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

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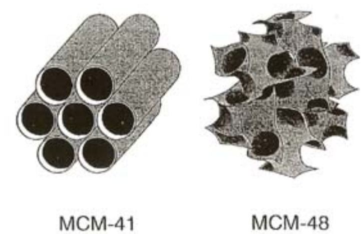
Mesoporous Silica

• Mesopores 2 - 30 nm

→MCM-41 & MCM-48:



+ Fast diffusion
+ Good accessibility

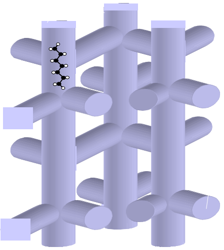
- No shape selectivity
- Inferior stability
- Weaker acidity

Introduction: Porous Adsorbents

Biporous Hierarchical Material

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

Silicalite-1 framework



Micropores: 0.55 nm

First level of porosity

Zeolite nuclei

- Nanoslabs: 1.3 x 1.3 x 4.0 nm^3

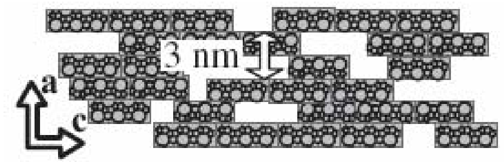
Kirschhock *et al.*, Chem.Eur.J., 2005

Materials

Zeogrid

Half-nanoslab suspension

CTMABr template



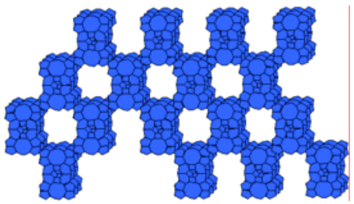
- Ultra-micropores: **0.55 nm**
- Rectangular mesopores: **3.0 nm**

Zeotile-2

Half-nanoslab suspension

CTMABr template

Stirred & Heated



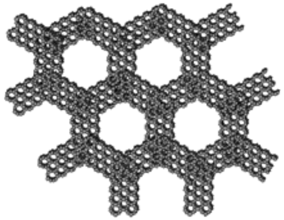
- Ultra-micropores: **0.55 nm**
- Cubic mesopores: **2.7 nm**

Zeotile-4

Double nanoslab suspension

P123

HCL_{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

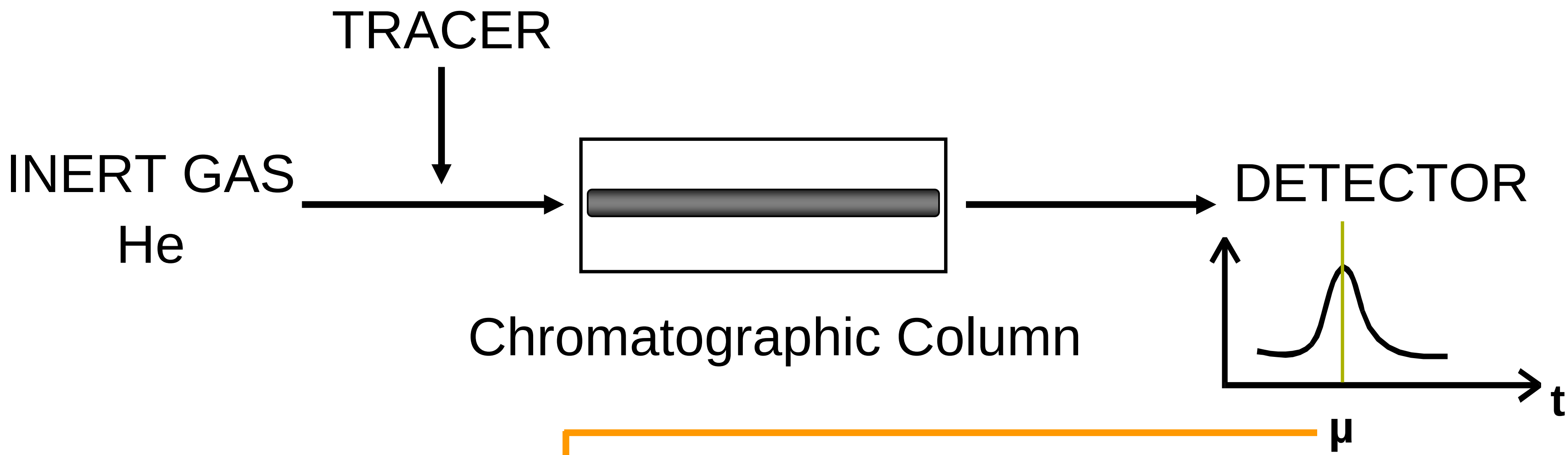
Goal

Study of the Gas phase Adsorption properties

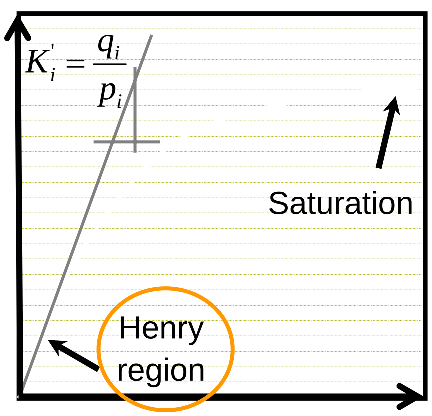
→ Low and High surface coverage

→ Compare to Zeolites and Mesoporous solid

Low Coverage: Pulse gas chromatography



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

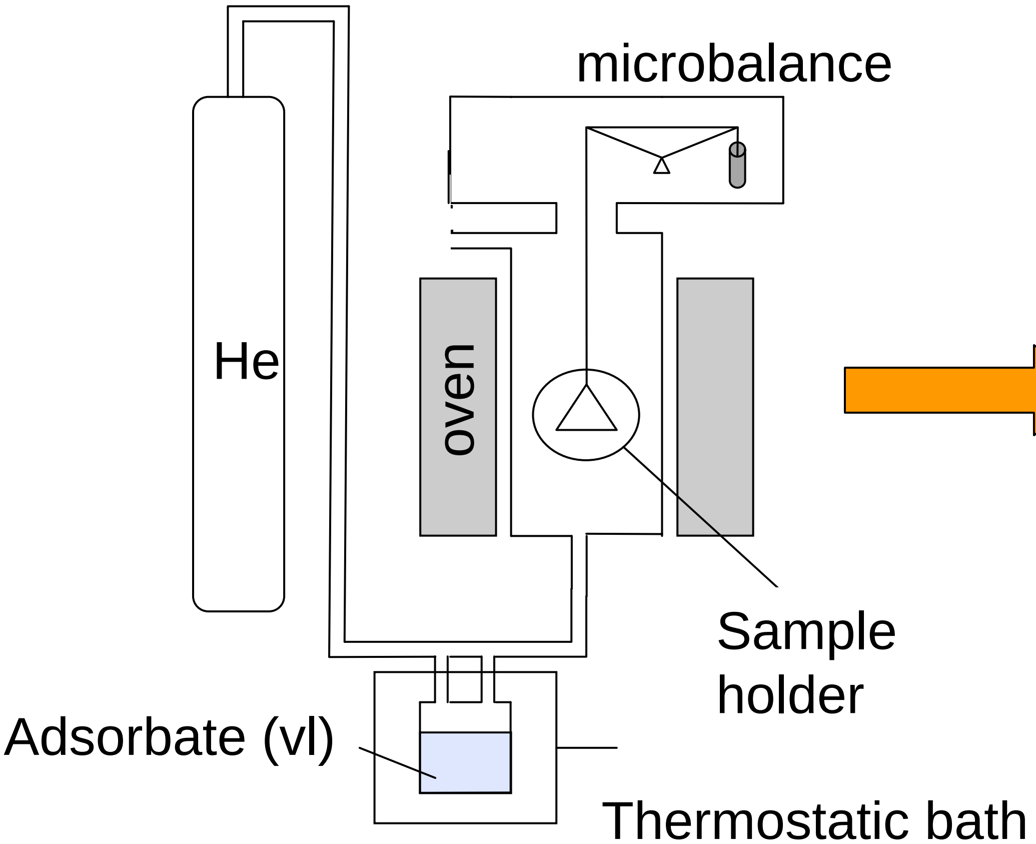


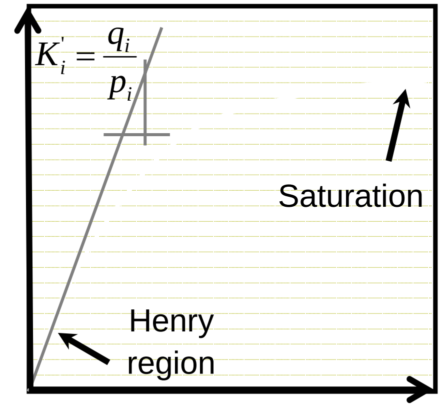
Henry Constant **K'**

Adsorption Enthalpy **ΔH_0**

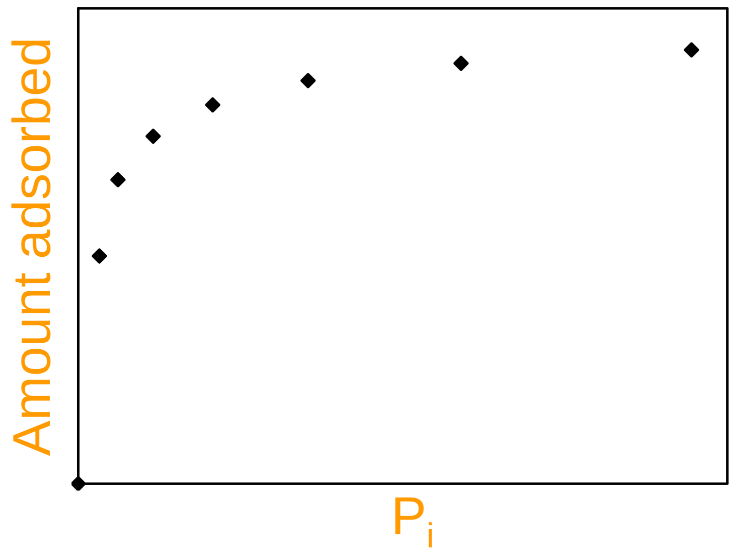
Adsorption Entropy **ΔS_0**

High Coverage: Gravimetric Technique





Adsorption Isotherm:



Results: Overview

Low Coverage: Pulse gas chromatography

→ Aspecific interactions: *n*-alkanes

→ Shape Selective Properties: *n*- and iso-alkanes

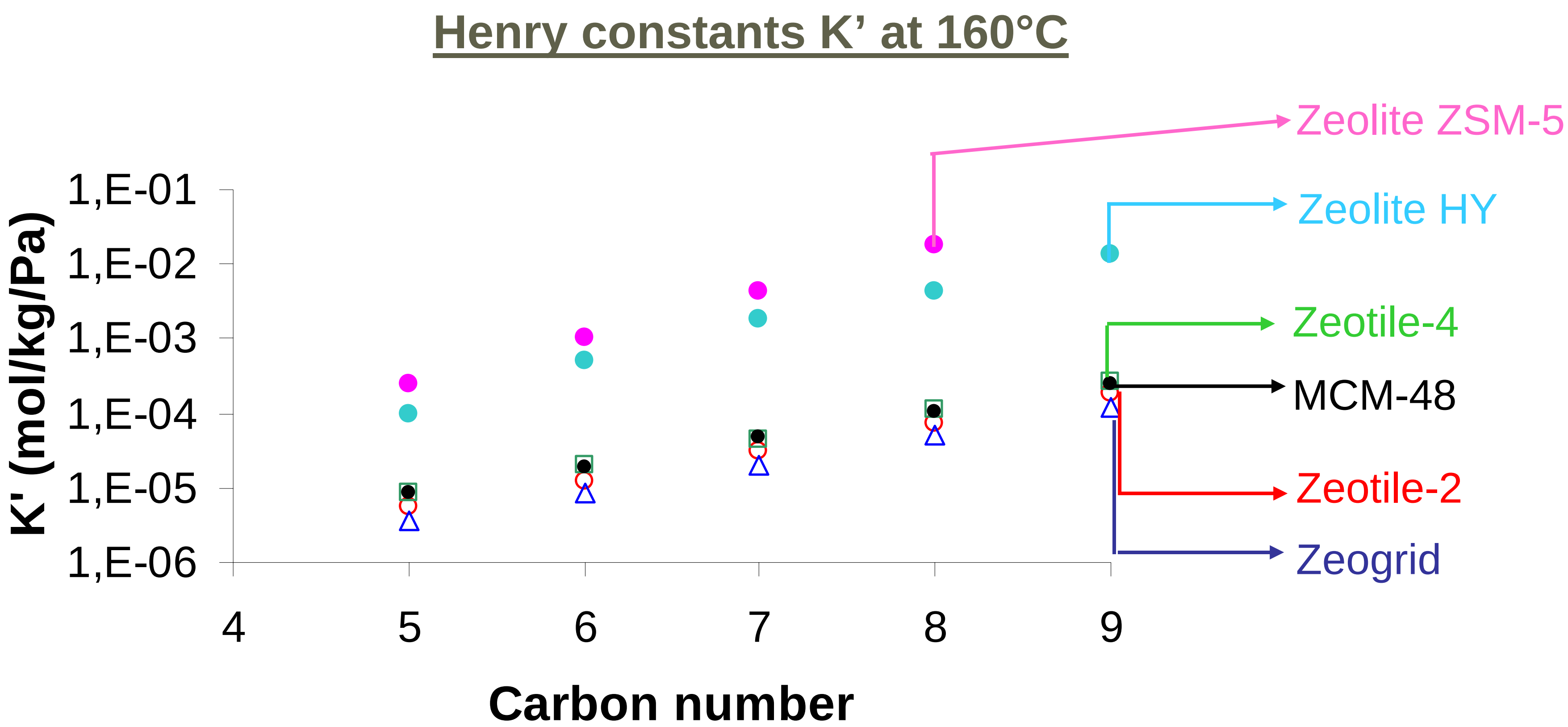
→ Specific interactions: 1-alkenes & aromatics

High Loading: Gravimetric experiments

→ Aspecific interactions: *n*-octane

→ Specific interactions: 1-alkenes & aromatics

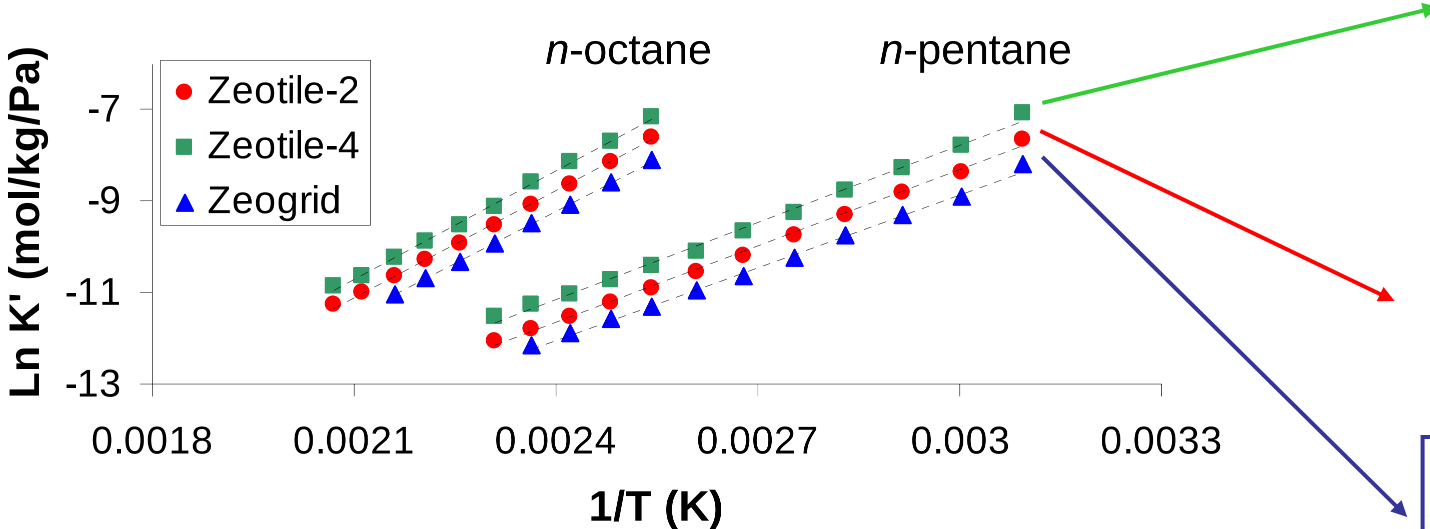
Low Coverage, Aspecific interactions

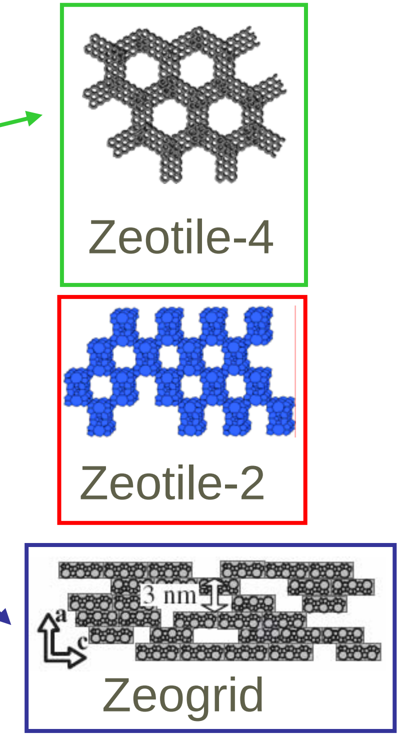


- Exponential increase
- $K'_{ZEOLITES}$ >> $K'_{BIPOROUS\ MATERIALS}$ = $K'_{MCM\text{-}48}$

Low Coverage, Aspecific interactions

Van 't Hoff plot (50-250°C):



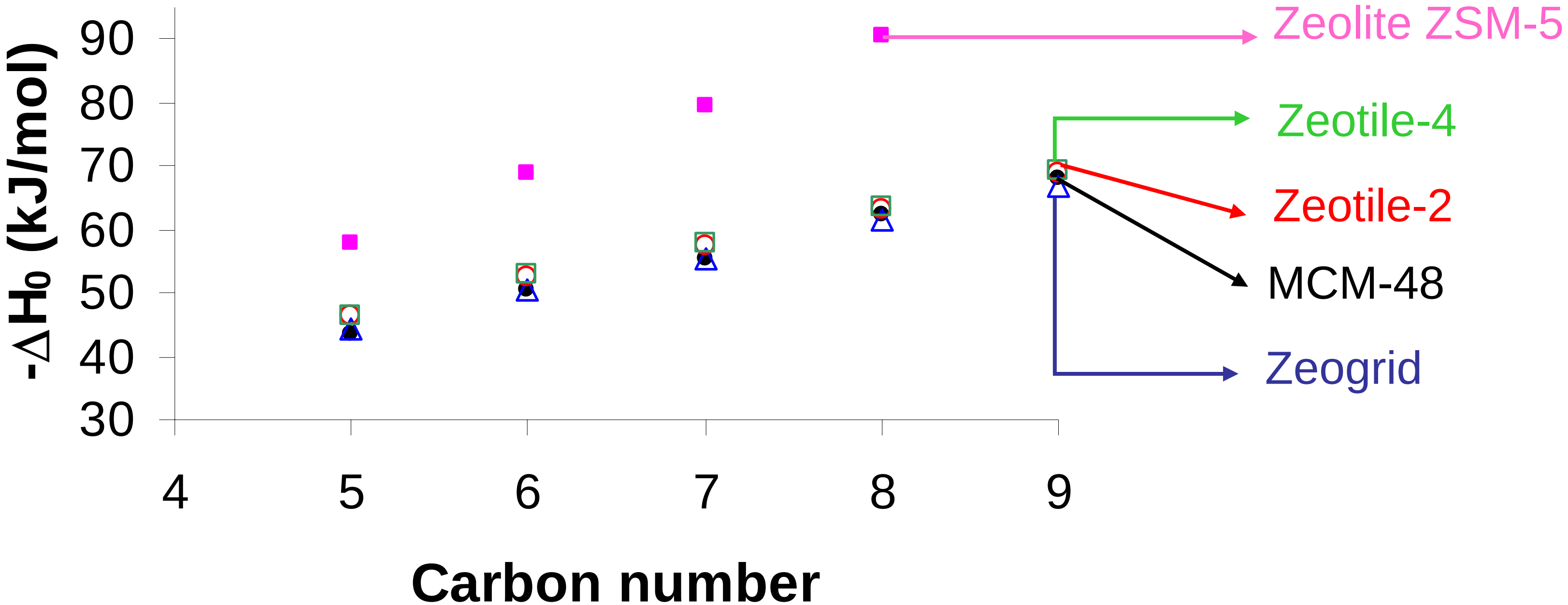


- Highly linear for all alkane components
- Differences in K' related to:
  - → Adsorption enthalpy ΔH_0
  - → Adsorption entropy ΔS_0
  - → number of adsorption sites

Low Coverage, Aspecific interactions

Adsorption Enthalpy

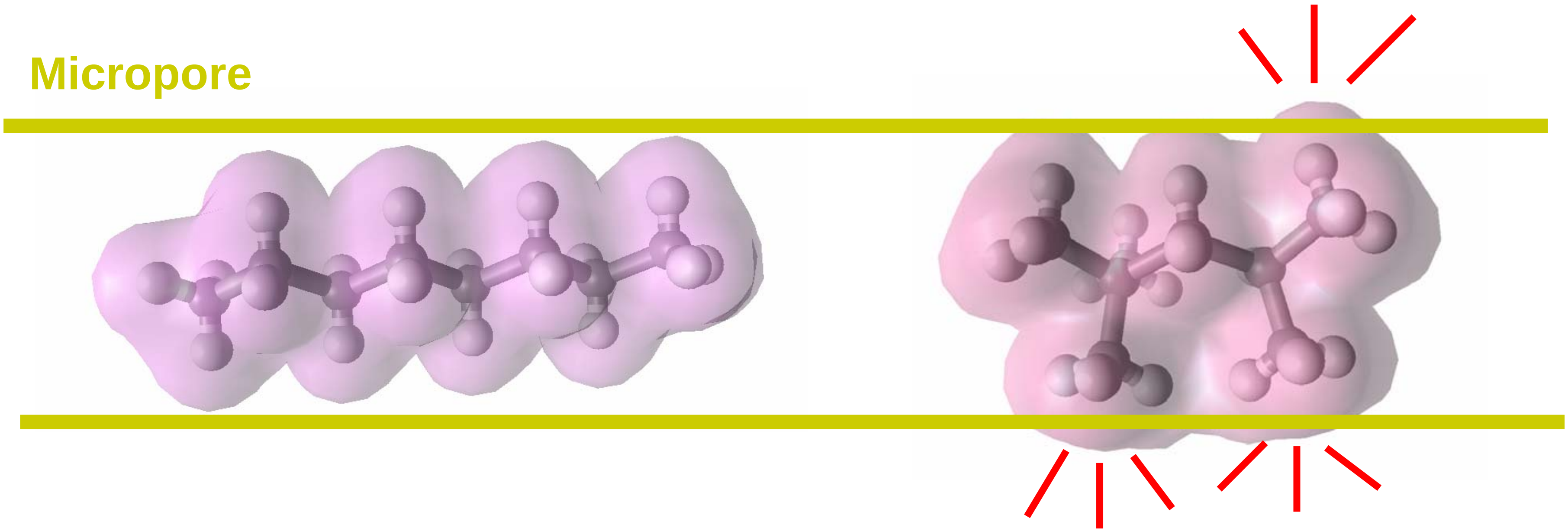
$$K' = K'_0 . \exp^{-\Delta H_0 / RT}$$

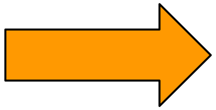


- Microporous Zeolites: highest adsorption enthalpy
- Only subtle differences between Mesoporous and Biporous

Low Coverage, Shape Selectivity

<u>*n*- and iso-alkanes</u>





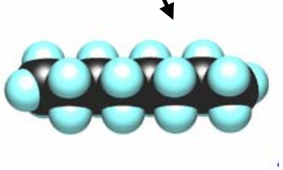
- Branched alkanes: less adsorption
- Shape Selective Property

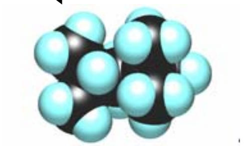
Low Coverage, Shape Selectivity

Separation factors at 160°C

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

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

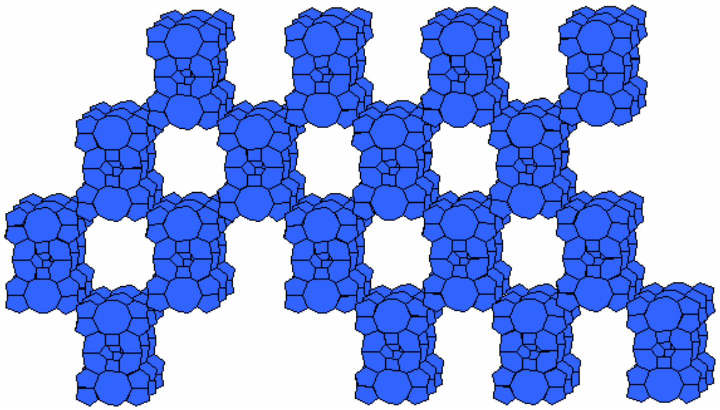


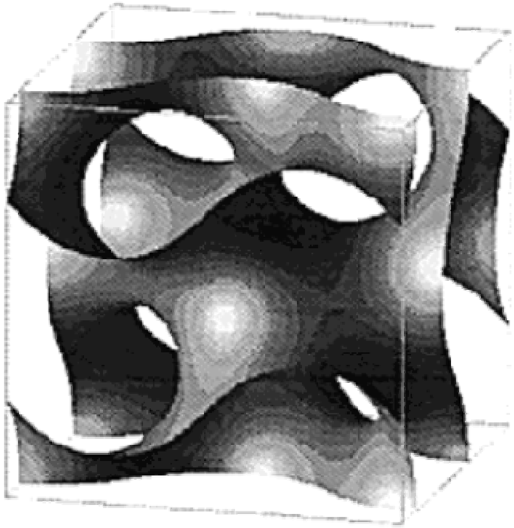


- α: ZSM-5 >> Zeotile-2 > Zeogrid, Zeotile-4 and MCM-48
- Biporous materials: separating linear from branched alkanes

Low Coverage, Shape Selectivity

Zeotile-2 versus MCM-48





Zeotile-2

Cubic structure

Micropores: 0.55 nm

Mesopores: 2.7 nm

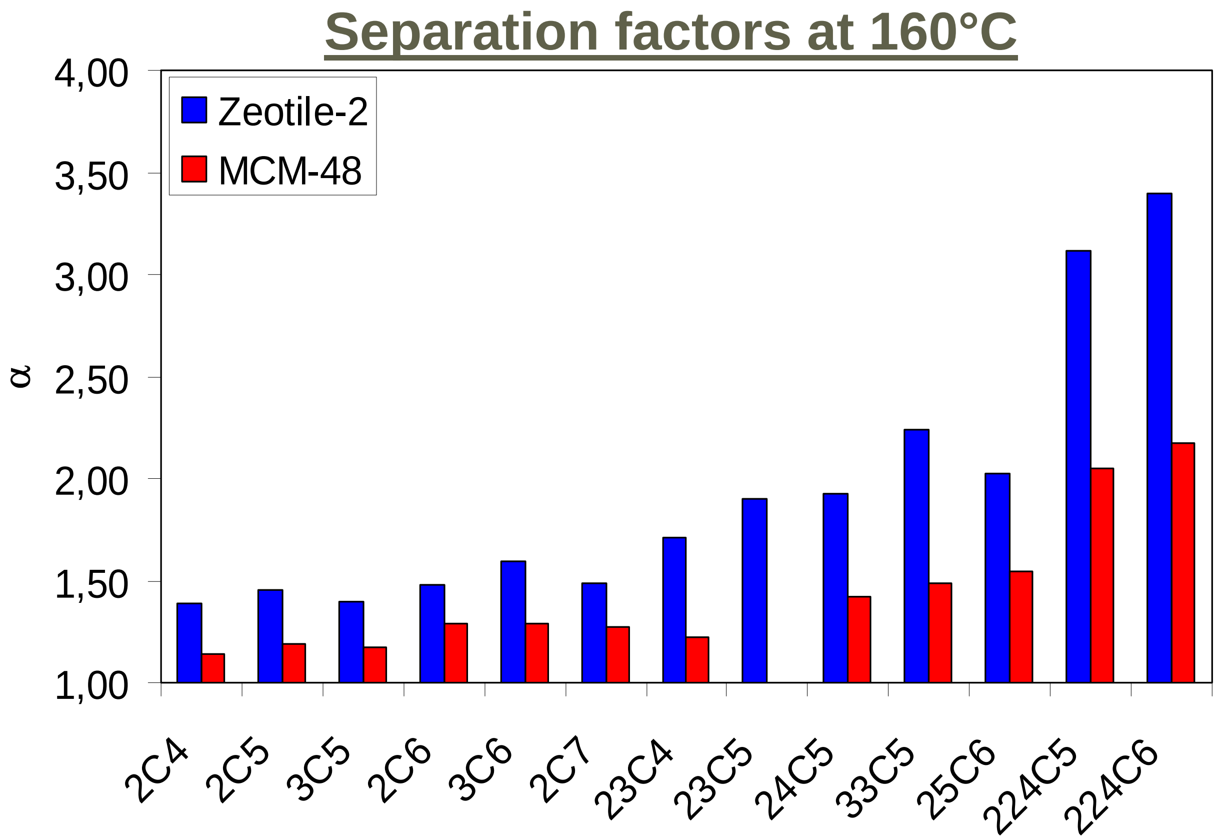
MCM-48

Cubic structure

NO micropores

Mesopores: 2.5 nm

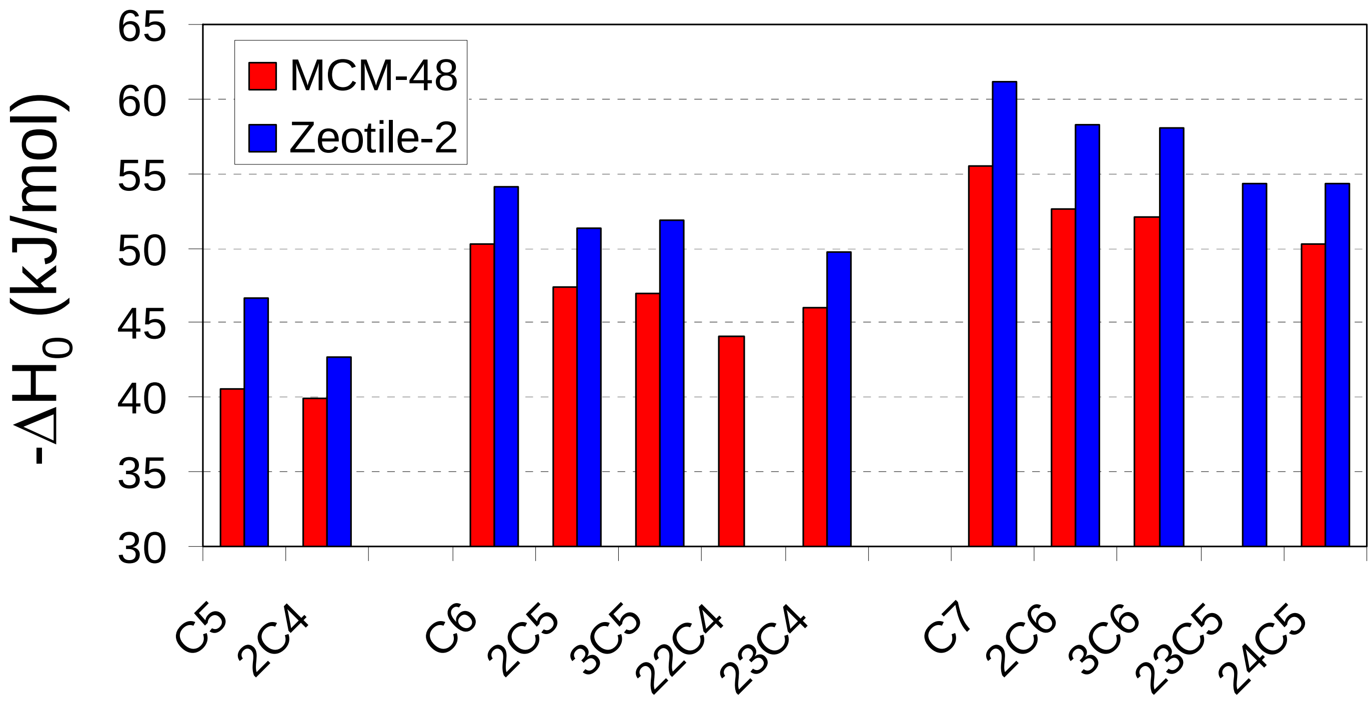
Low Coverage, Shape Selectivity



- Separation factors: Zeotile-2 > MCM-48

Low Coverage, Shape Selectivity

Adsorption enthalpy

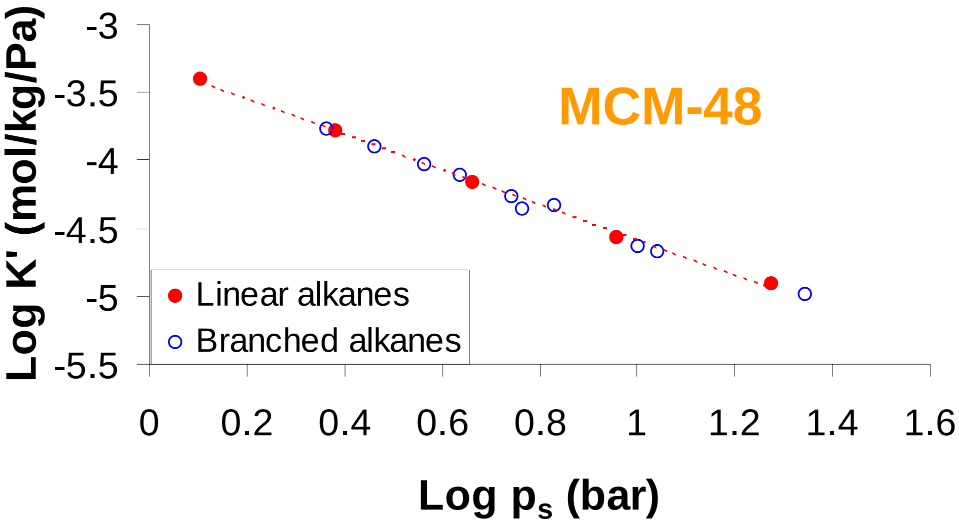


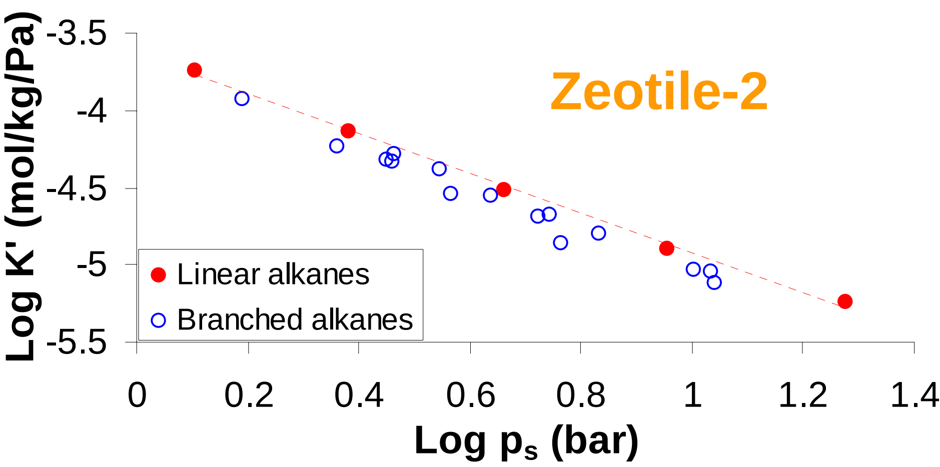
- Interaction energy: Zeotile-2 > MCM-48
- Micropore adsorption

Low Coverage, Shape Selectivity

Vapour Pressure

$$\log K' = a \cdot \log p_s + b$$



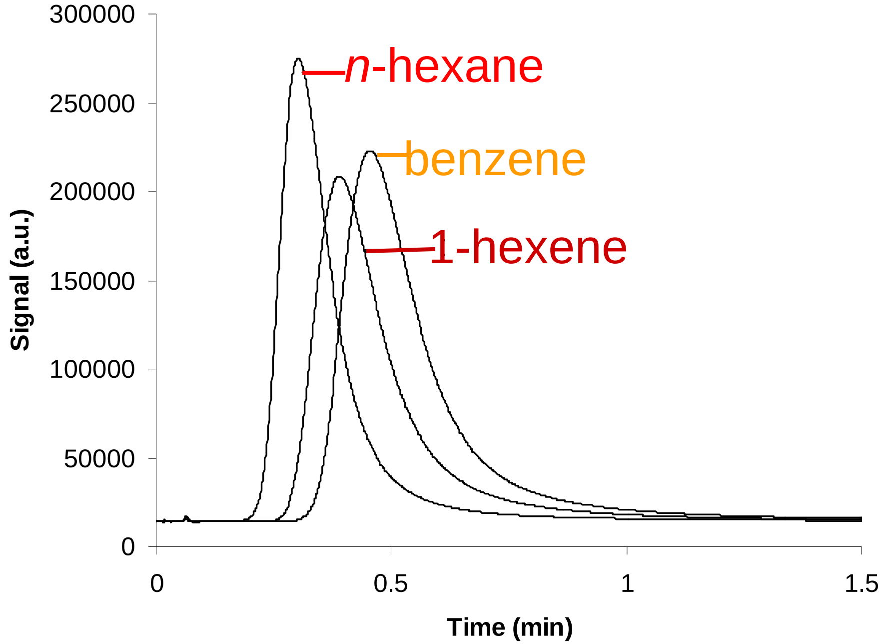


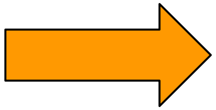
No Shape Selective Properties

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

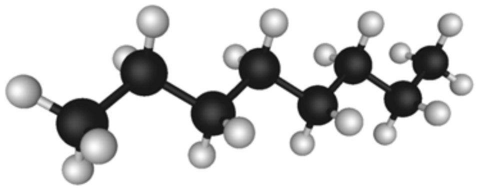
$\alpha = K'_i / K'_j$

α	Zeotile-2	Zeotile-4	Zeogrid
benzene/ *n*-hexane	2.3	1.8	1.4
1-hexene/ *n*-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

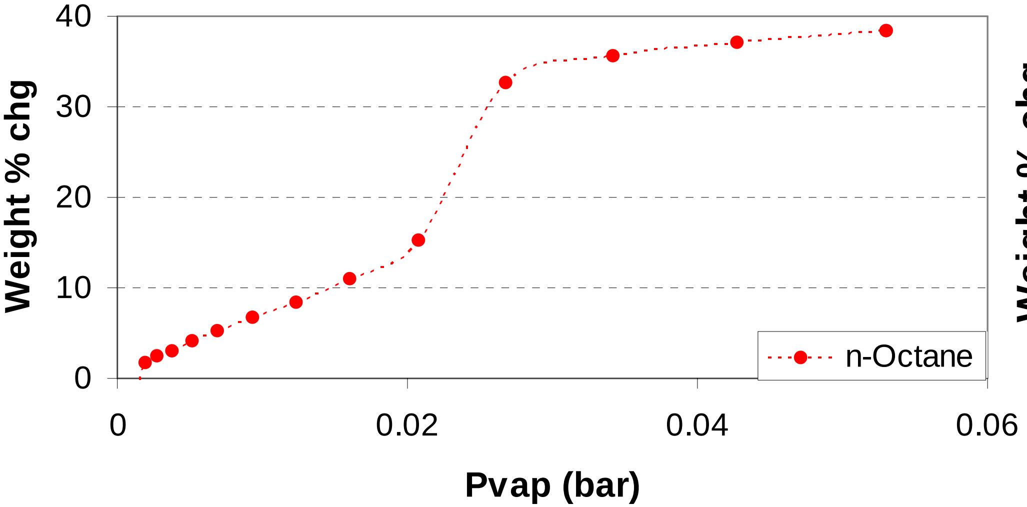
- Preference in adsorption: aromatics > alkenes > alkanes
- Xylene isomers: no separation

High Coverage, Aspecific interactions

n-octane (70°C)

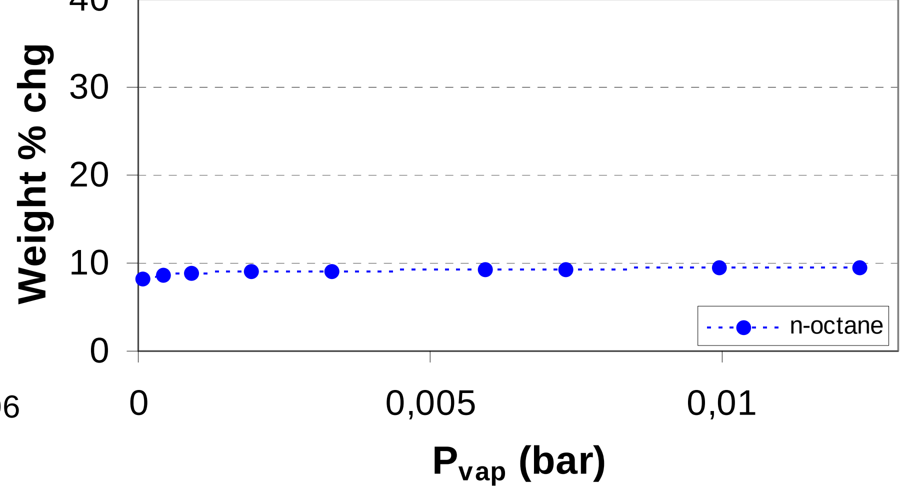


Zeotile-2



Silicalite

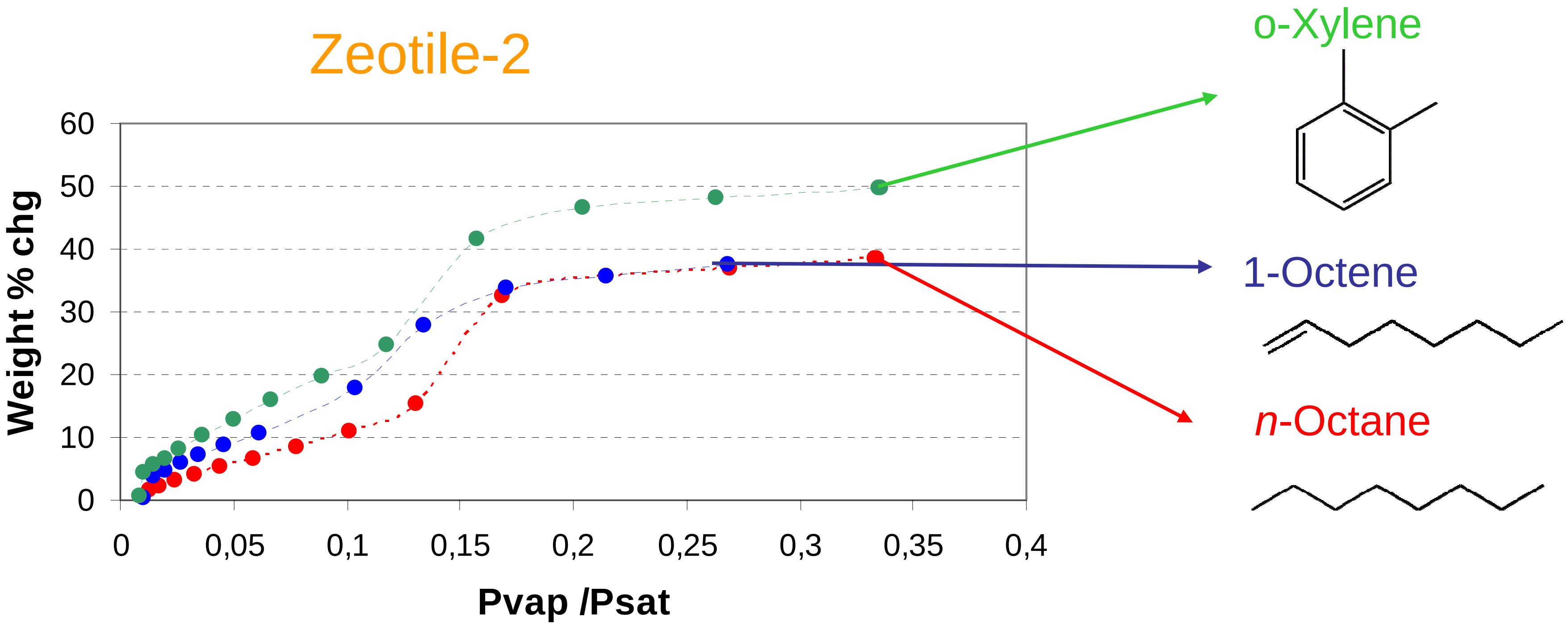
Sun *et al*., J.Phys.Chem., 1996



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

High Coverage, Specific interactions

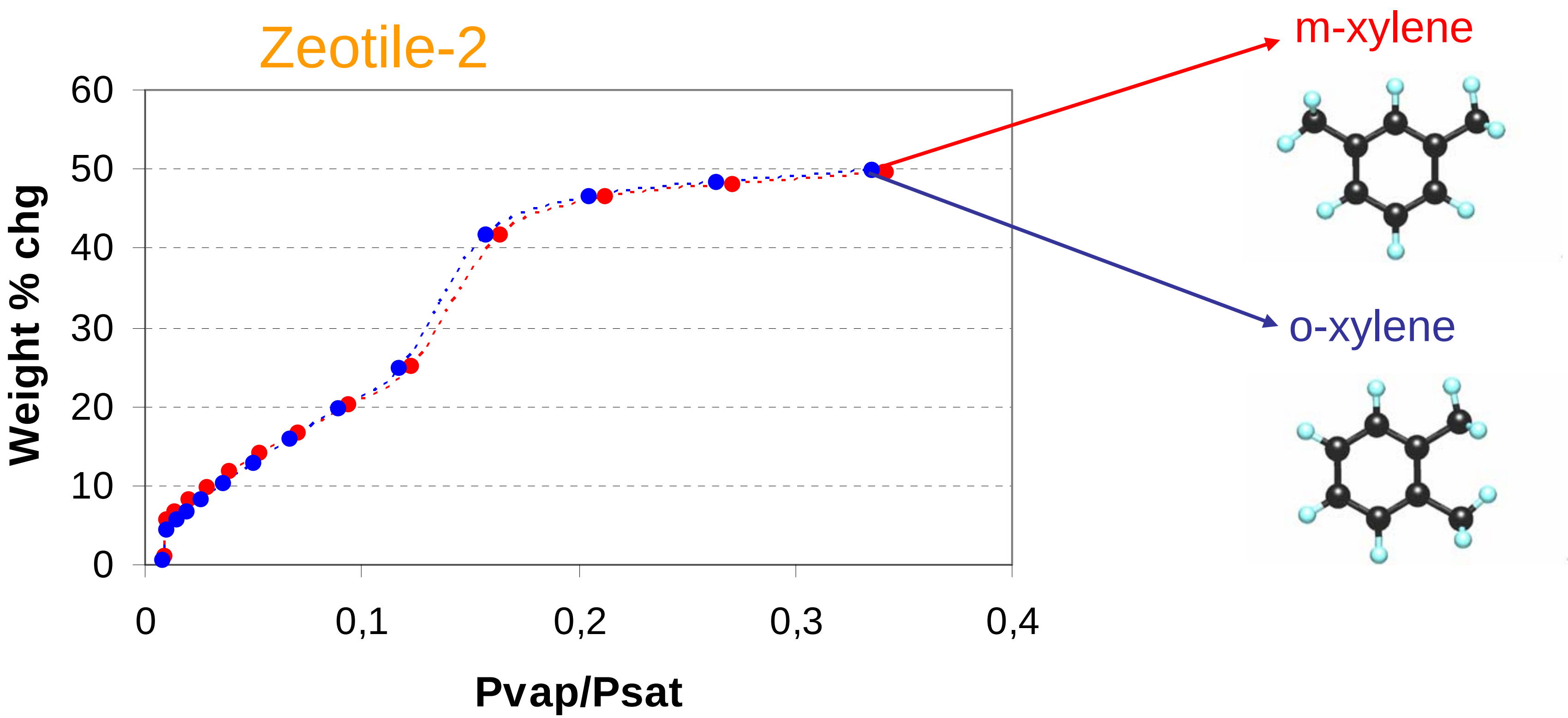
o-xylene, 1-octene and *n*-octane (70°C)



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

High Coverage, Specific interactions

Xylene isomers (70°C)



- 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’)
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Thank you