Flexible MOFs for Gas Separation – A Case Study Based on Static and Dynamic Sorption Experiments

Dr. Robert Eschrich[1]

Christian Reichenbach[1], Andreas Möller[1], Jens Möllmer[2], Marcus Lange[2], Hannes Preißler[2], Roger Gläser[2], Matthias Thommes[3]

[1] 3P INSTRUMENTS GmbH & Co. KG

[2] INC Leipzig e.V.

[3] Quantachrome Instruments

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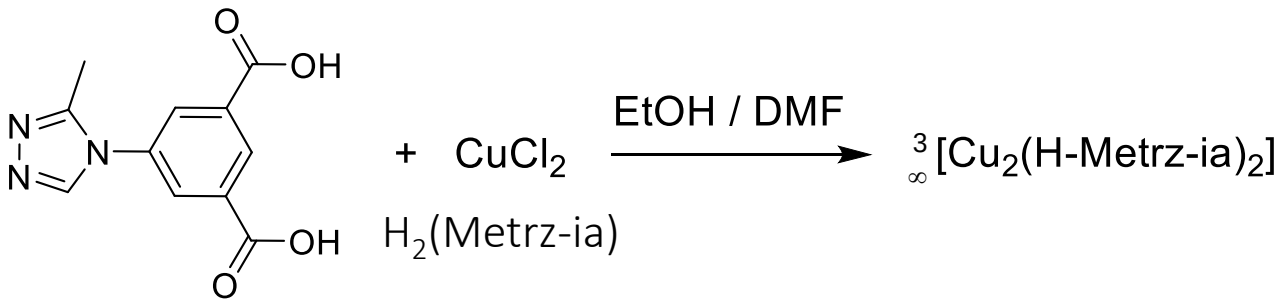
www.dynamicsorption.com

$^{3}_{\infty}[Cu_2(H-Metrz-ia)_2]$ – a flexible compound?



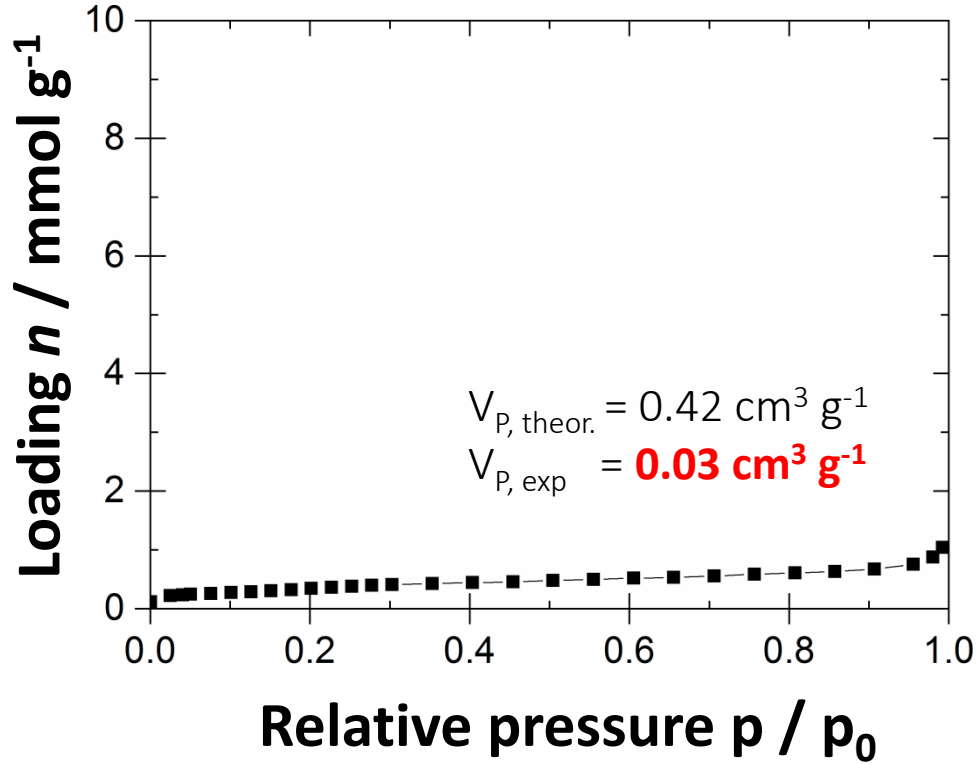
Accessible in a multigramm scale

X-ray cristallography

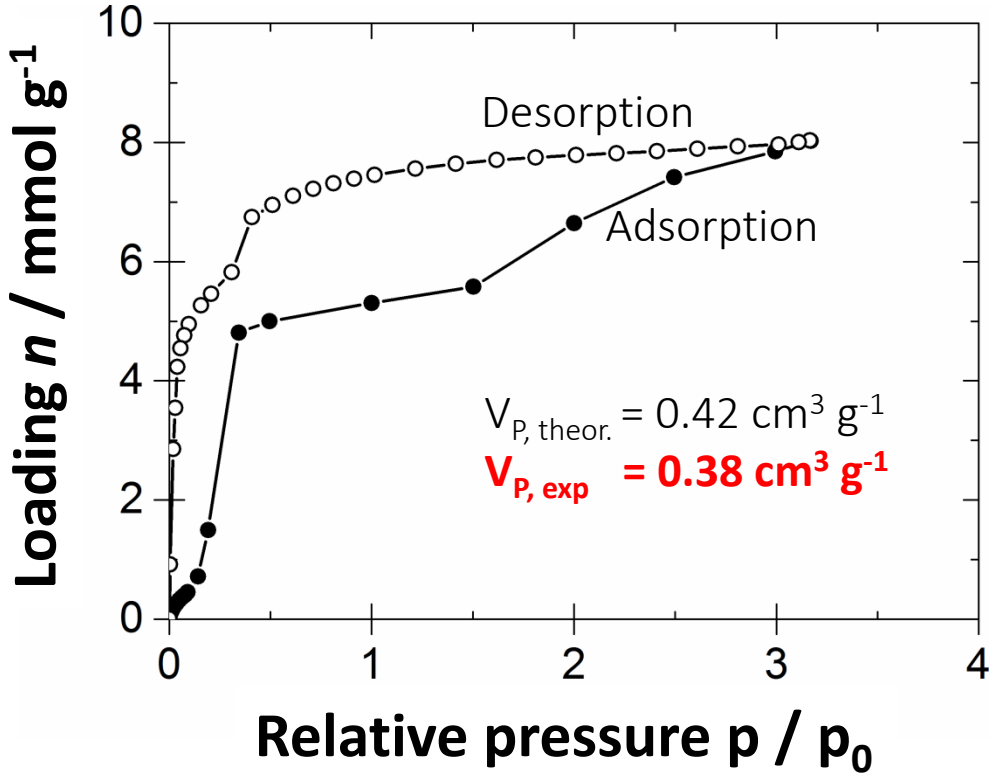
47 % porosity→

$V_{Pore,theor.} = 0.42\ cm^3\ g^{-1}$

N_2 / 77 K



CO_2 / 273 K



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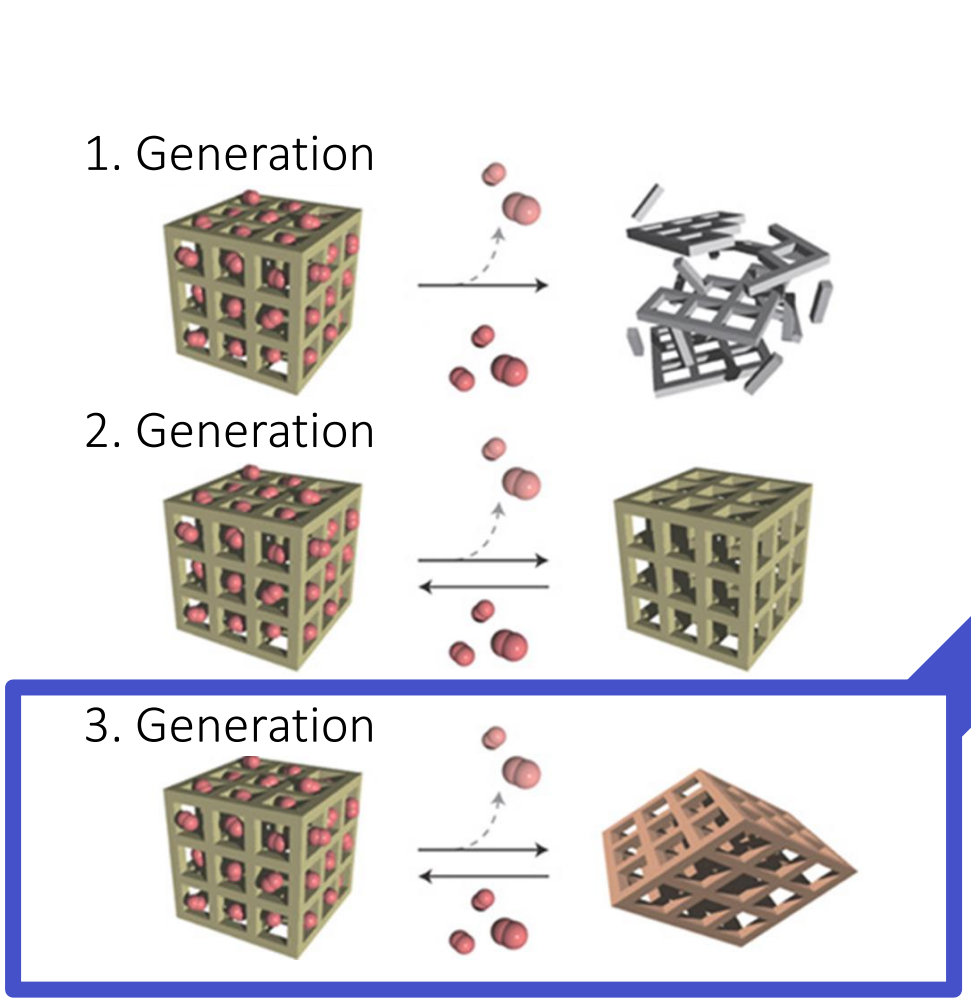
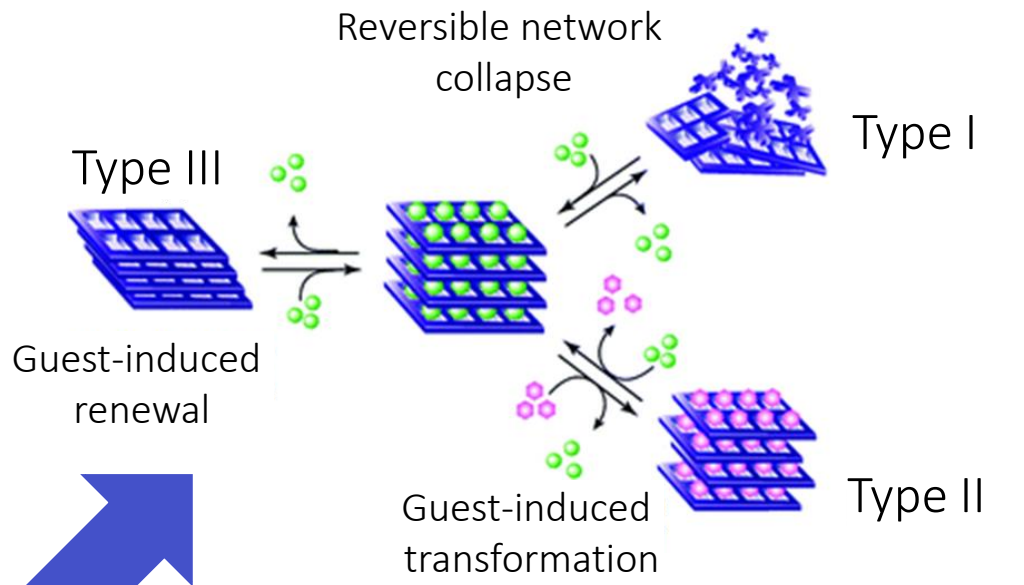
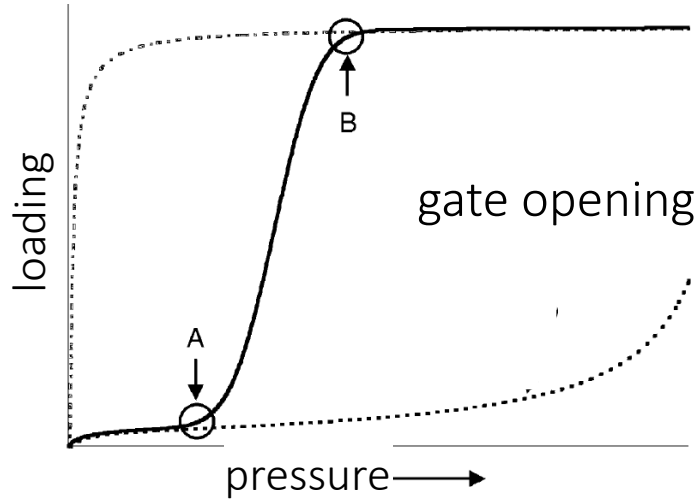
Structurally flexible coordination polymers







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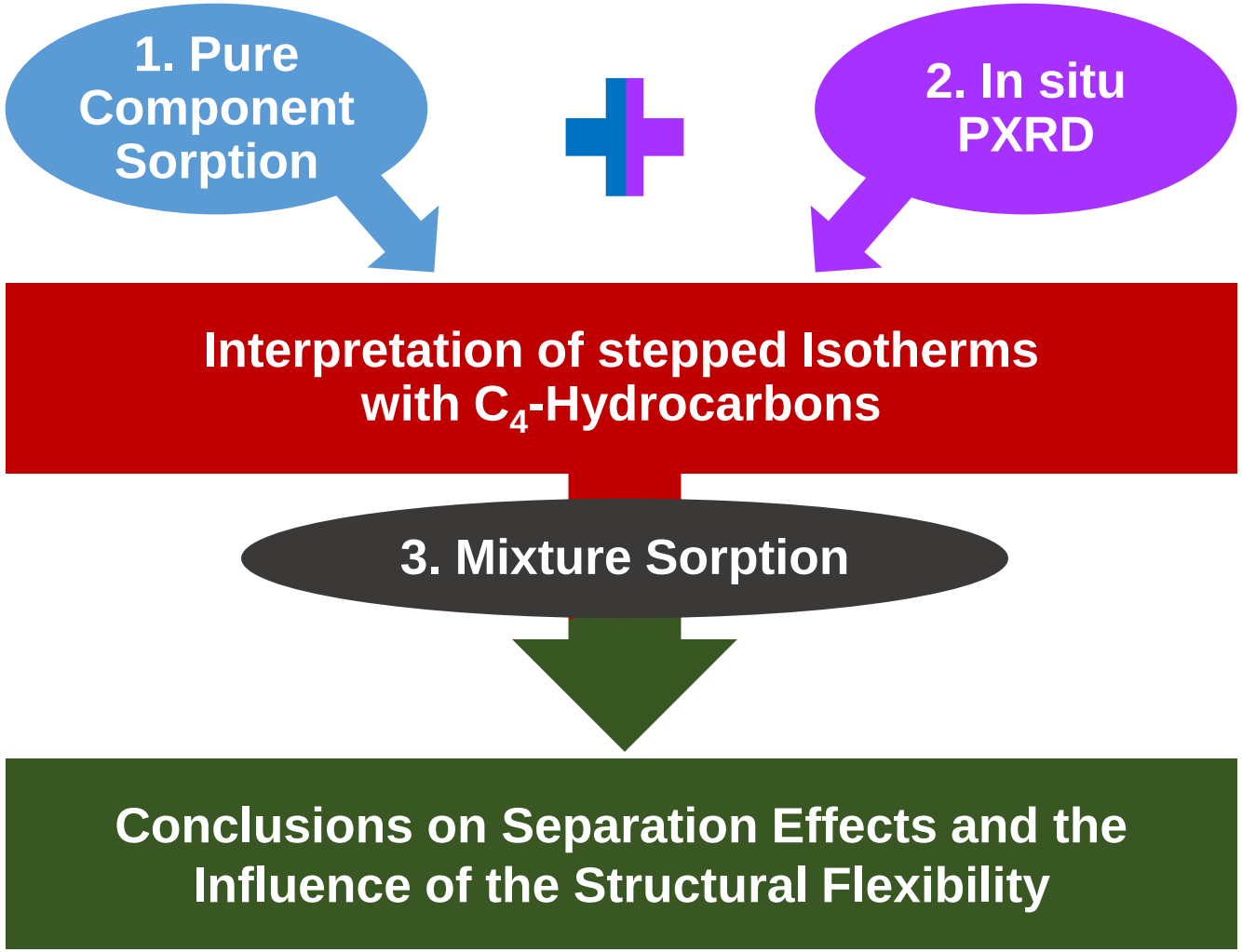
Outline



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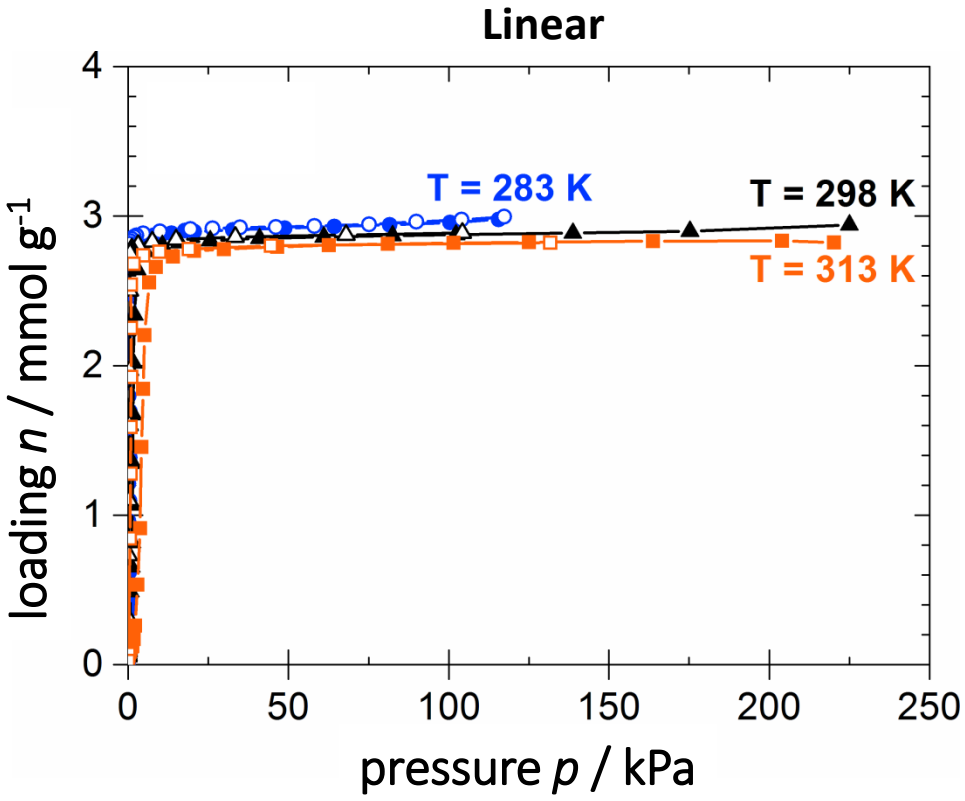
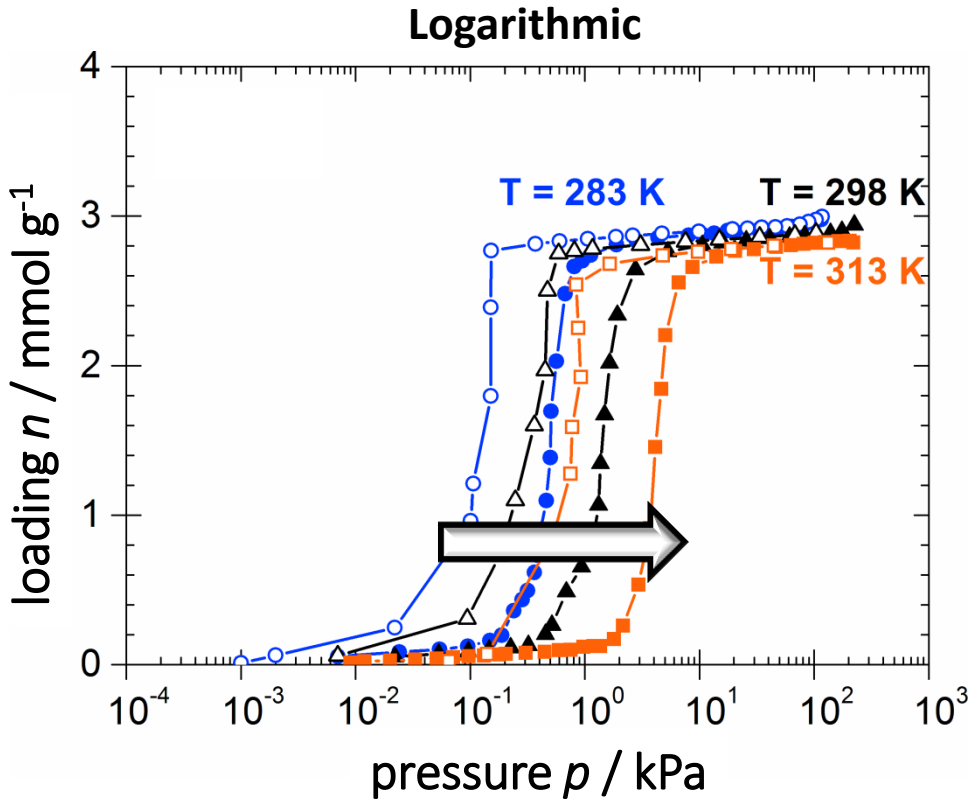
1. Pure Components Isotherms

n-Butane Isotherms



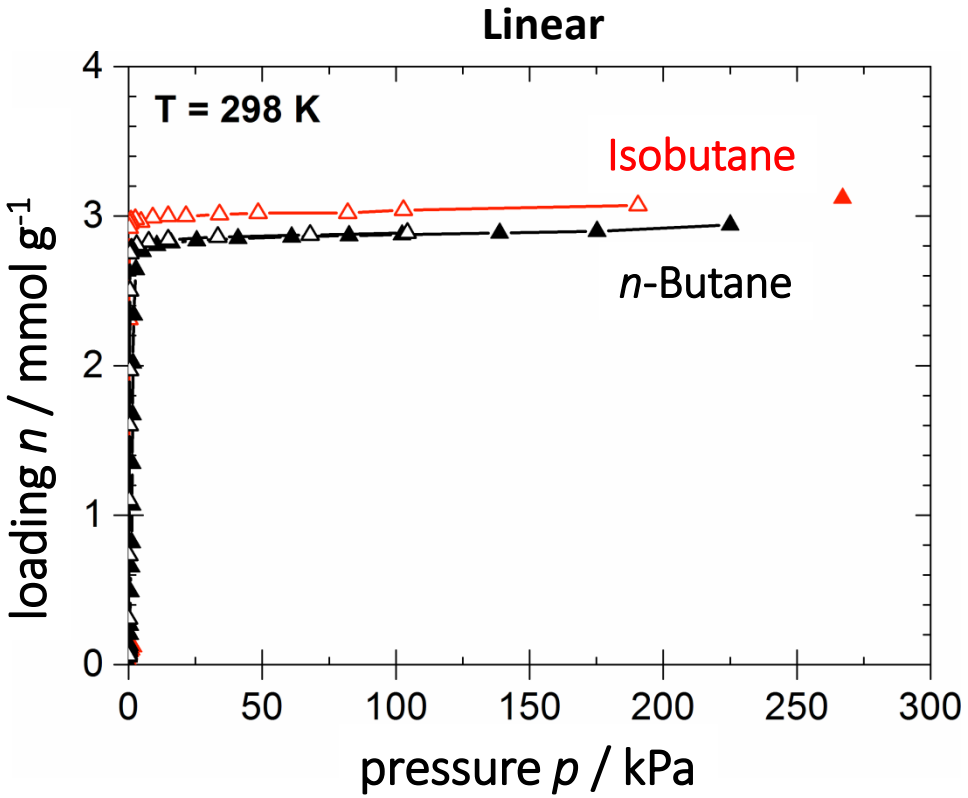


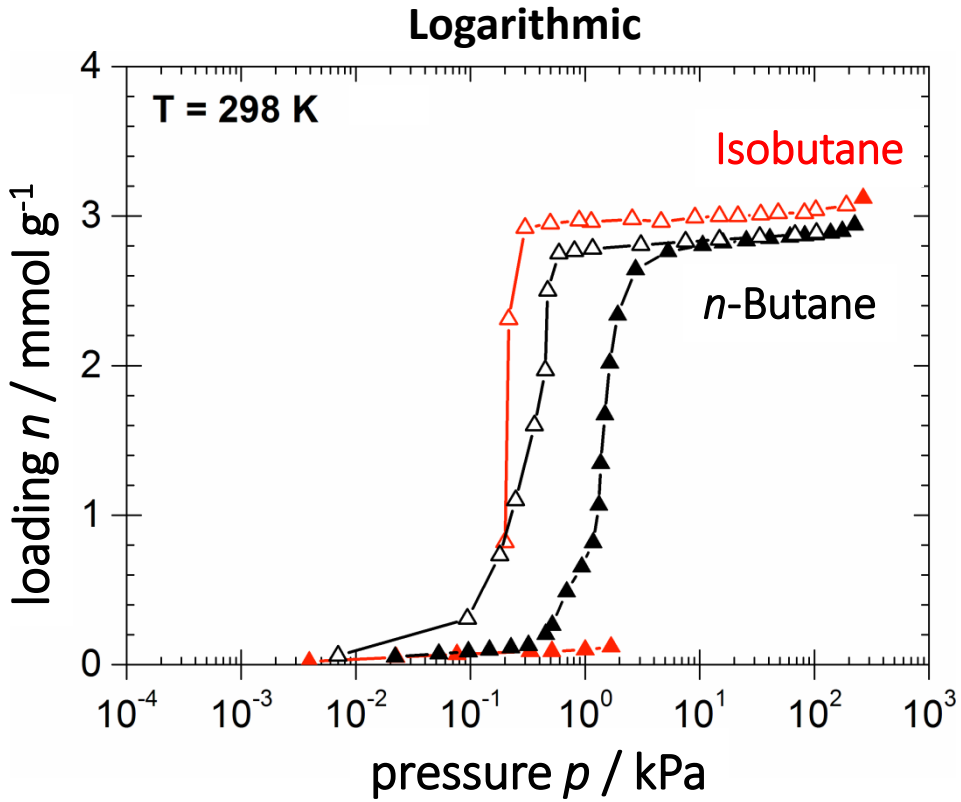
- **stepped isotherm** with strong hysteresis in **low pressure region** (< 5 kPa)
- hysteresis dependent on pressure and temperature

→ Structural change?

1. Pure Components Isotherms

Comparison of *n*-Butane and Isobutane at 298 K

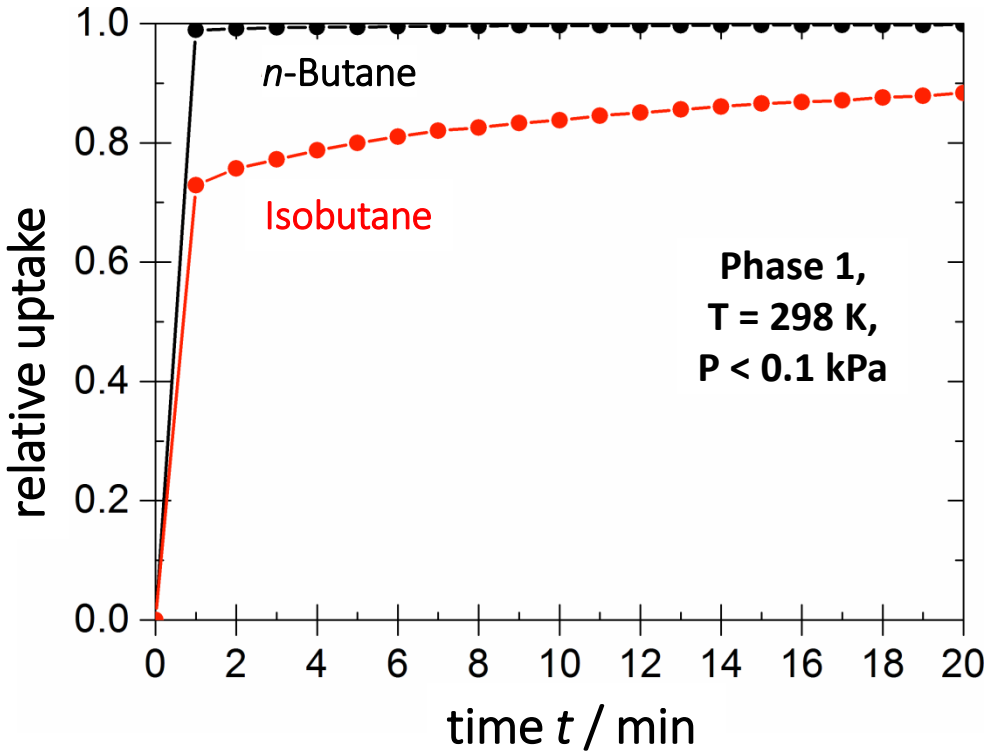


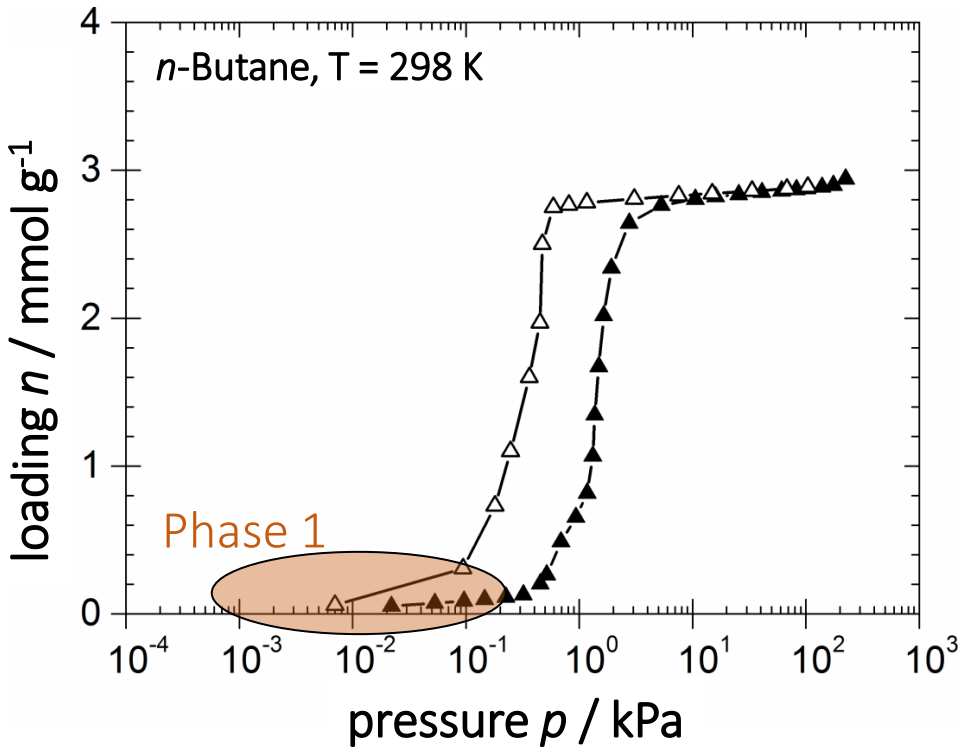


- $V_{P,\,exp}$ = 0.31 cm^3 g^{-1} (*n*-Butane) and 0.34 cm^3 g^{-1} (Isobutane)
- Isobutane adsorption is **much slower** than *n*-Butane adsorption!

1. Pure Components Isotherms

Uptake Curves – an indication for the rate of adsorption





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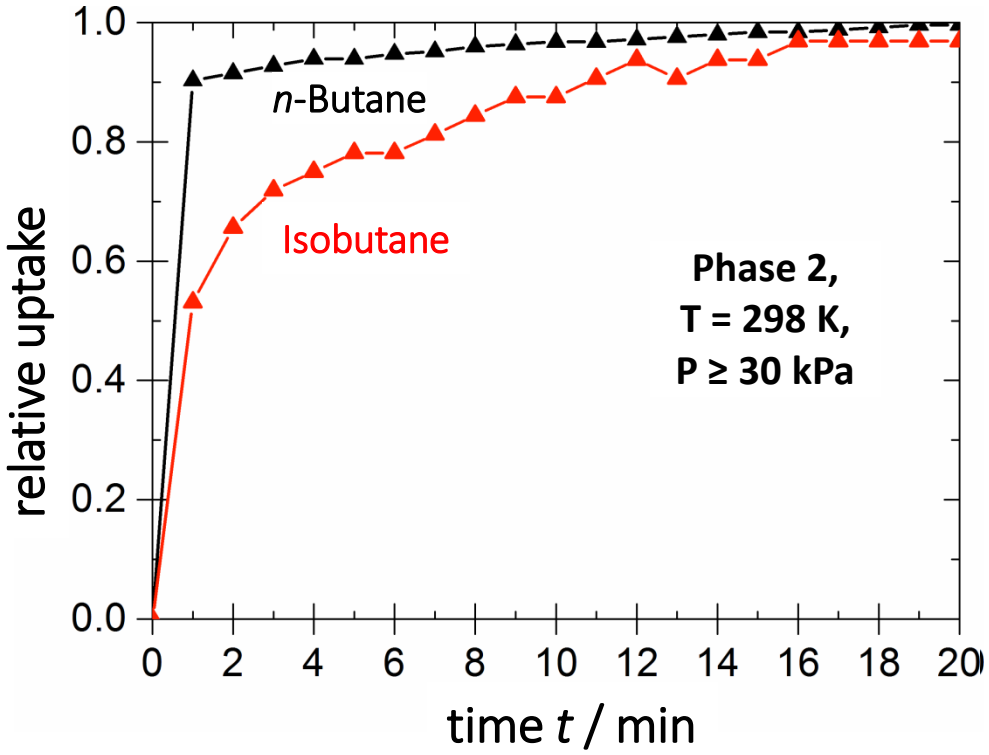

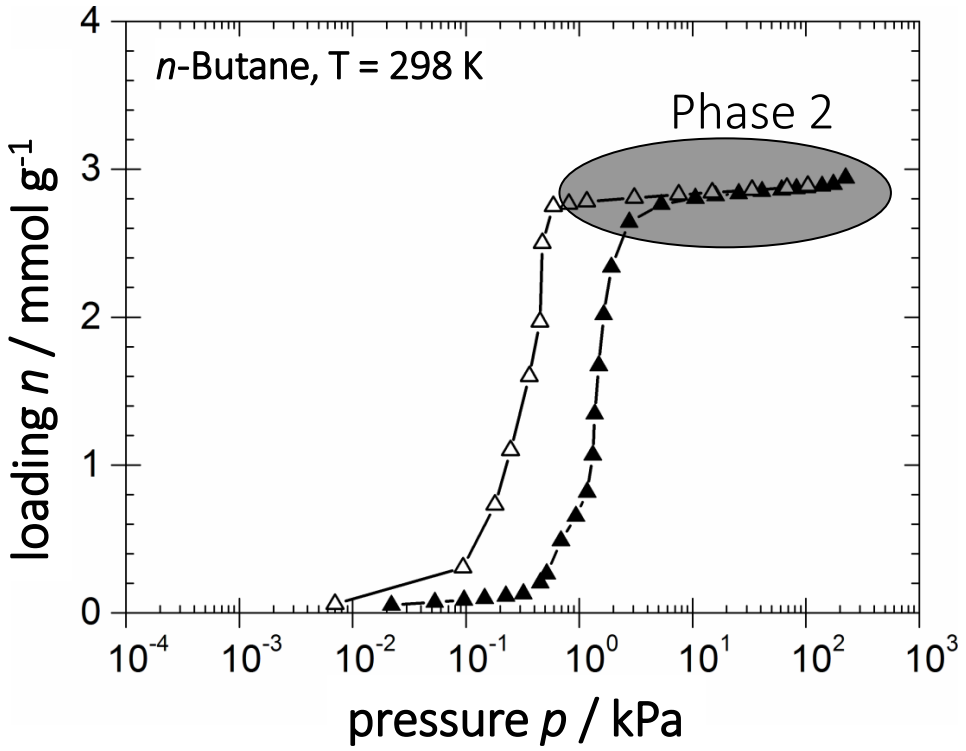

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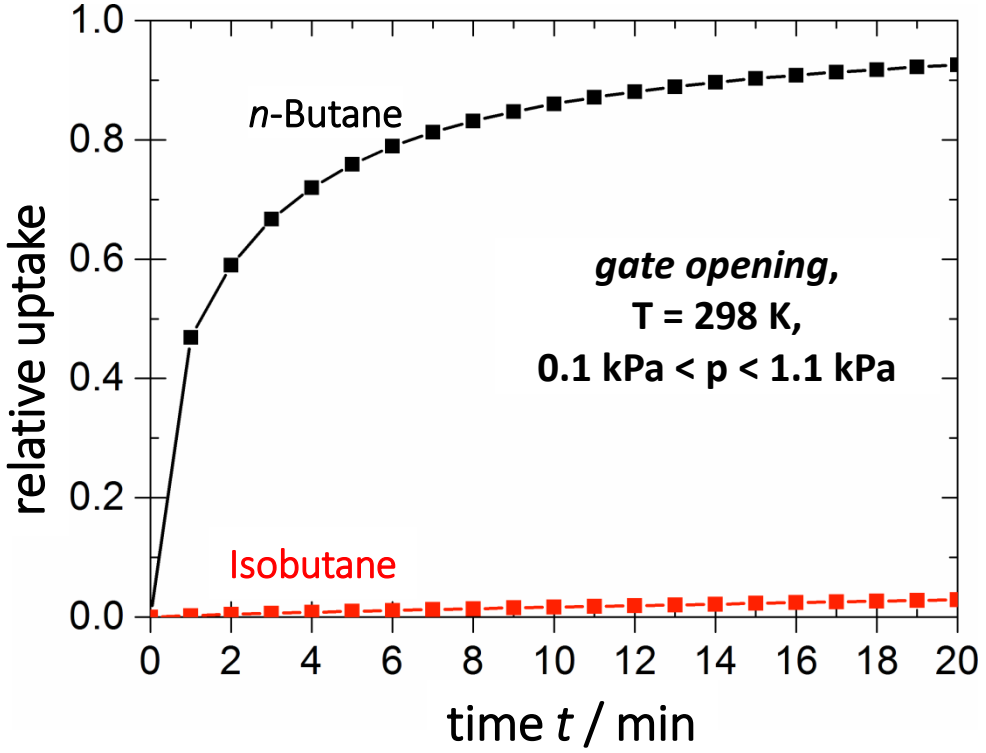
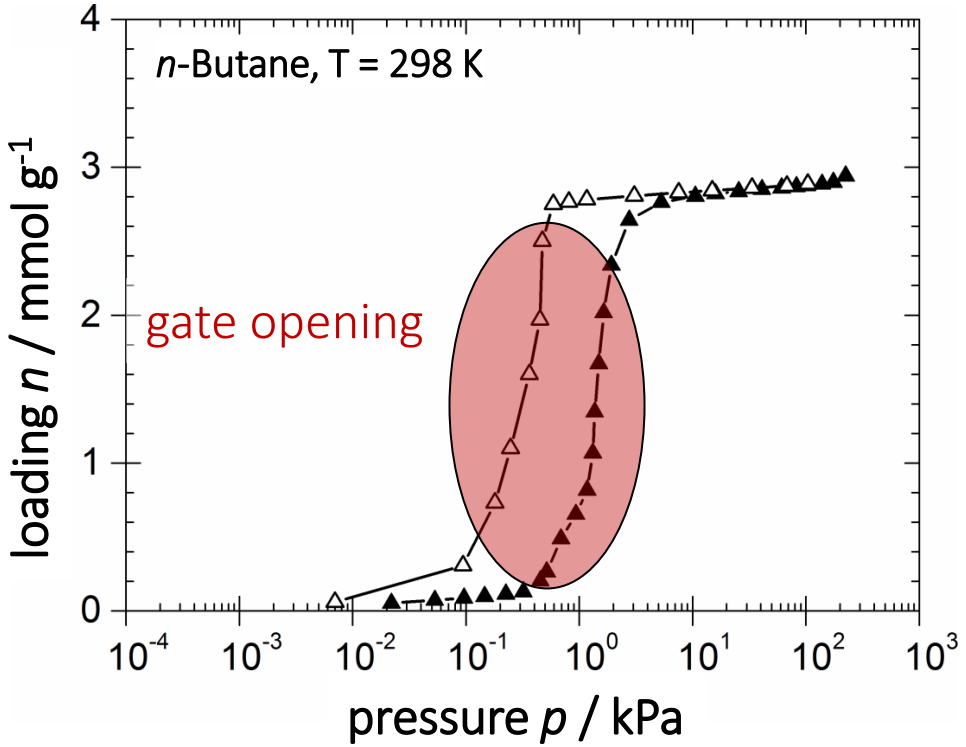
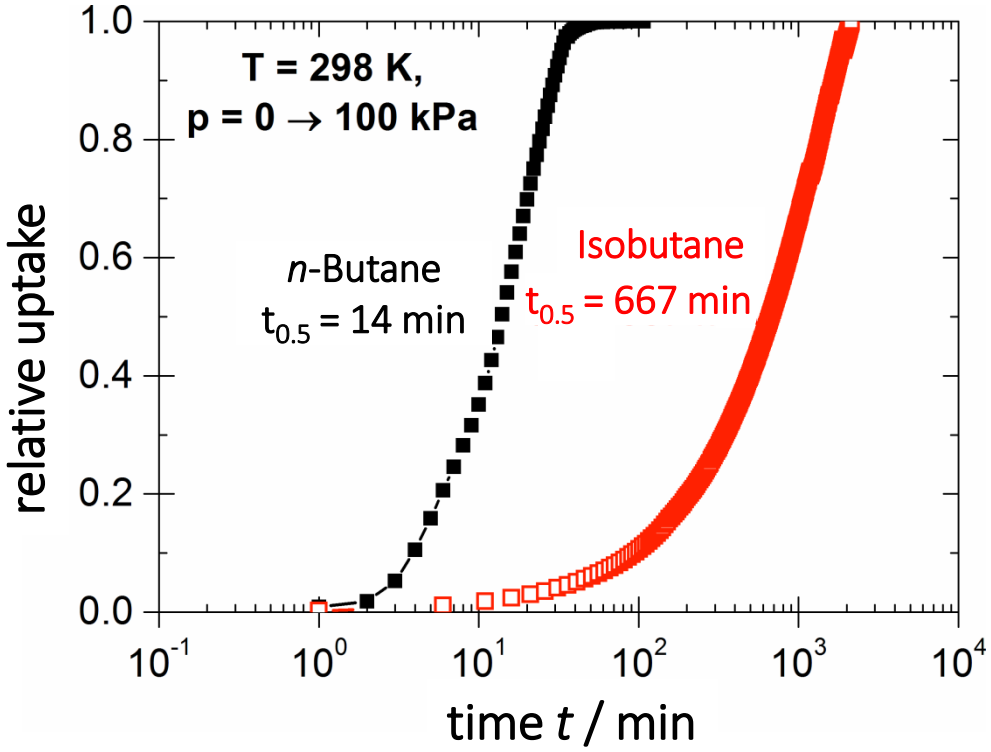
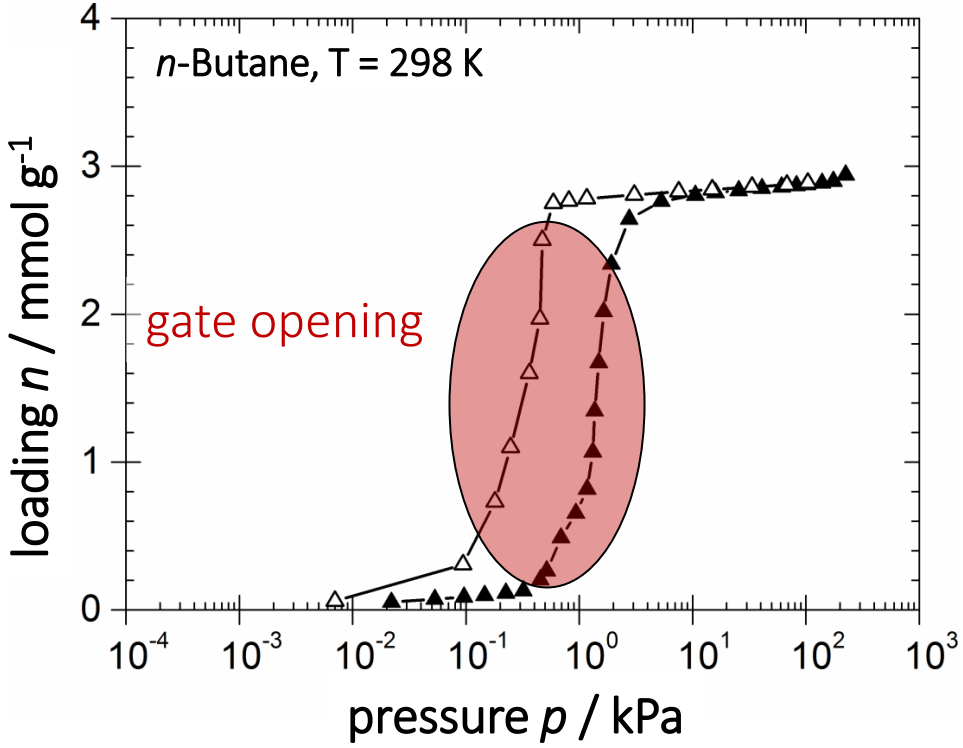




- **gate opening** has influence on rate of adsorption
- *Can this be utilized for a kinetic separation?*

Uptake Curves – an indication for the rate of adsorption





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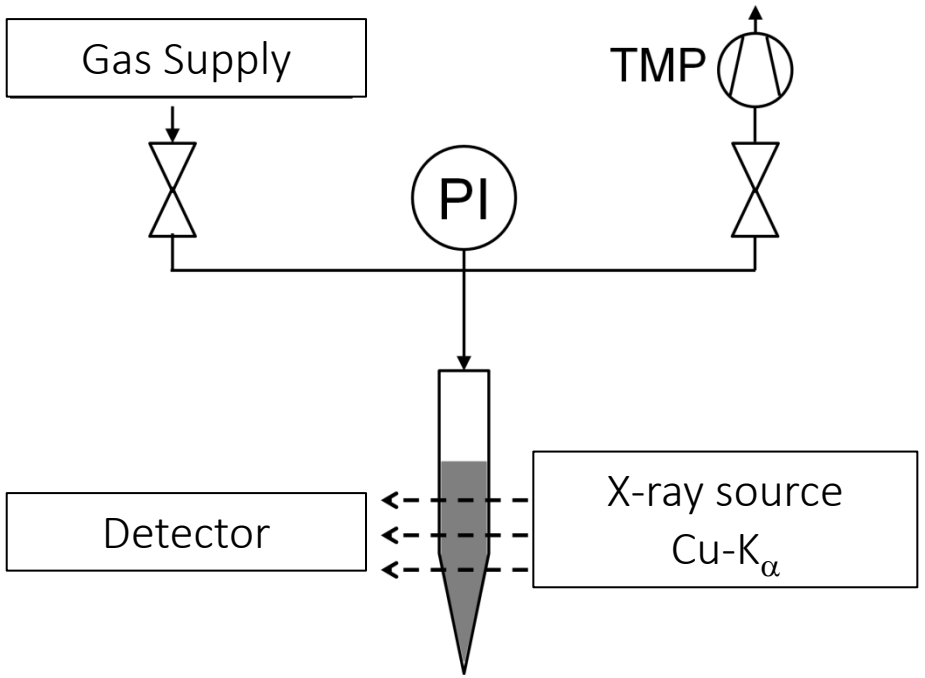
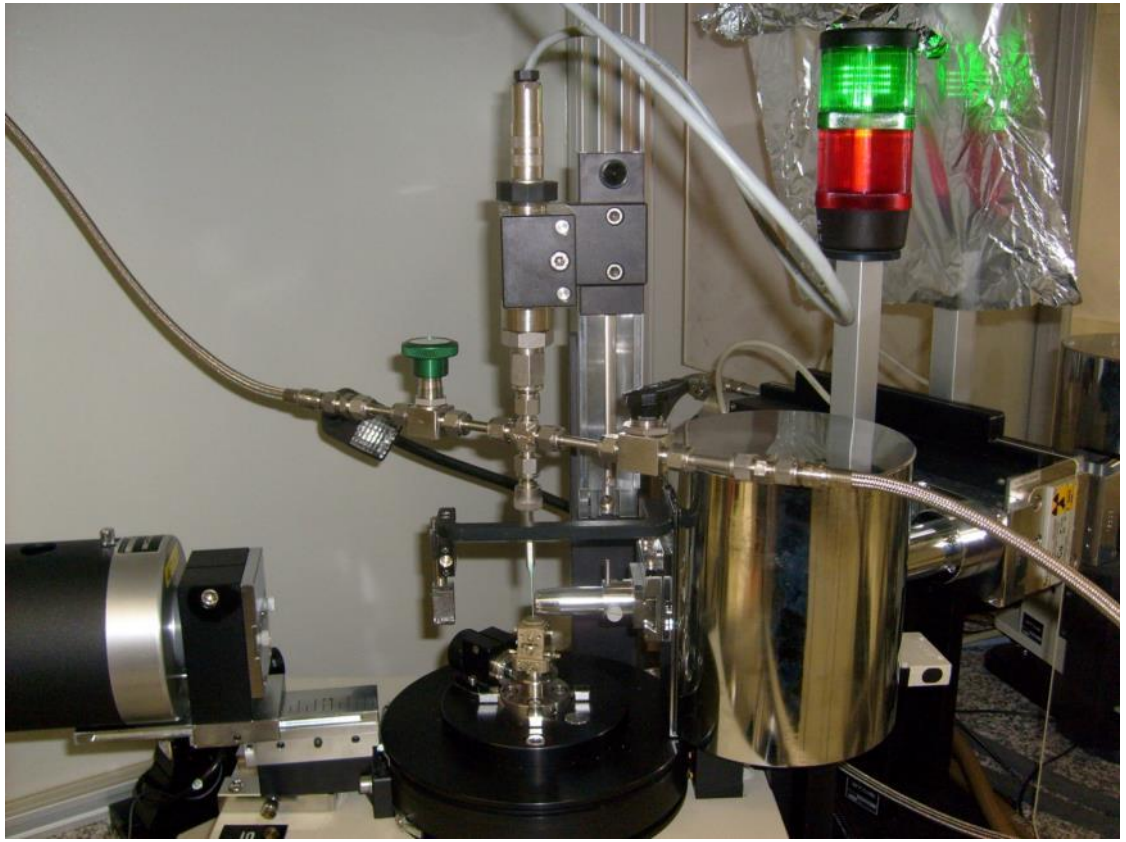
Experimental Setup

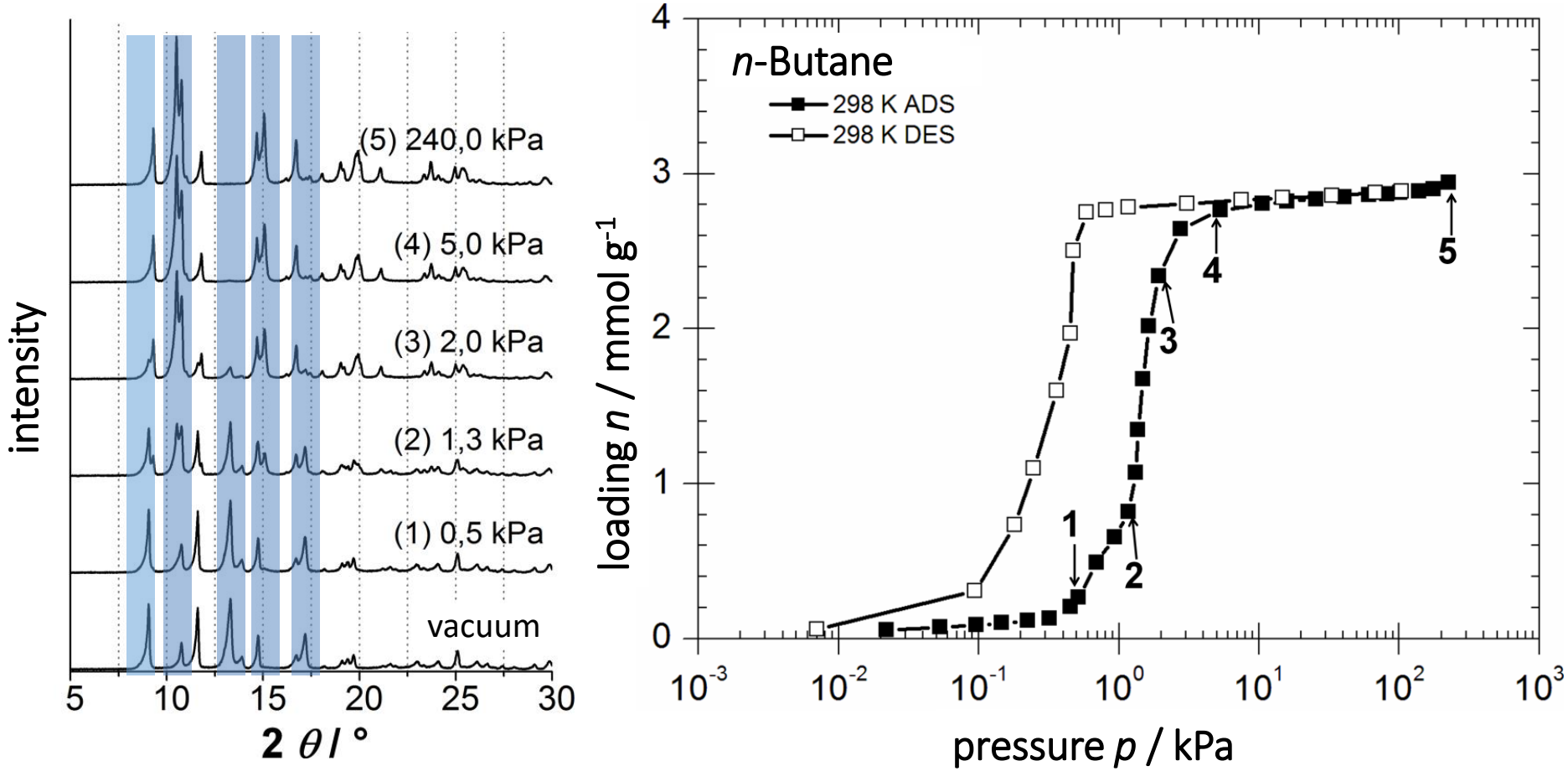
Coupling of sorption experiments with powder x-ray diffractometry
→ structural changes oberservable?





2. In situ PXRD

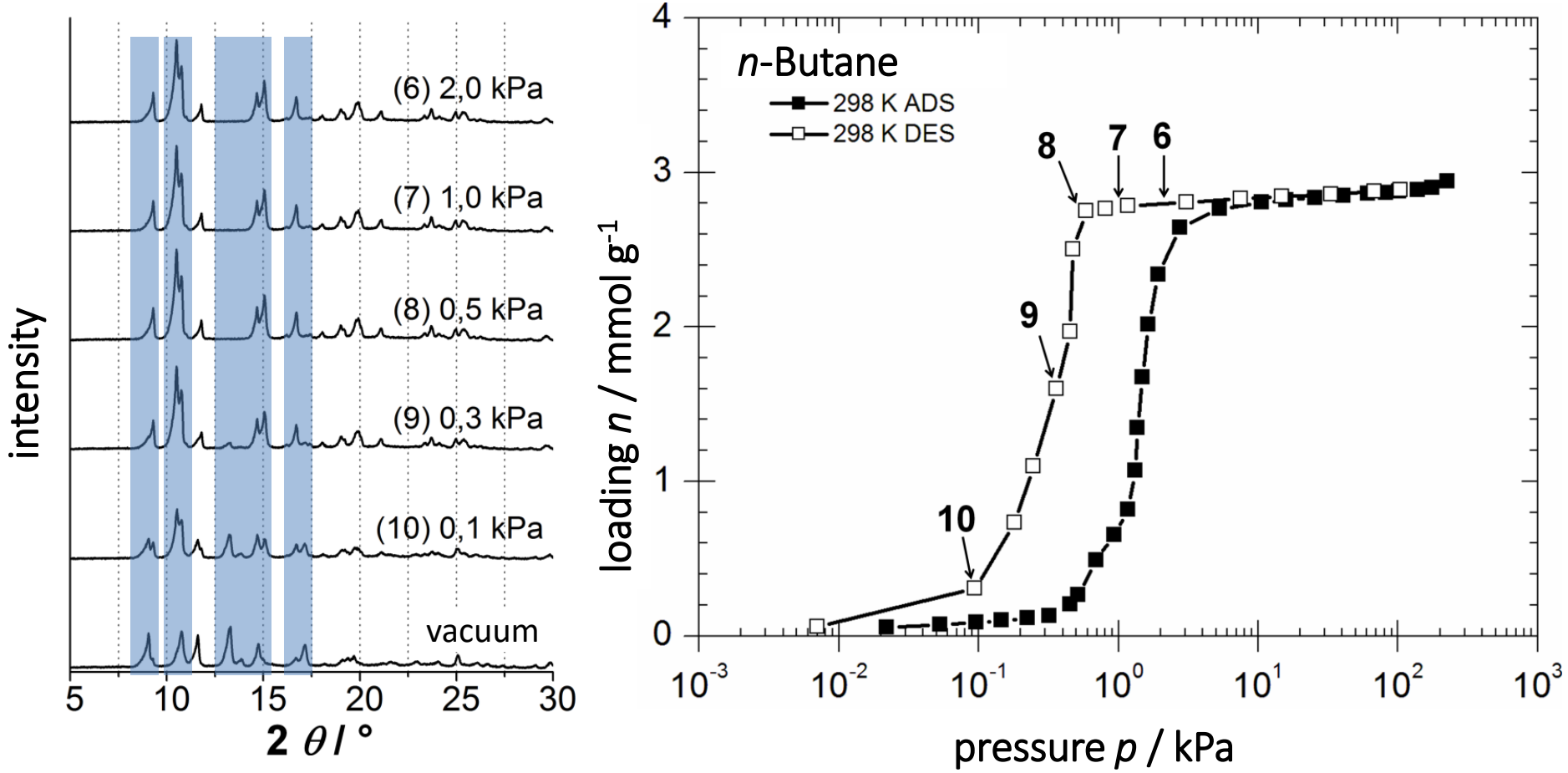
Adsorption of *n*-Butane



- **Structural Change** observable during *n*-Butane adsorption

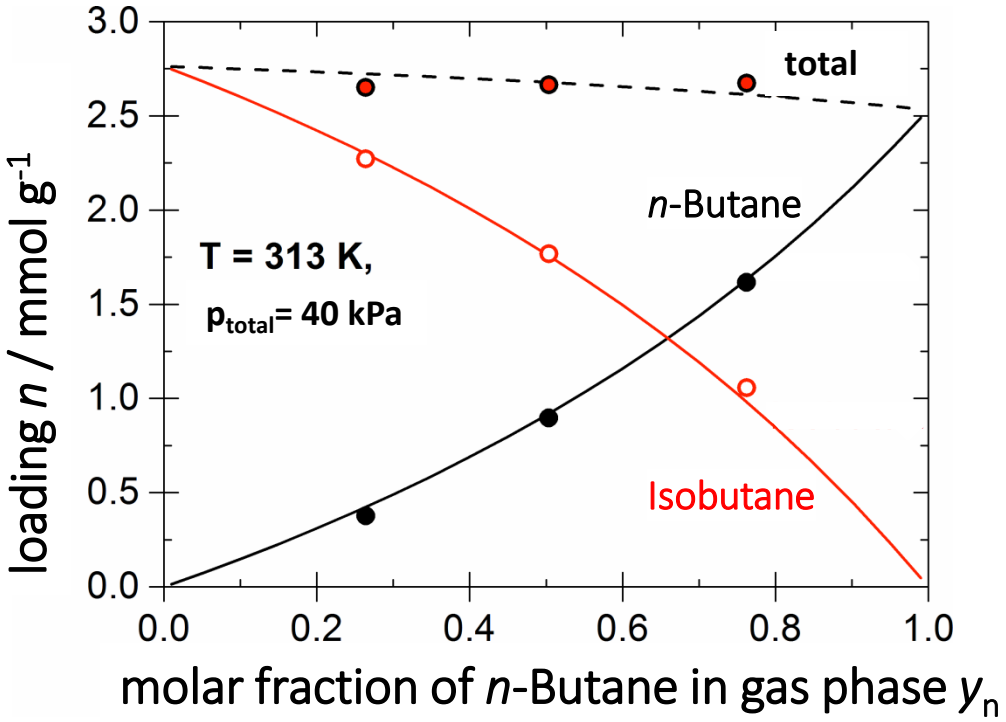
2. In situ PXRD

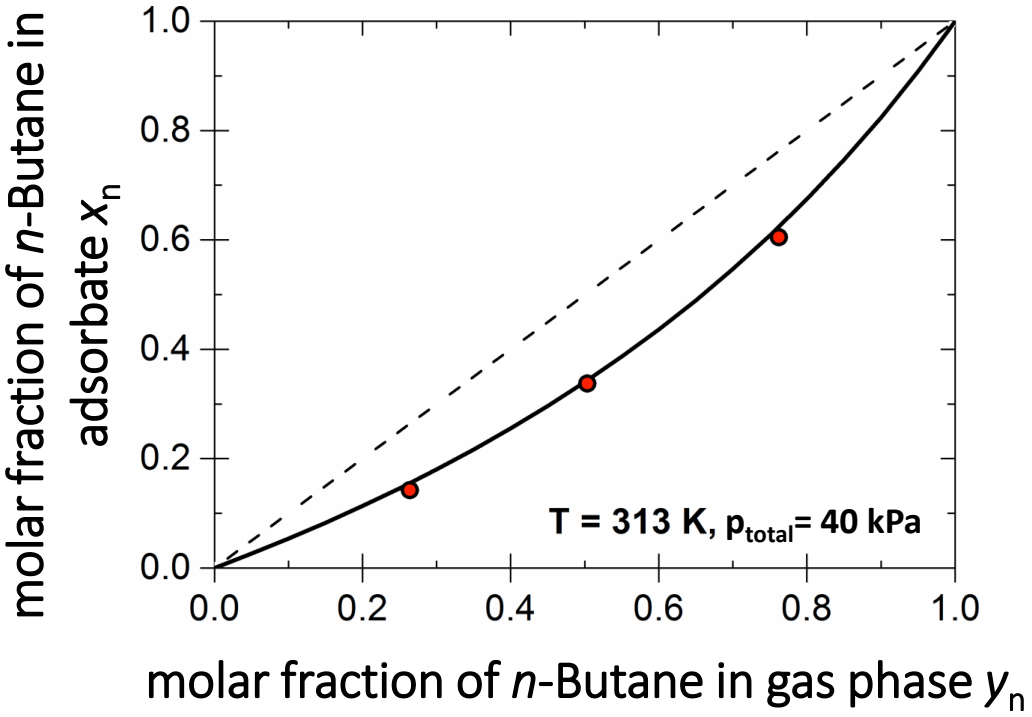
Desorption of *n*-Butane



- Closed structure is **retained** after desorption. Open structure is retained after resolvatization
- **Monoclinic** crystal structure before and after gate-opening
- With *n*-Butane → **Guest-induced transformation** → 3. Generation – Type II

Static Volumetric-Gravimetric Measurements with *n*-Butane/Isobutane Gas Mixtures

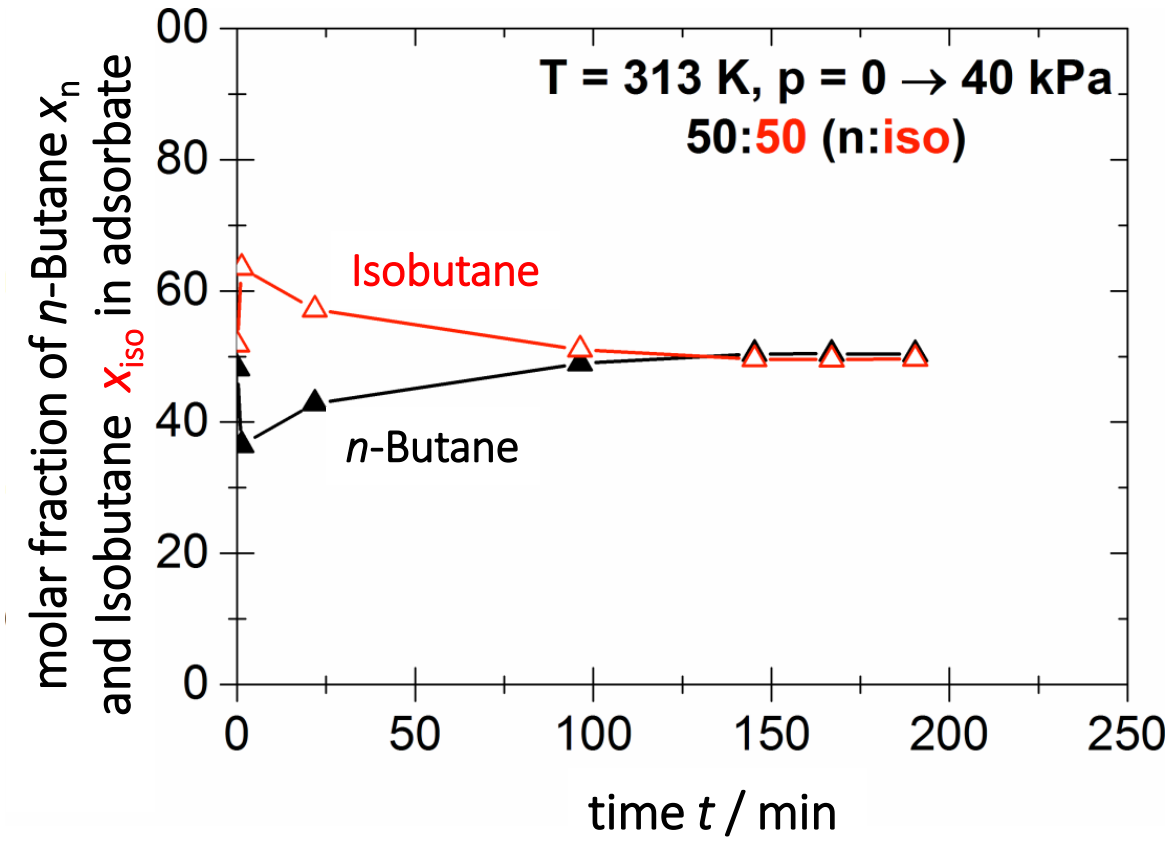


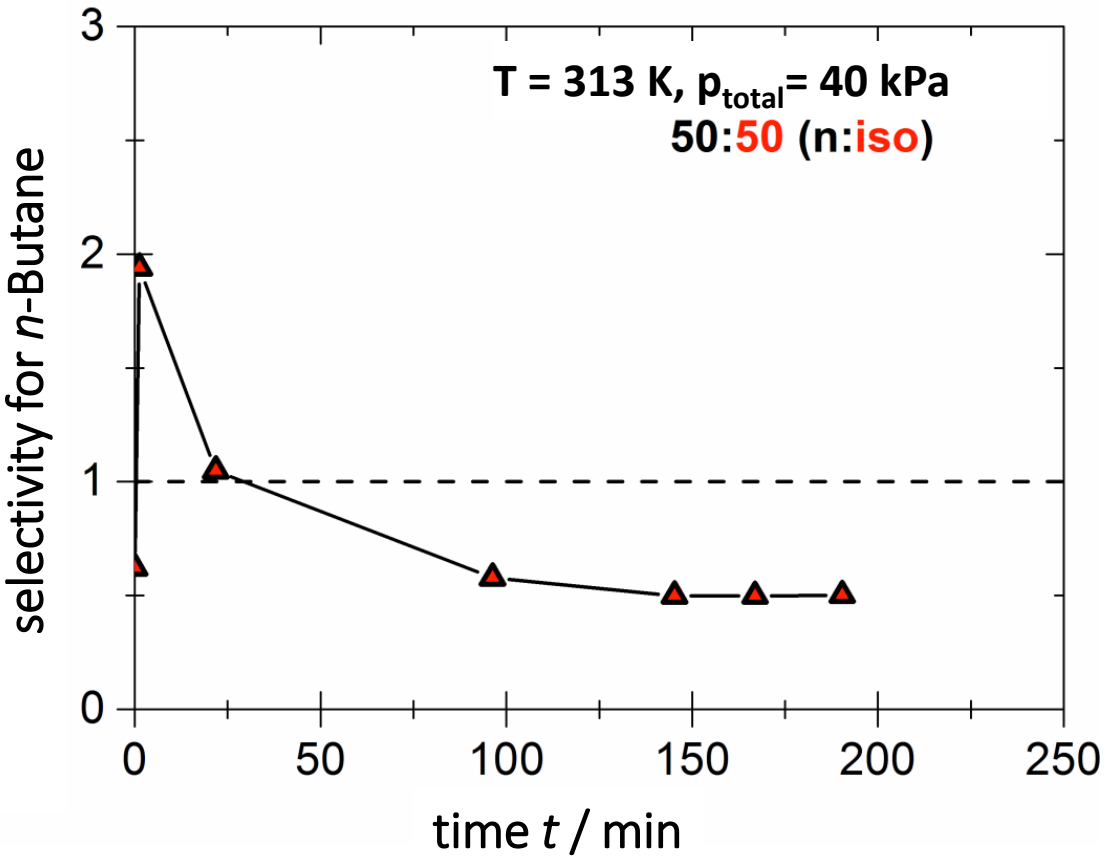


- High experimental effort – **continous mixing** of the gas phase
- GC analysis before and after each experiment → **partial loadings**
- Calculation of the mixture isotherm with the IAST

→ **thermodynamically ideal behaviour**

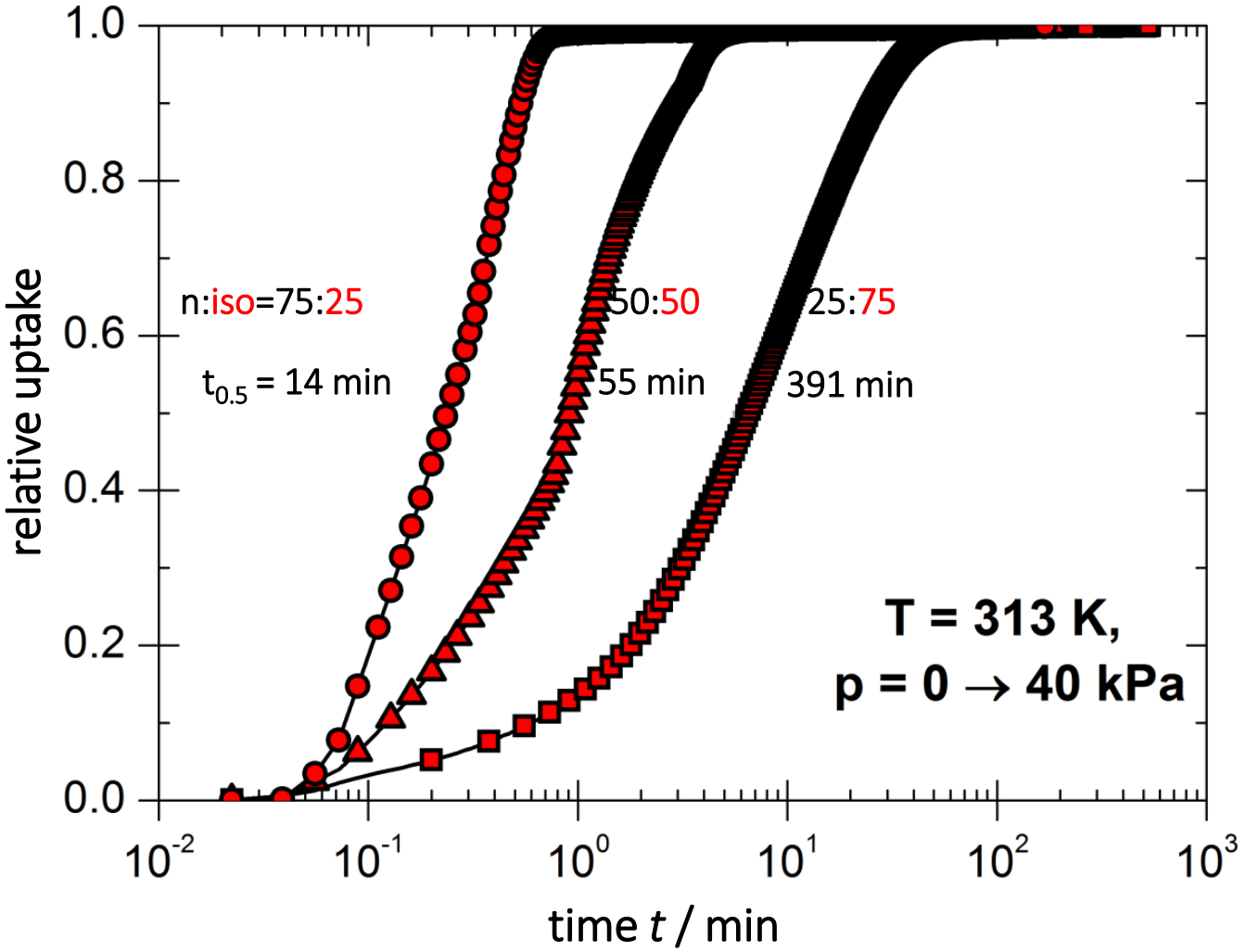
Static Volumetric-Gravimetric Measurements with *n*-Butane/Isobutane Gas Mixtures





- faster adsorption of *n*-Butane opens pore structure
- **change in selectivity** over time can be observed

Static Volumetric-Gravimetric Measurement: Uptake Curves

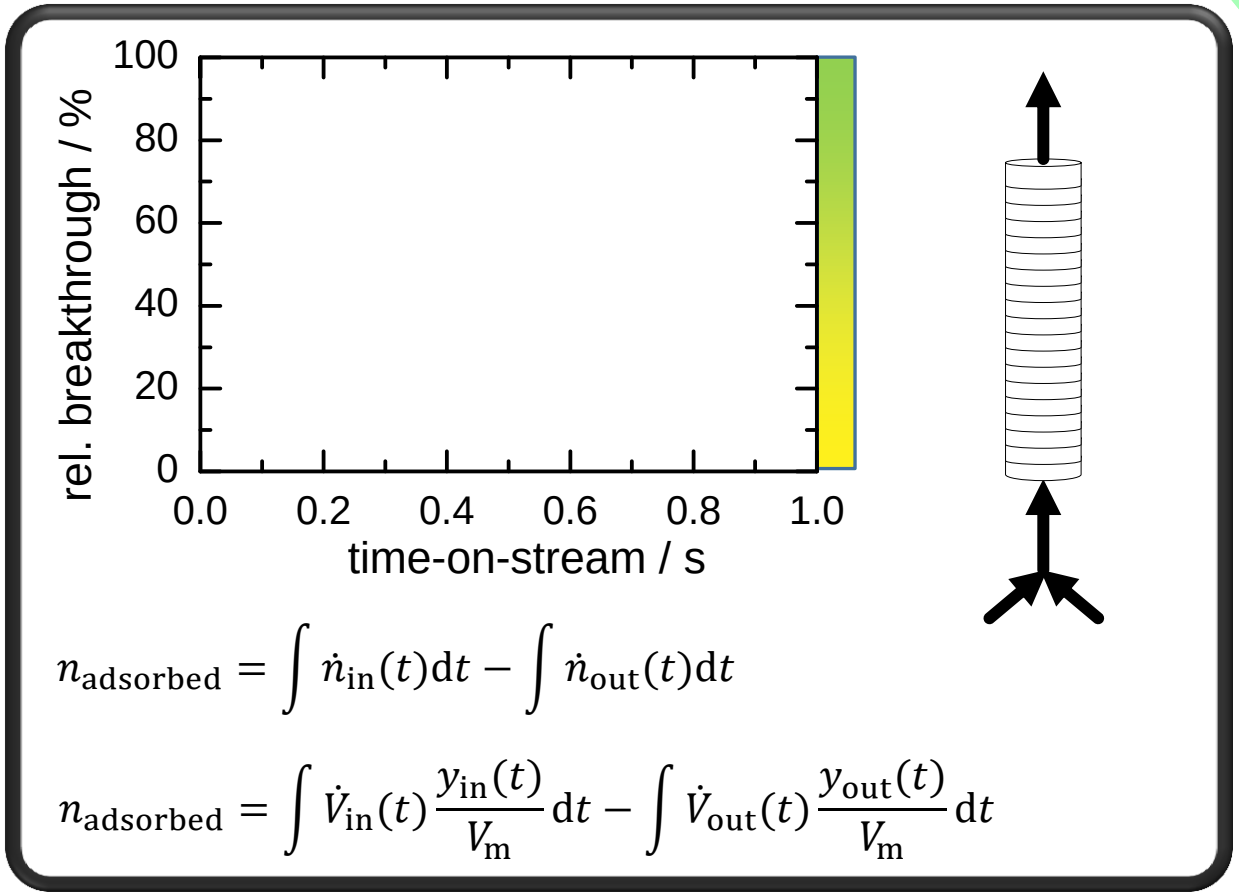


- **Equilibrium times** for different gas mixtures
- Partial pressure of ***n*-Butane** determines the time until equilibrium

→ more *n*-Butane = **faster** equilibrium time

Breakthrough Curve Experiment

- Sorption takes place in **open system**
- Pressure is constant
- Gas Mixtures only
- **Outlet composition** is recorded over time
- **Fixed Bed Adsorber**: Gas must not pass without interaction



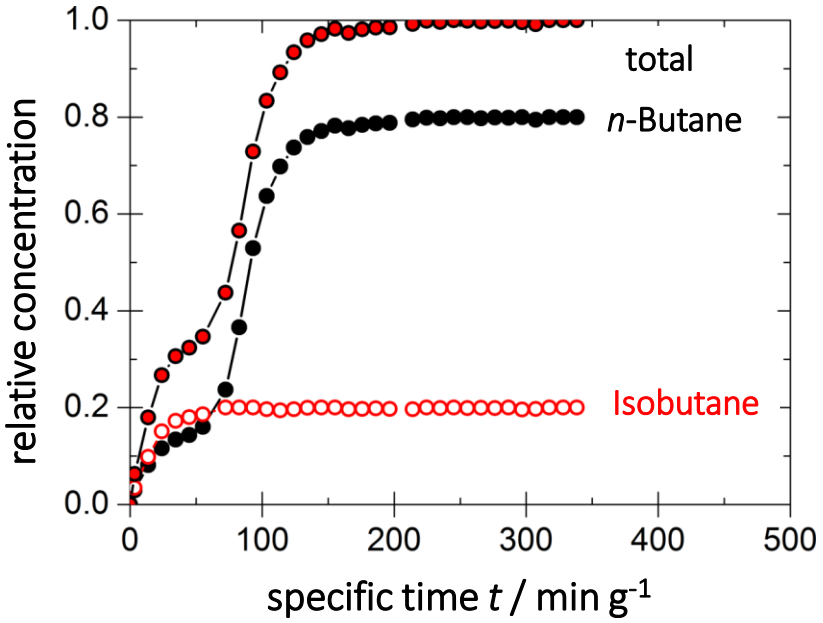
$$n_{\text{adsorbed}} = \int \dot{n}_{\text{in}}(t)\mathrm{d}t - \int \dot{n}_{\text{out}}(t)\mathrm{d}t$$

$$n_{\text{adsorbed}} = \int \dot{V}_{\text{in}}(t)\frac{y_{\text{in}}(t)}{V_{\text{m}}}\mathrm{d}t - \int \dot{V}_{\text{out}}(t)\frac{y_{\text{out}}(t)}{V_{\text{m}}}\mathrm{d}t$$

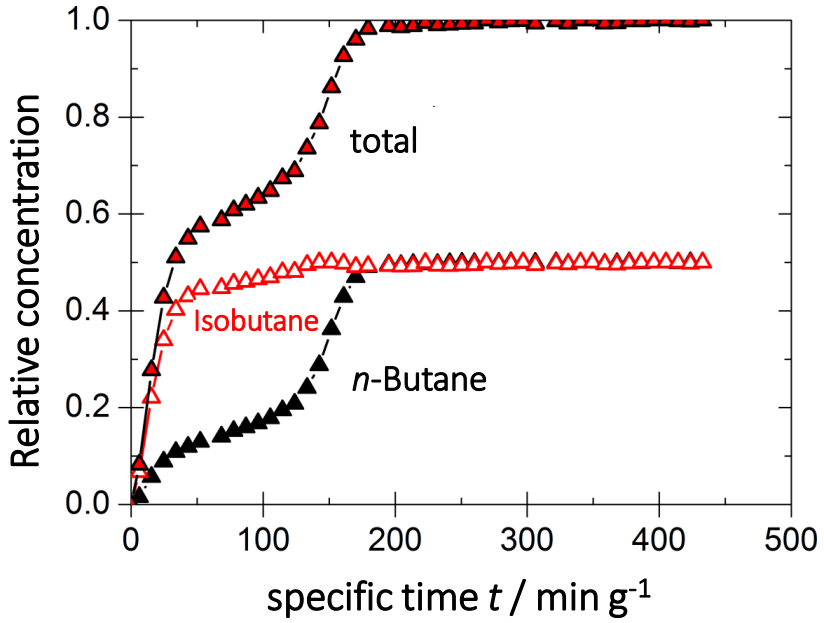
3. Mixture Adsorption

Breakthrough Curves

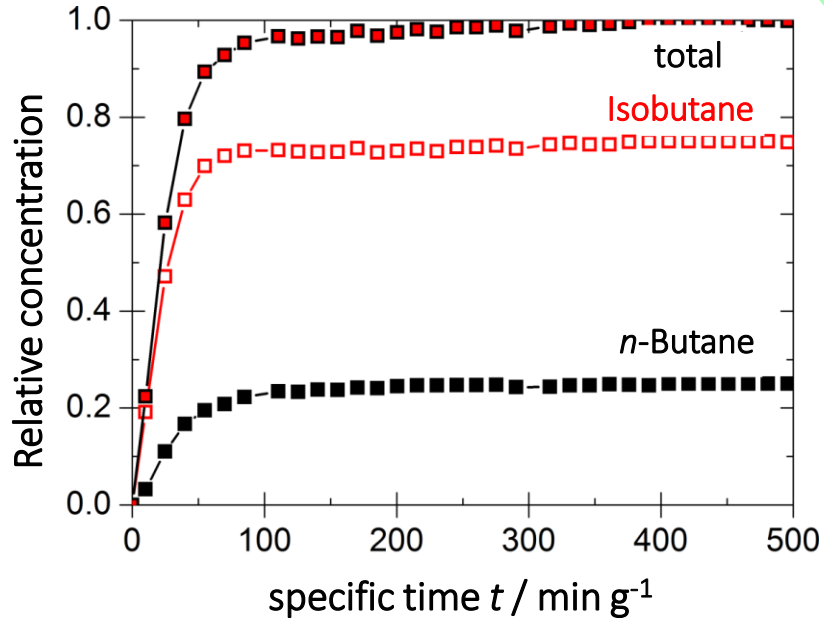
n : iso = 80:20



n : iso = 50:50



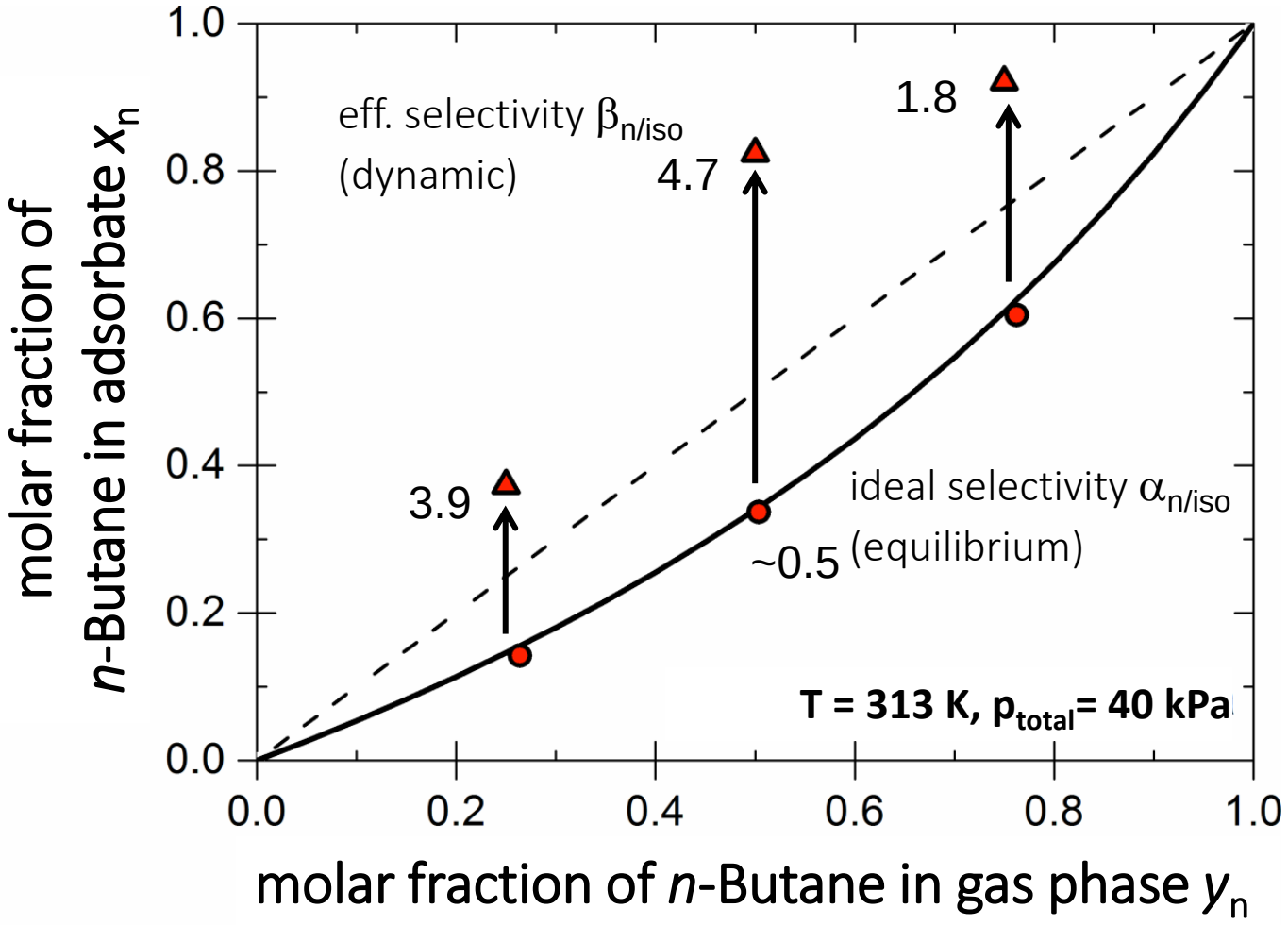
n : iso = 25:75



- BTC from *n*-Butane and Isobutane
  → Combination of equilibrium and **kinetic effects**
- Adsorption of ***n*-Butane is favored** in the **dynamic** measurement

C_4 mixtures in N_2:
313 K, Flow: 3 cm^3 min^{-1}
p_{total} = 100 kPa, p_{C4} = 40 kPa

Comparison of Selectivities: Dynamic vs. Static



- Calculating the **partial loadings** by integrating over the Breakthrough curves → Determining **effective selectivity β**
- Values are **very different** from thermodynamic selectivity α
- **Gate opening influences selectivity in dynamic processes**

Conclusions

- Enrichment of **Isobutane** on the surface in **equilibrium**
- **Sorption-induced structural changes** determined with XRD
- **gate opening** dependent on ***n*-Butane** partial pressure
- **Stepwise breakthrough curves** for *n*-Butane; spontaneous Breakthrough for Isobutane
- Enrichment of ***n*-Butane** on the surface in **dynamic measurements**
- **Kinetics** of gate-opening determine **selectivities**
  → **interesting for gas separation applications**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