Influence of temperature on binary adsorption of light hydrocarbons on FAU zeolites

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Motivation

The separation of light alkanes and alkenes of the same chain length (C_2-C_4) at trace concentrations is of great importance in petrochemical industry and in technical environmental protection. Because of similar structural and thermophysical properties of the alkane and the alkene, the separation is very expensive. Adsorption processes at low temperatures may be an alternative. Due to different temperature dependencies, a temperature optimum may be found for separation. As yet, no systematic data are available on binary adsorption of light hydrocarbons at low temperatures. With this in mind, this work investigates the adsorption thermodynamics of ethane and ethene mixtures on different faujasite zeolites over a wide temperature range. In particular, the influence of the zeolite cations on the separation will be discussed.

Methods & Materials

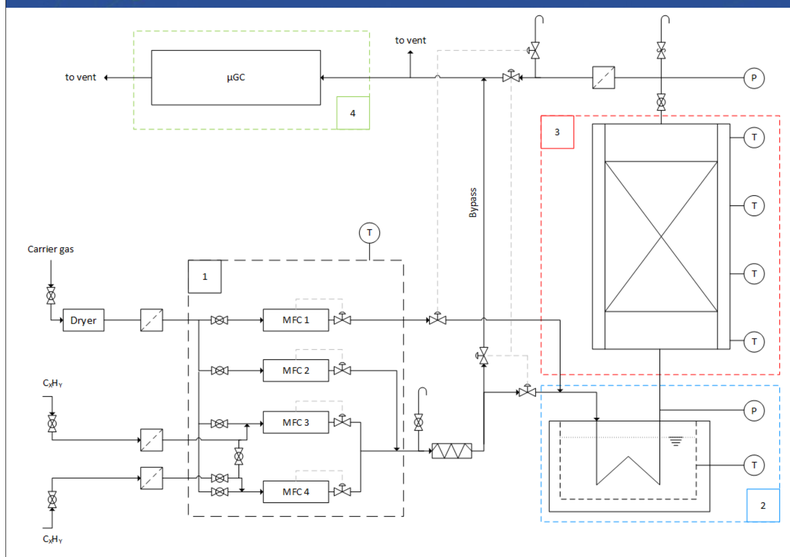


Figure 1: Experimental setup

- Alkane/Alkene/Nitrogen mixture with thermal mass flow controllers
- Cooling with cryogenic thermostat down to -75 °C
- Double jacket adsorber equipped with thermocouples
- Continuous gas analysis with gas chromatograph (µGC)

Measurement of cumulative breakthrough curves

Calculation of adsorbent loading via mass balancing

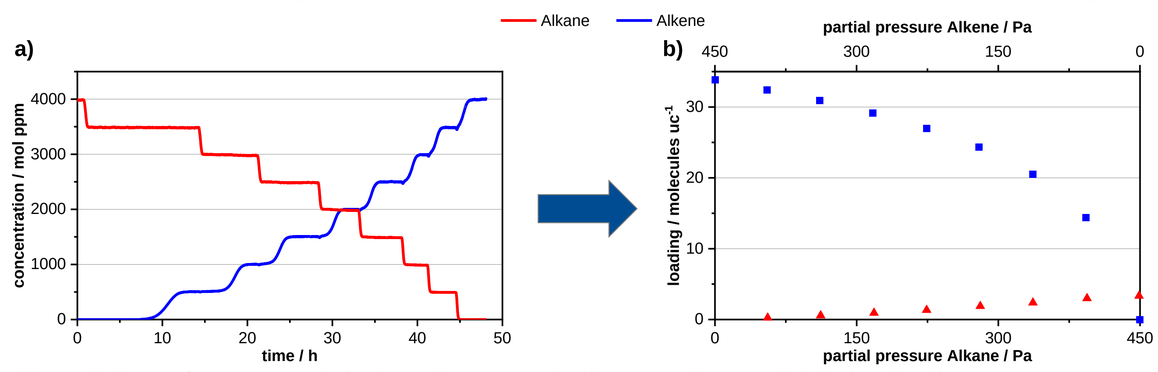
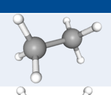


Figure 2: Exemplary curves of a) adsorptive concentrations over time and b) derived isotherms

Table 1: Thermodynamic and structural properties of the adsorptives

	Structure	Critical diameter / nm	Polarizability / $\cdot 10^{-30}$ m^3	Quadrupole moment / $\cdot 10^{-40}$ C·m^2
Ethane / C_2H_6		0.45	4.47	3.34
Ethene / C_2H_4		0.34	4.25	6.67

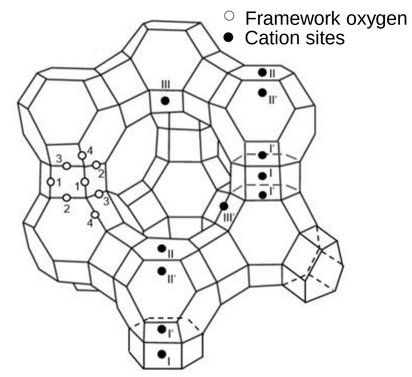


Figure 3: Structure of a faujasite zeolite

Faujasite (FAU) zeolites:

- Sodalite cages linked via D6R
- Framework consists of SiO_4 and AlO_4 tetrahedra
- Aluminum causes negative charge, balanced by exchangeable cations
- Number of cations depends on Si/Al ratio and charge of cations

Results & Discussion

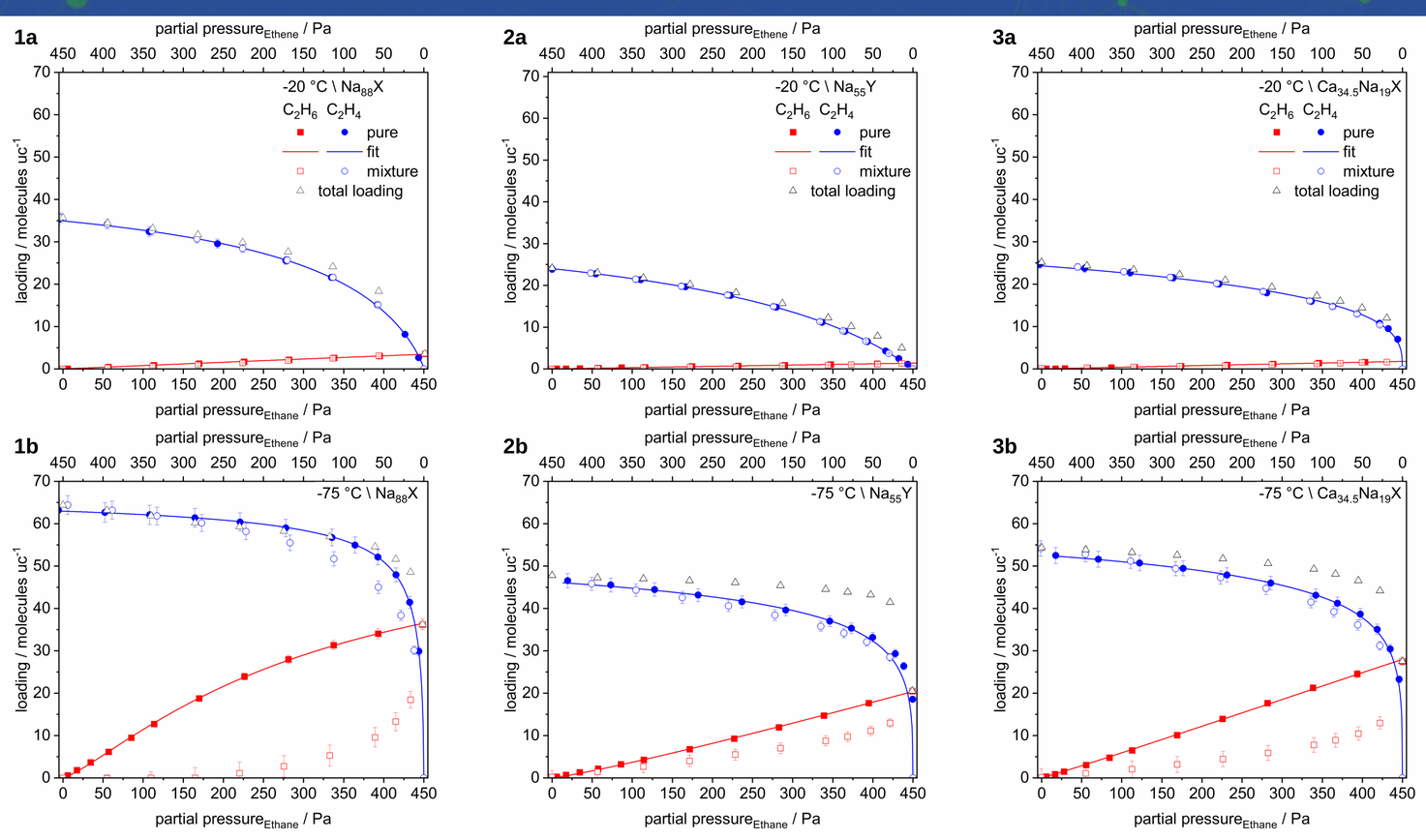


Figure 4: Adsorption isotherms of ethane and ethene as pure components and in mixture at temperatures of (a) -20 °C and (b) -75 °C on zeolites (1) $Na_{88}X$, (2) $Na_{55}Y$ and (3) $Ca_{34.5}Na_{19}Y$

Table 2: Total number of cations and number of reachable cations in FAU zeolites

Zeolite	Aluminum atoms per unit cell	Cations		Number of reachable cations
		Na^+	Ca^{2+}	
$Na_{88}X$	88	88	0	56
$Na_{55}Y$	55	55	0	32
$Ca_{34.5}Na_{19}X$	88	19	34.5	32

-20 °C:
- Mixture measurements of ethane and ethene are congruent with pure component isotherms for all three zeolites
- No competition for adsorption sites between the two adsorptives

-75 °C:
- Displacement of ethane by ethene in the mixture, which is most pronounced for $Na_{88}X$
- At low partial pressures of ethene in the mixture, even the alkene does not reach the pure component loading
  - ➢ **Loading is strongly dependent on the number of accessible cations**
  - ➢ **Displacement results from saturation of the zeolite**

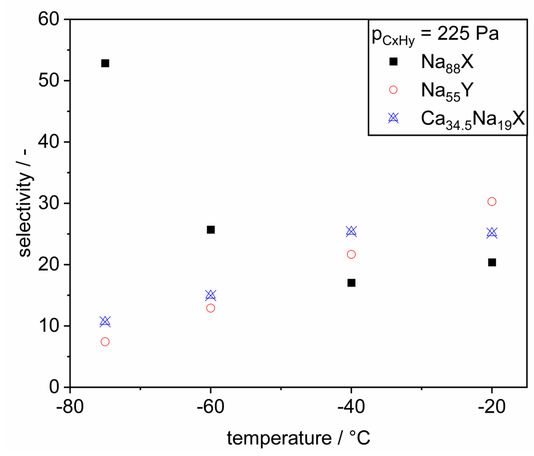


Figure 5: Selectivity of ethane-ethene separation for equimolar adsorptive composition

Selectivity: $S(T) = \frac{X_{Ethene}}{X_{Ethane}}$

- Increases sharply from -40 °C onwards for $Na_{88}X$
- Decreases for $Na_{55}Y$ and $Ca_{34.5}Na_{19}X$ with lowering of the temperature

Summary & Prospect

To determine the effect of temperature on the binary adsorption of ethane and ethene at trace concentrations, isotherms were measured on $Na_{88}X$, $Na_{55}Y$ and $Ca_{34.5}Na_{19}X$ zeolites at temperatures between -20 °C and -75 °C. The mixture measurements on all three zeolites show similar behavior when the temperature is lowered. At -20 °C, no competition of the adsorptives for the adsorption sites occurs. At -75 °C, the limited number of adsorption sites leads to a strong competition between the adsorptives, resulting in a displacement of ethane by ethene. Zeolite $Na_{88}X$ is the most saturated and thus has a high selectivity for the alkene. Further work will investigate the influence of the hydrocarbon chain length and the isomerism on multi-component adsorption at different temperatures. Additionally, zeolites with a different framework structure will be used as adsorbents.

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