Chabazite: A zeolite allowing selective adsorption of short chain alcohols

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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 occurring zeolite
• Elipsoidal cages connected through 8 MR windows of 3.8 x 4.2 Å
• Separation of N\textsubscript{2} and O\textsubscript{2} from Ar
• Propane / propene separation
• Isostructural to SAPO-34: Methanol to Olefins (MTO) catalyst
Chabazite

Double 6-ring connecting 2 cages

Chabazite cage

Elipsoidal cages with access through 8 MR 3.8 x 4.2 Å

8-ring window
Molecular Assembling in Confined Spaces

Entropy $\Delta S$
- Loss of freedom in pore

Enthalpy $\Delta H$
- Energetic interaction

$K' = K_0' e^{\frac{-\Delta H_0}{RT}}$

$\Delta G_0 = -RT \ln(K' \rho_c RT)$*

$\Delta S_0 = \frac{\Delta H_0 - \Delta G_0}{T}$

*Molecular packing:
- Optimisation enthalpy / entropy

Chain length exclusion in CHA zeolite

Linear hydrocarbon chains
n-alkanes
alcohols
alkenes
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 Na₂O : 2.0 K₂O : 5.18 SiO₂ : Al₂O₃ : 224 H₂O

Si/Al ratio of 2.59

UC: Na₀.₈K₉.₅[Al₁₀.₃Si₂₅.₇O₇₂] N₂-porosimetry 0.17 ml/g (486 m²/g), activated 350°C
## Ion exchanged CHA

### UC composition of exchanged Na-K-CHA

<table>
<thead>
<tr>
<th>Type</th>
<th>Formula</th>
<th>ML/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-CHA</td>
<td>$K_{10.7} \ [Al_{10.7}Si_{25.3}O_{72}]$</td>
<td>0.17 ml/g</td>
</tr>
<tr>
<td>Na-CHA</td>
<td>$Na_{9.5}K_{0.9} \ [Al_{10.4}Si_{25.6}O_{72}]$</td>
<td>0.23 ml/g</td>
</tr>
<tr>
<td>Ca-Cha</td>
<td>$Ca_{4.7}K_{0.8} \ [Al_{10.2}Si_{25.8}O_{72}]$</td>
<td>0.19 ml/g</td>
</tr>
</tbody>
</table>

![Ca-CHA isotherm](image)

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Molecular Simulations

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

\[ K' \]

\[ \text{Carbon number of } n\text{-alkane} \]

\[ \begin{align*}
\text{OFF-type silica} & \quad \text{ERI-type silica} \\
\text{CHA-type silica} & \quad \text{AFX-type silica} \\
\text{RHO-type silica} & \quad \text{KFI-type silica}
\end{align*} \]

1David 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

-\ln(K_0') (mol/kg/Pa) vs. -\Delta H_0 (kJ/mol)

Adsorption entropy vs. Adsorption enthalpy
Adsorption mechanism

\[ C_1 \text{ to } C_5 \]

Alkanes to \( C_5 \): stretched in cages

8.84 Å
Adsorption thermodynamics

\[ \ln(K_{0}' (mol/kg/Pa)) = -\Delta H_0 (kJ/mol) \]

Graph showing the relationship between \(-\ln(K_{0}')\) and \(-\Delta H_0\) for various points labeled C1 to C12.
Adsorption mechanism

\[ \text{C}_6 \text{ to C}_{10} \]

- \( \text{C}_6 \) to \( \text{C}_{10} \) alkanes: coiled configuration
- Maximally 10 CH\(_2\) groups per cage
Adsorption thermodynamics

![Graph showing adsorption thermodynamics with data points labeled C1 to C12.](image)
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

\[ q = \frac{hC}{1+bC} \]  and  \[ q' = \frac{K' C}{1+bC} \]

\[ q'_{s} \quad \text{adsorption constant} \]

\[ q_{s} \quad \text{saturation capacity} \]
n-alkanes on CHA in liquid phase

Complete cage filling

Cut-off between C2 and C3

Ca-CHA 299K
1-alcohols on CHA in liquid phase

- Cut-off between C2 and C3
- 2nd cut-off between C4 and C5

Graph showing the number of molecules per cage for various alcohols with different carbon counts.
1-alcohols on CHA in liquid phase

Cation effect

Na-CHA 299K

⇒ No clear cut-off
⇒ Cations affect adsorption mechanism
1-alcohols on CHA in liquid phase

Cation effect

K-CHA
299K

Cut-off between C4 and C5

methanol
ethanol
1-propanol
1-butanol
1-pentanol
1-hexanol
1-heptanol

q (molec / SC)

q (C-at / SC)

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CBMC modelling

With cations!

Gas phase versus Liquid phase

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

1 pentanol molecule / cage
4 ethanol molecules / cage
Liquid phase, mixtures?

Column separation experiments
Ethanol / propanol mixture adsorption

Ca-CHA

Ethanol

Propanol

Na-CHA

Ethanol

Propanol

Mole fraction 1-propanol

Mole fraction 1-propanol
Breakthrough curves Ca-CHA

\[ \text{ethanol/1-propanol} \]

\[ \Rightarrow \text{preferential adsorption of the shortest molecule ethanol} \]
Ethanol – Hexanol binary equilibrium

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

The diagram shows the concentration of CH$_4$ and CO$_2$ over time, with CH$_4$ and CO$_2$ labeled on the graph. The concentration values are given in $10^{-6}$ units. The time axis is in seconds, ranging from 0 to 1800 seconds.
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

Thank you!
Very difficult, slow desorption

**Ca CHA:** Desorption with octane

- Absoute concentration (wt %)
- D~$2 \times 10^{-17}$ m$^2$/s

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- Concentration (wt %)
- Volume (ml)
- Ethanol
- 0.01 ml/g CHA
Alkane conformations in CHA

C1  C2  C3  nC4
nC5  nC6  nC7  nC8
Vapor phase isotherms Ca-CHA 70°C

- Higher capacity for methanol

![Graph showing isotherms for methanol and 1-butanol with a Langmuir fit for 1-butanol.](image-url)
Liquid phase in iso-C8 on Ca-CHA

- Methanol
- Ethanol
- 1-Propanol
- 1-Butanol
- 1-Pentanol
- 1-Hexanol
- 1-Heptanol

q (molec / SC)

Ca CHA tweede staal (2007)
Ca CHA eerste staal (2004)
Equimolar mixture simulations
Window effect - Commensurate diffusion

Erionite

Low coverage – Henry constants

Exponential increase of $K'$ with CN

$K'$ (mol/kg/Pa)

$1 \times 10^{-1}$

$1 \times 10^{1}$

$1 \times 10^{2}$

$1 \times 10^{3}$

$1 \times 10^{4}$

$1 \times 10^{5}$

$1 \times 10^{6}$

$1 \times 10^{7}$

Carbon number

4

6

8

10

12

Beta

Mordenite

Y

Silicalite

CBV760

ZSM-22

Montmorillonite
Retention n-alkanes in vapor phase

→ longer chains more strongly adsorbed

n-hexane
n-heptane
n-octane
n-nonane
n-decane

NaY (325 °C)

0 200 400 600 800

\( t \) (s)
Molecular assembling is the arrangement of adsorbed molecules inside confined pore systems, hereby optimizing the balance between energetic ($\Delta H$) and steric ($\Delta S$) contributions.

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

Enthalpy = $\Phi_R + \Phi_D + \Phi_P + \Phi_\mu + \Phi_q + \Phi_S$

- van der Waals
- electrostatic
- adsorbate-adsorbate

Entropy
Gas phase:

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

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- 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

CHA crystal
Molecular Assembling in Confined Spaces

High Adsorption Potential $\Rightarrow$ High Energetic Interaction

Limited space $\Rightarrow$ Large entropy losses / Steric effects $\Rightarrow$ Molecular packing critical