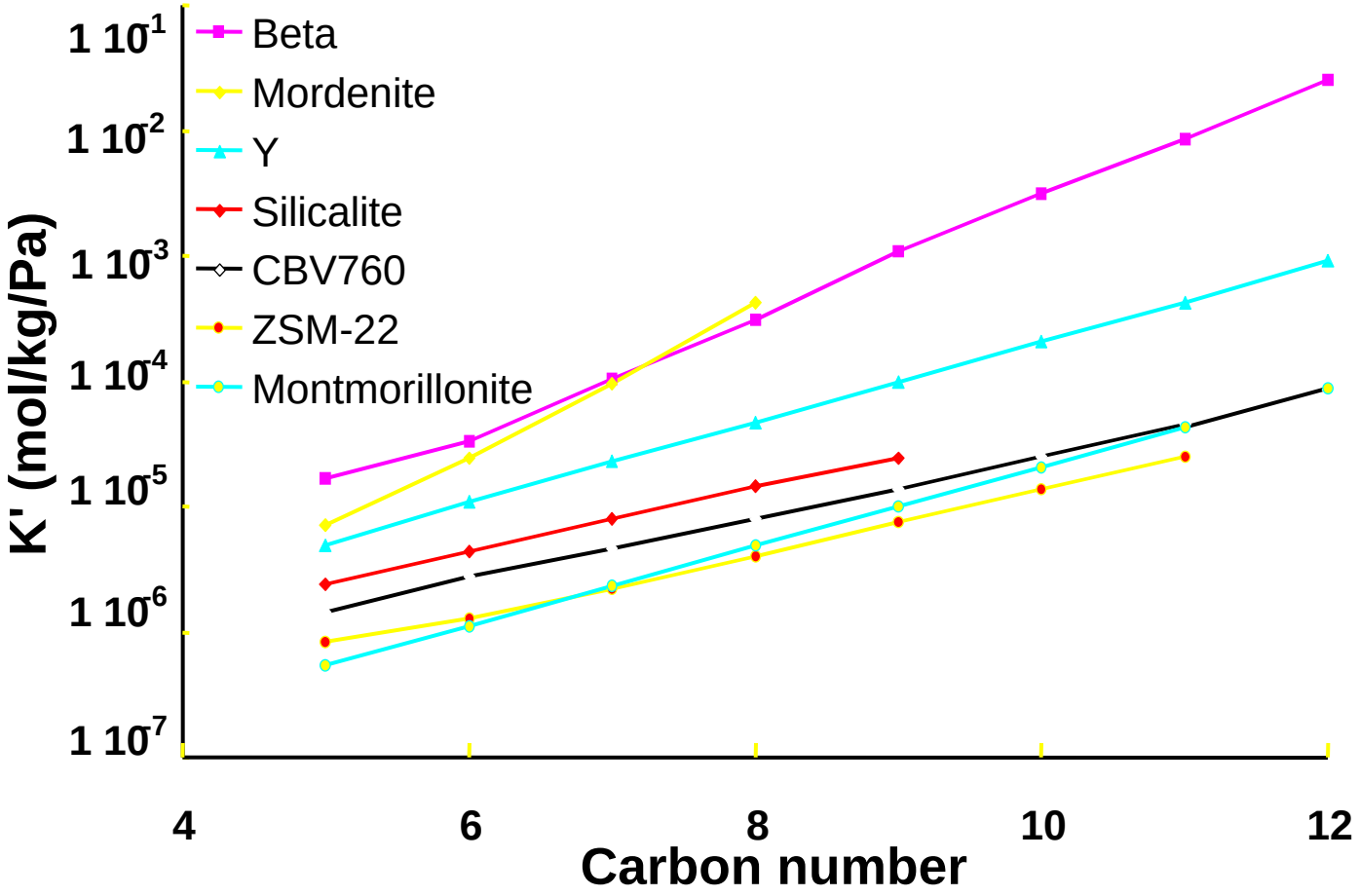
Erionite



Dubbeldam and Smit, *J. Phys. Chem. B, Vol. 107, No. 44, 2003*

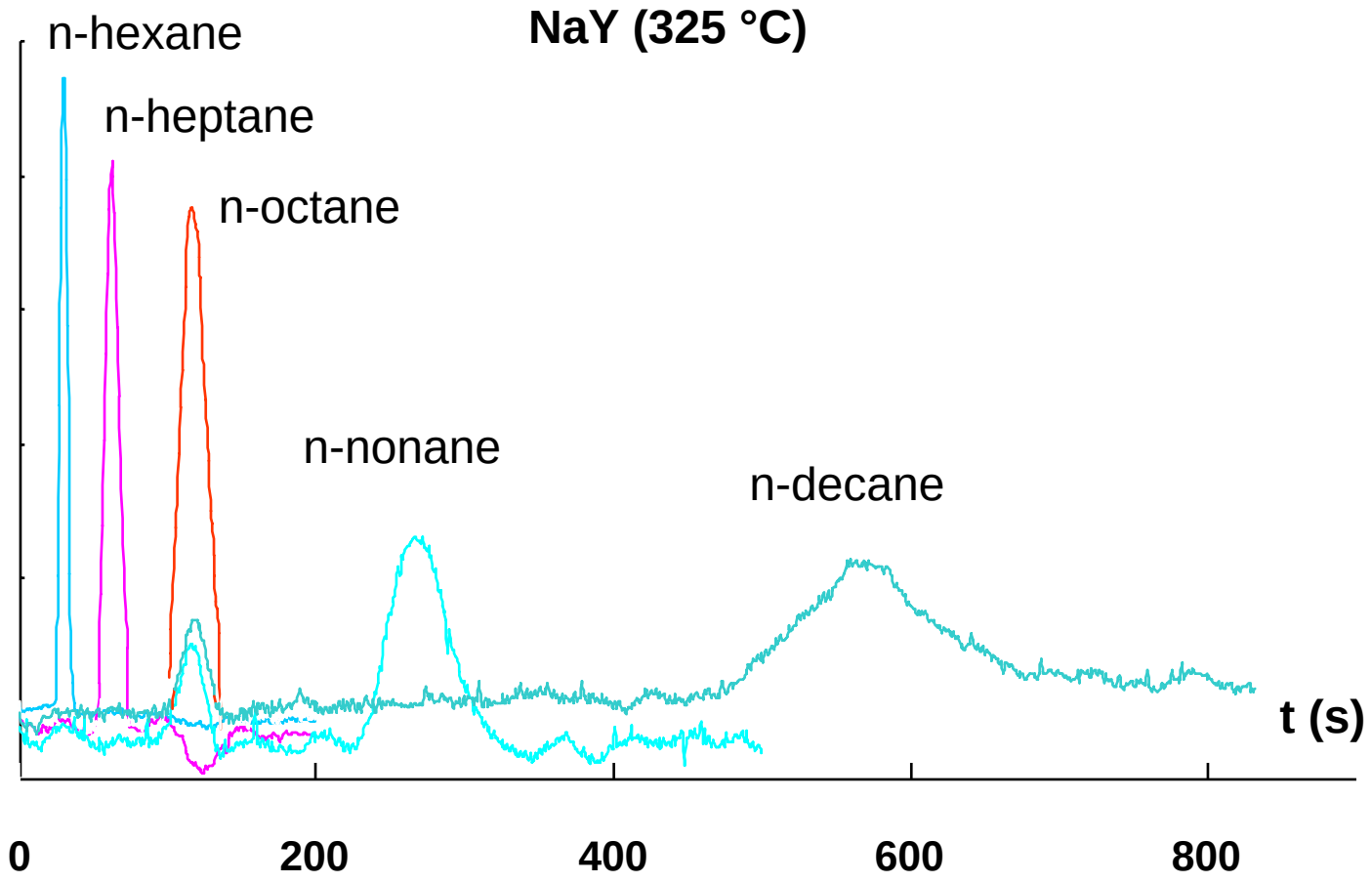
Low coverage – Henry constants

Exponential increase of K' with CN



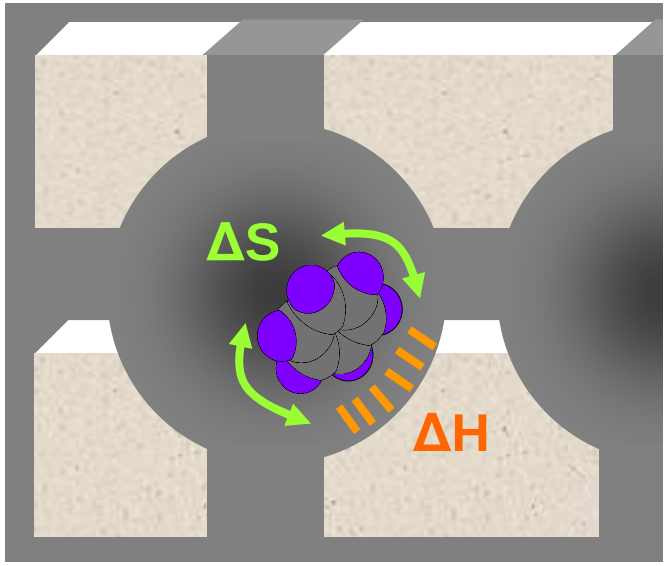
Retention n-alkanes in vapor phase

→ **longer chains more strongly adsorbed**



Molecular assembling

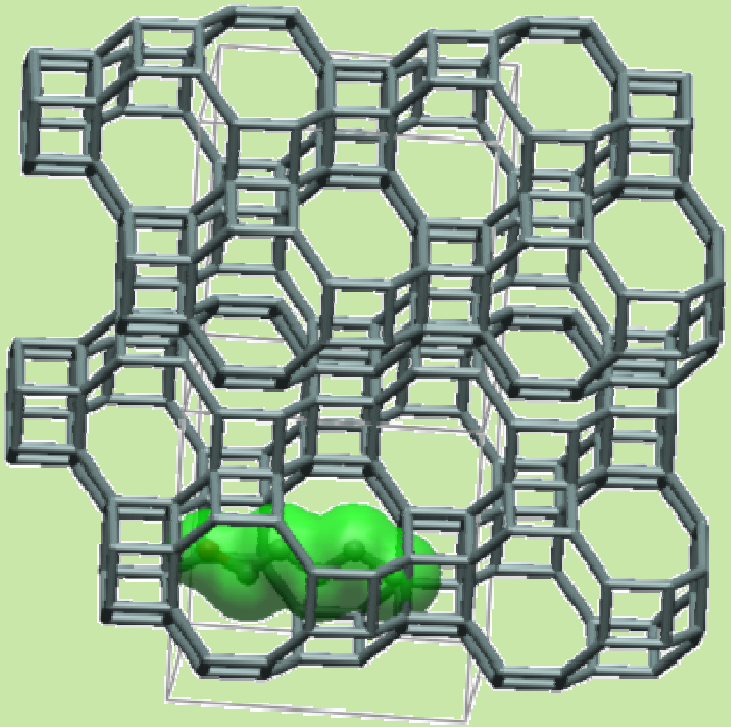
Molecular assembling is the arrangement of adsorbed molecules inside confined pore systems, hereby optimizing the balance between energetic (ΔH) and steric (ΔS) contributions.



$$\Delta G = \Delta H - T\Delta S$$

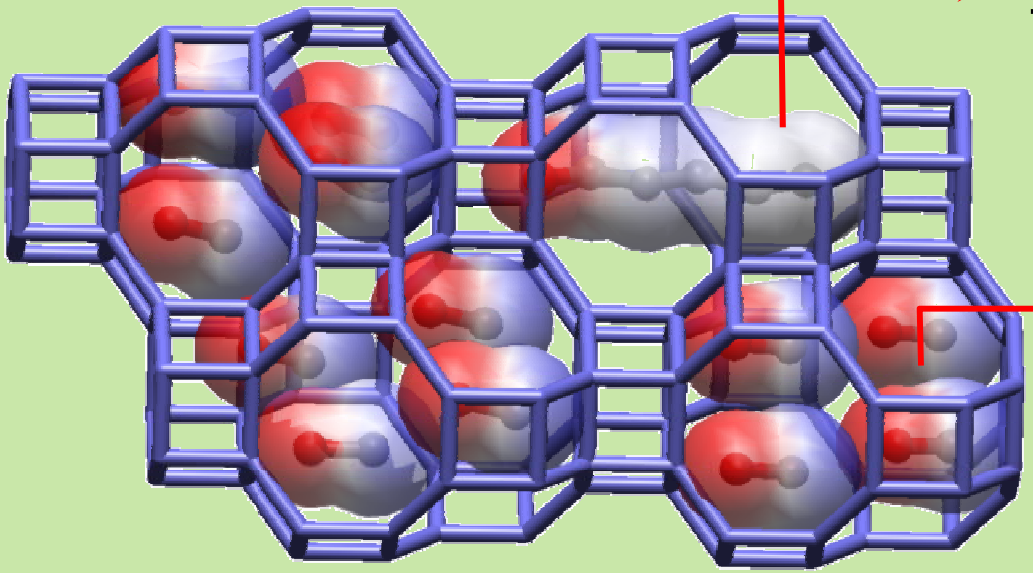
Entropy

$$\text{Enthalpy} = \underbrace{\Phi_R + \Phi_D}_{\text{van der Waals}} \; \underbrace{+\Phi_P + \Phi_\mu + \Phi_q}_{\text{electrostatic}} \; \underbrace{+\Phi_S}_{\text{adsorbate-adsorbate}}$$



Gas phase:

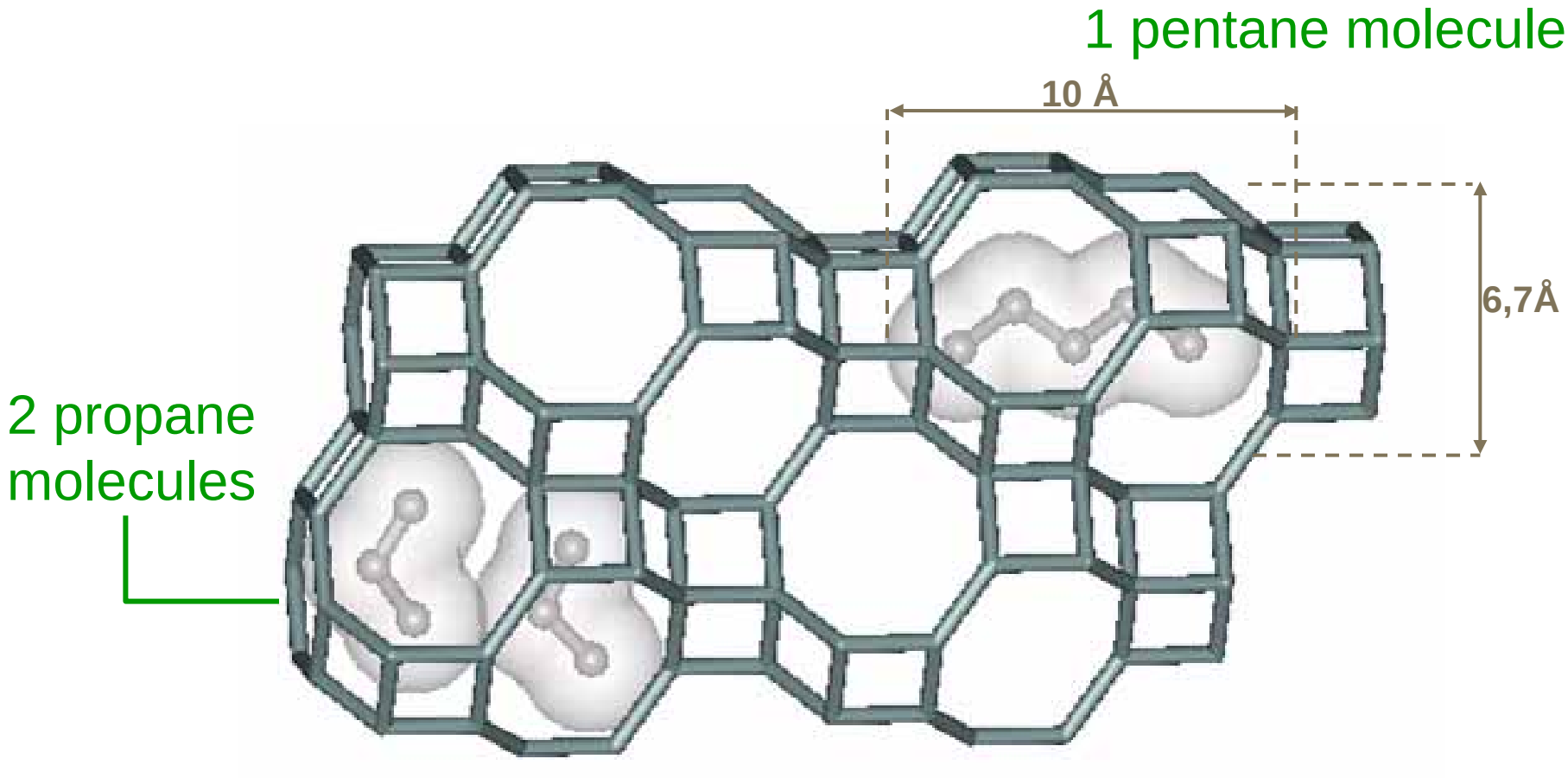
- Low degree of pore filling
- Unrestricted motion from cage to cage
- No “packing” or “assembly” problems



Liquid phase:

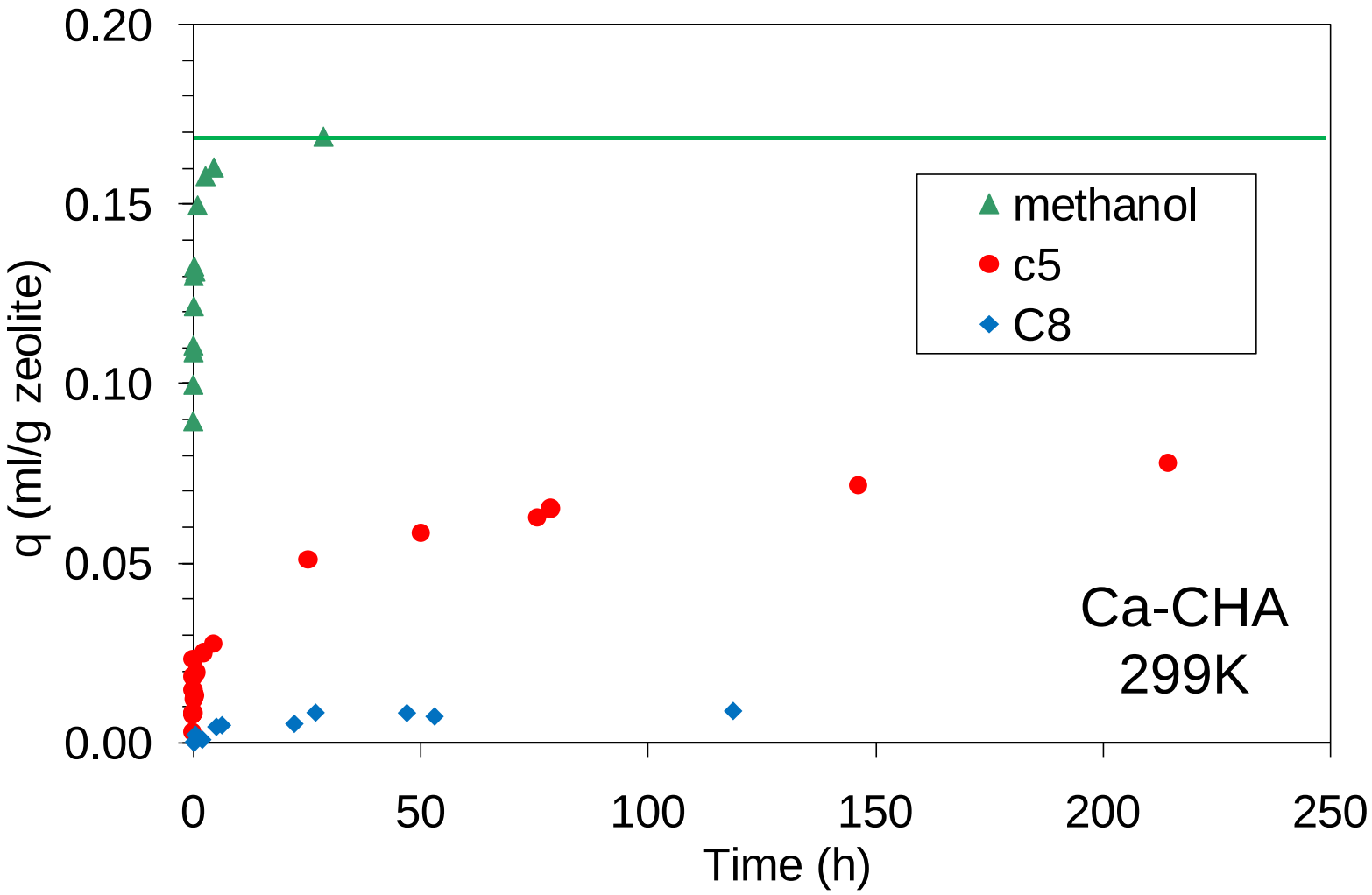
- High degree of pore filling
- Restricted motion from cage to cage
- Molecular packing becomes critical
- Small molecules pack better: configurational entropy advantage

Chabazite and adsorbed molecules



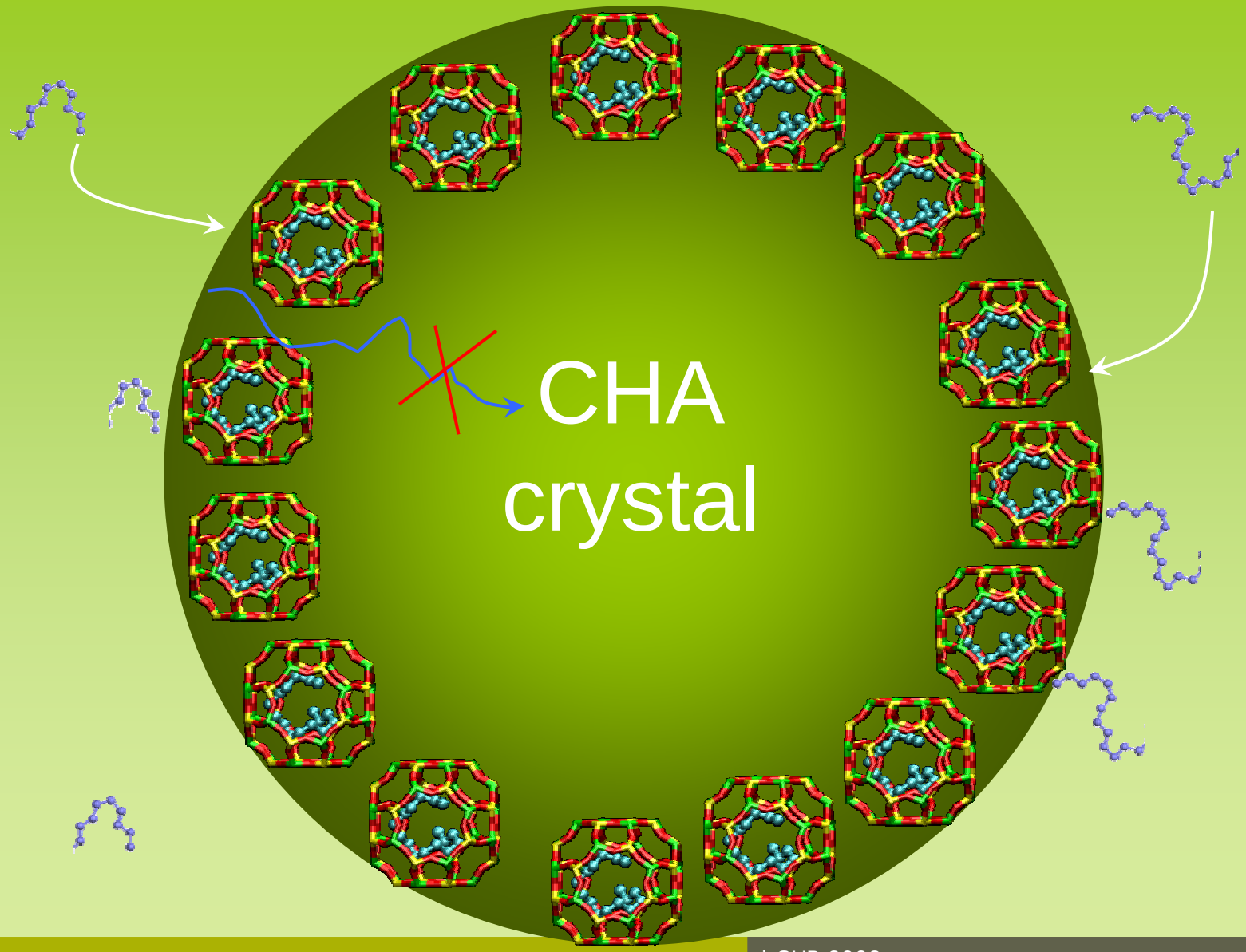
Smaller molecules pack better: Configurational entropy advantage

Adsorption kinetics



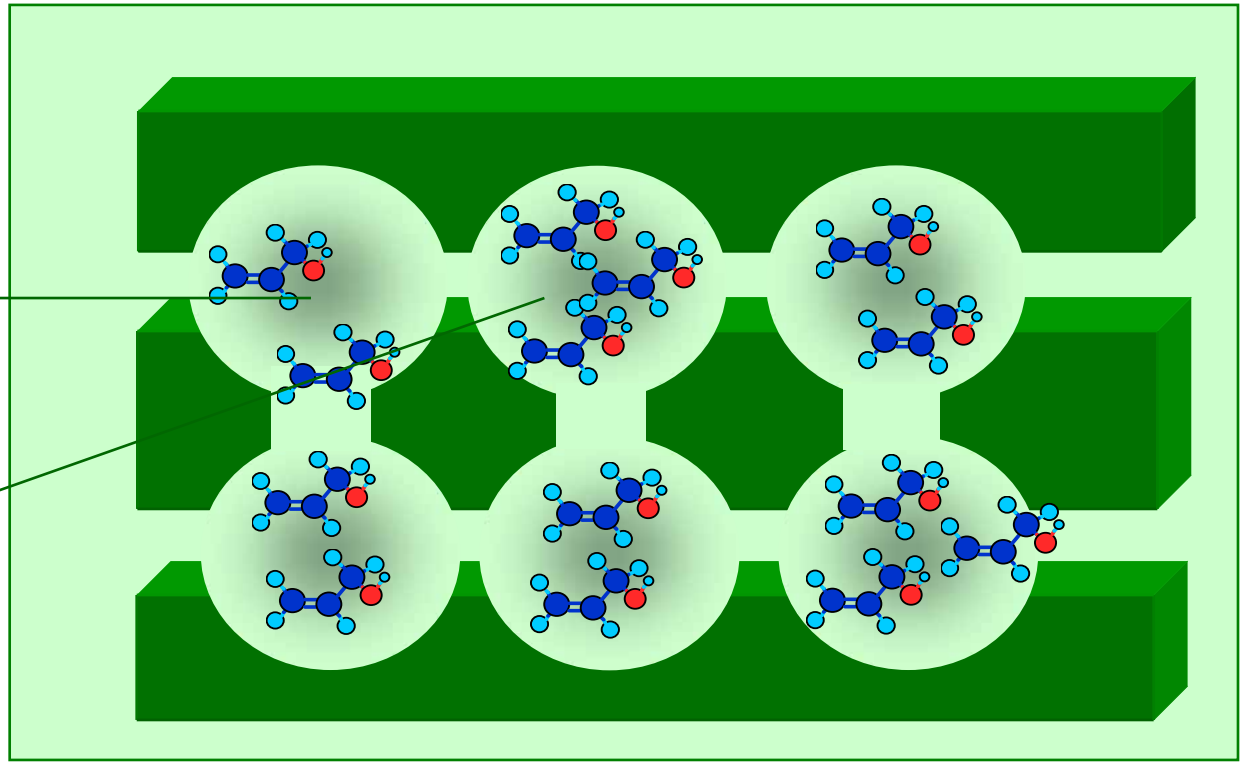
Diffusion limitations for C5 – Possibly also for longer chains

Access blocking by coiled molecules



Molecular Assembling in Confined Spaces

High Adsorption Potential ⇒ High Energetic Interaction



Limited space ⇒ Large entropy losses / Steric effects

⇒ Molecular packing critical