Breakthrough Curves of Propane and CO_2 at Different Relative Humidities

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3P INSTRUMENTS

Characterization of

particles · powders · pores

Introduction

Application of porous materials as adsorbents

- Adsorbents for waste air and indoor air cleaning (VOCs like propane)
- Adsorbents for CO_2 separation from waste gas streams
- Adsorbents for direct air capture of CO_2

➡ For such applications:
Humidity plays an important role

Competitve Sorption of H_2O leads to changes in:

- Sorption equilibrium
- Sorption capacity
- Sorption kinetics

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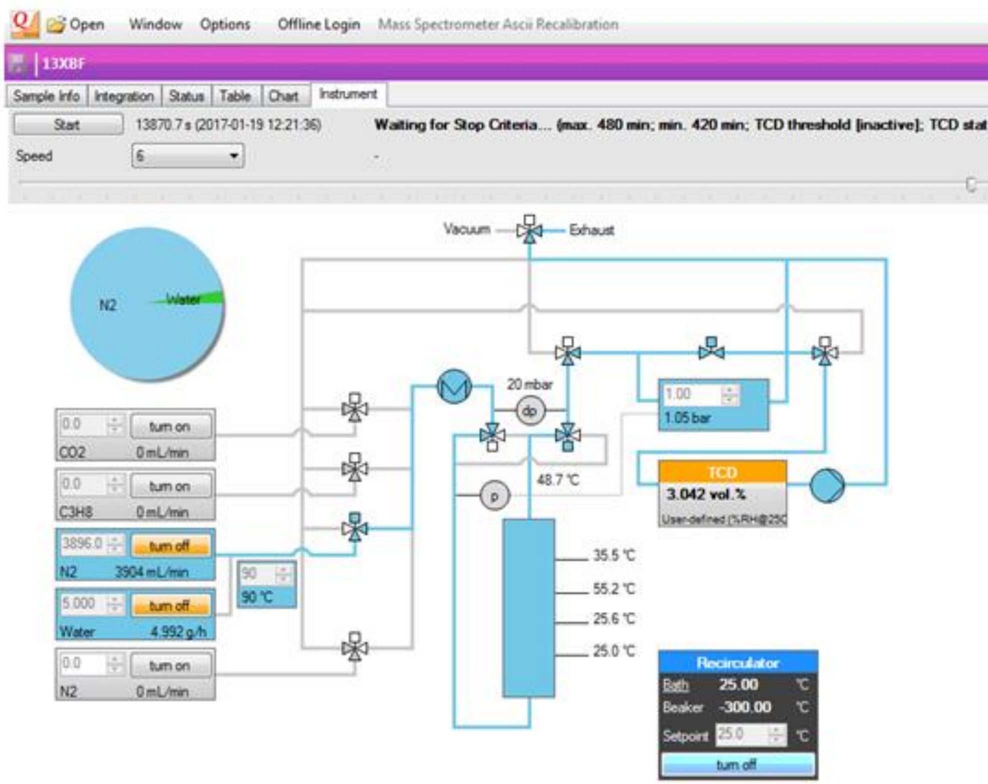
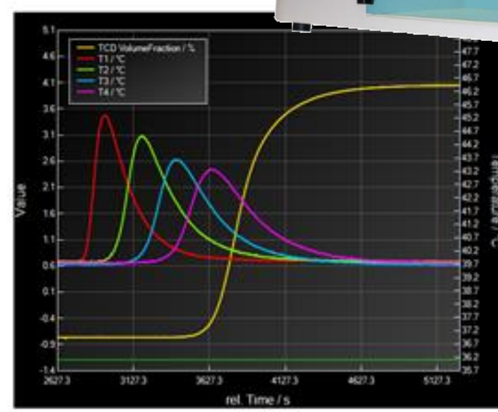
Gutknecht et al., Energy Procedia 146 (2018) 129-134; Climeworks AG

Methods

Experimental Setup





MixSorb **L**

- ➢ Flow through the regenerated sample with a predefined gas mixture
- ➢ Signal detecting (Temp., WLD, etc.) at the outlet for **a specified pressure and gas mixture**

Materials

Microporous Carbon

Microporous Zeolite 4A

Microporous Zeolite 5A

Amin-functionalized microporous Polymer (Lewatit)

Example 1 - Propane

Sequence of three Breakthrough curve measurements of propane and H_2O on AC

Segment 1

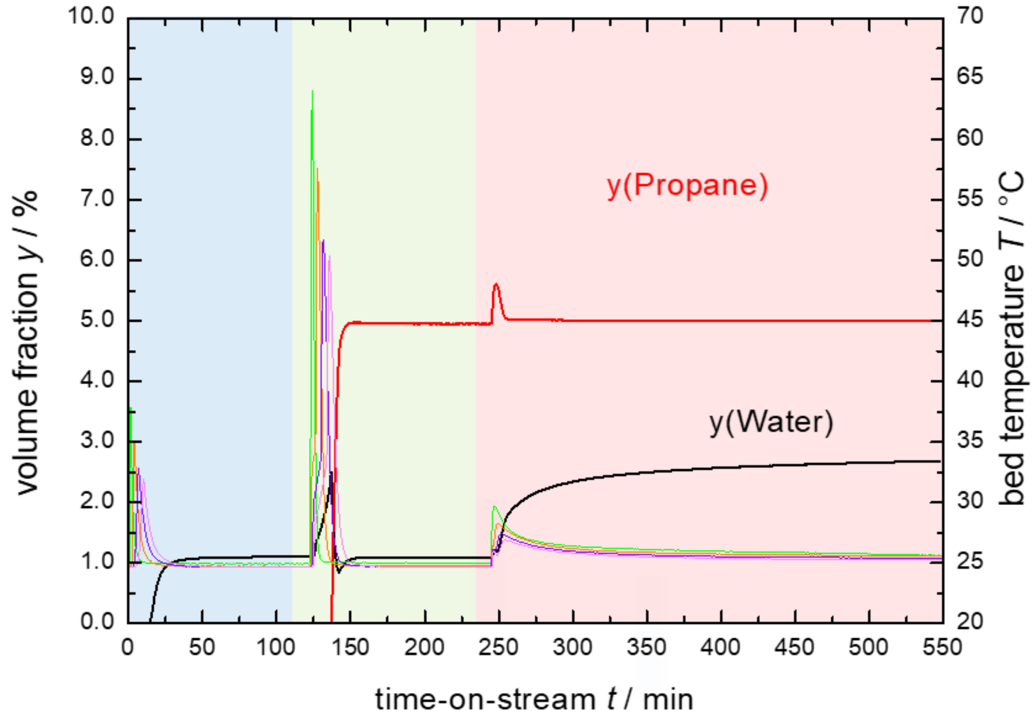
volume fraction $y(H_2O)$ = **0.95 %**, relative humidity approx. **30 % @ 25 °C**

Segment 2

volume fraction $y(C_3H_8)$ = **5.00 %,** volume fraction $y(H_2O)$ = 0.95 %, relative humidity approx. 30 % @ 25 °C

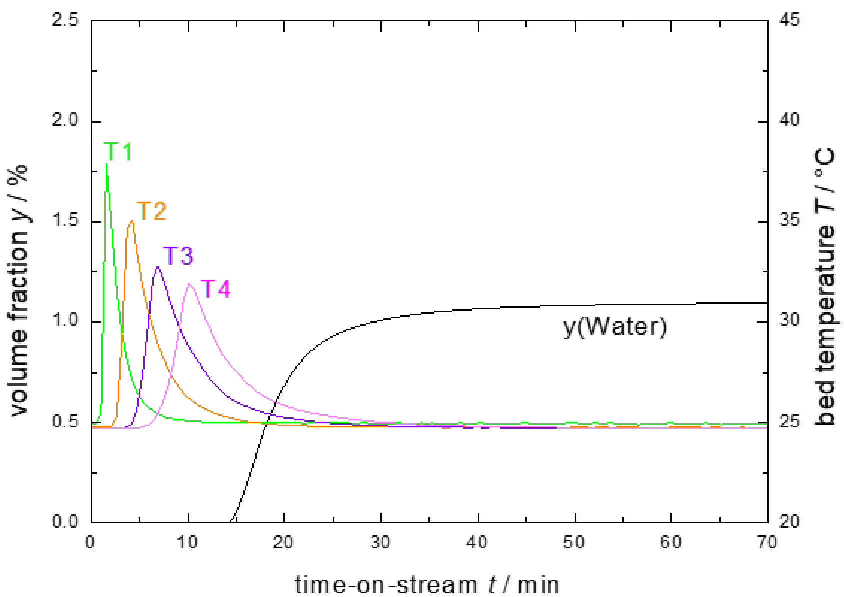
Segment 3

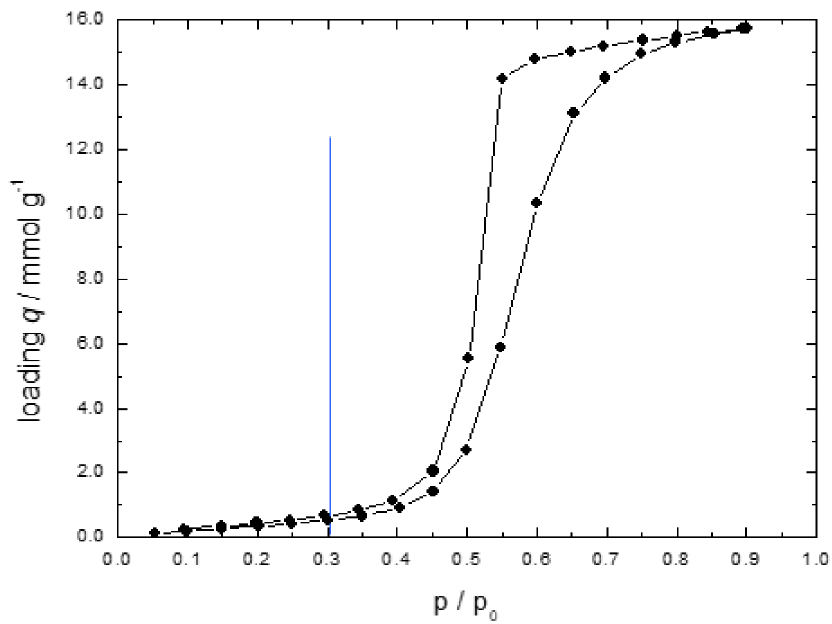
volume fraction $y(C_3H_8)$ = 5.00 %, volume fraction $y(H_2O)$ = **2.70 %**, relative humidity approx. **85 % @ 25 °C**



Example 1 - Propane

Segment 1 (volume fraction $y(H_2O)$ = **0.95 %**, relative humidity approx. **30 % @ 25 °C**

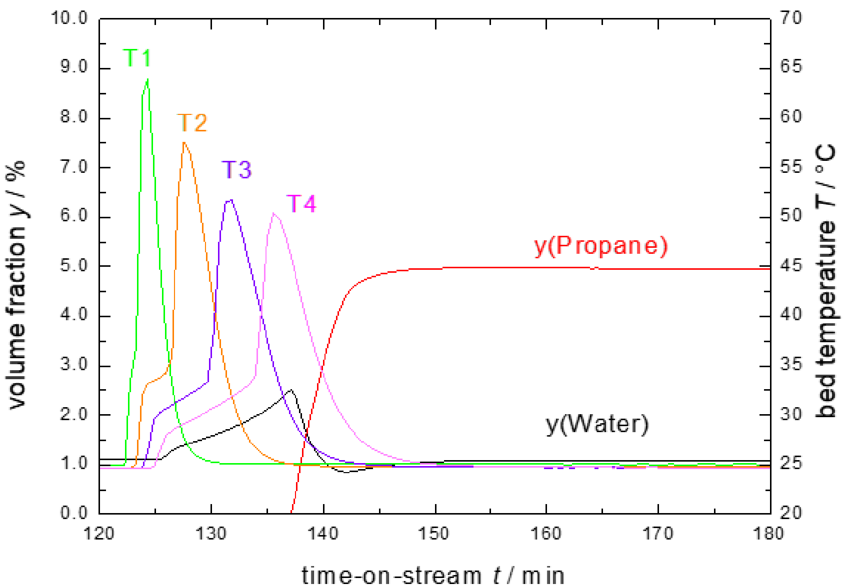


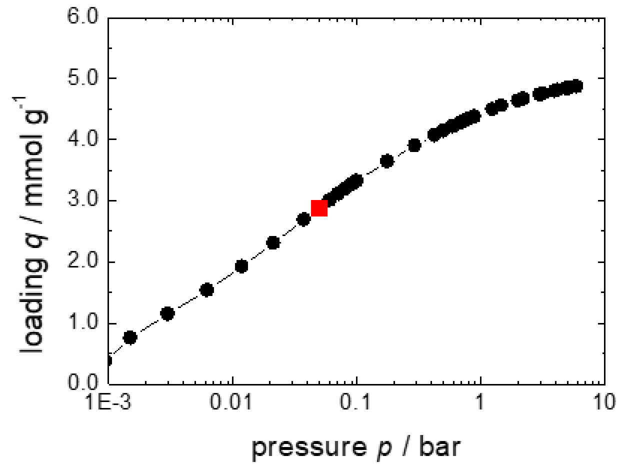


- Breakthrough curve and temperature curves show regular shape
- **No distinct condensation** observable
- Loading: $\boldsymbol{q(H_2O) = 0.64\ \mathrm{mmol\ g^{-1}}}$
- Very good agreement with water isotherm measured on typical volumetric setup

Example 1 - Propane

Segment 2 (volume fraction $y(C_3H_8)$ = **5.00 %,** volume fraction $y(H_2O)$ = 0.95 %, relative humidity approx. 30 % @ 25 °C

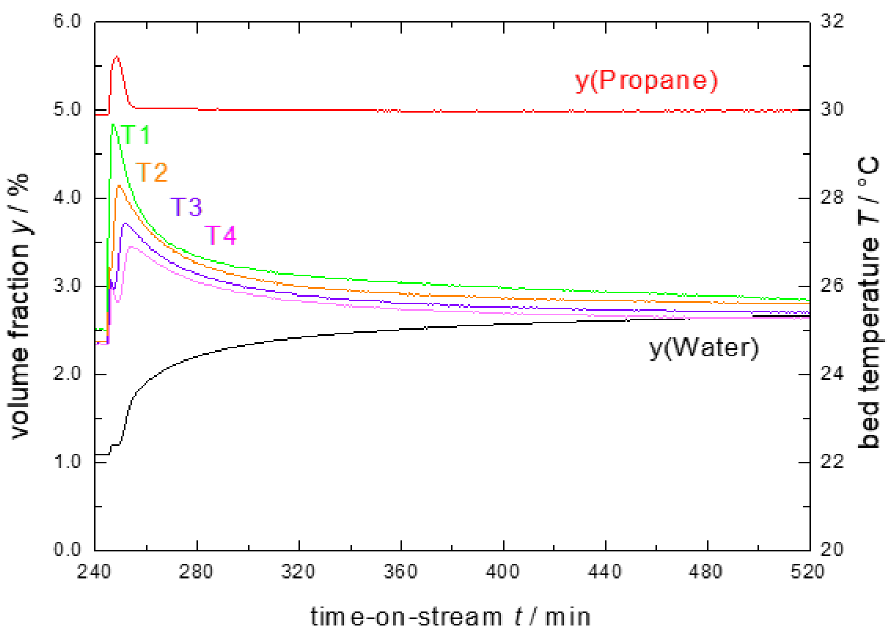


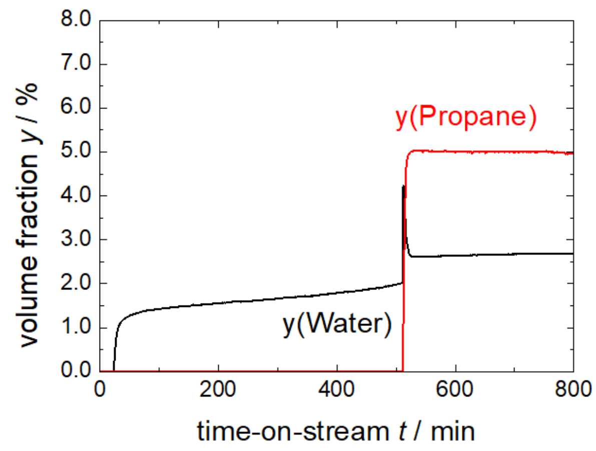


- Loading: $q(C_3H_8)$ = **2.84 mmol g^{-1}**, good agreement with loading at dry conditions: **2.88 mmol g^{-1}**
- H_2O isotherm Loading: $q(H_2O)$ = **0.64 mmol g^{-1}**
- Very good agreement with water isotherm measured on typical volumetric setup
- Heat of adsorption by propane is used to desorb water
- Released water can now adsorb in the next adsorbent layer, which is also an exothermal process
- Slight slope in temperature, before big peak observed caused by propane adsorption

Example 1 - Propane

Segment 3 (volume fraction $y(C_3H_8)$ = 5.00 %, volume fraction $y(H_2O)$ = **2.70 %**, relative humidity approx. **85 % @ 25 °C**)



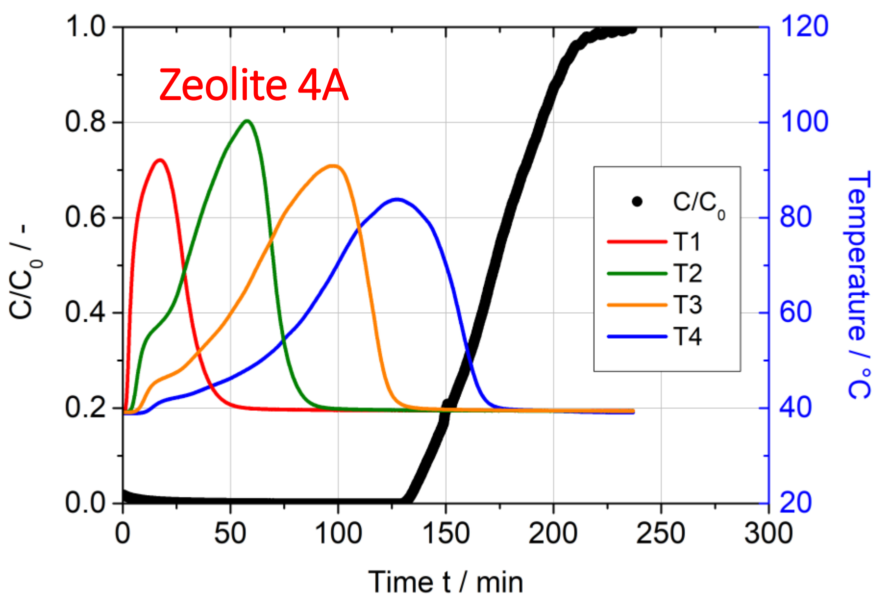


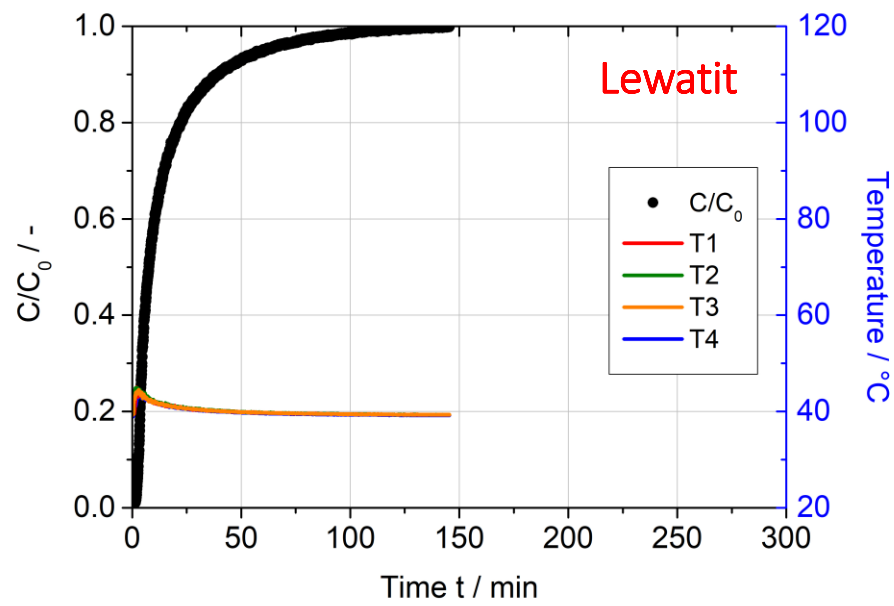
- **Slight displacement** of propane, not equilibrated after 5 h → very slow process due to **condensation** of water in the pores → No replacement of propane on the surface
- By inverting the experiment (1. breakthrough curve with RH 85 % and 2. adding of propane) → a lower propane loading (**0.79 mmol g^{-1}**) is observed
- When adsorbent is pre-saturated with high RH → pore filling → limited access to adsorption sites

Example 2 – Carbon dioxide

Breakthrough curve of H_2O on Zeolite 4A and Lewatit

(313 K, relative humidity 50 % in N_2 at 0.1 MPa, total flow: 5 Nl min^{-1})



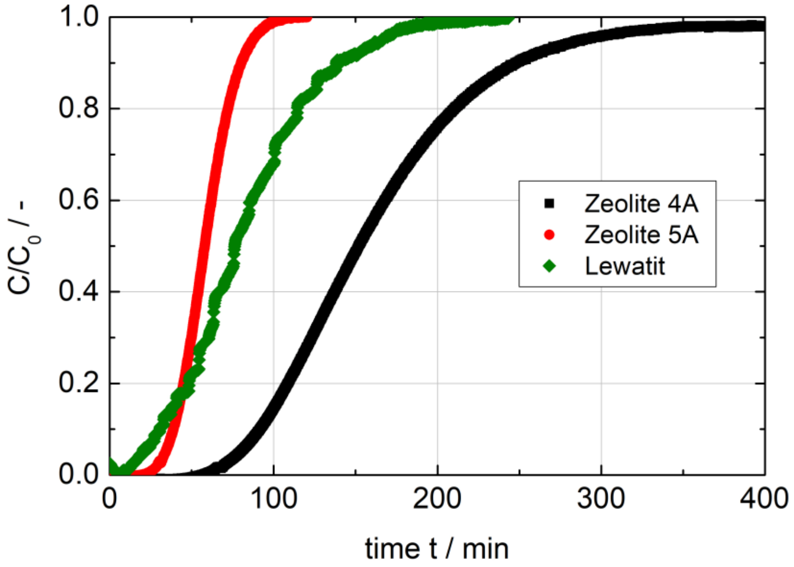


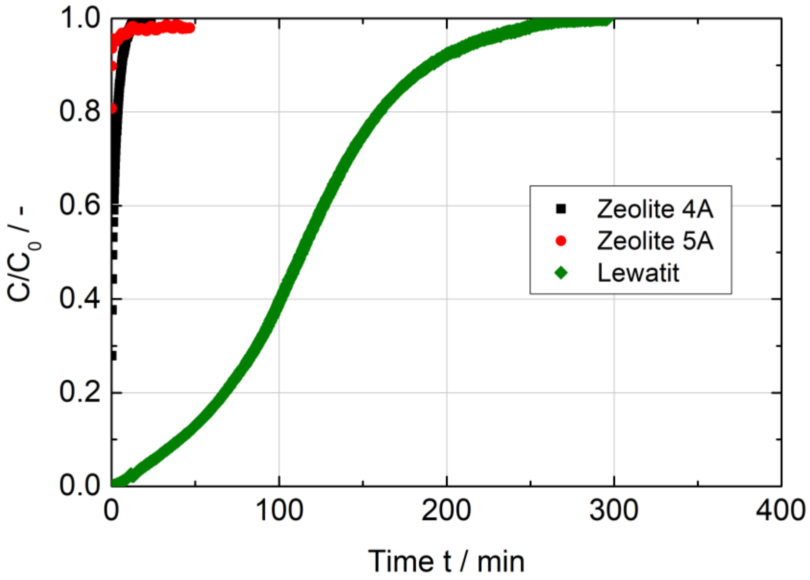
- **Zeolite 4A** shows **high H_2O sorption capacity** compared to Lewatit (due to lower surface area)
- **Large heat effects** are observed for sorption on **zeolite 4A**
- Due to **lower surface area** of Lewatit → the adsorbed amount of H_2O and **resulting heat effects** are **much lower compared to zeolite 4A**

Example 2 – Carbon dioxide

Breakthrough curve on zeolite 4A, 5A and Lewatit – dry vs. wet conditions

(313 K, 2000 ppm CO_2 balanced by N_2 at 0.1 MPa, total flow: 5 Nl min^{-1}, relative humidity 50 %)





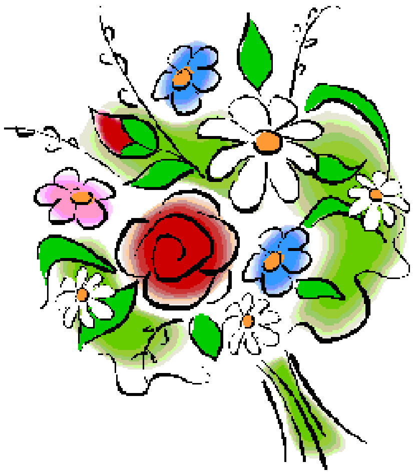
- **Zeolite 4A and 5A** show **drastically reduced CO_2 capacities** in **presence of humidity**
- **Lewatit** shows **higher CO_2 capacity** in **presence of water** due to **supported reaction** of **CO_2** with **amino-functionality** on the surface of the polymer

Sorbent	CO_2 loading at dry conditions / mmol g^{-1}	CO_2 loading at wet conditions / mmol g^{-1}
Zeolite 4A	**0.77**	**< 0.01**
Zeolite 5A	**0.34**	**< 0.01**
Lewatit	**0.61**	**0.82**

Summary – Influence of Humidity

- **Breakthrough experiments** are **suitable to characterize samples** under dynamic conditions in the presence of humidity
- **Presence of humidity** can have large effects on sorption equilibrium and sorption kinetics
- At **humidities > 40 %**, the loading **capacity of propane or CO_2 on AC and zeolite** will be **reduced**
- **pre-loaded H_2O** will **drastically reduce** the **capacity** of propane and CO_2 and thus, the **breakthrough time** in dynamic experiments
- Competitive sorption in terms of **condensation of H_2O** (hydrophobic AC, mesoporous adsorbents) can **lead** to a **long equilibration process** in dynamic experiments
  → as a result: **no equilibrium can be observed** from such measurement
- Presence of H_2O is essential in sorption process during amine-functionalized sorbents

Thank you for your attention!



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