

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

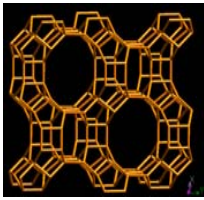
- Diffusion limitations
- Pore obstruction
- Limited access

Introduction: Porous Adsorbents

Zeolites

- Micropores < 1 nm

→ MOR:



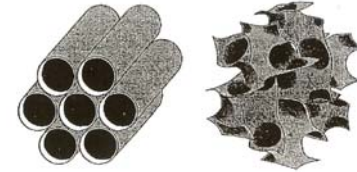
- + Shape selectivity
- + Good stability

- Diffusion limitations
- Pore obstruction
- Limited access

Mesoporous Silica

- Mesopores 2 - 30 nm

→ MCM-41 & MCM-48:



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

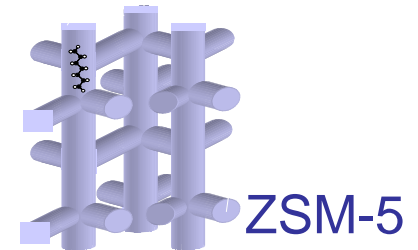
+ Shape selectivity
+ Good stability
+ Large number of sites

Zeolite nuclei

- Nanoslabs: $1.3 \times 1.3 \times 4.0 \text{ nm}^3$

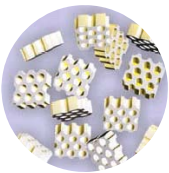
Kirschhock *et al.*, Chem.Eur.J., 2005

Silicalite-1 framework



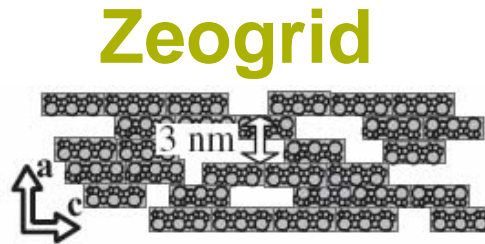
Micropores: 0.55 nm

First level of porosity



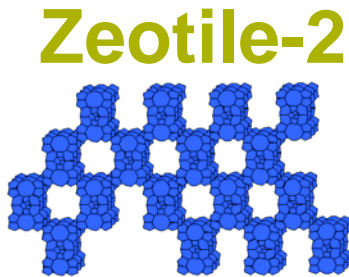
Materials

Half-nanoslab suspension
CTMABr template



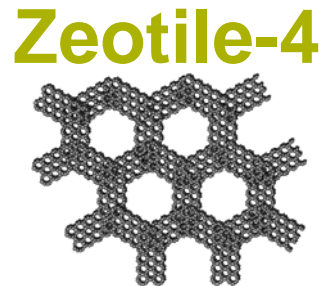
- Ultra-micropores: **0.55 nm**
- Rectangular mesopores: **3.0 nm**

Half-nanoslab suspension
CTMABr template
Stirred & Heated



- Ultra-micropores: **0.55 nm**
- Cubic mesopores: **2.7 nm**

Double nanoslab suspension
P123
HCL_{aq} solution



- Ultra-micropores: **0.55 nm**
- Hexagonal mesopores: **7.3 nm**

Kremer *et al.*, Adv.Funct.Mater, 2002
Kremer *et al.* Solid State Sciences, 2005

Kremer *et al.* Adv.Mater, 2003
Kirschhock *et al.*, Chem.Eur.J., 2005

Kremer *et al.*, C.R.Chimie, 2005

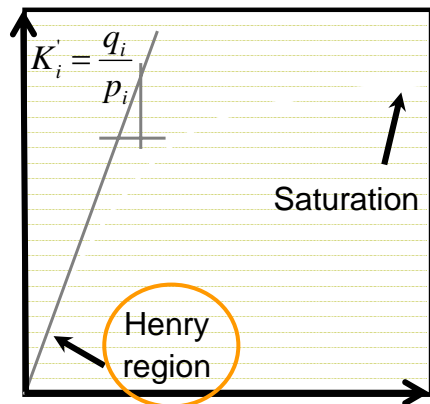
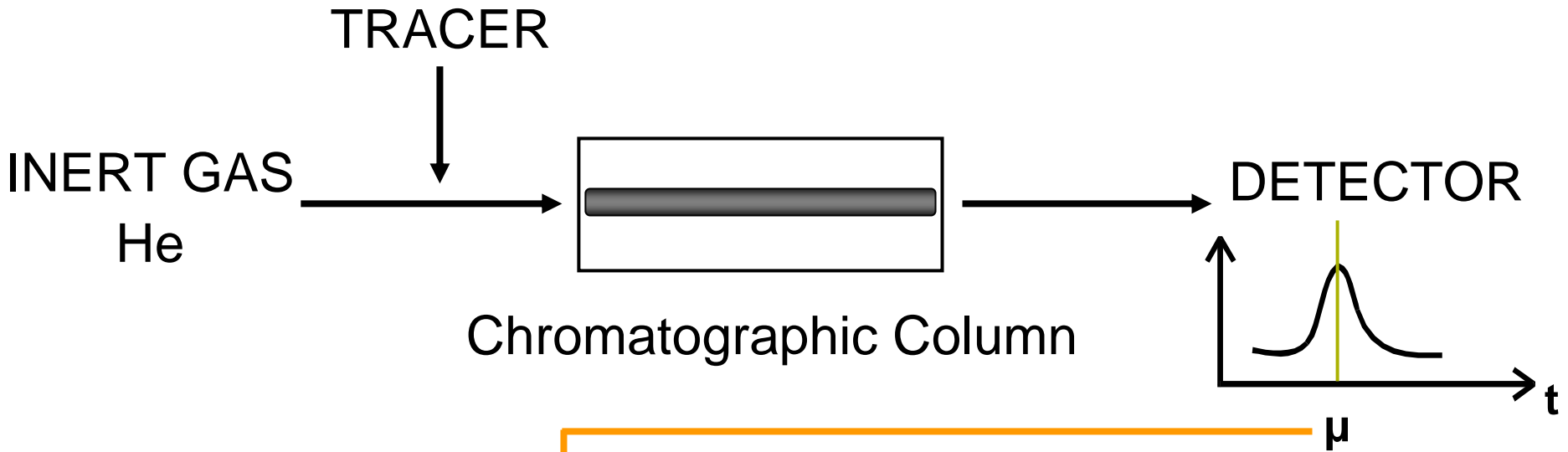
Goal

Study of the Gas phase Adsorption properties

→ Low and High surface coverage

→ Compare to Zeolites and Mesoporous solid

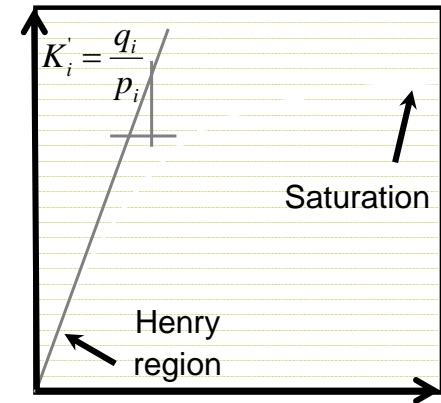
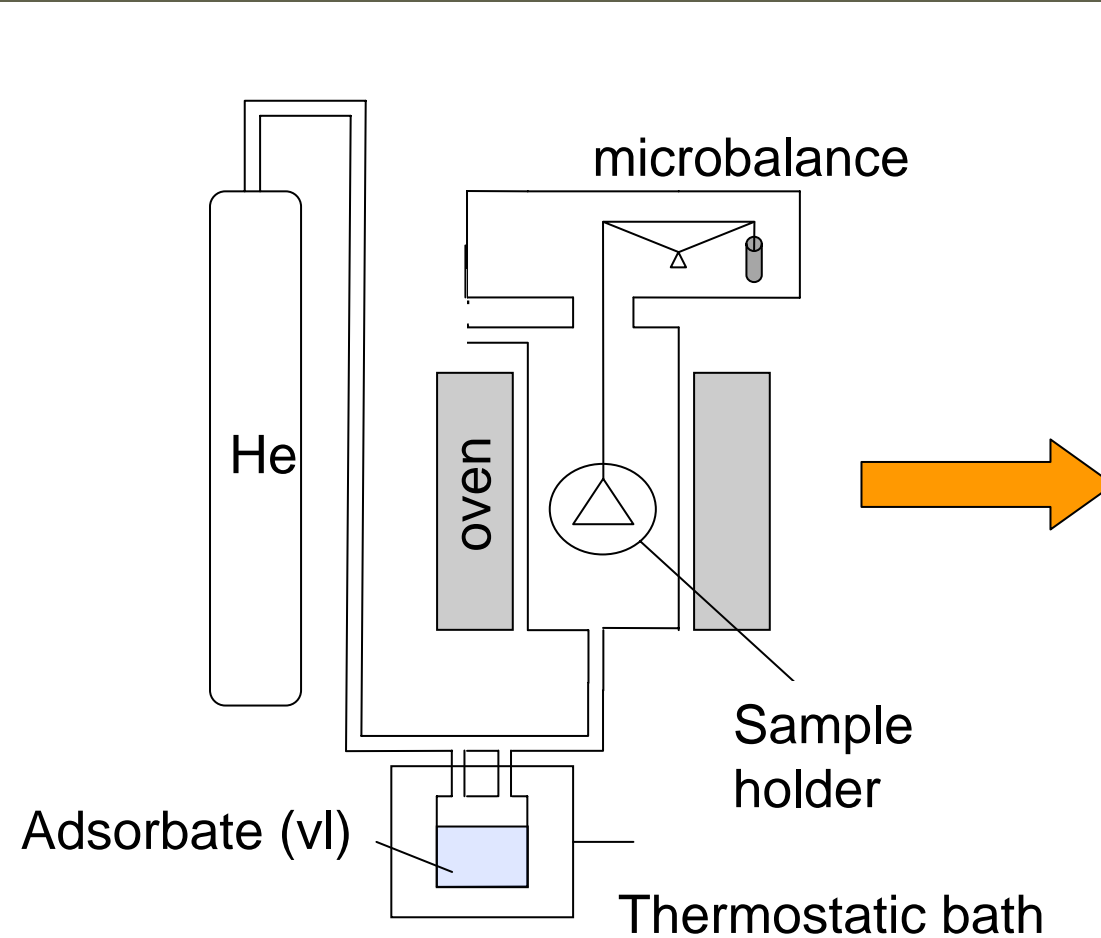
Low Coverage: Pulse gas chromatography



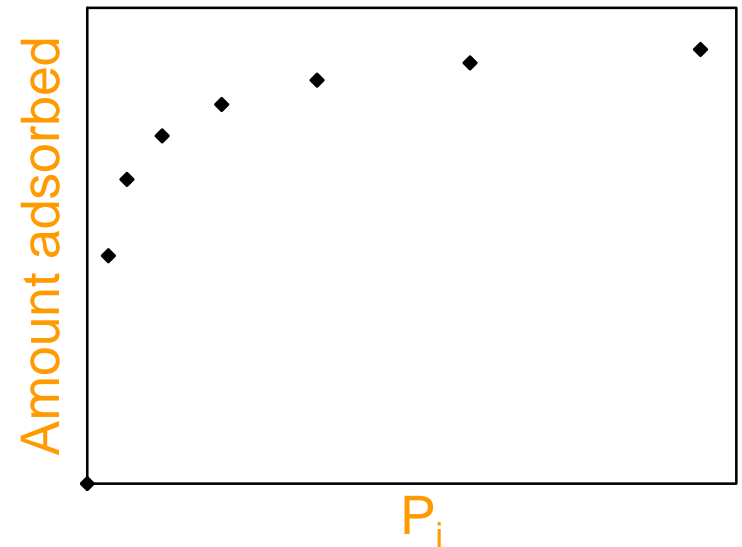
$$\mu = \frac{L}{v_f} \left[(\epsilon_{\text{ext}} + \epsilon_{\text{macr}}) + (1 - \epsilon_{\text{ext}} - \epsilon_{\text{macr}}) RT \rho_c K' \right]$$

Henry Constant K'
 Adsorption Enthalpy ΔH_0
 Adsorption Entropy ΔS_0

High Coverage: Gravimetric Technique



Adsorption Isotherm:



Results: Overview

Low Coverage: Pulse gas chromatography

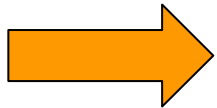
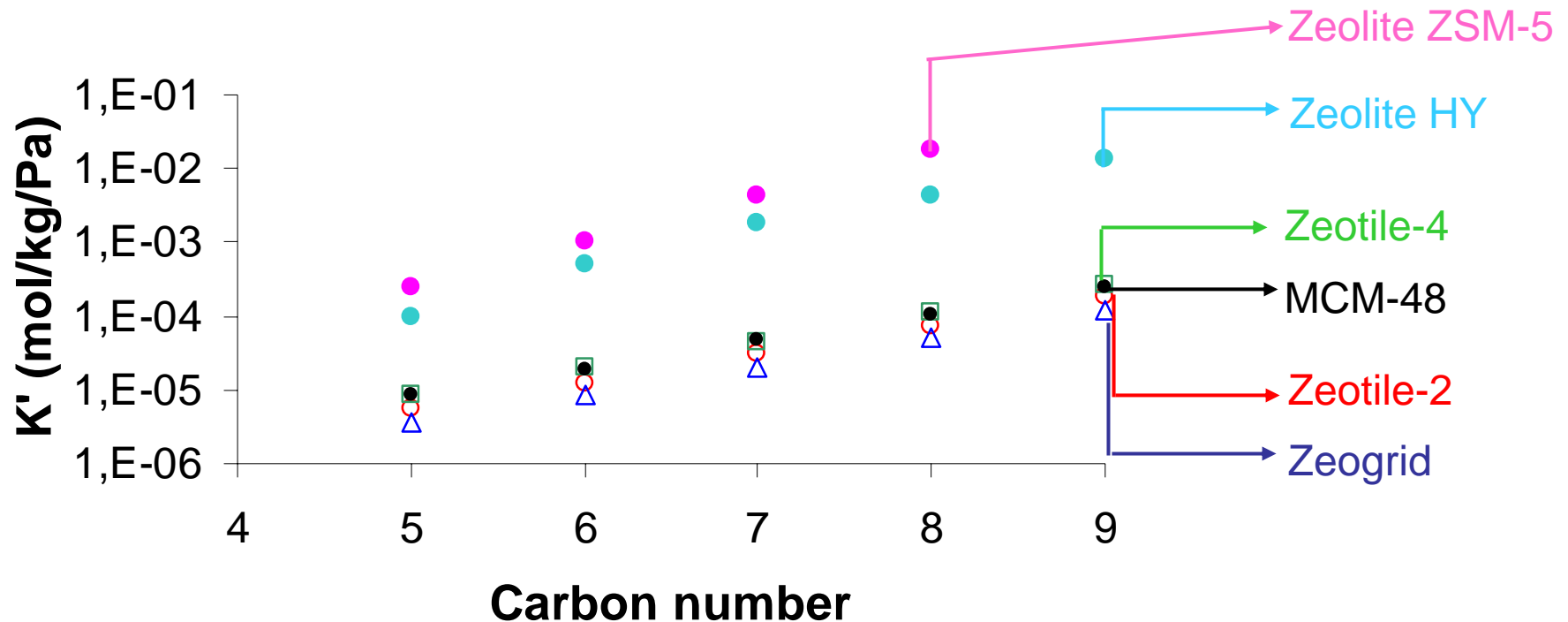
- Aspecific interactions: *n*-alkanes
- Shape Selective Properties: *n*- and iso-alkanes
- Specific interactions: 1-alkenes & aromatics

High Loading: Gravimetric experiments

- Aspecific interactions: *n*-octane
- Specific interactions: 1-alkenes & aromatics

Low Coverage, Aspecific interactions

Henry constants K' at 160°C

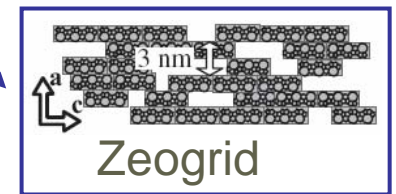
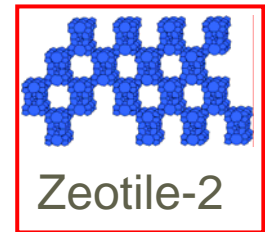
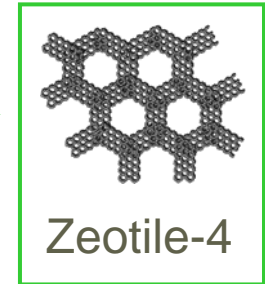
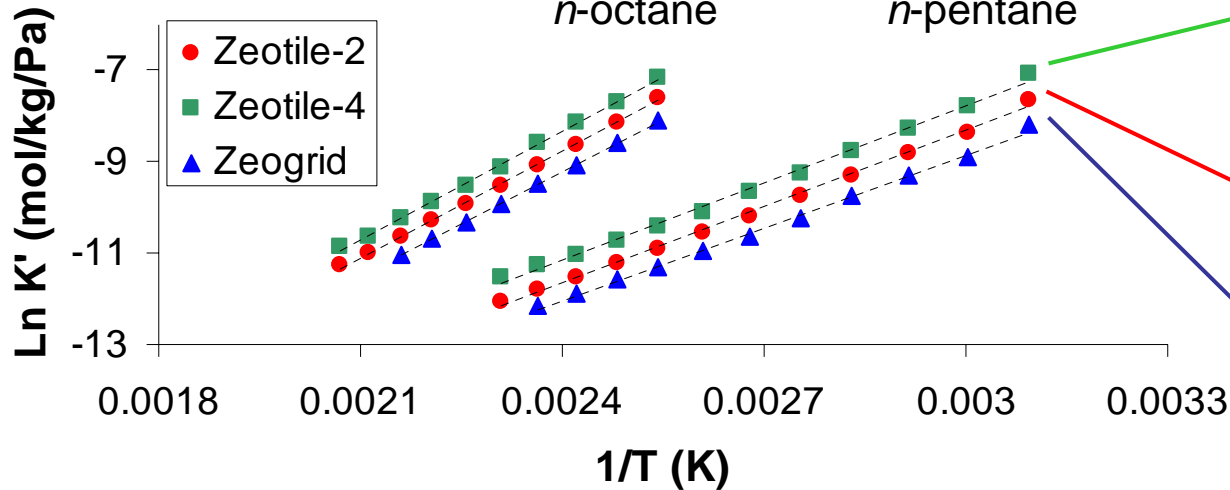


- Exponential increase

- $K'_{\text{ZEOLITES}} \gg K'_{\text{BIPOROUS MATERIALS}} = K'_{\text{MCM-48}}$

Low Coverage, Aspecific interactions

Van 't Hoff plot (50-250°C):



- Highly linear for all alkane components

- Differences in K' related to:

→ Adsorption enthalpy ΔH_0

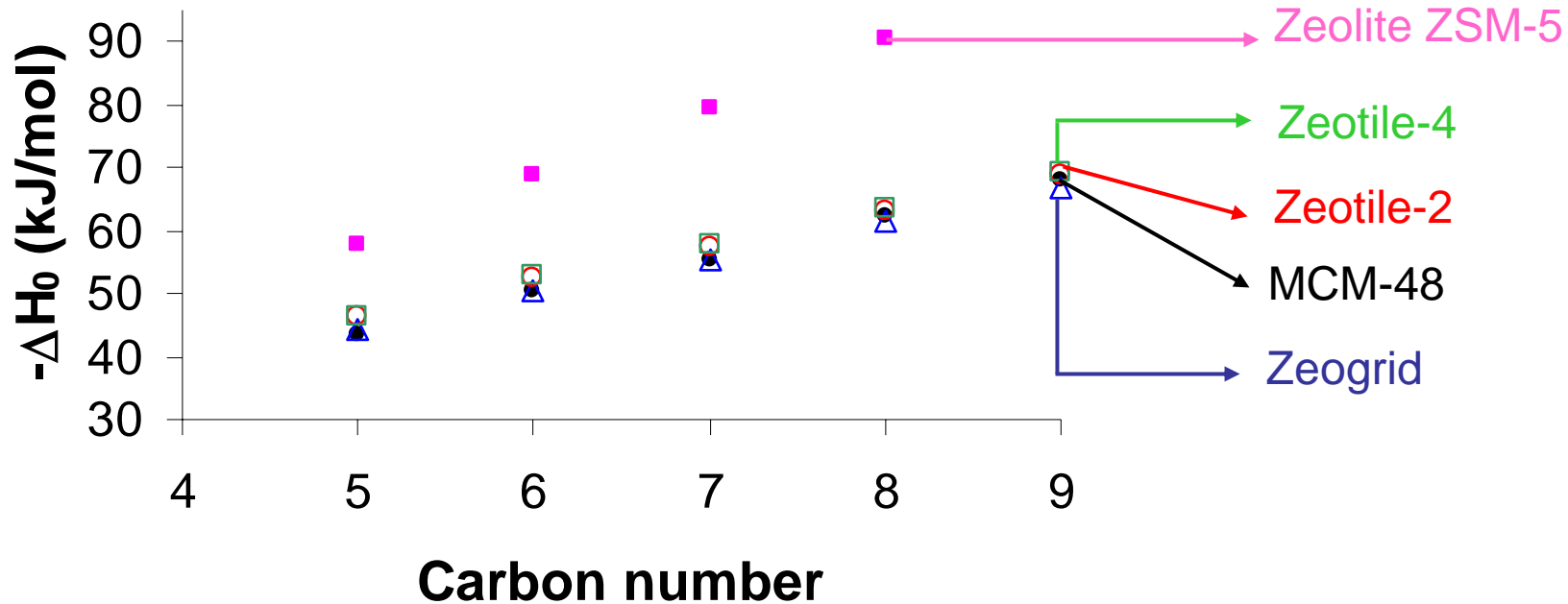
→ Adsorption entropy ΔS_0

→ number of adsorption sites

Low Coverage, Aspecific interactions

Adsorption Enthalpy

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

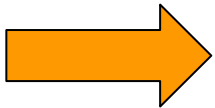
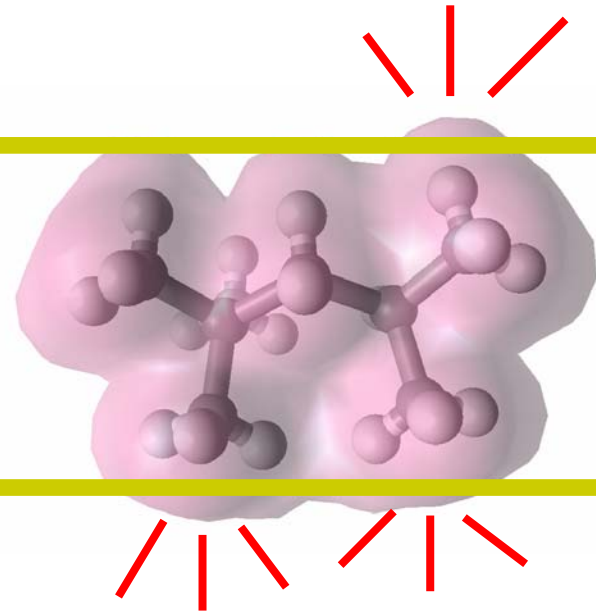
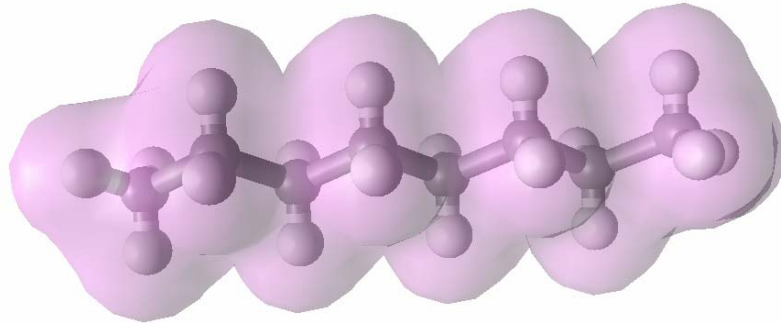


- Microporous Zeolites: highest adsorption enthalpy
- Only subtle differences between Mesoporous and Biporous

Low Coverage, Shape Selectivity

n- and iso-alkanes

Micropore



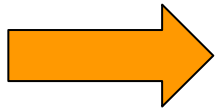
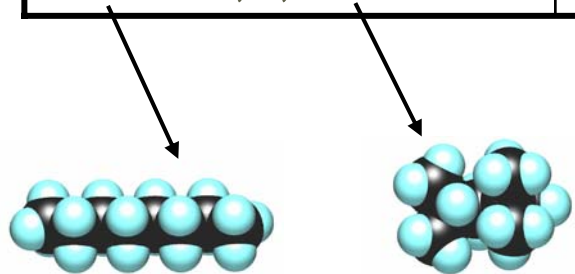
- Branched alkanes: less adsorption
- Shape Selective Property

Low Coverage, Shape Selectivity

Separation factors at 160°C

$$\alpha = K'_{n\text{-alkane}} / K'_{\text{iso-alkane}}$$

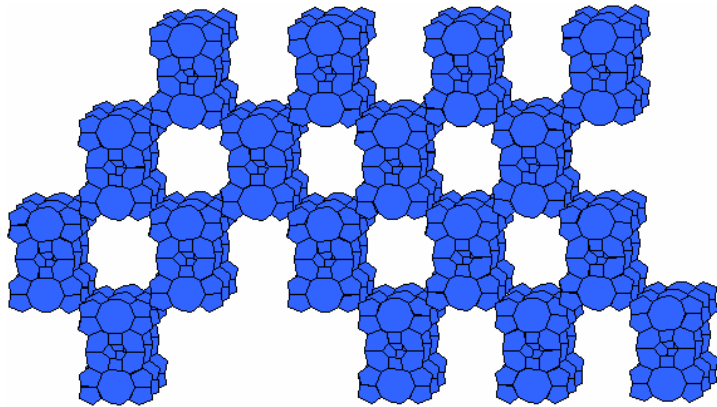
α	Zeotile-4	Zeogrid	MCM-48	Zeotile-2	ZSM-5
<i>n</i> -C8 / 2-MeC7	1.2	1.2	1.3	1.5	2.1
<i>n</i> -C8 / 2,5diMeC6	1.4	1.4	1.5	2.0	-
<i>n</i> -C8 / 2,2,4-triMeC5	1.8	1.7	2.0	3.1	>100



- α : 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

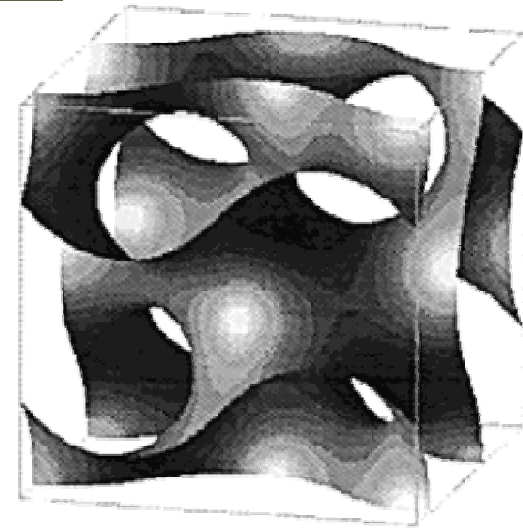


Zeotile-2

Cubic structure

Micropores: 0.55 nm

Mesopores: 2.7 nm



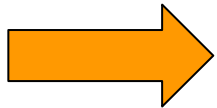
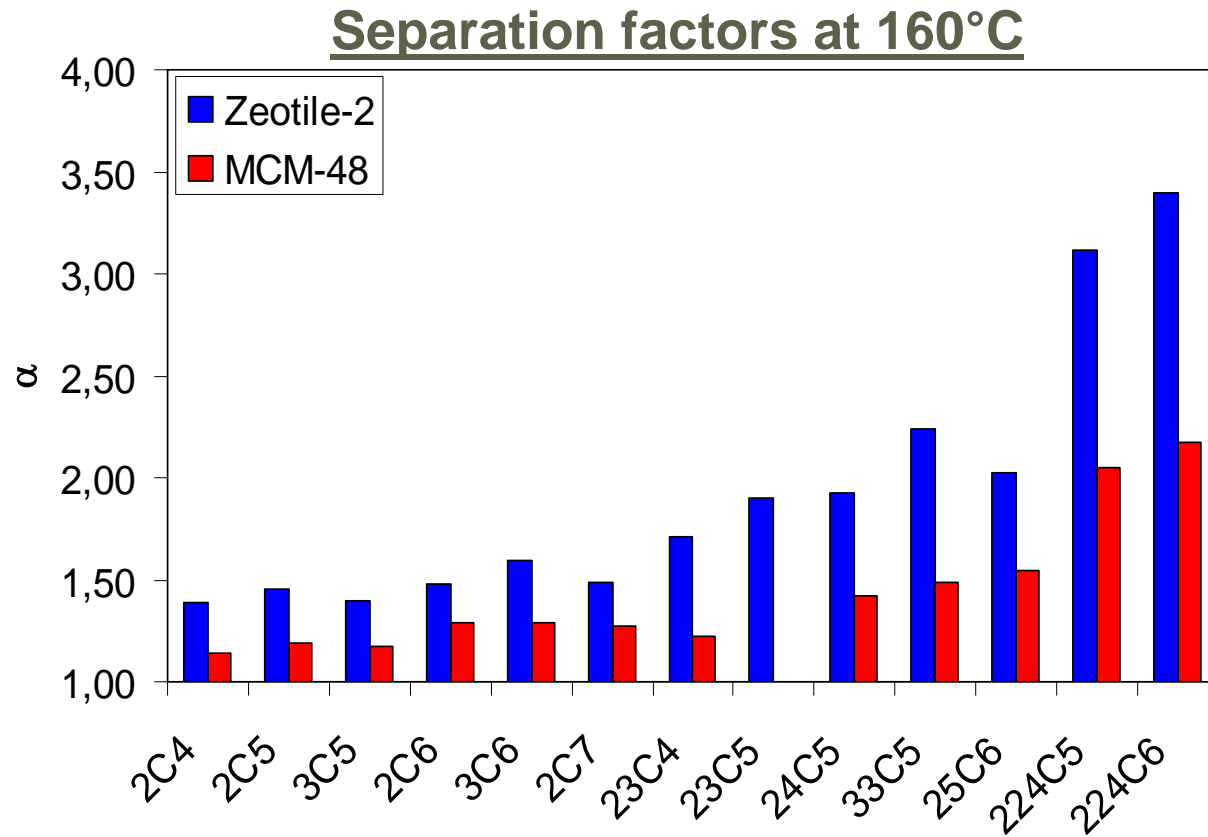
MCM-48

Cubic structure

NO micropores

Mesopores: 2.5 nm

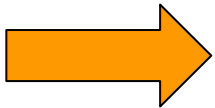
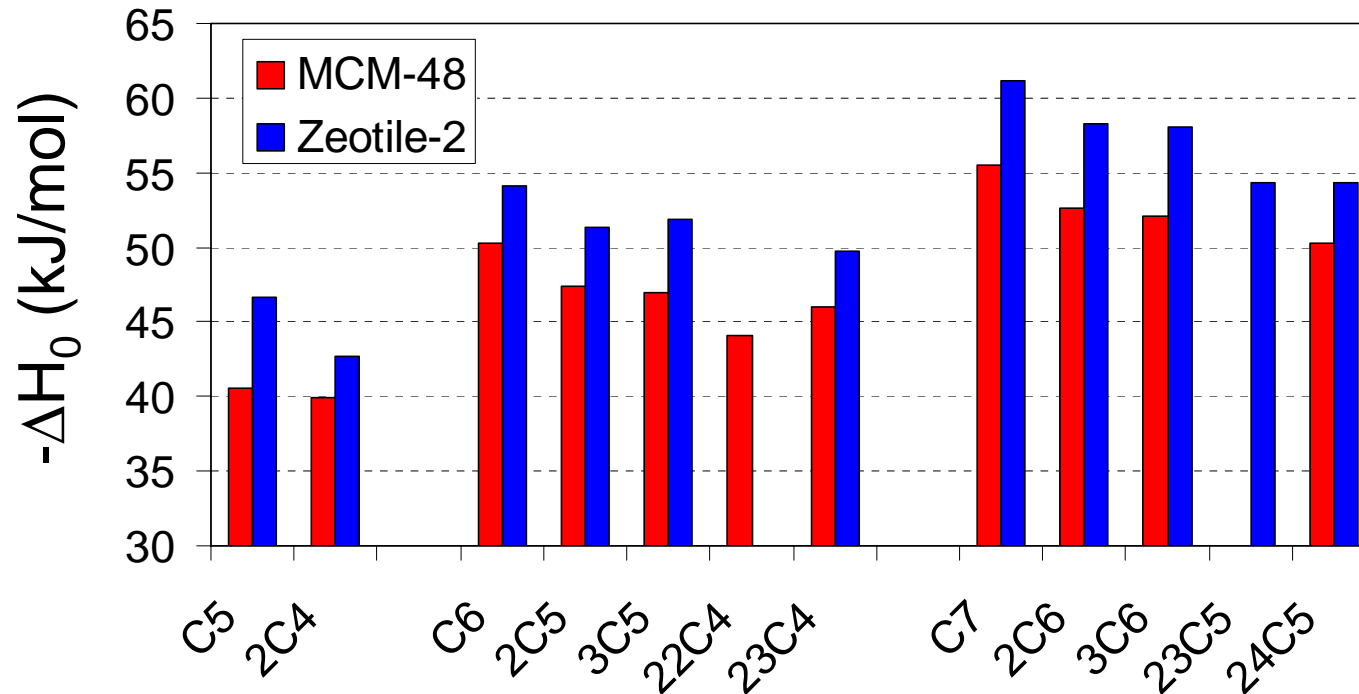
Low Coverage, Shape Selectivity



- Separation factors: **Zeotile-2** > **MCM-48**

Low Coverage, Shape Selectivity

Adsorption enthalpy

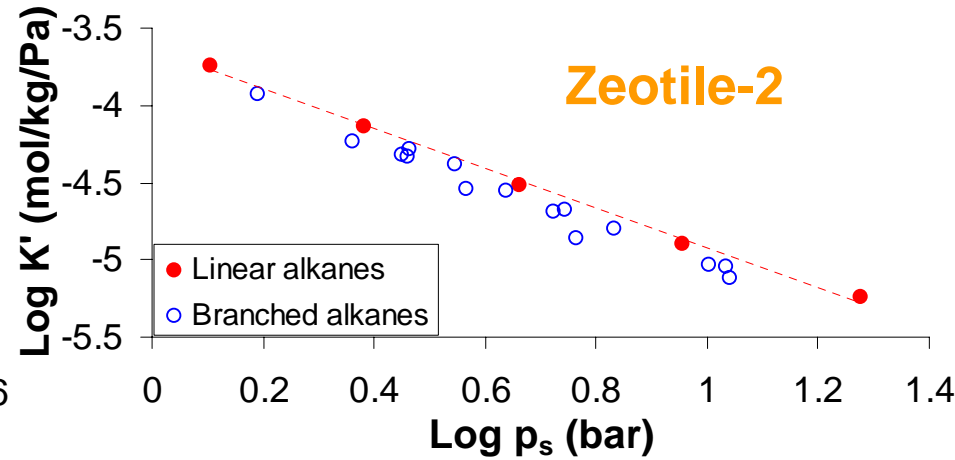
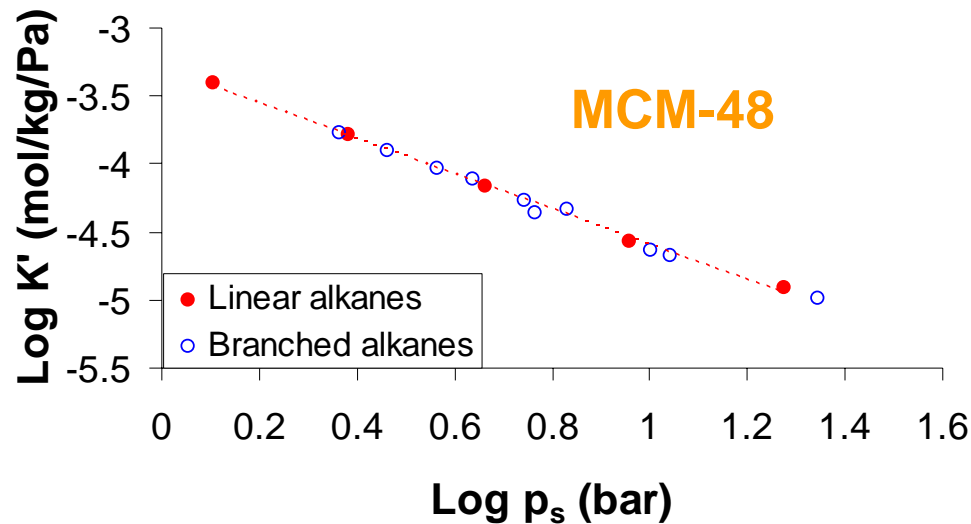


- Interaction energy: Zeotile-2 > MCM-48
- Micropore adsorption

Low Coverage, Shape Selectivity

Vapour Pressure

$$\text{Log } K' = a \cdot \text{Log } p_s + b$$

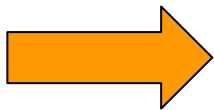
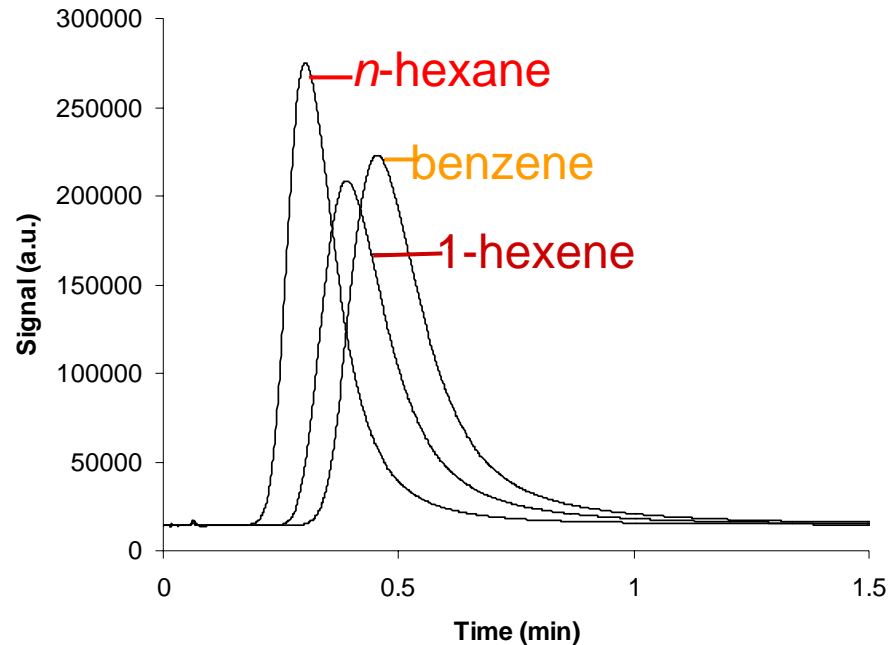


No Shape Selective Properties

Shape Selective Properties !

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

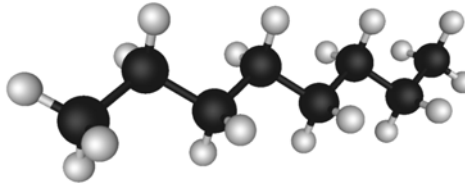
$$\alpha = K'_i / K'_j$$

α	Zeotile-2	Zeotile-4	Zeogrid
benzene/ <i>n</i> -hexane	2.3	1.8	1.4
1-hexene/ <i>n</i> -hexane	1.9	1.3	1.7
o-xylene/ m-xylene	1.0	1.1	1.0
p-xylene/ m-xylene	1.1	1.0	1.0

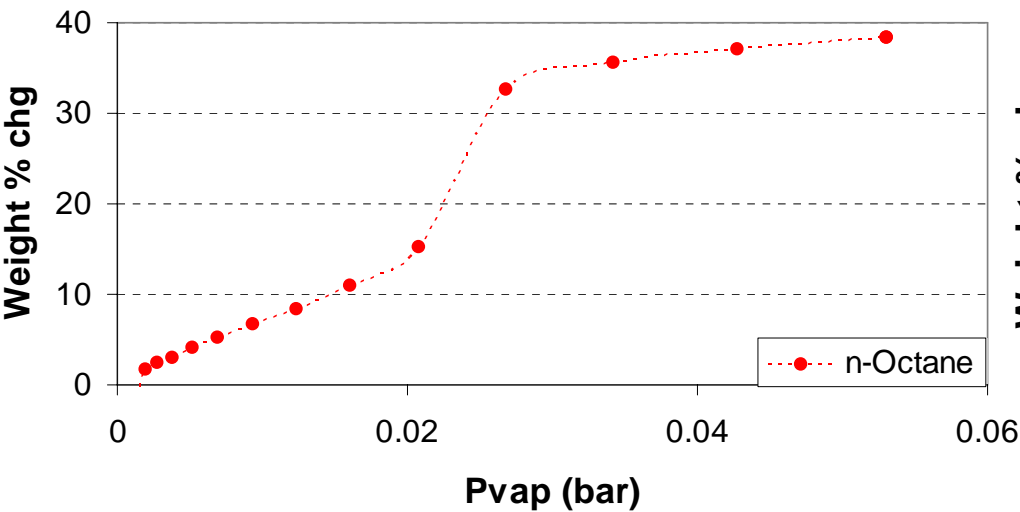
- 
- Preference in adsorption: aromatics > alkenes > alkanes
 - Xylene isomers: no separation

High Coverage, Aspecific interactions

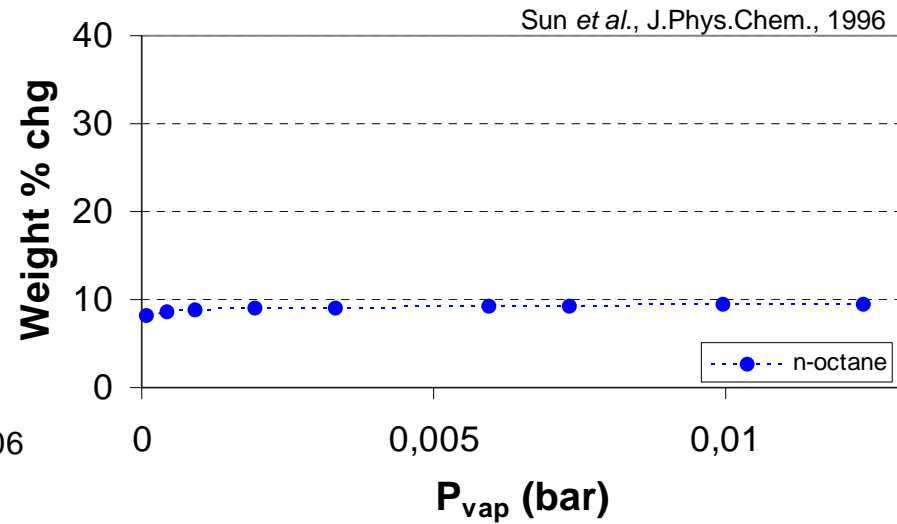
n-octane (70°C)

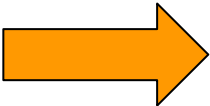


Zeotile-2



Silicalite

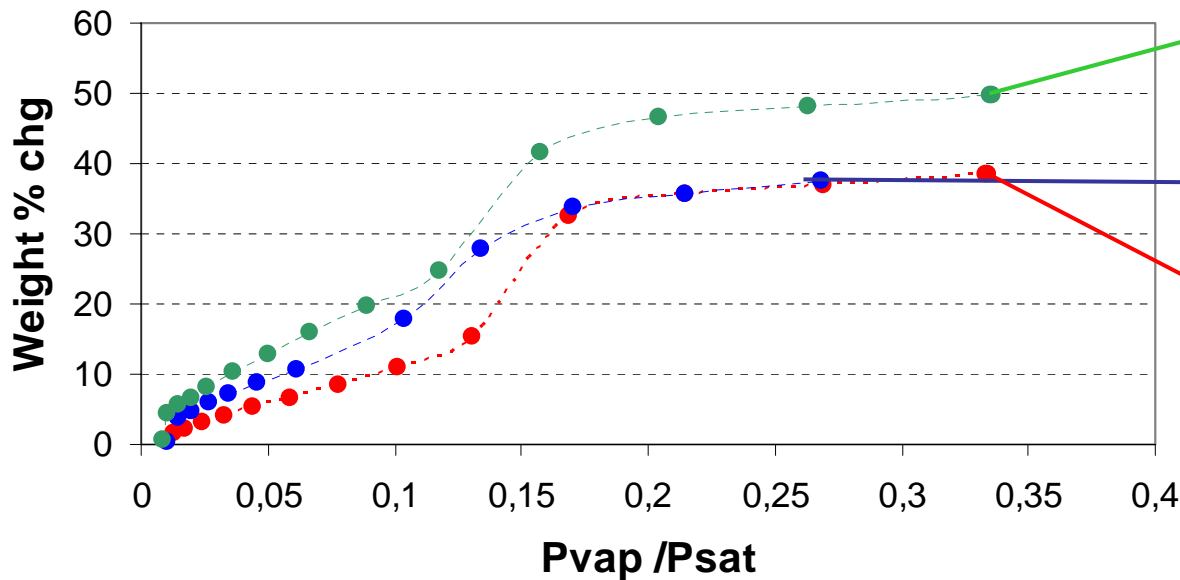


- 
- Two Step Behaviour
 - High adsorption capacities! → 40-50 wt%
 - Zeolites → Max 35 wt%, Typical < 20 wt%

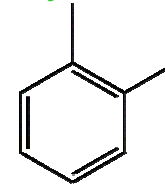
High Coverage, Specific interactions

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

Zeotile-2



o-Xylene

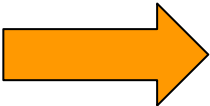


1-Octene



n-Octane

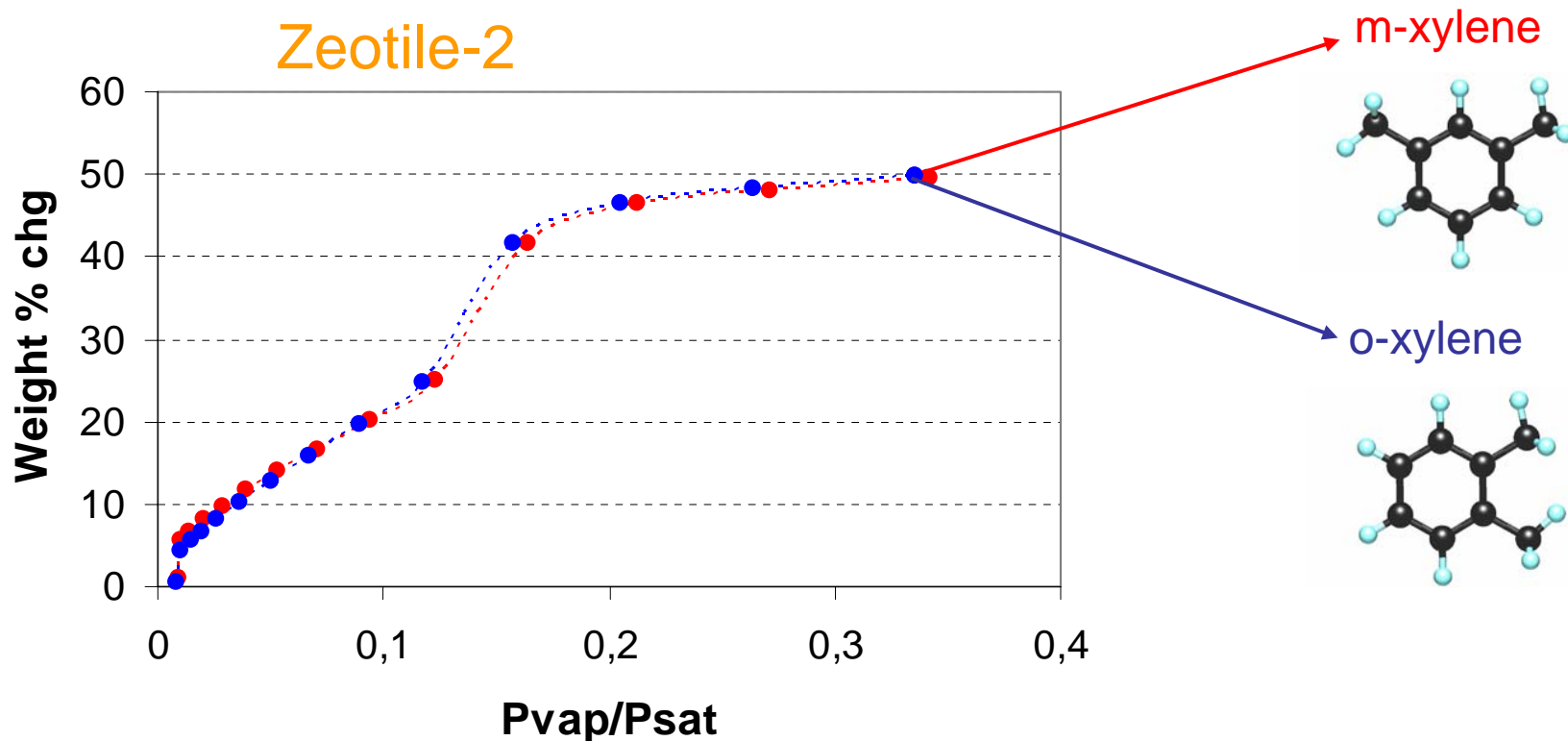


- 
- 1-octene & *n*-octane: similar adsorption capacities
 - o-xylene: stronger adsorption + higher adsorption capacity

High Coverage, Specific interactions

Xylene isomers (70°C)

Zeotile-2



- Xylene isomers: no separation
- High capacities

Conclusions

- Lower K' and ΔH_0 compared to zeolites
- Significant higher adsorption capacities
→ Up to 50 weight %
- Selectivity: aromatics > alkenes > alkanes
- Presence of micropores
→ Shape Selectivity at low coverage: Zeotile-2

Acknowledgements

- IWT Vlaanderen (SBO 'BIPOM')
- FWO Vlaanderen (J. Denayer)

Thank you