Investigation of the temperature dependence of adsorption enthalpy

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Motivation

The heat of adsorption represents a crucial design parameter for industrial adsorption and desorption processes, as the temperature has a considerable impact on adsorption capacity and process kinetics. The temperature dependence of the heat of adsorption is of particular importance in the context of TSA (temperature swing adsorption) processes, which are characterized by pronounced temperature shifts between adsorption and desorption. Accordingly, an understanding of the load- and temperature-dependent behavior of the heat of adsorption offers potential for process optimization.

The heat of adsorption, as a process variable, is obtained by adding an RT-term (R: universal gas constant, T: temperature) to the adsorption enthalpy, which is a variable of state. The adsorption enthalpy provides a measure of the strength of intermolecular interactions between the adsorbent surface and adsorptive molecules. Consequently, the load- and temperature-dependent measurement of adsorption enthalpies allows conclusions regarding the adsorption behavior.

Methods and Materials

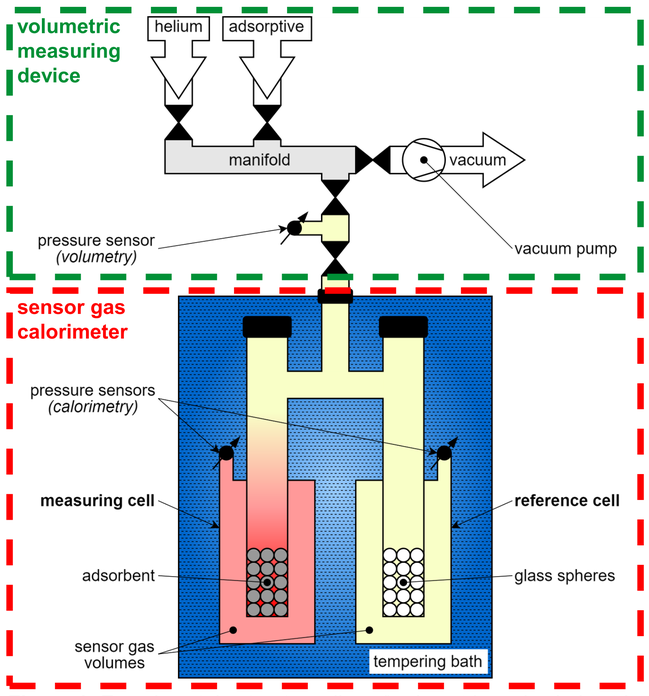

Figure 1: *Experimental setup (coupling of volumetric and calorimetric measurement)*

Volumetric Measurement:

- Time-dependent measurement of the pressure inside the sample vessel
- Pressure plateaus represent adsorption steps

→ **Adsorption isotherm** (cumulative measurement)

→ Calculation of isosteric adsorption enthalpy according to Clausius-Clapeyron

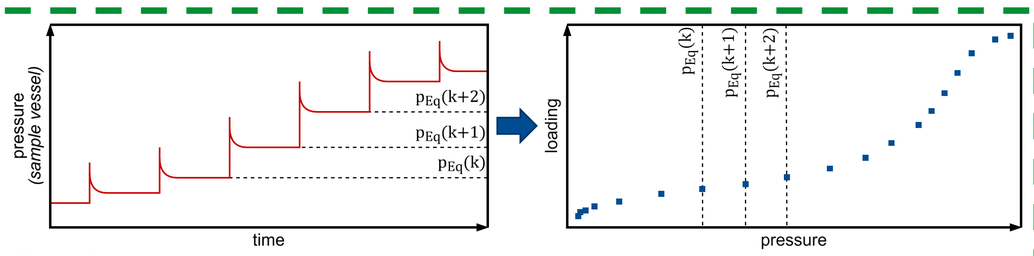

Figure 2: *Volumetric measurement signal (left) to determine the adsorption isotherm (right)*

Clausius-Clapeyron equation: $\left.\frac{d(\ln(p))}{d(1/T)}\right|_X = -\frac{\Delta h_{ads}}{R}$

Calorimetric Measurement:

- Time-dependent measurement of the pressure difference between both sensor gas volumes
- Each pressure difference peak results from one adsorption step
- Areas below the peaks correspond to released heat of adsorption

→ **Adsorption enthalpy** (Δh_{Ads})

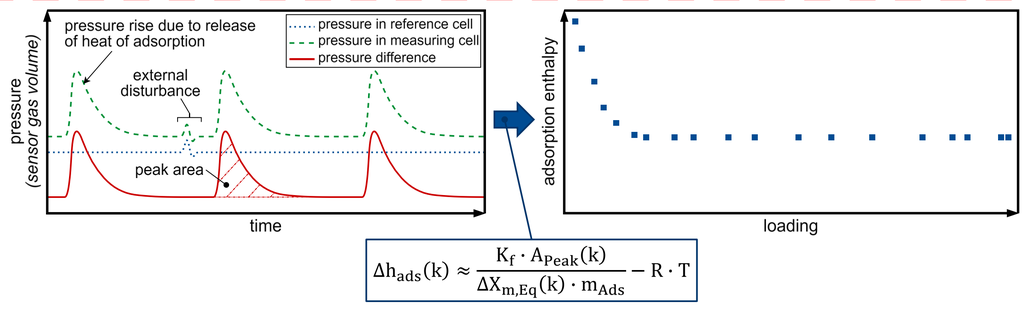

Figure 3: *Calorimetric measurement signal (left) to determine the adsorption enthalpy (right)*

Adsorptive:

- Ethene
  - π-bonding due to sp^2 hybrid orbital
  - Planar molecule

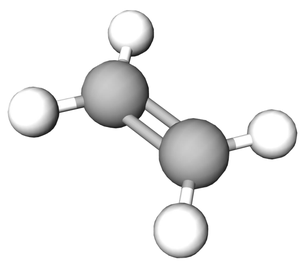

Figure 4: *Molecular structure of ethene*

Adsorbents:

- Faujasite (FAU) zeolites
  - Sodalite cages connected by double six rings
  - Extra framework cations for charge balancing
- Extra framework cations: Na^+- and Ca^{2+}-cations

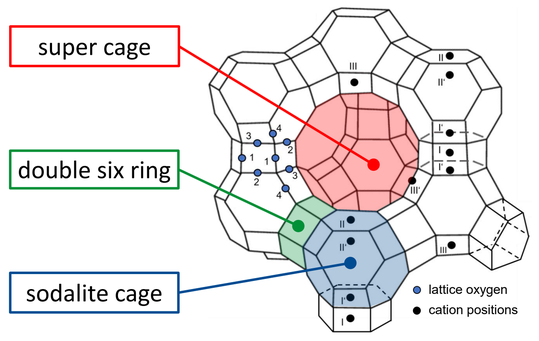

Figure 5: *Topology of FAU zeolites*

Table 1: *Cation distributions of FAU zeolites*

Cation Position	NaX	CaNaX 80%	
	Na^+	Na^+	Ca^{2+}
I	0	0	17
I'	32	0	0
II	32	14	18
II‘	0	0	0
III + III‘	24	4	0
Sum	88	18	35

Results and Discussion

Adsorption of ethene on FAU zeolite NaX:

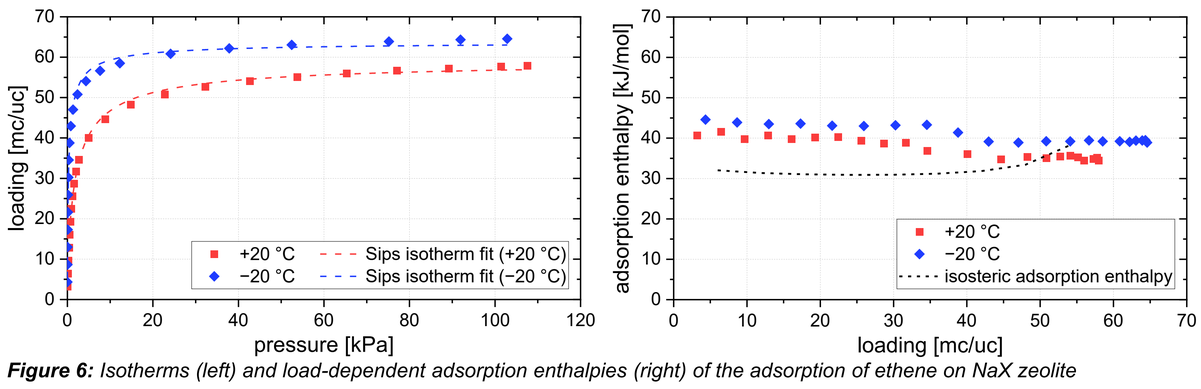

Figure 6: *Isotherms (left) and load-dependent adsorption enthalpies (right) of the adsorption of ethene on NaX zeolite*

- Equilibrium loading decreases with increasing temperature
- Two plateaus of constant adsorption enthalpy
  → Two energetically different adsorption sites ($\Delta(\Delta h_{Ads})$ = 5 kJ/mol)
- Decrease of adsorption enthalpy by 5 kJ/mol with increase in temperature of 40 K
- Isosteric adsorption enthalpy cannot describe shape and values of measured data

Adsorption of ethene on FAU zeolite CaNaX 80%:

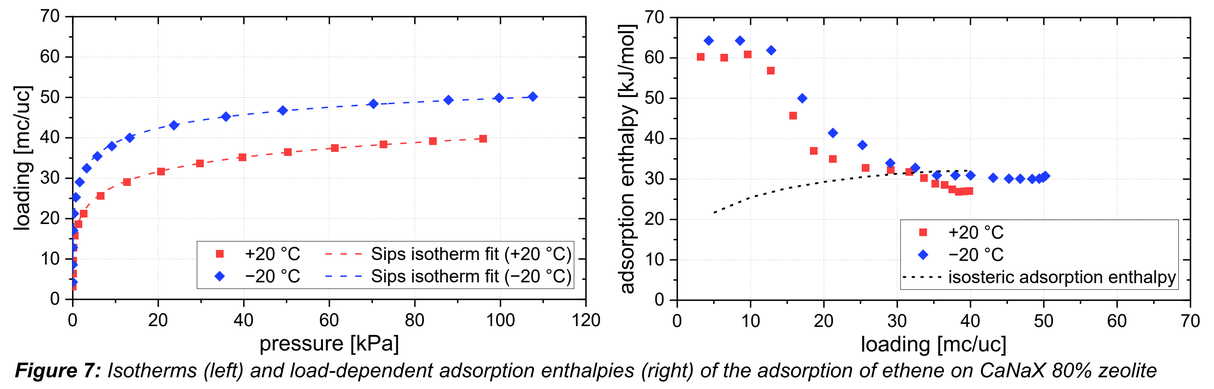

Figure 7: *Isotherms (left) and load-dependent adsorption enthalpies (right) of the adsorption of ethene on CaNaX 80% zeolite*

- Equilibrium loading decreases with increasing temperature
- Two plateaus of constant adsorption enthalpy
  → Two energetically different adsorption sites ($\Delta(\Delta h_{Ads})$ = 35 kJ/mol)
  → Higher adsorption enthalpies and adsorption enthalpy difference between plateaus on CaNaX 80% than on NaX due to additional divalent Ca^{2+}-cations
- Decrease of adsorption enthalpy by 5 kJ/mol with increase in temperature of 40 K
- Isosteric adsorption enthalpy cannot describe shape and values of measured data

Summary and Outlook

The temperature-dependent adsorption behavior is investigated systematically using a sensor gas calorimeter to simultaneously measure adsorption isotherms and enthalpies. Exemplarily, the results for the adsorption of ethene on a zeolite NaX and a cation exchanged zeolite CaNaX are shown. Significant differences in the load-dependent adsorption enthalpies indicate different kinds and strengths of molecular interactions. Despite these differences, a comparable temperature dependence is exhibited by both systems between -20 °C and +20 °C, with a decrease in adsorption enthalpy of approximately 5 kJ/mol being observed over the entire range of loading investigated.

A comparison of the measured adsorption enthalpies with the results of the isostere method obtained using the Sips isotherm model demonstrates significant deviations of the isosteric adsorption enthalpies from the measured data.
In further investigations, additional systems and temperatures will be studied to get a deeper mechanistic understanding of the temperature dependence of adsorption and prevailing interactions. As the accuracy of isosteres increases with increasing quantity of isotherms, the comparison between the measured adsorption enthalpies and those obtained from the Clausius-Clapeyron equation will also be further elaborated.

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