Sorption Measurements on Zeolites under Equilibrium and Non-Equilibrium

Project 2

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Aim of Project 2

- macroscopic measurement of transport diffusivities in adsorption/desorption experiments
- comparison of the obtained results with other techniques (NMR, QENS, ZLC etc.)
- supplying equilibrium data (isothermes)

Systems under Investigation - period 1

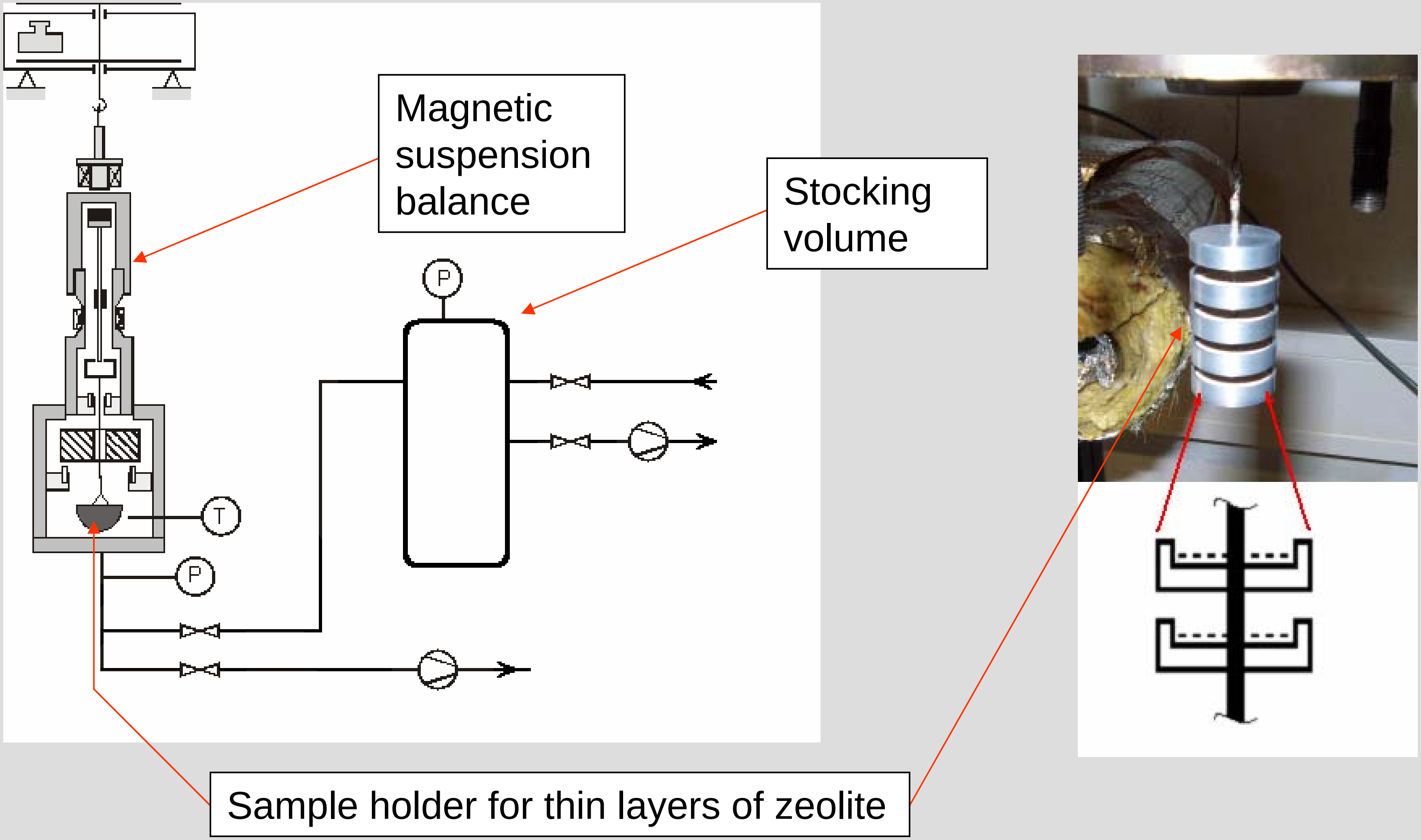
Equilibrium data for:

- methane, i-butane on ZSM-5 and silicalite-1
- n-butane, n-hexane, n-octane and n-decane on zeolite A (XY-155 NaCa 76A)
- propane, n-butane on zeolite A XY-293 NaCaA
- propane, n-butane on modified zeolite A XY-293 TEOS-NaCaA

Transport diffusivities for:

- propane, n-butane on zeolite A (XY-155 NaCa 76A, XY-293 NaCaA, and XY-293 TEOS-NaCaA)

Instrumental Setup

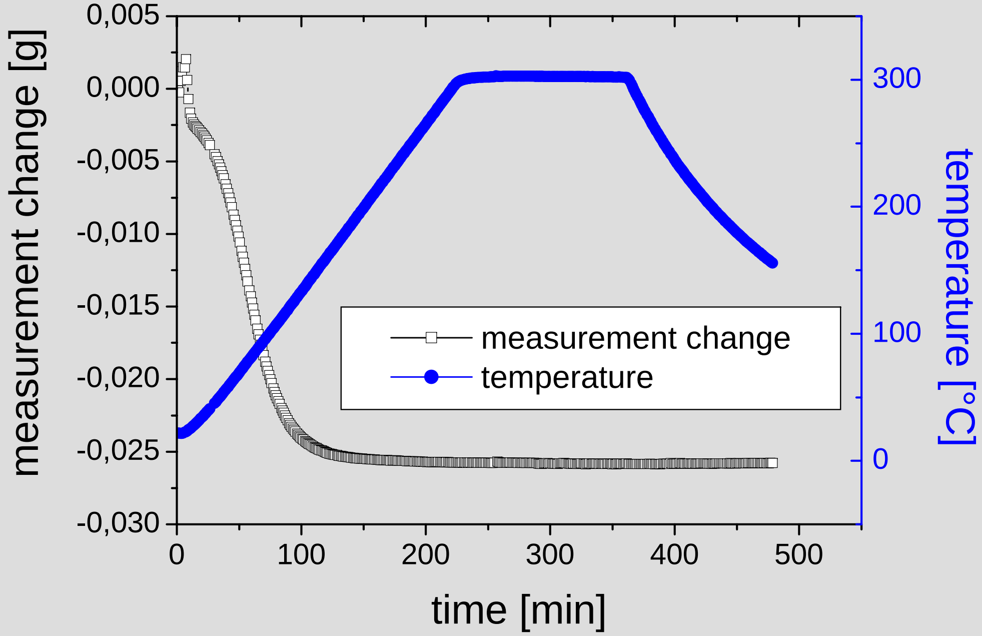


Magnetic suspension balance

Stocking volume

Sample holder for thin layers of zeolite

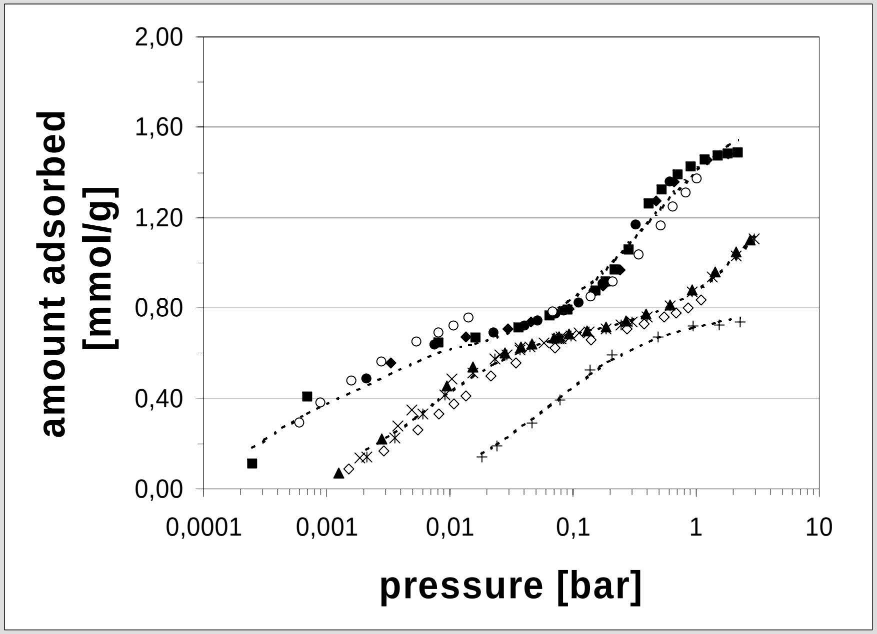
Preparation of the Samples

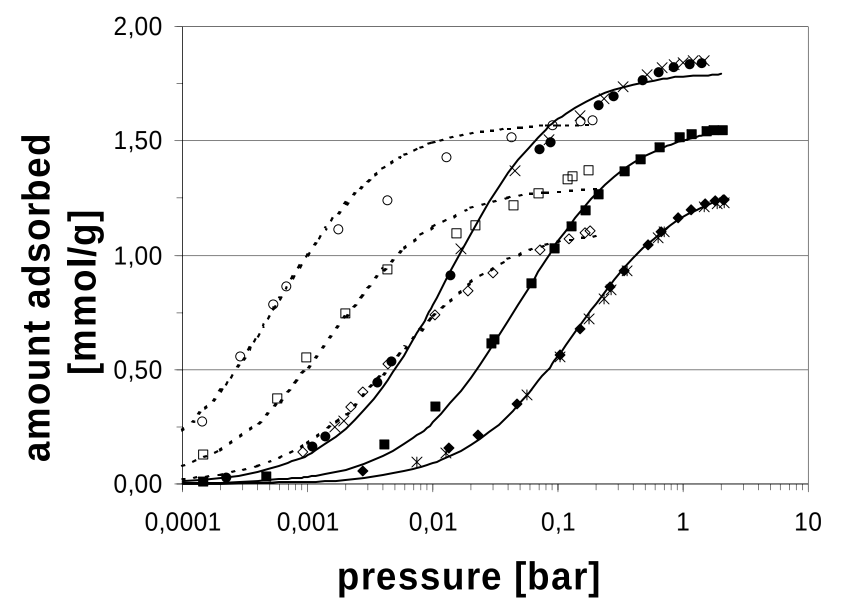


- m_{sample} about 300 mg
- evacuating of samples
- heating of samples
  - heating-rate 100 K/h
  - max. temperature 400 °C
- cooling down of sample

- Weight of silicalite-1 and ZSM-50 is constant above 200 °C.
- A-Zeolite were heated up to 380 °C.

Isotherms





Isotherms on silicalite-1

■, ◆, ● i-butane at 30°C
▲, x, ∗ i-butane at 60°C
+ i-butane at 120°C
○, ◇ sun et al.

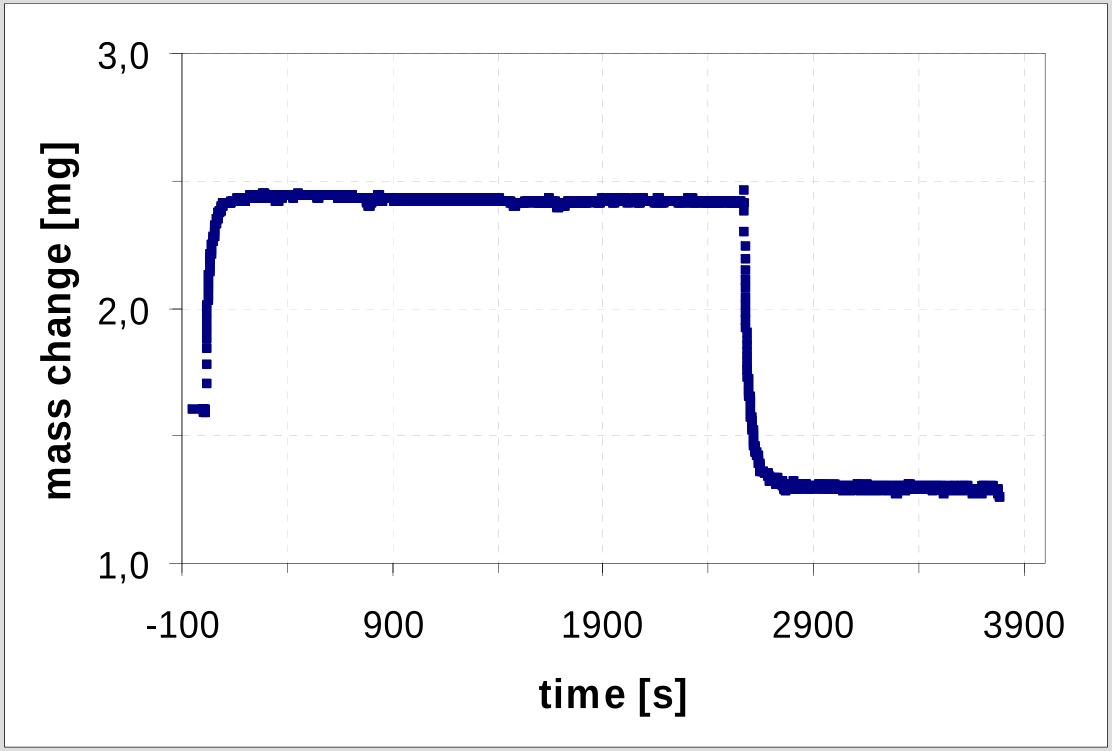
Isotherms on zeolite A

●, ■, ◆∗n-butane at 98°C, 151°C, 208°C
○, □, ◇ n-hexane at 104°C, 153°C, 195°C

Ref : M. S. Sun, D. B. Shah, H.H.Xu, O. Talu Adsorption Equilibira of C1 to C4 Alkanes, CO2 and SF6 on Silicalite, J. Phys. Chem. B, 1998, 102, S. 1466-1473,

Adsorption-Desorption curve

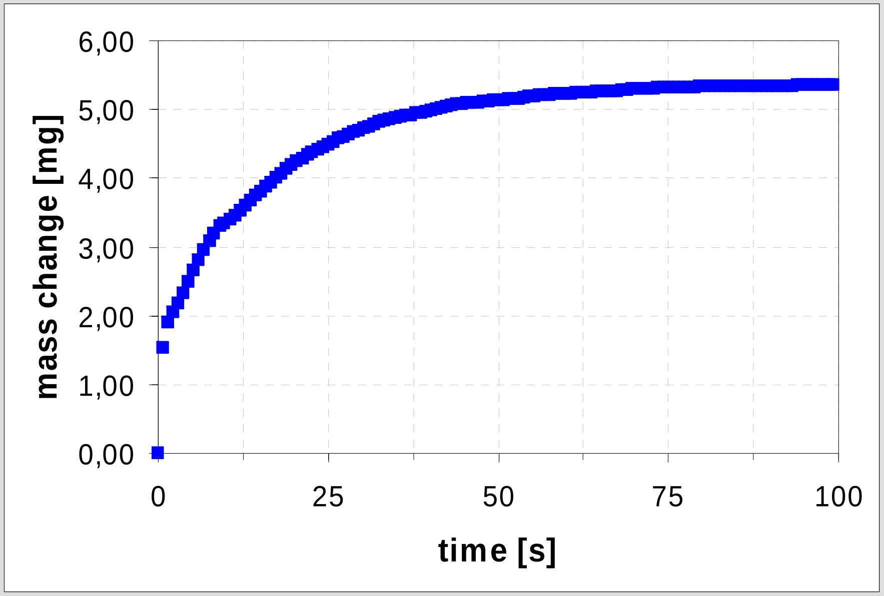
- Curve of an adsorption step and a desorption step of n-butane on XY-155 NaCa76A at 200°C

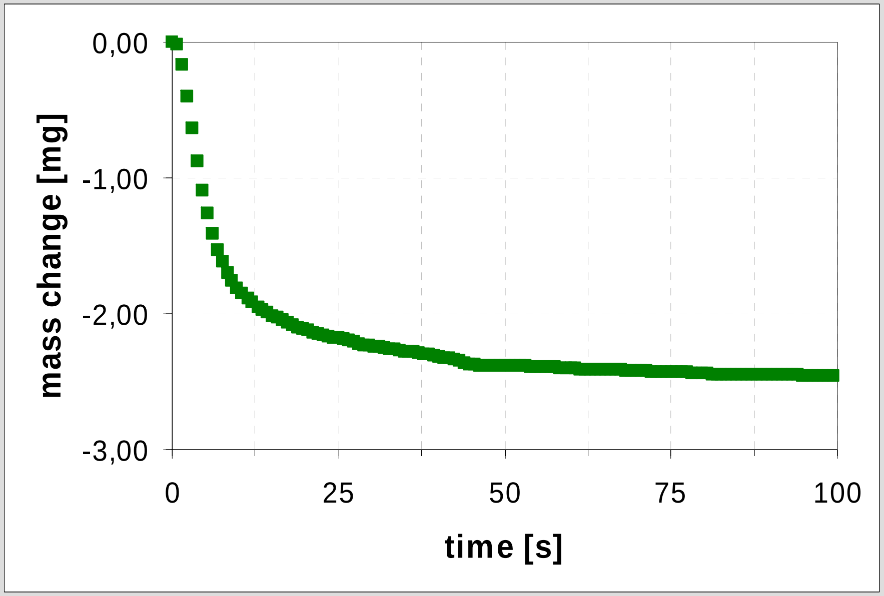


adsorption from 4,6 mbar to 10,6 mbar

desorption from 10,6 mbar to 2,6 mbar

Kinetic Behavior of n-butane





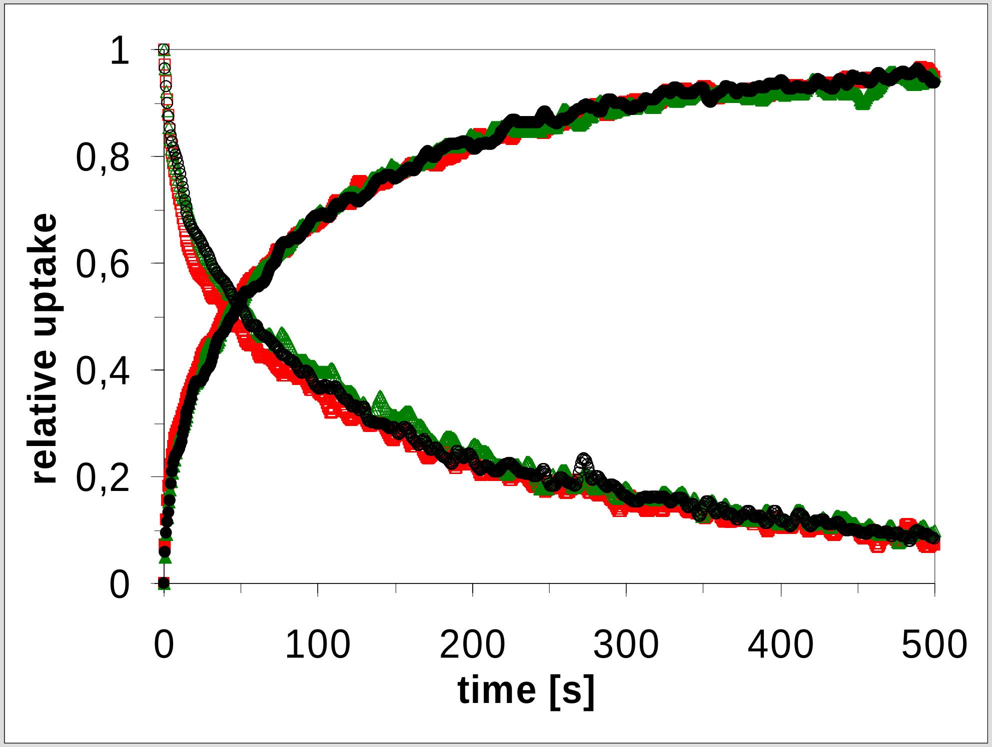
mass change for an adsorption step

(n-butane on XY-155 NaCa76A; 200 °C; p_0=Vacuum, p_E=16 mbar)

mass change for a desorption step

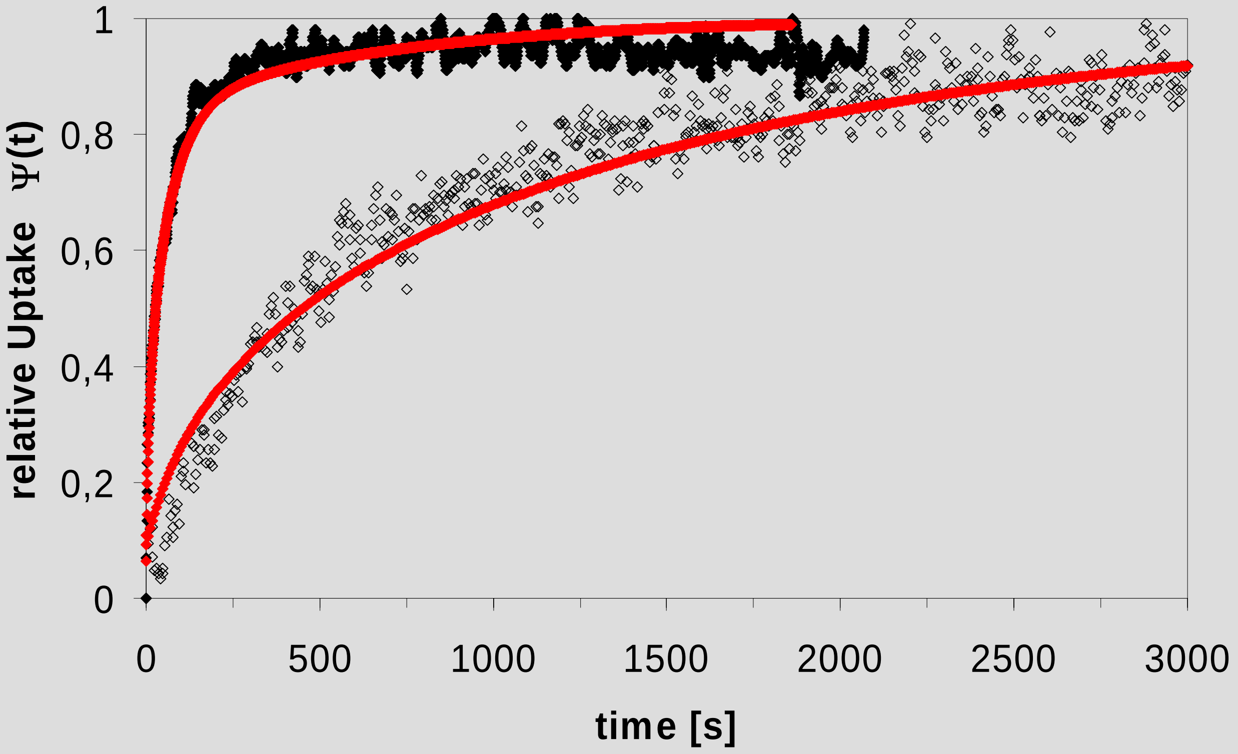
(n-butane on XY-155 NaCa76A; 200 °C; p_0=10 mbar, p_E=3 mbar)

Reproducibility of kinetics



Plot of relative uptakes for adsorption and desorption steps for n-butane on XY-293 NaCaA at 100 °C
p_0=2 mbar, p_{End}=10 mbar

Influence of a Surface barrier



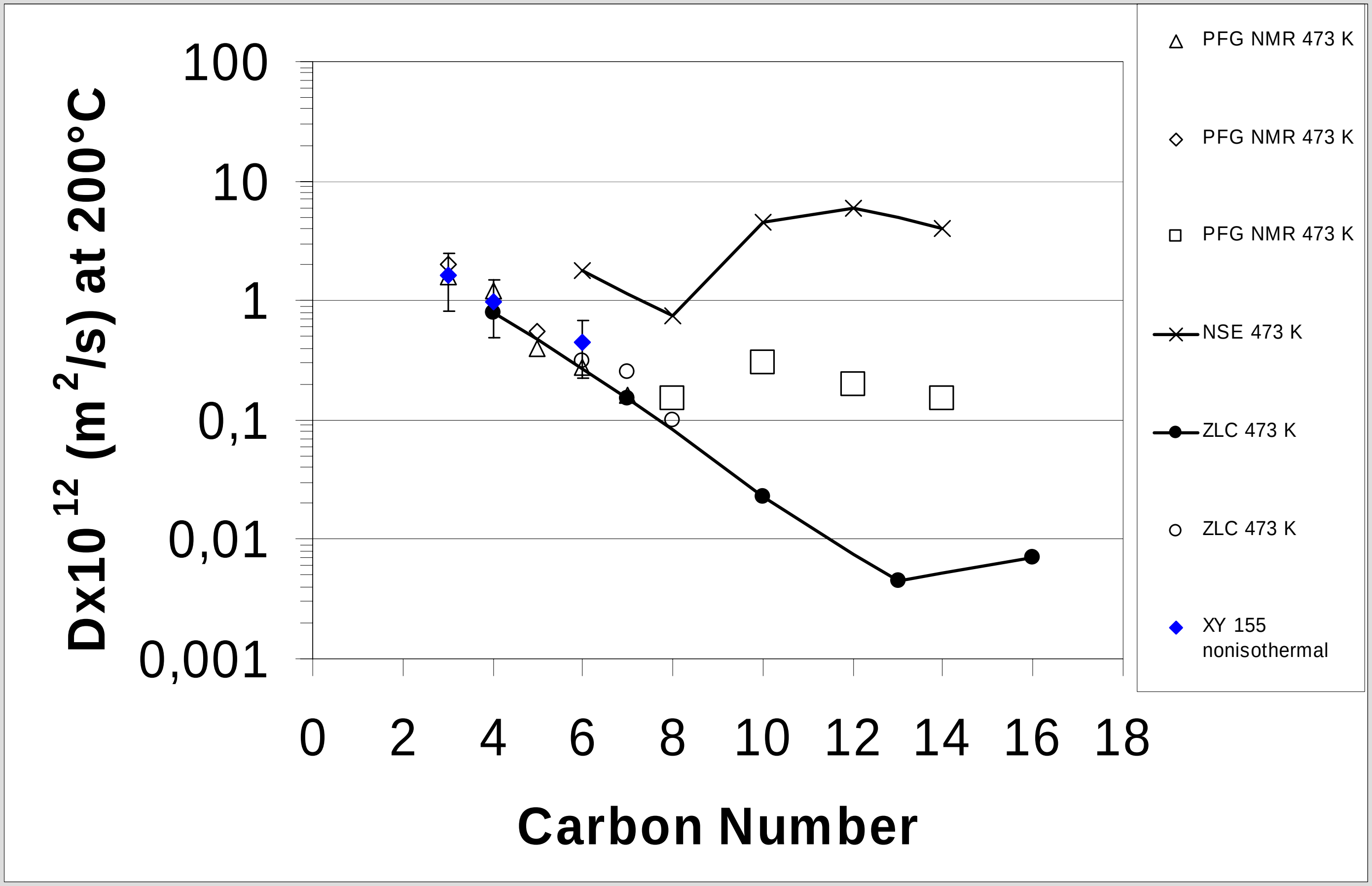
relative Uptakes for a untreated and a modified zeolite material for propane at 100 °C: ◆ untreated NaCaA p_0=3,1 mbar p_{Eq}= 14,5 mbar, ◇ TEOS modified p_0=2,5 mbar p_{Eq}= 21,4 mbar, ◆ fitted with Nonisothermal and isothermal model, respectively

Calculated Transport diffusivities: ◆ $4*10^{-13}$ m^2/s, ◇ $3*10^{-14}$ m^2/s

Results of kinetic measurements

alkane	temperature [°C]	Diffusivities [m^2/s]
XY-155-NaCaA		
propane	200	$(1,6\pm0,6)*10^{-12}$
n-butane	200	$(7\pm5)*10^{-13}$
XY-293-2-CaA		
propane	101	$(6\pm4)*10^{-13}$
	145	$(2,5\pm1,2)*10^{-12}$
	200	$(4,5\pm0,6)*10^{-12}$
n-butane	101	$(2,7\pm0,3)*10^{-13}$
	145	$(7\pm2)*10^{-13}$
	200	$(3,2\pm0,9)*10^{-12}$

Comparison with other Data



- Diffusivities of propane, n-butane and n-hexane on zeolite A (XY-155 NaCa76A); 200 °C

Ref : J. Kärger et al.,Diffusion Fundamentals I, Leipzig 2005

Non-Isothermal Model

- Non-isothermal model was developed and published by D.M. Ruthven, L.K. Lee and H. Yucel.
  - Assumptions:
    - sample consists of uniform spherical particles,
    - significant heat transfer resistance can only be observed at the external surface of the sample,
    - intraparticle diffusion is significant resistance to mass transfer,
    - the diffusivity is assumed constant (isotherms in Henry regime).

Ref : *D.M. Ruthven, L.K. Lee, H. Yucel, Kinetics of Non-Isothermal Sorption in Molecular Sieve Crystals, AiChE, Vol. 26, No. 1 (1980)*

Equations of the Model

- solution of the Non-Isothermal model:

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=1}^{\infty} \frac{9\left[\frac{q_n \cot q_n - 1}{q_n^2}\right]^2 \cdot EXP\left(-q_n^2 \cdot \frac{D}{r^2} \cdot t\right)}{\frac{1}{\beta} + \frac{3}{2}\left[\frac{q_n \cot q_n \left(q_n \cot q_n - 1\right)}{q_n^2} + 1\right]} \qquad (1)$$

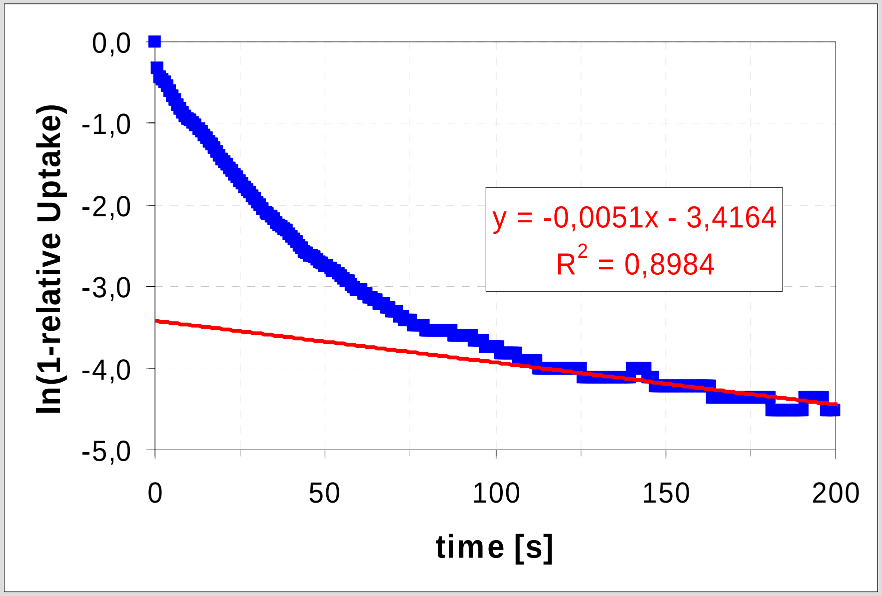
$$3\beta\left(q_n \cot q_n - 1\right) = q_n^2 - \alpha \qquad (2)$$

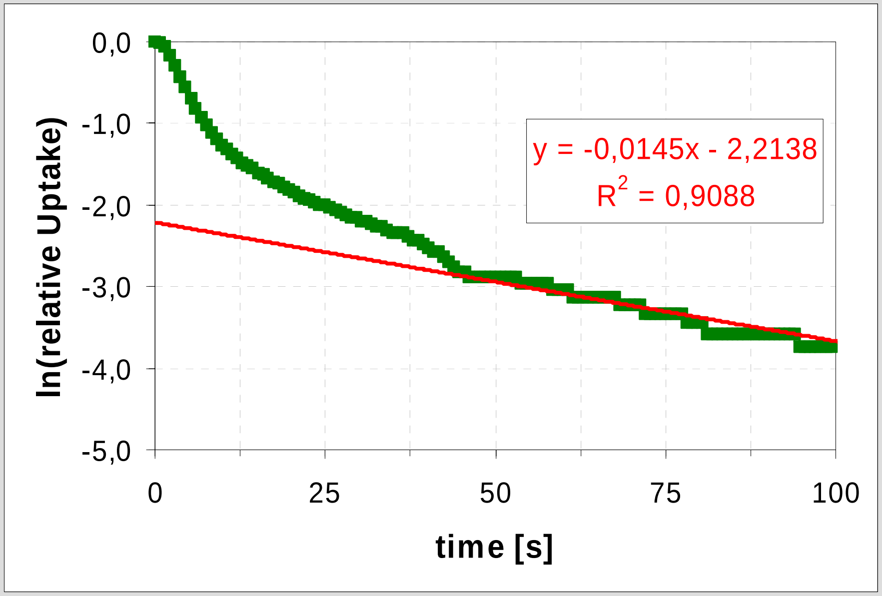
$$\frac{m_t}{m_\infty} = 1 - \frac{\beta}{1+\beta} \cdot EXP\left(-\frac{\alpha \cdot t}{1+\beta}\right) \qquad (3)$$

- calculation of α and β from the long time region with equation (3)
- numerical determination of q_n for n=[1..10] as roots of equation (2)
- insertion of the q_n values in equation (1) and applying them to exp. data

Ref : *D.M. Ruthven, L.K. Lee, H. Yucel, Kinetics of Non-Isothermal Sorption in Molecular Sieve Crystals, AiChE, Vol. 26, No. 1 (1980)*

Long time region

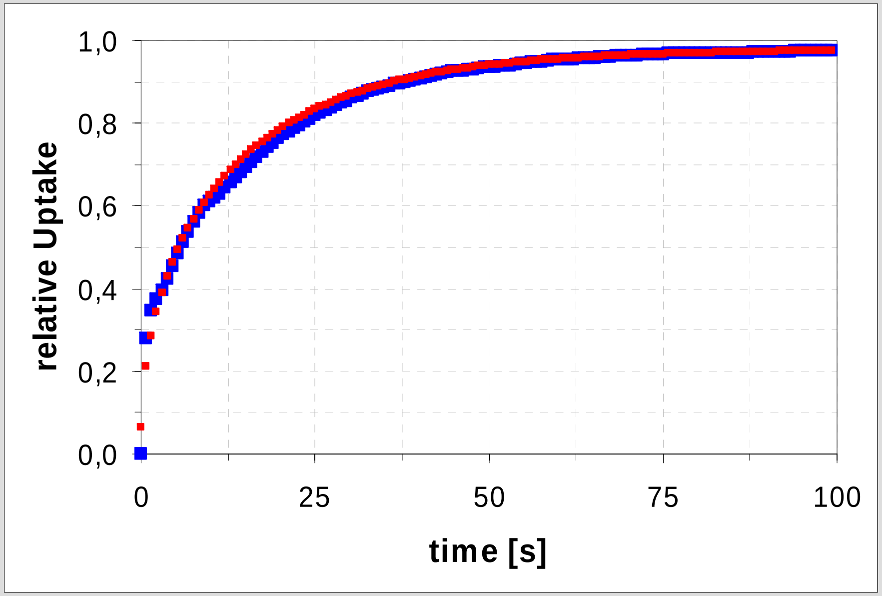


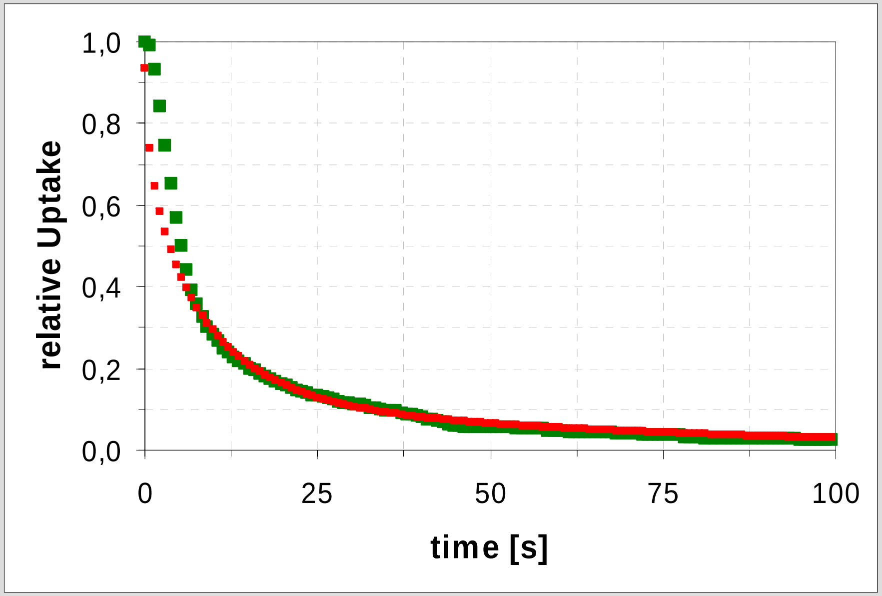


estimation of slope and intercept for the non-isoth. model
(n-butane on XY-155 NaCa76A; 200 °C;
p_0=Vacuum, p_E=16 mbar)

estimation of slope and intercept for the non-isoth. model
(n-butane on XY-155 NaCa76A; 200 °C;
p_0=10 mbar, p_E=3 mbar)

Fit on Experimental Data





D/r^2=5,8*10^{-3} s^{-1}

r=9,3*10^{-6} m

D=5*10^{-13} m^2/s

(n-butane on XY-155 NaCa76A;

200 °C;

p_0= Vacuum, p_E= 16 mbar)

D/r^2= 9,6*10^{-3} s^{-1}

r=9,3*10^{-6} m

D=8*10^{-13} m^2/s

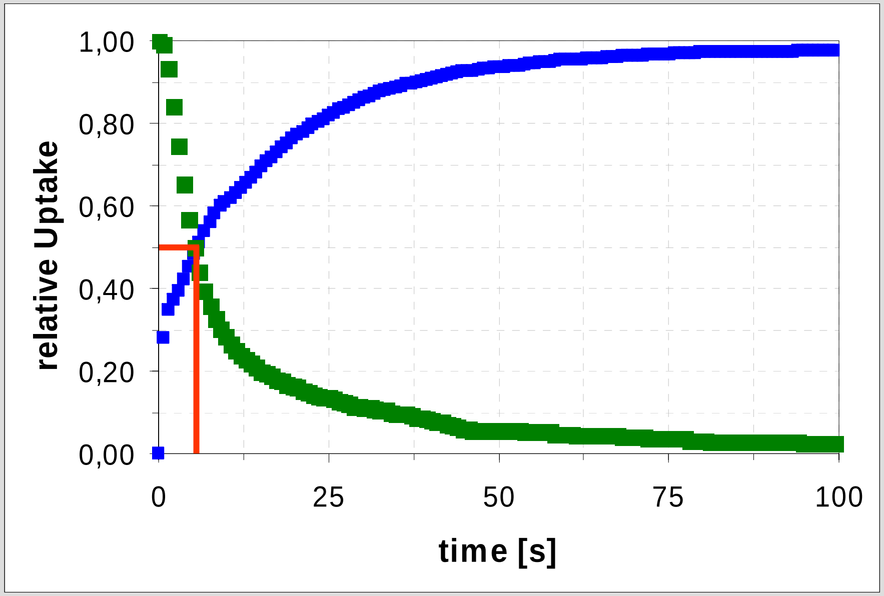
(n-butane on XY-155 NaCa76A;

200 °C;

p_0= 10 mbar, p_E= 3 mbar)

Half time for the fractional uptake

- $t_{0,5}$ is the time to reach the half of relative uptake
- for linear isotherms should be the same for adsorption and desorption steps



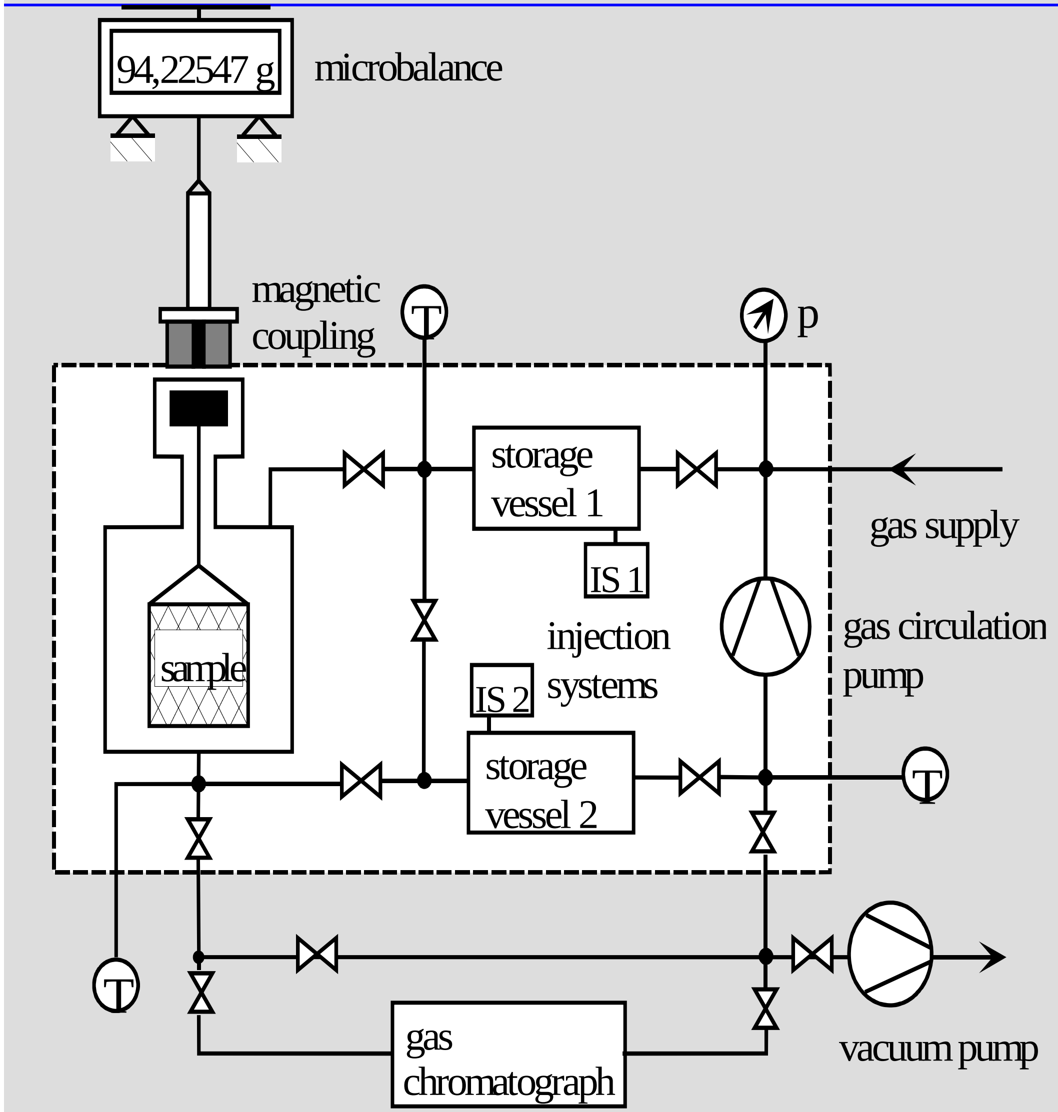
Adsorption: n-butane on XY 155 NaCa76A at 200°C; p_0=vacuum; p_E=10,9 mbar

Desorption: n-butane on XY 155 NaCa76A at 200°C; p_0=10 mbar; p_E=3 mbar

- $t_{0,5}$ experimental 5,5 s

Ref : *D. D. Do ,Adsorption Analysis: Equilibria and Kinetics, (1998)*

Volume-Gravimetry & Volumetry with GC



Calibration:
Volume of vessel & sample holder, GC ...

Volume-Gravimetry:

Measurement: p, T, m

Calculation:

$m^{fl}_1, m^{fl}_2, m_1, m_2$

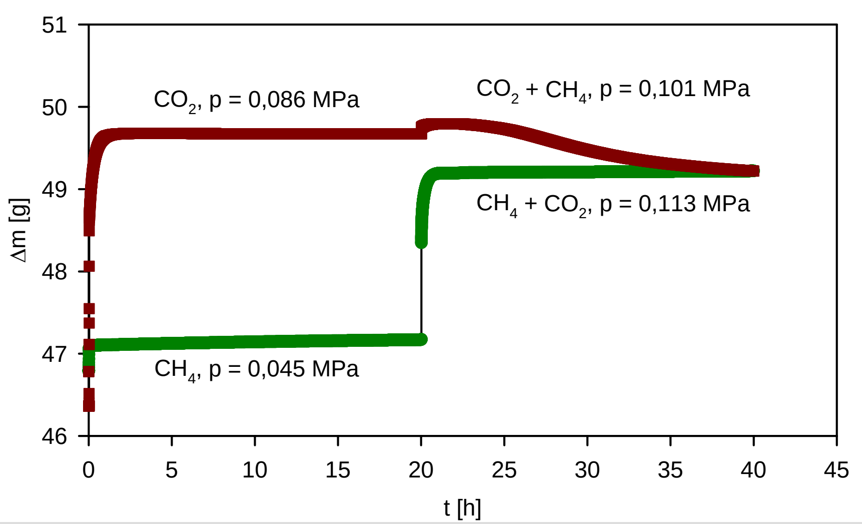
Volumetry with GC:

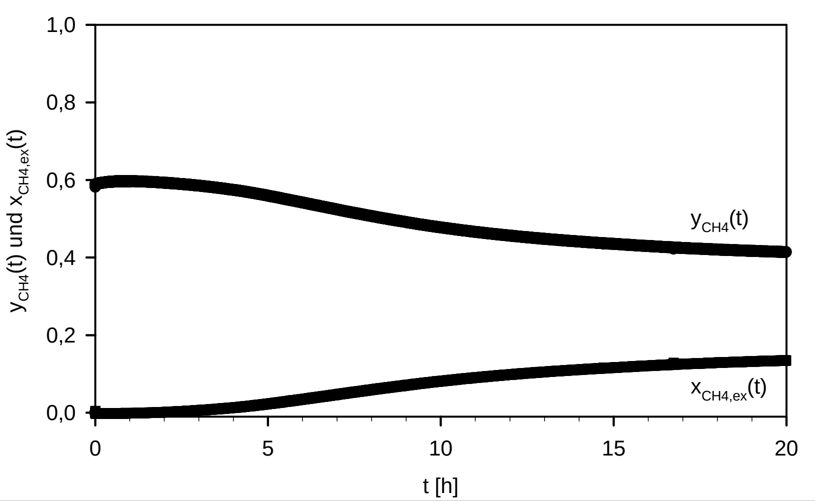
Measurement: p, T, c

Calculation:

$m^{fl}_1, m^{fl}_2, m_1, m_2$

Adsorption Kinetics of binary mixture on Activated Carbon

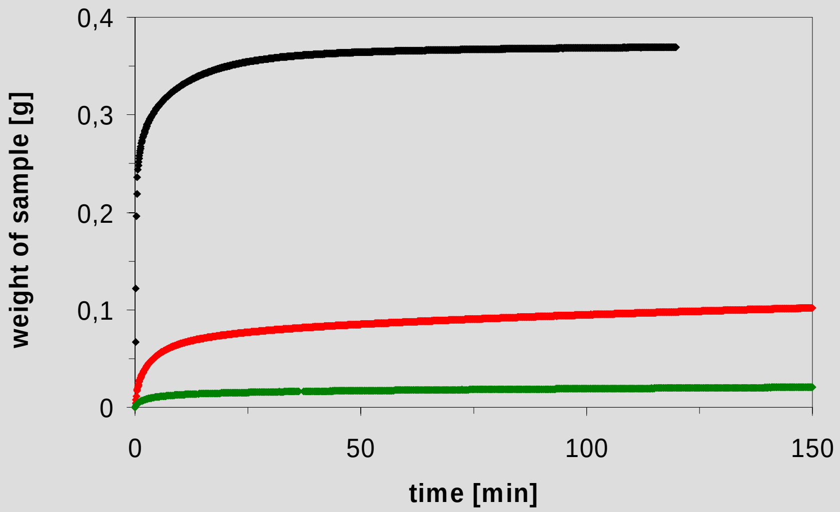




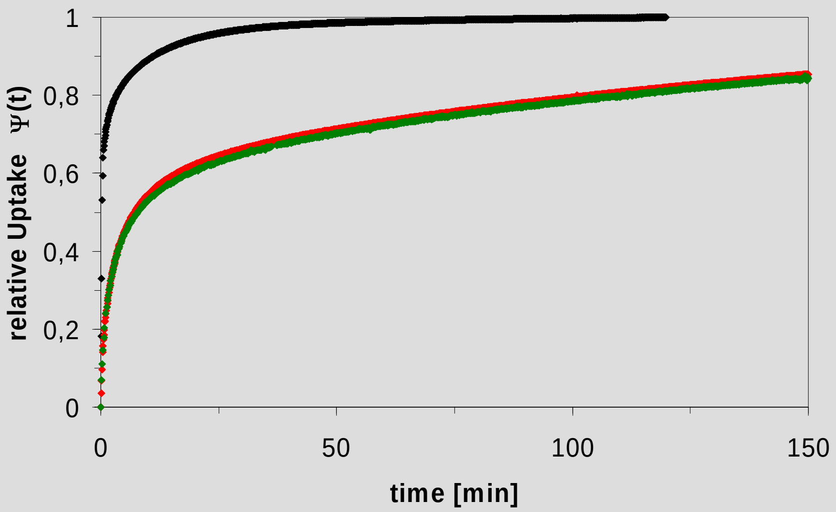
Microbalance signal
CH4/CO2 on AC Norit R1,
T = 298 K, P = 0,113 MPa
and P = 0,101 MPa.

Molar concentration of methane
in the adsorptive (yCH4(t))
and in the adsorbate (xCH4(t))
for the adsorption of CH4/CO2 mixture
on preloaded AC Norit R1

Kinetics of CO_2, CH_4 and a mixture on 4A pellets



weight of a 4A zeolite sample during an adsorption step for ◆ CO_2 (30°C; $p_{Eq,CO2}$=0,22 bar), ◆ CH_4+CO_2 (30°C; $p_{Eq,CH4+CO2}$=5,07 bar) und ◆ CH_4 (30°C; $p_{Eq,CH4}$=1,02 bar)

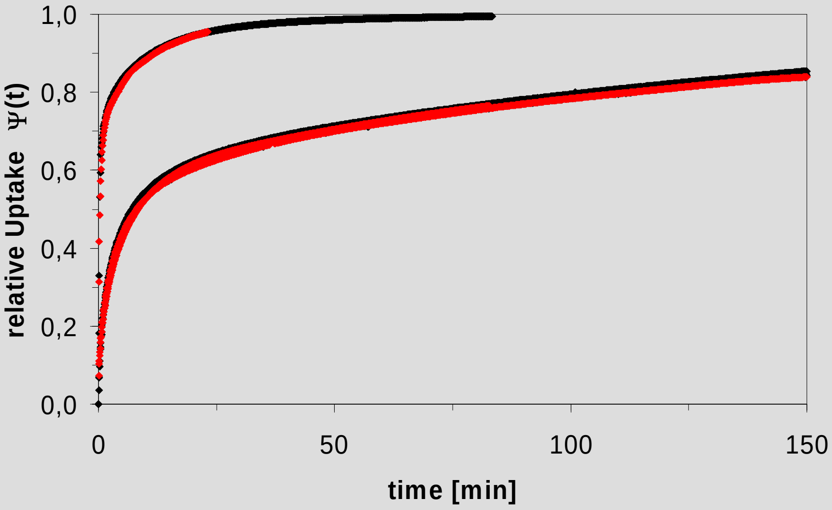


relative Uptake of a 4A zeolite sample during an adsorption step for ◆ CO_2 (30°C; $p_{Eq,CO2}$=0,22 bar), ◆ CH_4+CO_2 (30°C; $p_{Eq,CH4+CO2}$=5,07 bar) und ◆ CH_4 (30°C; $p_{Eq,CH4}$=1,02 bar)

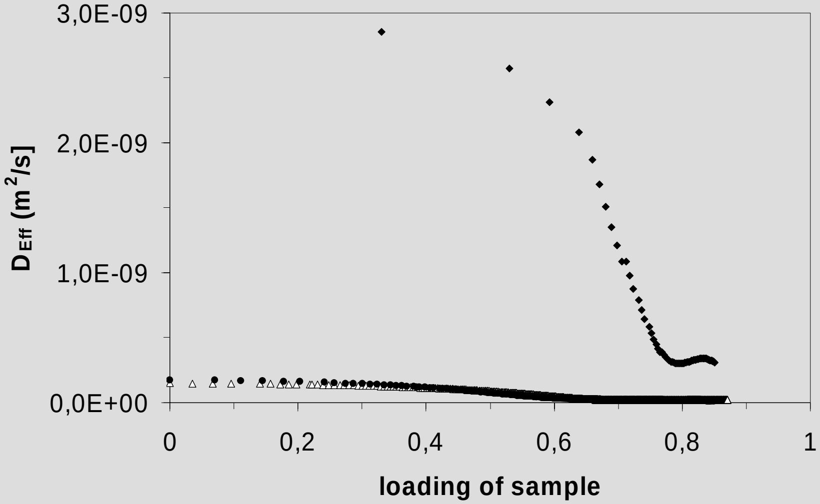
Used Model : $D_{Eff} = \frac{r^2}{\pi \cdot t} \cdot \left(1 - \sqrt{1 - \frac{\pi \cdot \Psi(t)}{3}}\right)^2$

Ref : *F. Dreisbach, Fortschritt-Berichte, VDI, 3, 547,* ***1998****, 131; W. Kast, Adsorption aus der Gasphase, VCH-Verlag, Weinheim, 1988*

Kinetics of CO_2, CH_4 and a mixture on 4A pellets

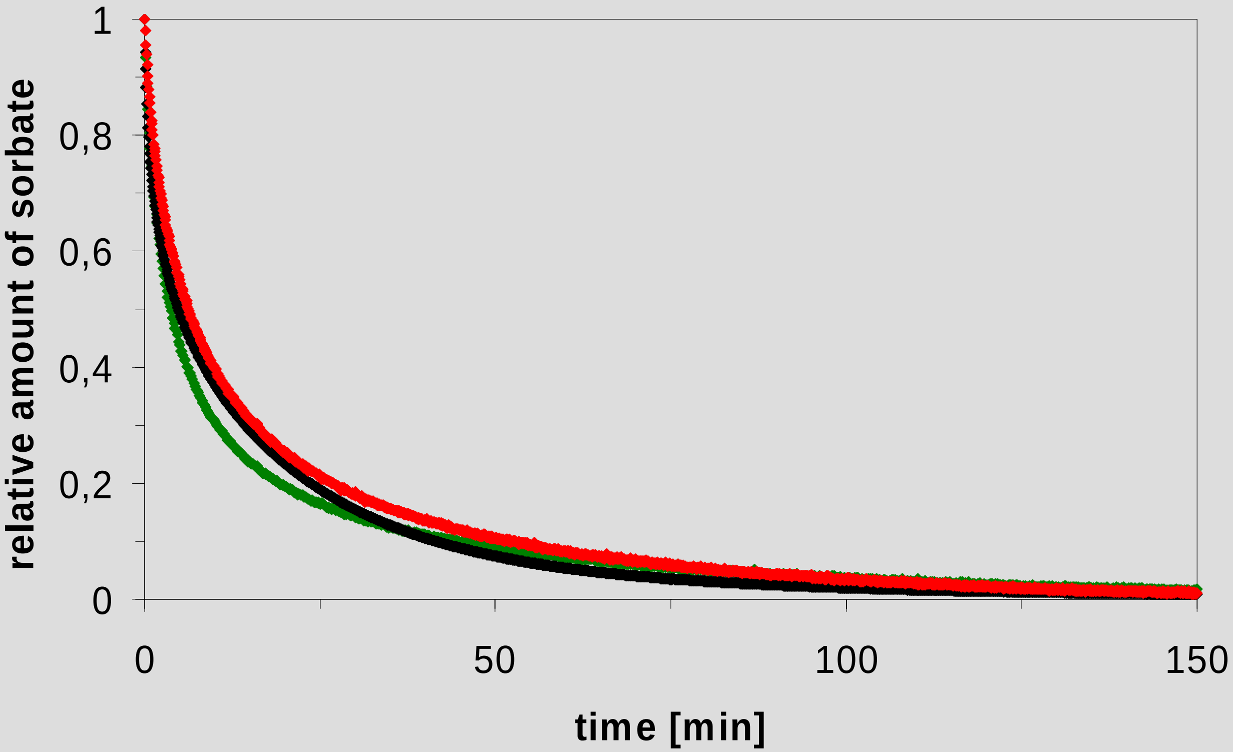


relative Uptake of a 4A zeolite sample during an adsorption step for ◆ CO_2 (30°C; $p_{Eq,CO2}$=0,22 bar), ◆ CH_4+CO_2 (30°C; $p_{Eq,CH4+CO2}$=5,07 bar) und ◆ CH_4 (30°C; $p_{Eq,CH4}$=1,02 bar); ◆ Fit of experimental data



effektive transport coefficients as a function of loading for ◆ CO_2 (30°C; $p_{Eq,CO2}$=0,22 bar), Δ CH_4+CO_2 (30°C; $p_{Eq,CH4+CO2}$=5,07 bar) und ● CH_4 (30°C; $p_{Eq,CH4}$=1,02 bar)

Kinetics of CO_2, CH_4 and a mixture on 4A pellets



relative amount of sorbate in 4A zeolite pellets during a desorption step at 30°C ◆ CO_2, ◆ CH_4+CO_2 and ◆ CH_4

Work Programm

- Completion of the transient sorption device
- Measurements of binary adsorption equilibria
- Studies of existence and quantification of possible surface barriers
- Two component diffusion in one dimensional channels
- Compare and discuss results from other techniques in this project

Requested Financial Support

Personnel

- 1 PhD student BAT IIa/2, for performing and analysing the gravimetric and volume-gravimetric experiments
- 1 Research Assistant (80 h/month), for the routine measurement of adsorption isotherms

Durable Equipments

- Pressure sensors (ultrahigh precision), € 2,500.-
- Data acquisition system, € 2,500.-
- Gas circulator pump, € 800.-
- Gas storage vessel for volumetric part of apparatus, € 1200.-

Consumables

- Sorptive gases (ultra-high purity), € 6,000.-
- Delivery and handling of gas steel bottles, € 1,500.-
- Valves, Sealings etc., € 3,500.-
- Computer & Printer Supply, € 1,000.-

Travelling 2000 € per year