A new generation of hierarchical structured materials with high adsorption capacity and selectivity

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Introduction: Porous Adsorbents

Zeolites

- Micropores < 1 nm

→ MOR:

+ Shape selectivity
+ Good stability

- Diffusion limitations
- Pore obstruction
- Limited access
# Introduction: Porous Adsorbents

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>Mesoporous Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Micropores &lt; 1 nm</td>
<td>• Mesopores 2 - 30 nm</td>
</tr>
</tbody>
</table>

→ **MOR:**
+ Shape selectivity
+ Good stability
- Diffusion limitations
- Pore obstruction
- Limited access

→ **MCM-41 & MCM-48:**
+ Fast diffusion
+ Good accessibility
- No shape selectivity
- Inferior stability
- Weaker acidity
Introduction: Porous Adsorbents

Biporous Hierarchical Material

- Micropores AND Mesopores
- Mesoporous Material
  + Fast diffusion
  + Good accessibility
- Zeolite
  + Shape selectivity
  + Good stability
  + Large number of sites

Zeolite nuclei
- Nanoslabs: 1.3 x 1.3 x 4.0 nm³

Silicalite-1 framework
- First level of porosity
  - Micropores: 0.55 nm

Kirschhock et al., Chem.Eur.J., 2005
Materials

**Zeogrid**
- Half-nanoslab suspension
- CTMABr template
- • Ultra-micropores: 0.55 nm
- • Rectangular mesopores: 3.0 nm

**Zeotile-2**
- Half-nanoslab suspension
- CTMABr template
- Stirred & Heated
- • Ultra-micropores: 0.55 nm
- • Cubic mesopores: 2.7 nm

**Zeotile-4**
- Double nanoslab suspension
- P123
- HCL\textsubscript{aq} solution
- • Ultra-micropores: 0.55 nm
- • Hexagonal mesopores: 7.3 nm

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Kremer et al., C.R.Chimie, 2005  
Kirschhock et al., Chem.Eur.J., 2005

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Goal

Study of the Gas phase Adsorption properties

→ Low and High surface coverage

→ Compare to Zeolites and Mesoporous solid
Low Coverage: Pulse gas chromatography

\[ K' = \frac{q_i}{p_i} \]

\[ \mu = \frac{L}{V_f} \left[ (\varepsilon_{ext} + \varepsilon_{macr}) + (1 - \varepsilon_{ext} - \varepsilon_{macr})RT \rho_c K' \right] \]

Henry Constant \( K' \)
Adsorption Enthalpy \( \Delta H_0 \)
Adsorption Entropy \( \Delta S_0 \)
High Coverage: Gravimetric Technique

\[ K_i' = \frac{q_i}{p_i} \]

Adsorption Isotherm:
Results: Overview

Low Coverage: Pulse gas chromatography
→ Aspecific interactions: $n$-alkanes
→ Shape Selective Properties: $n$- and iso-alkanes
→ Specific interactions: 1-alkenes & aromatics

High Loading: Gravimetric experiments
→ Aspecific interactions: $n$-octane
→ Specific interactions: 1-alkenes & aromatics
Henry constants $K'$ at 160°C

- Exponential increase
- $K'_{\text{ZEOLITES}} \gg K'_{\text{BIPOROUS MATERIALS}} = K'_{\text{MCM-48}}$
Low Coverage, Aspecific interactions

Van ‘t Hoff plot (50-250°C):

- Highly linear for all alkane components
- Differences in $K'$ related to:
  → Adsorption enthalpy $\Delta H_0$
  → Adsorption entropy $\Delta S_0$
  → number of adsorption sites
Low Coverage, Aspecific interactions

\[ K' = K'_0 \cdot \exp^{-\Delta H_0 / RT} \]

- Microporous Zeolites: highest adsorption enthalpy
- Only subtle differences between Mesoporous and Biporous

Adsorption Enthalpy

<table>
<thead>
<tr>
<th>Carbon number</th>
<th>-(\Delta H_0) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>70</td>
</tr>
<tr>
<td>9</td>
<td>90</td>
</tr>
</tbody>
</table>

Zeolite ZSM-5
Zeotile-4
Zeotile-2
MCM-48
Zeogrid
Low Coverage, Shape Selectivity

*n- and iso-alkanes*

- Branched alkanes: less adsorption
- Shape Selective Property
Low Coverage, Shape Selectivity

Separation factors at 160°C

\[ \alpha = \frac{K'_n \text{-alkane}}{K'_i \text{-iso-alkane}} \]

<table>
<thead>
<tr>
<th></th>
<th>Zeotile-4</th>
<th>Zeogrid</th>
<th>MCM-48</th>
<th>Zeotile-2</th>
<th>ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)-C8 / 2-MeC7</td>
<td>1.2</td>
<td>1.2</td>
<td>1.3</td>
<td>1.5</td>
<td>2.1</td>
</tr>
<tr>
<td>(n)-C8 / 2,5diMeC6</td>
<td>1.4</td>
<td>1.4</td>
<td>1.5</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>(n)-C8 / 2,2,4-triMeC5</td>
<td>1.8</td>
<td>1.7</td>
<td>2.0</td>
<td>3.1</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

- \(\alpha\): ZSM-5 \(>>\) Zeotile-2 > Zeogrid, Zeotile-4 and MCM-48
- Biporous materials: separating linear from branched alkanes
Low Coverage, Shape Selectivity

**Zeotile-2 versus MCM-48**

Zeotile-2

- Cubic structure
- Micropores: 0.55 nm
- Mesopores: 2.7 nm

MCM-48

- Cubic structure
- NO micropores
- Mesopores: 2.5 nm
Low Coverage, Shape Selectivity

Separation factors at 160°C

- Separation factors: Zeotile-2 > MCM-48
Low Coverage, Shape Selectivity

Adsorption enthalpy

- Interaction energy: Zeotile-2 > MCM-48
- Micropore adsorption
Low Coverage, Shape Selectivity

Vapour Pressure

\[ \log K' = a \cdot \log p_s + b \]

<table>
<thead>
<tr>
<th>Log ( p_s ) (bar)</th>
<th>Log ( K' ) (mol/kg/Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-5.5</td>
</tr>
<tr>
<td>0.2</td>
<td>-5</td>
</tr>
<tr>
<td>0.4</td>
<td>-4.5</td>
</tr>
<tr>
<td>0.6</td>
<td>-4</td>
</tr>
<tr>
<td>0.8</td>
<td>-3.5</td>
</tr>
<tr>
<td>1</td>
<td>-3</td>
</tr>
<tr>
<td>1.2</td>
<td>-2.5</td>
</tr>
<tr>
<td>1.4</td>
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</tr>
<tr>
<td>1.6</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

- Linear alkanes
- Branched alkanes

MCM-48: No Shape Selective Properties
Zeotile-2: Shape Selective Properties

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Low Coverage, Specific interactions

Chromatogram: 200°C on Zeotile-2

- Preference in adsorption: aromatics > alkenes > alkanes
**Low Coverage, Specific interactions**

Separation factors at 160°C

\[ \alpha = \frac{K'_i}{K'_j} \]

<table>
<thead>
<tr>
<th></th>
<th>Zeotile-2</th>
<th>Zeotile-4</th>
<th>Zeogrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene/ ( n )-hexane</td>
<td>2.3</td>
<td>1.8</td>
<td>1.4</td>
</tr>
<tr>
<td>1-hexene/ ( n )-hexane</td>
<td>1.9</td>
<td>1.3</td>
<td>1.7</td>
</tr>
<tr>
<td>o-xylene/ m-xylene</td>
<td>1.0</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>p-xylene/ m-xylene</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

- Preference in adsorption: aromatics > alkenes > alkanes
- Xylene isomers: no separation
High Coverage, Aspecific interactions

- Two Step Behaviour
- High adsorption capacities! → 40-50 wt%
- Zeolites → Max 35 wt%, Typical < 20 wt%

$n$-octane (70°C)

Zeotile-2

Silicalite

Sun et al., J.Phys.Chem., 1996
High Coverage, Specific interactions

**o-xylene, 1-octene and n-octane (70°C)**

- 1-octene & n-octane: similar adsorption capacities
- o-xylene: stronger adsorption + higher adsorption capacity

Zeotile-2

![Graph showing weight % change vs. \( \frac{P_{vap}}{P_{sat}} \)]

- o-Xylene
- 1-Octene
- n-Octane

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High Coverage, Specific interactions

Xylene isomers (70°C)

- Xylene isomers: no separation
- High capacities
Conclusions

- Lower $K'$ and $\Delta H_0$ compared to zeolites
- Significant higher adsorption capacities
  $\rightarrow$ Up to 50 weight %
- Selectivity: aromatics $>$ alkenes $>$ alkanes
- Presence of micropores
  $\rightarrow$ Shape Selectivity at low coverage: Zeotile-2
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- IWT Vlaanderen (SBO ‘BIPOM’)

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