Characterization of sorption kinetics of CO_2 from N_2-rich gas mixtures studied by breakthrough experiments on Zeolites

Andreas Möller

Christian Reichenbach, Robert Eschrich

3P INSTRUMENTS

Characterization of particles · powders · pores

Application of porous materials as adsorbents

Fine cleaning of gases (e.g. purification of H_2, natural gas, bio methane…)

Waste air treatment, respiratory protection, solvent recovery, removal of pollutants…)

Gas separation (e.g. air separation…)

Modern and effective materials should have high sorption capacities, high selectivities , and a good kinetic performance.

➡ For such applications, one must consider sorption properties under process-near conditions.

Introduction – Characterization of Adsorbents

Number of Samples

Application Progress

Synthesis and First Characterization	Determination of Thermodynamic Data	Basic Process Design, Granulation of Adsorbents	Detailed Process Design, Application

Chemists

3P surface

- BET
- Pore Volume
- Pore Size Distribution

Chemists, Physicists

3P meso

- Isotherms
- Heat of Adsorption

Chemical Engineers

mixSorb L

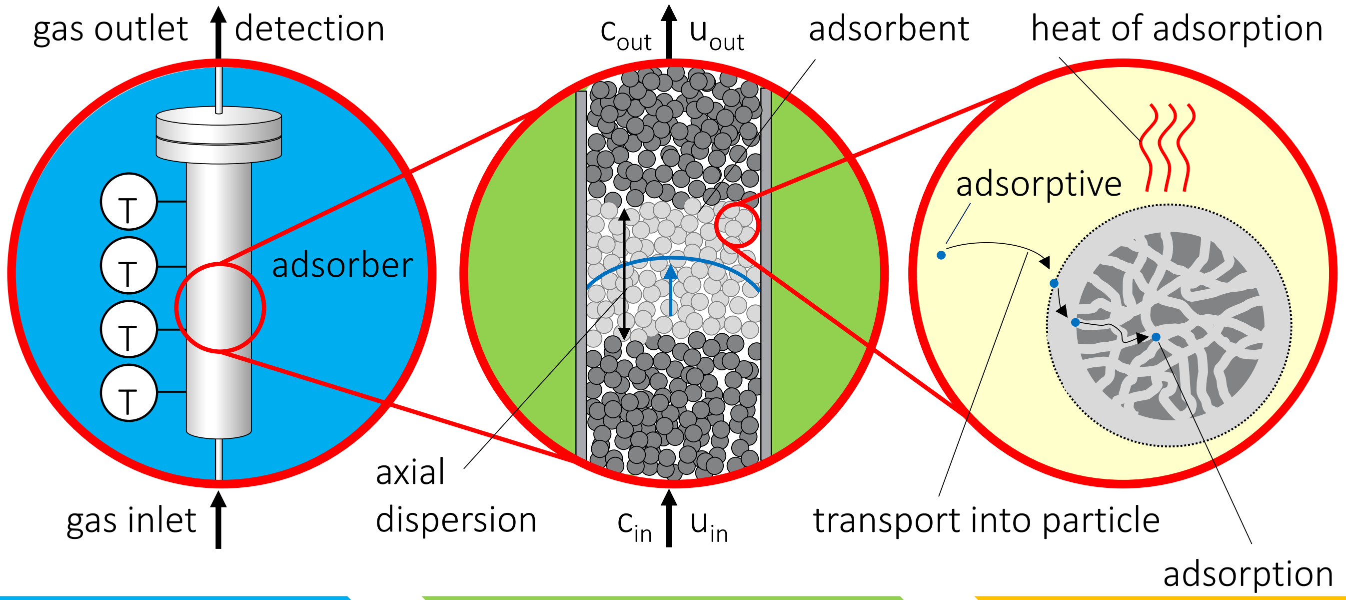
- Techn. Useable Sorption Capacity
- Gas Mixtures
- Selectivities
- Kinetics
- Cycle Stability

Engineers

Bench scale, Pilot plants, Industrial Plant

- Process Optimization
- Production

Basics – Dynamic Gas Sorption a multi-scale Process



Macroscopic

- Size of Adsorber
- Shape of Adsorber

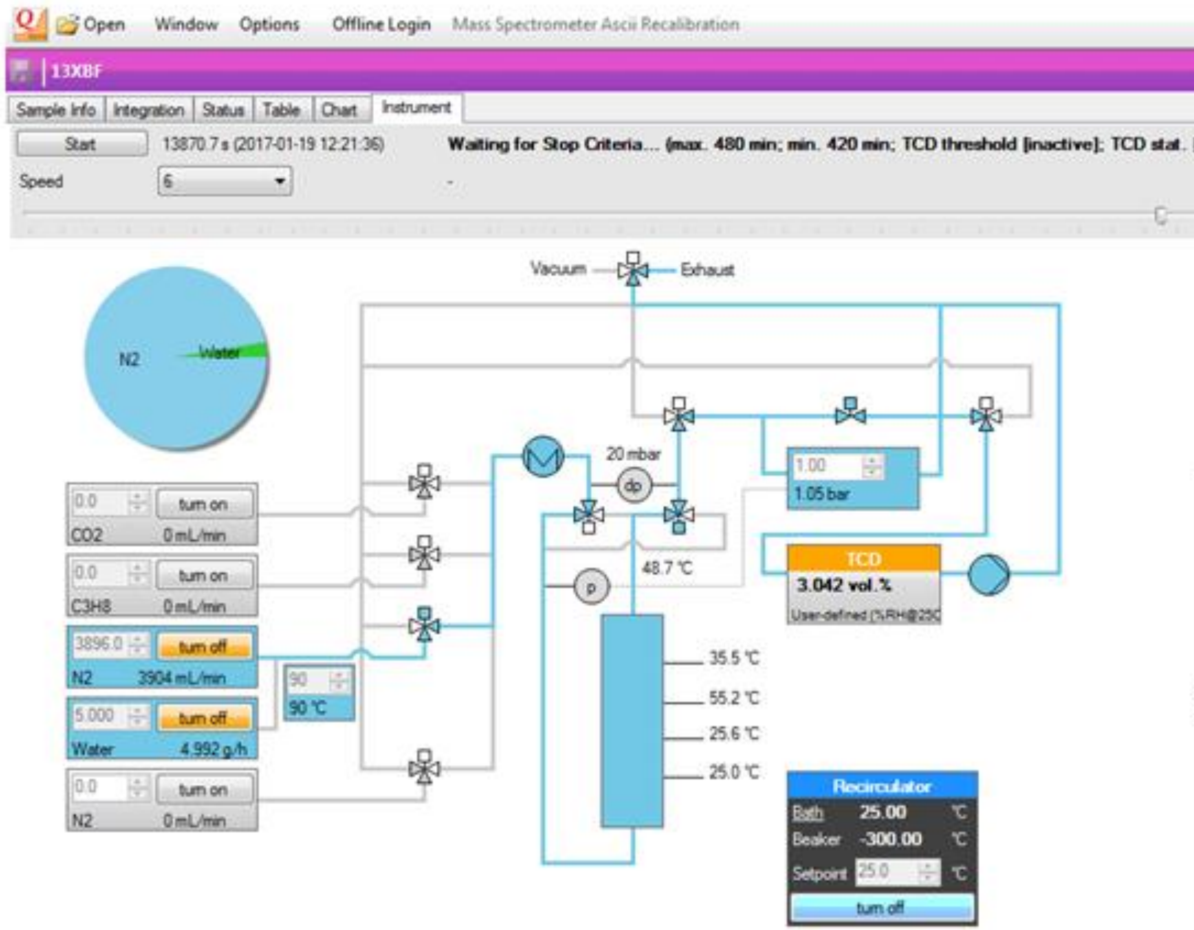
Mesoscopic

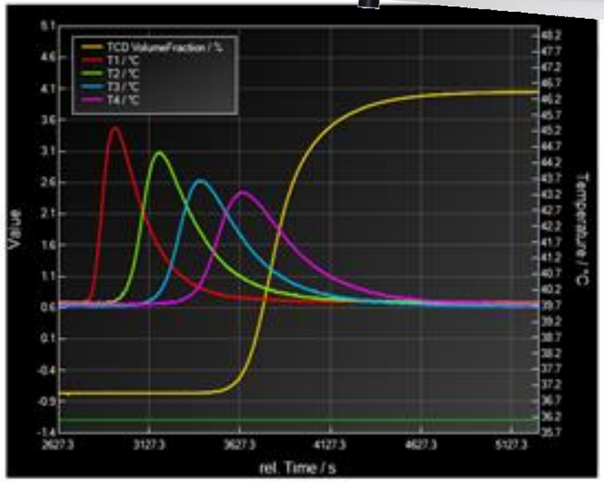
- Nature of the Fixed Bed
- Bed Porosity
- Shape of Particles

Microscopic

- Textural Properties
- Surface Characteristics
- Accessibility

Basics – Flow Plot of a Setup for Dynamic Measurements



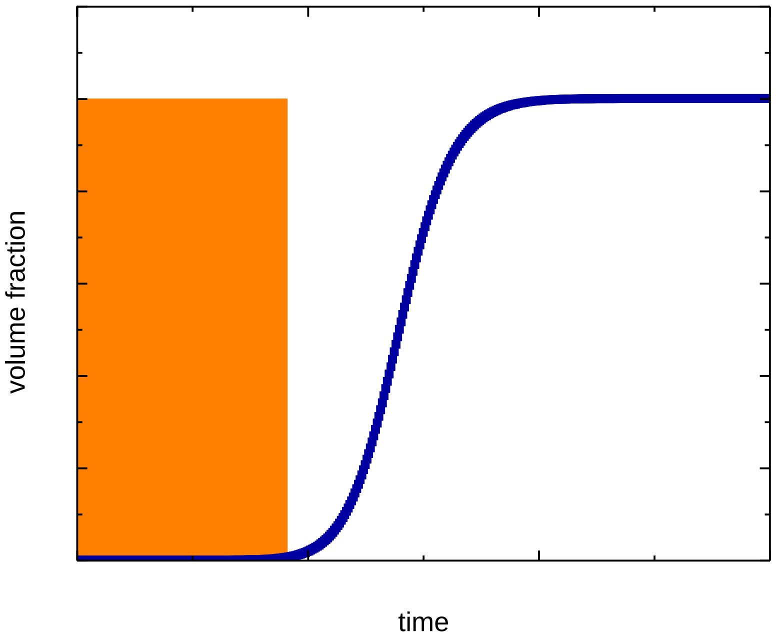


MixSorb **L**

- Flow through the regenerated sample with a predefined gas mixture
- Measurement of data at **a specified pressure and gas mixture**

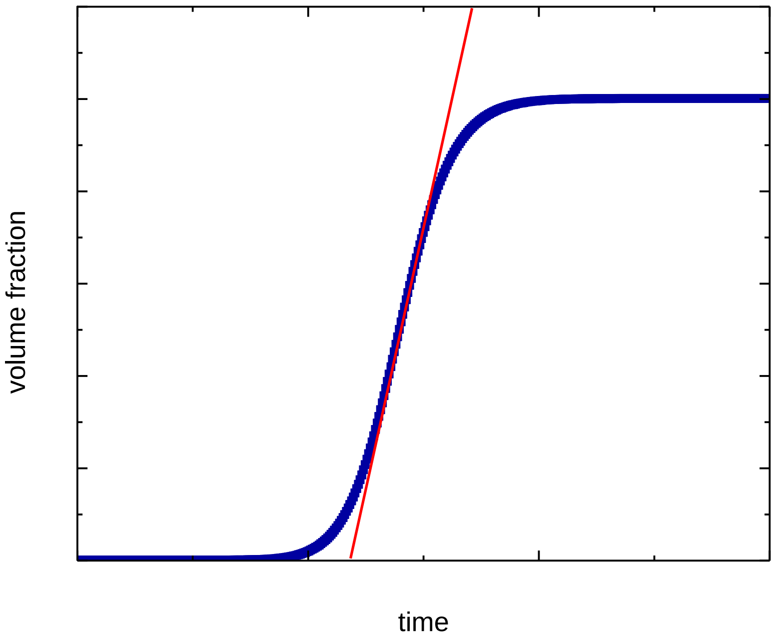
Basics – Different Segments of a Breakthrough Curve

Unsaturated Zone



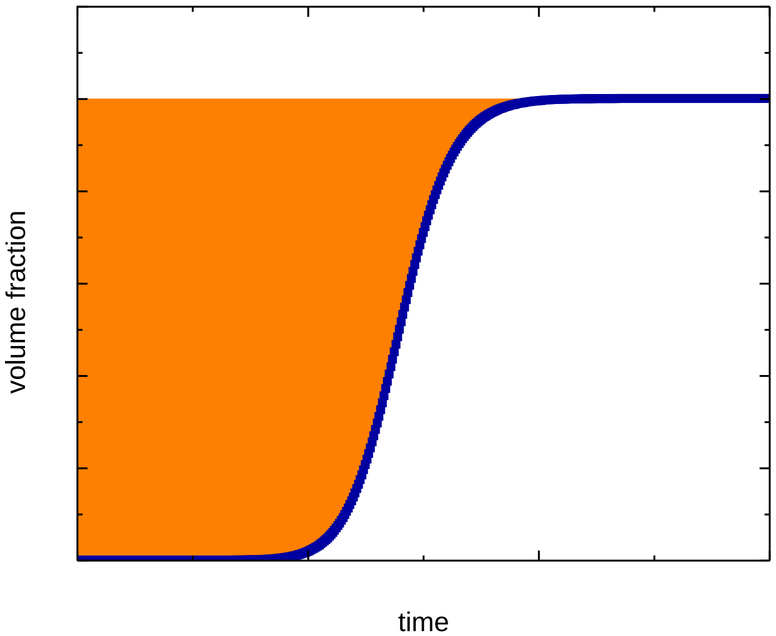
- Determination of technical usable sorption capacity
- Can be used as benchmark for separation performance of adsorbents

Mass Transfer Zone



- Mass transfer coefficient, axial dispersion, shape of isotherm
- Heat effects, heat dissipation
- The time interval of mass transfer zone has to be minimized

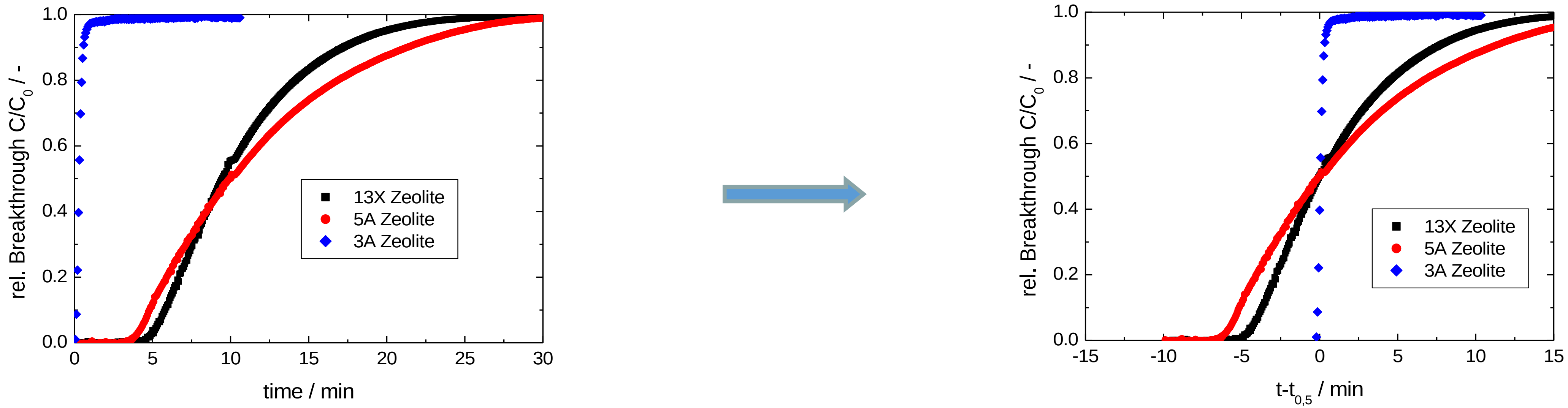
Saturated Zone



- Determination of saturation capacity
- By assuming of thermodynamic controlled system → Measurement of isotherms possible

Basics – Kinetics from Breakthrough Experiments

Breakthrough curves of 5% CO_2 in N_2 on Zeolites 13X, 5A, 3A (1 bar, 5 l/min (STP), 20°C)



Qualitative observation of Mass Transfer Zone:

- Zeolite 3A have a spontaneous breakthrough due to too narrow pores (kinetic-steric exclusion)
- Zeolite 5A exhibits a broad mass transfer zone
  → indicates obviously lower kinetic for 5A as 13X
- Both Zeolites, 5A and 13X have quite unsymmetrical breakthrough curves
  → indicate a **big influence of temperature effects** and shape of isotherms

Basics – Kinetics from Breakthrough Experiments

Question:

- Is it possible to get reliable kinetic data from such experiments?
- How is the influence of the isotherm shape, temperature effects, flow rates…?

Answer:

- Yes, but associated with high effort (model of mass- and energy balances is necessary)

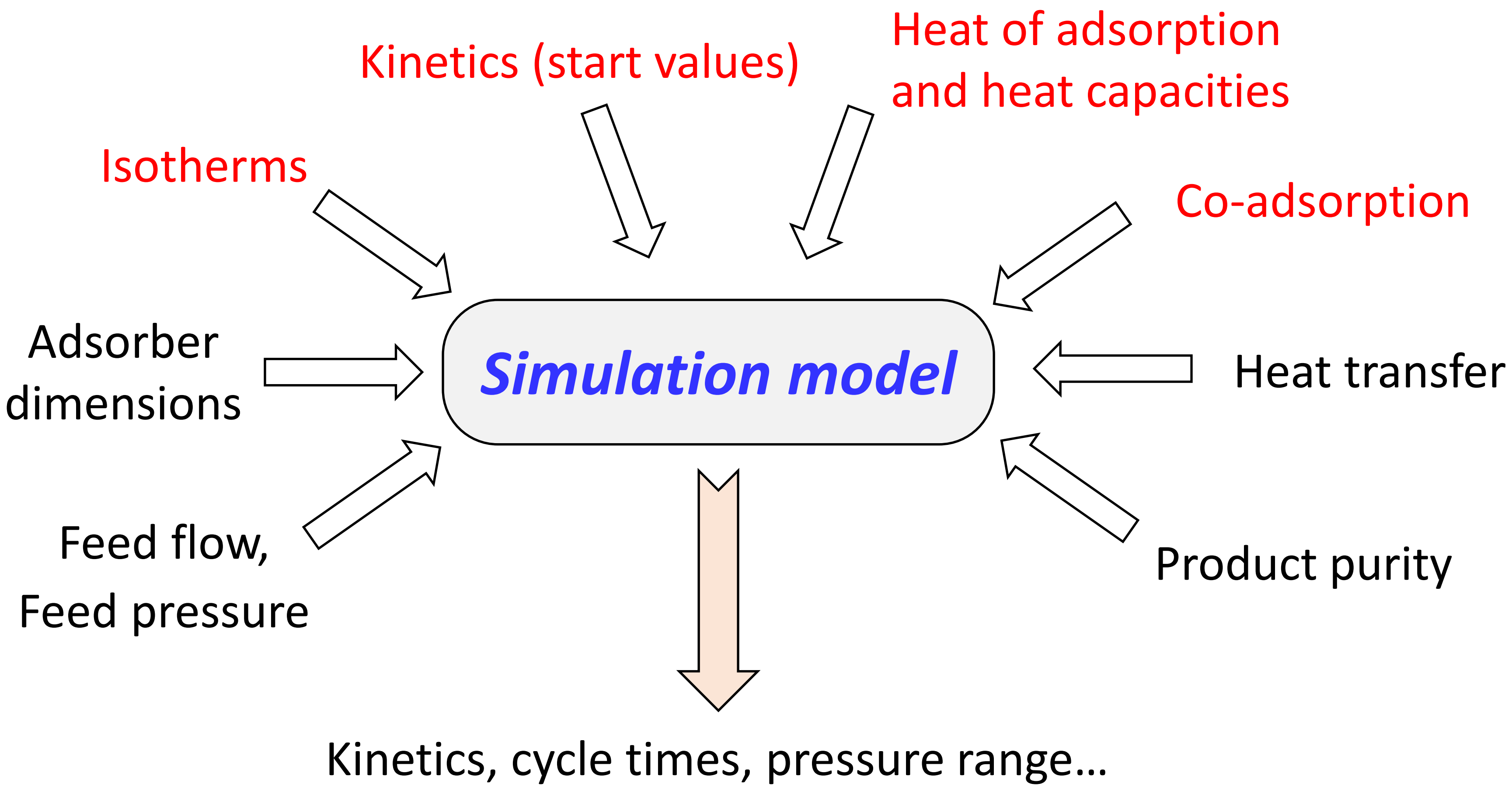
  → Simple comparison of slope can be erroneous

- For quantification of temperature effects also a model calculation must be performed!

  → I.e. in some cases heat effects can control nearly the whole curve

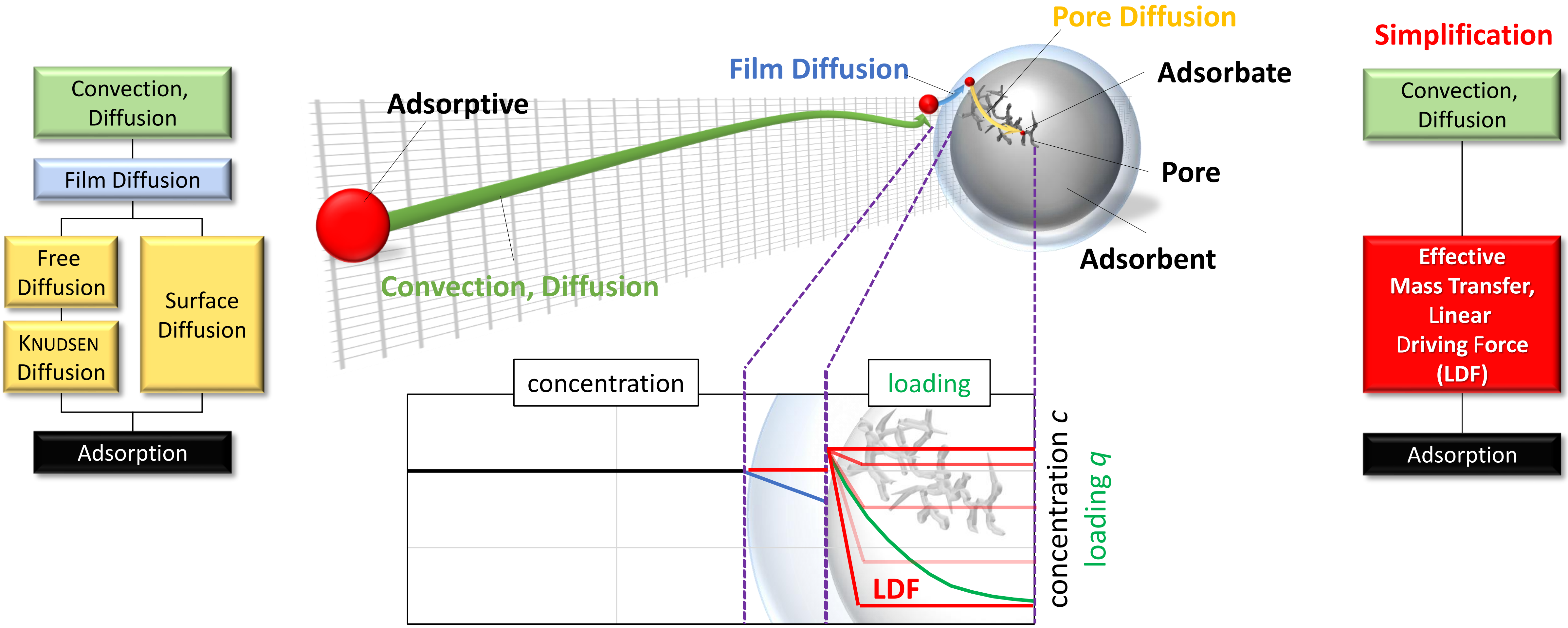
Model – Kinetics from Breakthrough Experiments

Input Parameters for calculation of breakthrough curves



Red: properties of adsorbent/adsorptive system
Black: properties of adsorber and adsorber wall

Kinetic considerations - Mass Transfer coefficient k_{LDF}



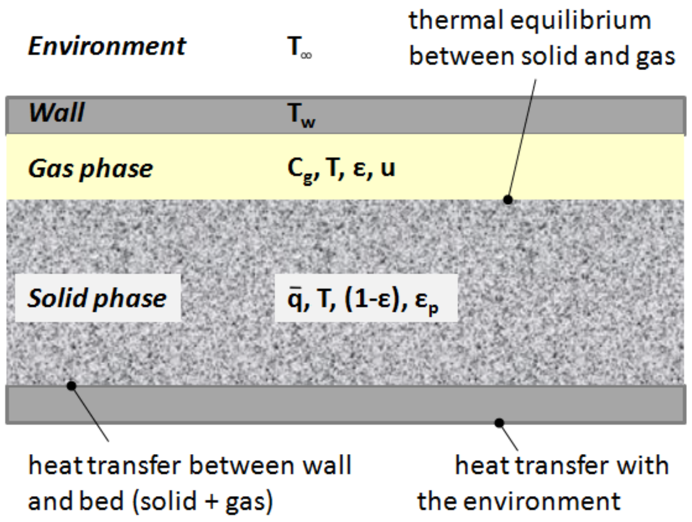
Model – Kinetics from Breakthrough Experiments

Mass Balance

$$\frac{\partial C_{g,i}}{\partial t} + \frac{1-\varepsilon}{\varepsilon}\rho_{Part}\frac{\partial \overline{q_i}}{\partial t} - Dax\frac{\partial^2 C_{g,i}}{\partial z^2} + u\frac{\partial C_{g,i}}{\partial z} + C_{g,i}\frac{\partial u}{\partial z} = 0$$

accumulation — dispersion — convection

$$\frac{\partial \overline{q_i}}{\partial t} = k_{LDF}\left(q_i^* - \overline{q_i}\right) \quad \text{LDF approach} \quad q_i^* = f(Isotherms)$$



Energy Balances

$$\frac{1-\varepsilon}{\varepsilon}\rho_{part}\sum_{i=1}^{n}\frac{\Delta H_i}{M_i}\frac{\partial \overline{q_i}}{\partial t} - \lambda\frac{\partial^2 T_g}{\partial z^2} + \left(\frac{1-\varepsilon}{\varepsilon}\rho_{part}cps + \rho_g cpg\right)\frac{\partial T_g}{\partial t} + u\rho_g cpg\frac{\partial T_g}{\partial z} + T_g\rho_g cpg\frac{\partial u}{\partial z} + 4\frac{h_w}{d_i}\left(T_g - T_w\right) = 0$$

generation — dispersion — accumulation — convection — transfer to wall

$$\alpha_w h_w\left(T_g - T_w\right) - \rho_w cpw\frac{\partial T_w}{\partial t} - \alpha_{wL}U_g\left(T_w - T_{Env}\right) = 0$$

gas to wall — accumulation — wall to environment

Equation for velocity / overall mass balance (isothermal)

$$\frac{\partial u}{\partial z} + \frac{RT}{p}\rho_{part}\frac{1-\varepsilon}{\varepsilon}\sum_{i=1}^{n}\frac{1}{M_i}\frac{\partial \overline{q_i}}{\partial t} + \frac{1}{p}\frac{\partial p}{\partial t} = 0$$

Change by adsorption — Change by compression

* A.M. Ribeiro et. al, *Chem. Eng. Sci.* 63 (**2008**)
* D.M. Ruthven, Principles of Adsorption (**1984**)
* M.S. Shafeeyan et. al, *Chem. Eng. Res. Des.* 92 (**2014**)

Model – Kinetics from Breakthrough Experiments

$$\frac{\partial \overline{q_i}}{\partial t} = k_{LDF}\left(q_i^* - \overline{q_i}\right)$$ **LDF approach** $$q_i^* = f\left(Isotherms\right)$$

1) $$k_{LDF,C} = const.$$

2) $$k_{LDF} = \frac{15 \cdot \varepsilon_p \cdot D}{R^2}\frac{c}{q} = k^*_{LDF,R}\frac{c}{q}$$

3) $$k_{LDF} = \frac{\rho_p}{A_{SP}}\frac{15 \cdot D}{R^2 \cdot \mu}\frac{1}{1 + \frac{\rho_p}{\varepsilon_p}\frac{\partial q}{\partial c}} = k^*_{LDF,M}\frac{1}{1 + \frac{\rho_p}{\varepsilon_p}\frac{\partial q}{\partial c}}$$

4) $$k_{LDF} \sim \frac{D}{R^2}\frac{\partial \ln c}{\partial \ln q} = k^*_{LDF,D}\frac{\partial \ln c}{\partial \ln q}$$

1) M.G. Plaza et al., *Ind. Eng. Chem. Res, 55* (**2016**)
2) N.S. Wilkins, A. Rajendran, *Adsorption 25* (**2019**)
3) Mersmann et al., *Chem. Ing. Tech. 55* (**1983**)
4) Darken, *Trans. AIME 175.1* (**1948**)

Note:

$$k_{LDF,C} \neq k^*_{LDF,M} \neq k^*_{LDF,R} \neq k^*_{LDF,D}$$

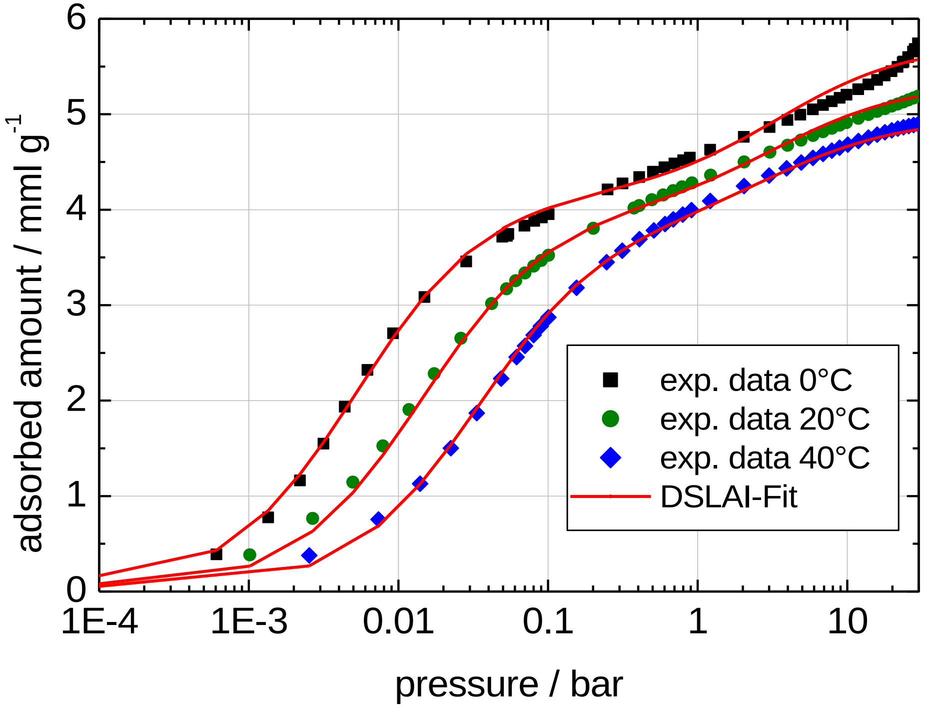
Comparison of LDF values from literature

- Possible, but used LDF approach must be taken into account!

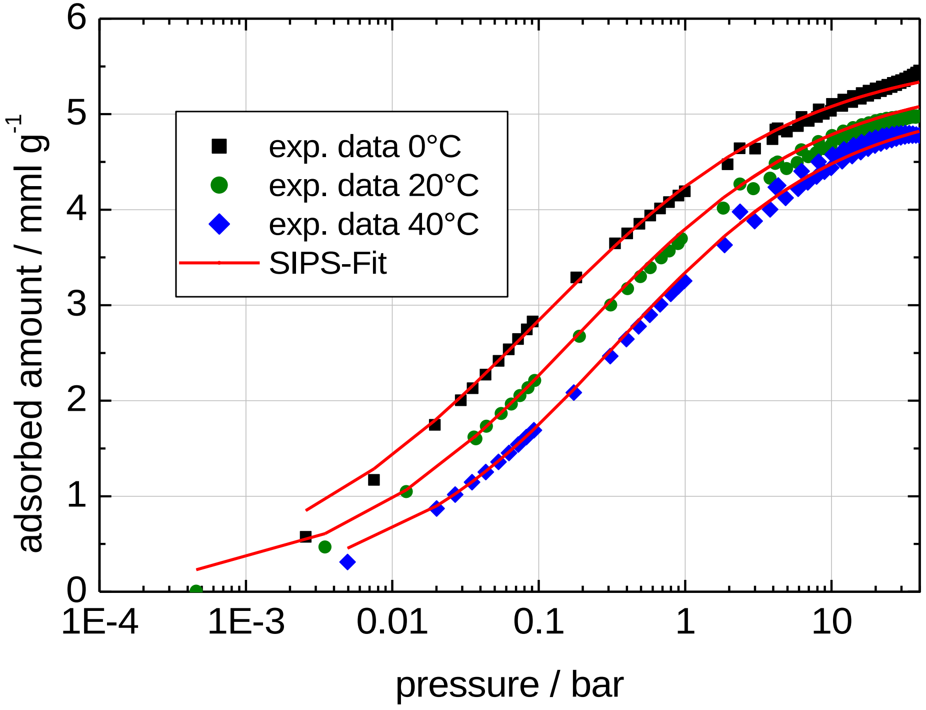
2,3…	Diffusion in macropores
4…	Diffusion in micropores

Results – Kinetics from Breakthrough Experiments

Isotherms as input parameter for calculations



CO_2 Isotherms on Zeolite 5A

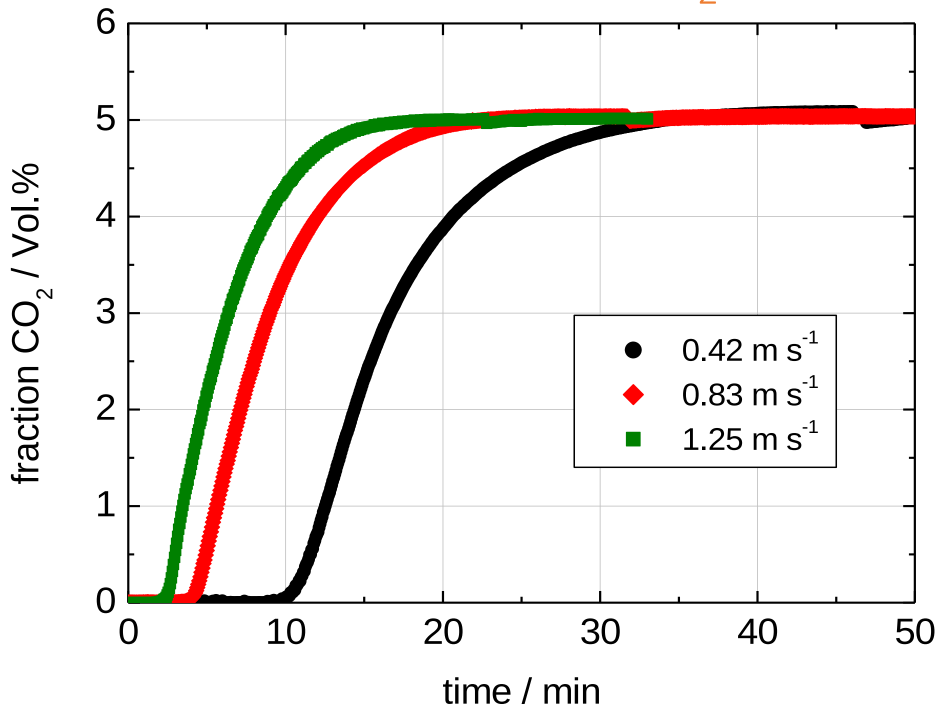


CO_2 Isotherms on Zeolite 13X

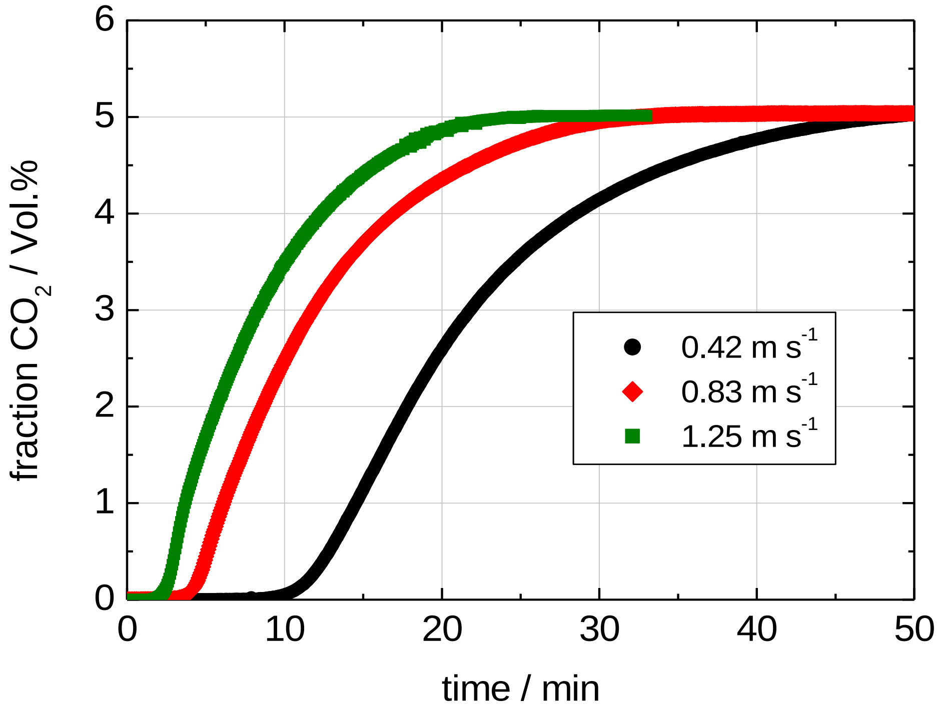
- Knowledge of isotherms necessary due to sharpening and softening of breakthrough curve
- Favored isotherm (e.g. Type I) shocks adsorption front and softening desorption

Results – Kinetics from Breakthrough Experiments

Breakthrough curves for 5% CO_2 on 13X and 5A Zeolite at different flow rates and 20°C



5% CO_2in N_2 on 13X, 1 bar at 20°C

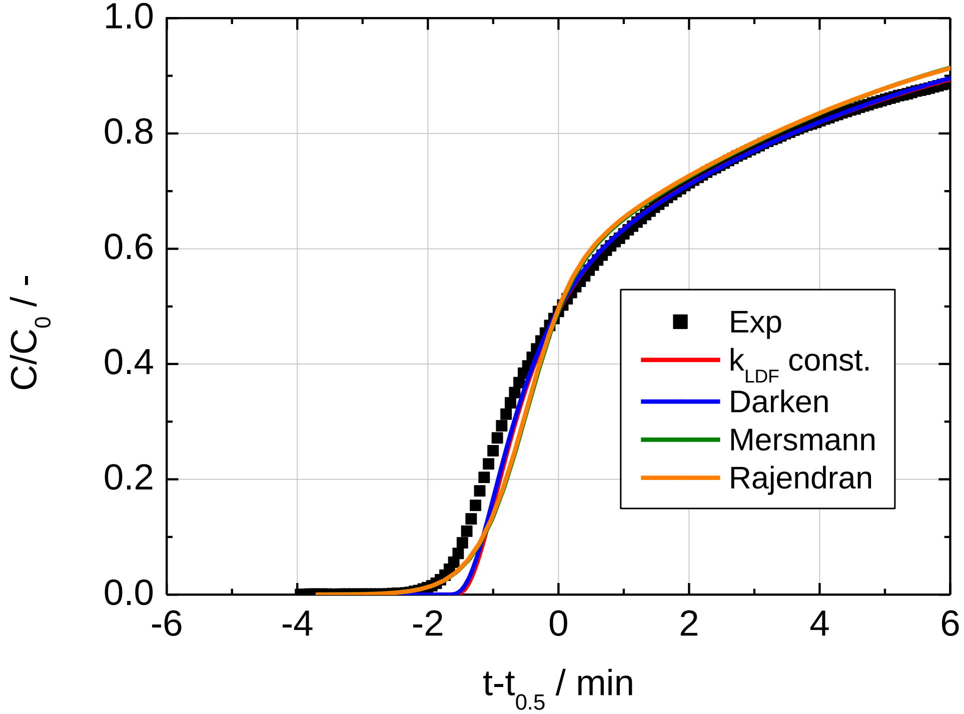


5% CO_2in N_2 on 5A, 1 bar at 20°C

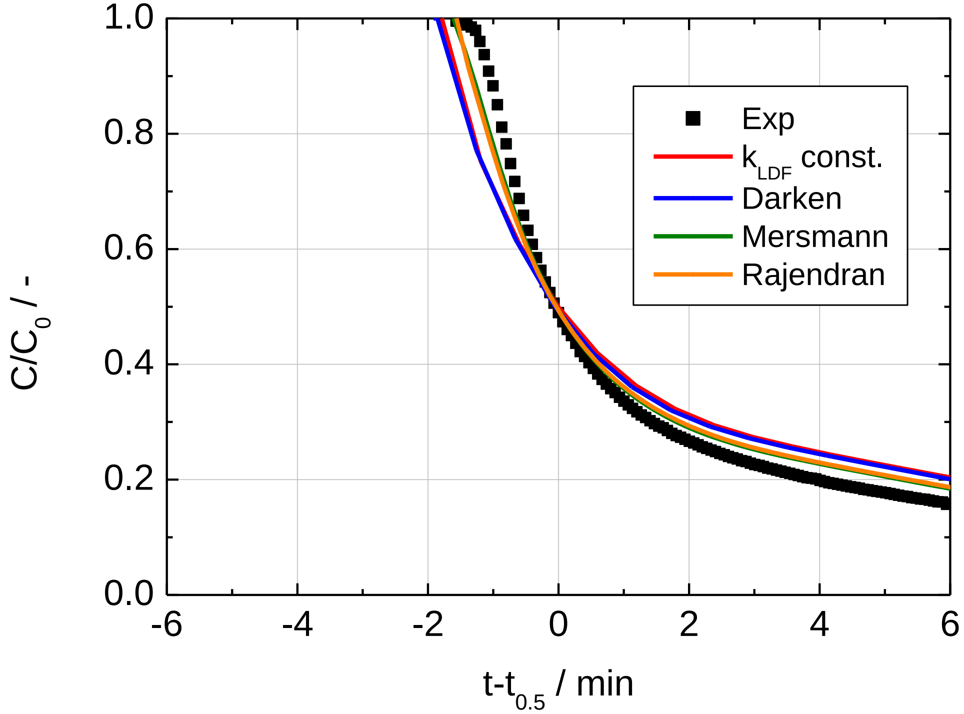
- Breakthrough curves shifts to shorter breakthrough times and are slightly steeper for higher flow rates
- Breakthrough curves on Zeolite 13X with smaller Mass Transfer Zone as for Zeolite 5A

Results – Kinetics from Breakthrough Experiments

Influence of selected model on transport parameter



5% CO_2 in N_2 on 13X, 1 bar, 60°C and 0.83 m s^{-1}



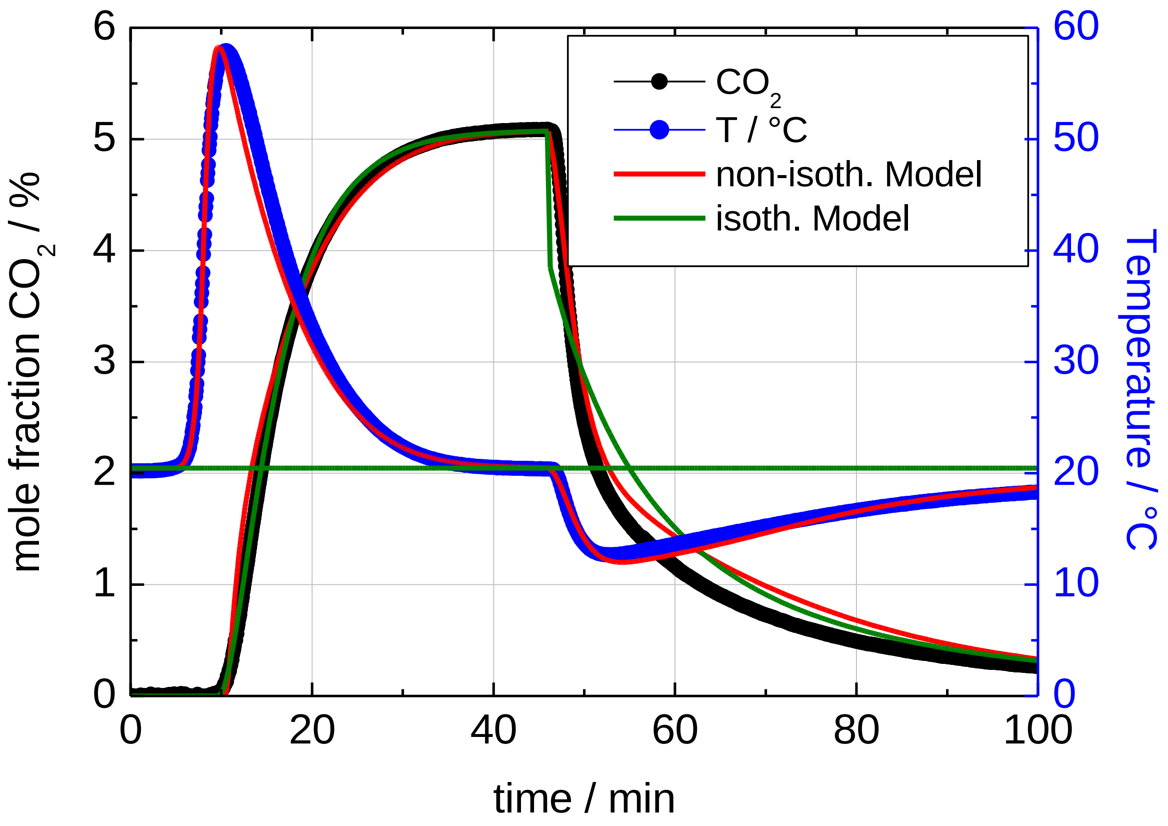
Pure N_2, 13X, 1 bar, 60°C and 0.83 m s^{-1}

$k_{LDF,Constant}$ = 1.2 min^{-1}; $k^*_{LDF,Darken}$ = 0.6 min^{-1}; $k^*_{LDF,Mersmann}$ = 120 min^{-1}; $k^*_{LDF,Rajendran}$ = 85 min^{-1}

- Best fits for constant k_{LDF} and Darken approach → curves coincides (both are micropore models)
- Best fits for Rajendran and Mersmann → curves coincides (both are macropore models)

Results – Kinetics from Breakthrough Experiments

Influence of temperature effects on transport parameter



Adsorption/ Desorption profile on Zeolite 13X

5% CO_2, 1 bar, 20°C and 0.417 m s^{-1}

Modeling with constant k_{LDF}

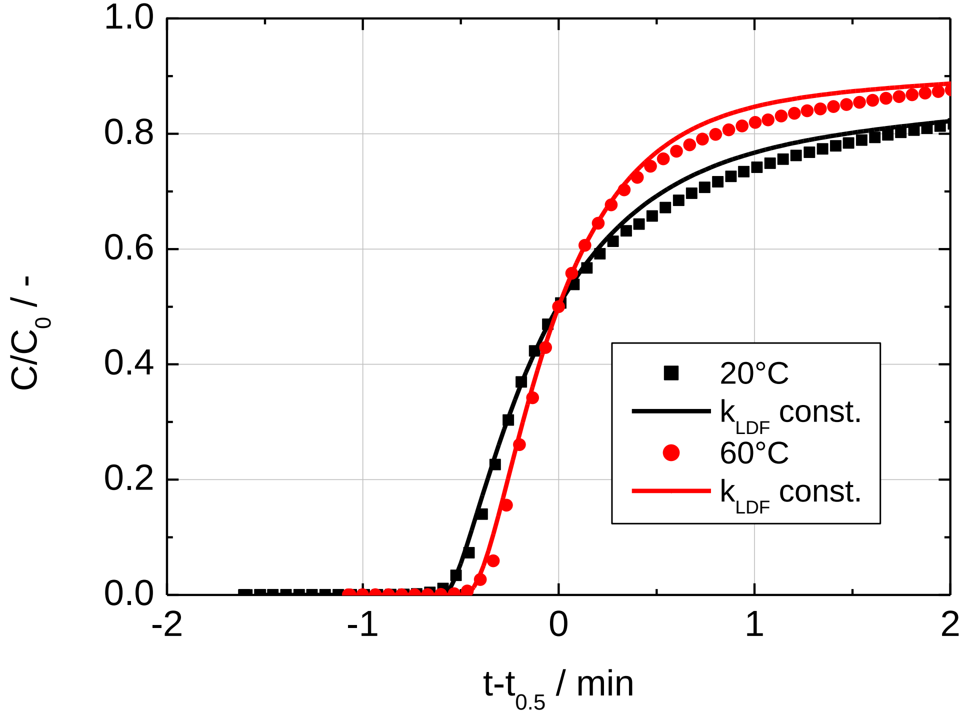
k_{LDF}(non-isotherm)= 1.20 min^{-1}
k_{LDF}(isotherm) = 0.25 min^{-1}

Ratio: $$\frac{k_{LDF}(nonisoth)}{k_{LDF}(isoth)} \approx 5$$

- Modeling of both, adsorption and desorption
  → Due to influence of isotherm
- Heat effect must be taken into account!

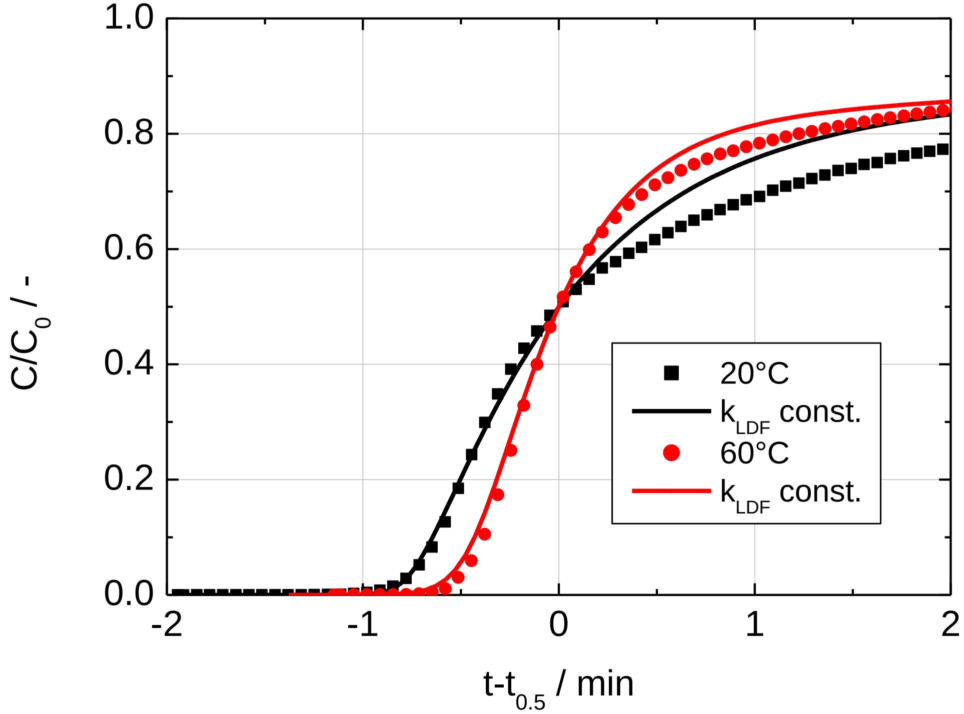
Results – Kinetics from Breakthrough Experiments

Influence of measurement temperature on LDF-Value (k_{LDF}=const.)



15% CO_2in N_2 on 13X, 1 bar and 1.25 m s^{-1}

$k_{LDF,C}$ (20°C)= 1.2 min^{-1}; $k_{LDF,C}$ (60°C)= 2.0 min^{-1}



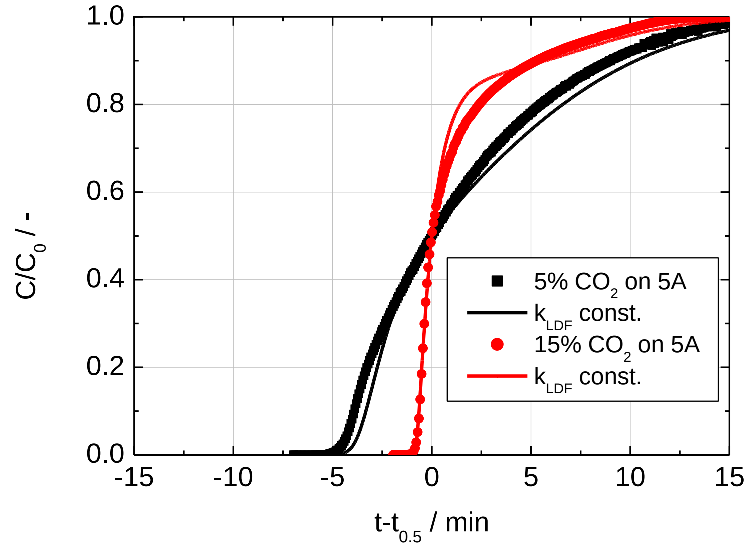
15% CO_2in N_2 on 5A, 1 bar and 1.25 m s^{-1}

$k_{LDF,C}$ (20°C)= 0.8 min^{-1}; $k_{LDF,C}$ (60°C)= 2.0 min^{-1}

- More symmetric breakthrough curves for higher temperature (smaller heat effects due to lower loading)
- Breakthrough curves steeper for higher temperatures (faster mass transfer)

Results – Kinetics from Breakthrough Experiments

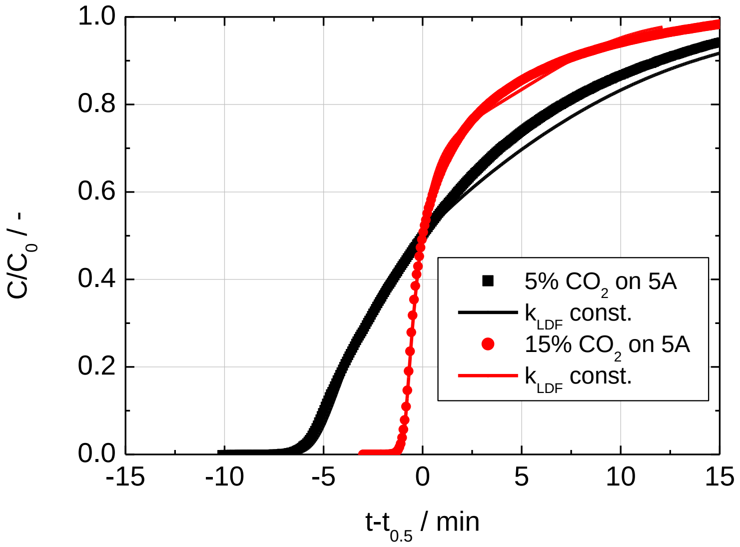
Comparison of breakthrough curves on 5A with different concentrations



1 bar, 20°C and 1.25 m s^{-1}

5% CO_2 on 5A $k_{LDF,C}$ = 0.4 min^{-1}

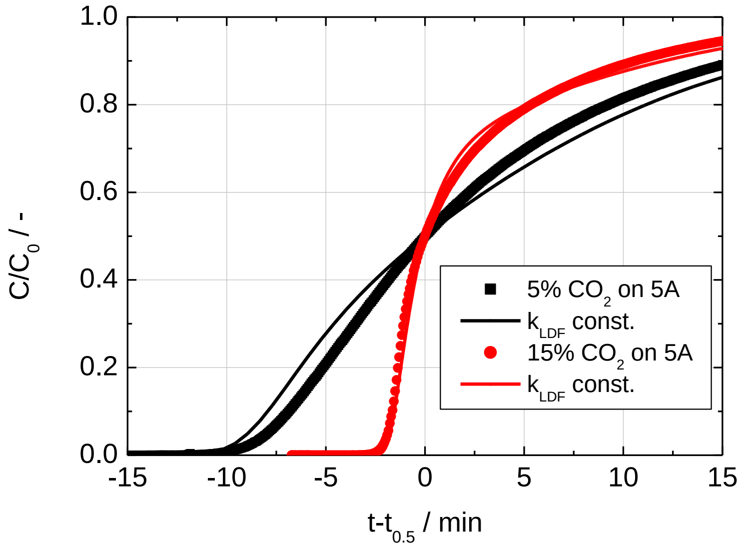
15% CO_2 on 5A $k_{LDF,C}$ = 0.8 min^{-1}



1 bar, 20°C and 0.83 m s^{-1}

5% CO_2 on 5A $k_{LDF,C}$ = 0.4 min^{-1}

15% CO_2 on 5A $k_{LDF,C}$ = 0.8 min^{-1}



1 bar, 20°C and 0.42 m s^{-1}

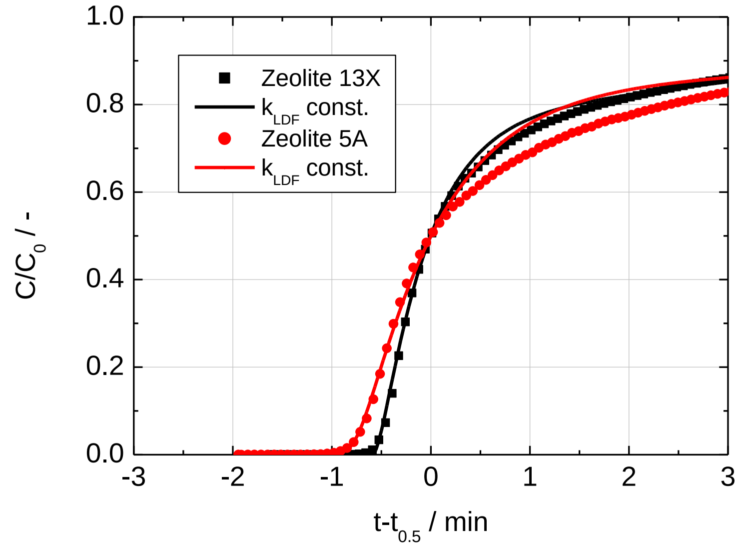
5% CO_2 on 5A $k_{LDF,C}$ = 0.4 min^{-1}

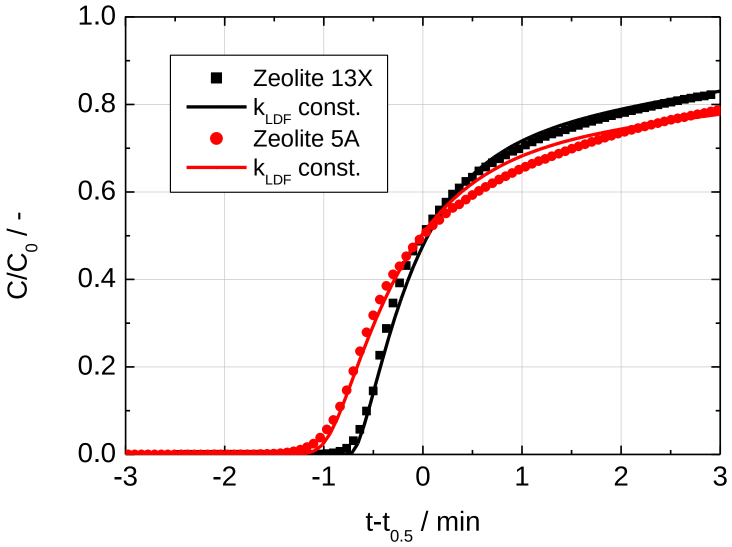
15% CO_2 on 5A $k_{LDF,C}$ = 0.5 min^{-1}

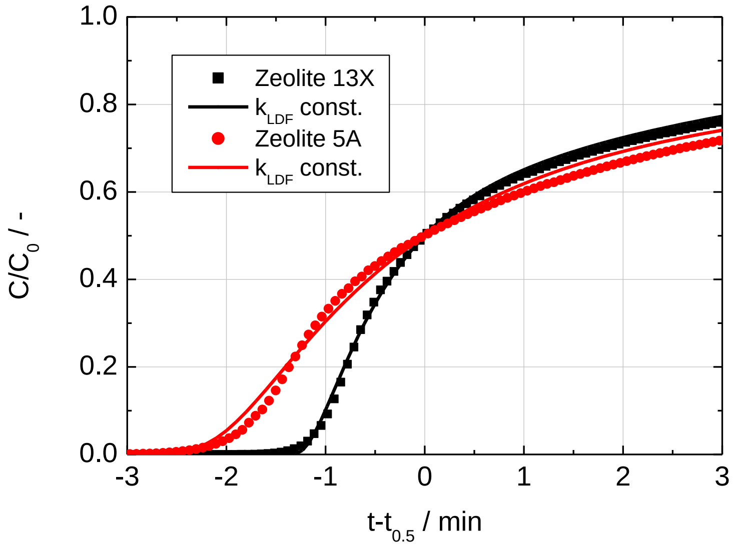
- Strong influence of concentration on breakthrough curves due to non-linearity of isotherm
- Higher LDF-values for higher concentrations

Results – Kinetics from Breakthrough Experiments

Comparison of breakthrough curves on 13X and 5A at different flow rates







15% CO_2, 1 bar, 20°C and 1.25 m s^{-1}

Zeolite 5A $k_{LDF,C}$ = 0.8 min^{-1}

Zeolite 13X $k_{LDF,C}$ = 1.2 min^{-1}

15% CO_2, 1 bar, 20°C and 0.83 m s^{-1}

Zeolite 5A $k_{LDF,C}$ = 0.8 min^{-1}

Zeolite 13X $k_{LDF,C}$ = 1.2 min^{-1}

15% CO_2, 1 bar, 20°C and 0.42 m s^{-1}

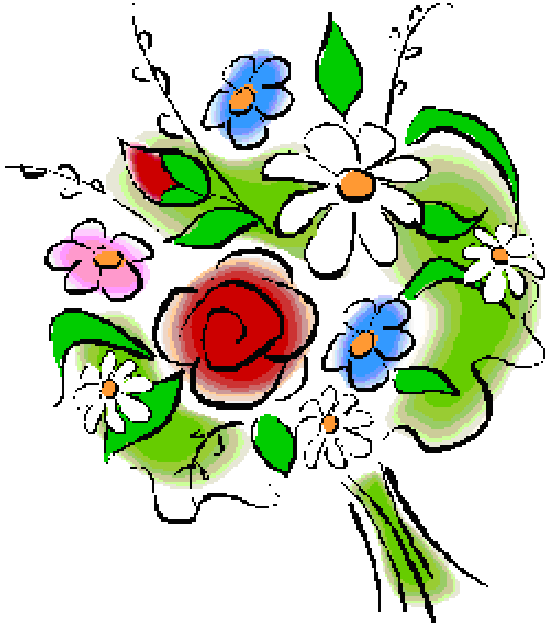
Zeolite 5A $k_{LDF,C}$ = 0.42 min^{-1}

Zeolite 13X $k_{LDF,C}$ = 1.2 min^{-1}

- Values same range, and rather independent from flow rate under this conditions
- External film fluid resistance can be neglected

Summary – Kinetics from Breakthrough Experiments

- **Model is necessary to get** reliable **transport parameter** → k_{LDF} **value, with used LDF-Approach**
- Strong **non-isothermal effects must be considered** for evaluation of kinetics → influence of dissipation of heat
- **Measurement of desorption** part is **helpful** → influence of isotherm, heat dissipation etc.
- k_{LDF} **values depend on concentration, total pressure** etc. → **measurements** under **same** conditions **like technical process** for up-scaling
- By **assuming macropore diffusion resistance of binder** → **further investigations with different particle sizes** from same supplier **necessary**



Thank you for your attention!

Please visit our website for further information

www.dynamicsorption.com

or contact our partner in US

www.altamirainstruments.com