

Motivation

The main component of natural gas is methane. Besides that, trace amounts of sulfuric components can be included. An industrial method to purify and dry the raw gas to high purity specifications such as Liquefied Natural Gas (LNG) is the fixed bed adsorption technology using cyclic temperature swing adsorption (TSA). A part of the purified dry gas stream is used in the desorption step. It contains residual concentrations of hydrogen sulfide (H₂S) and carbon dioxide (CO₂) which react in the zeolite bed in a catalytic reaction to water (H₂O) and carbonyl sulfide (COS).

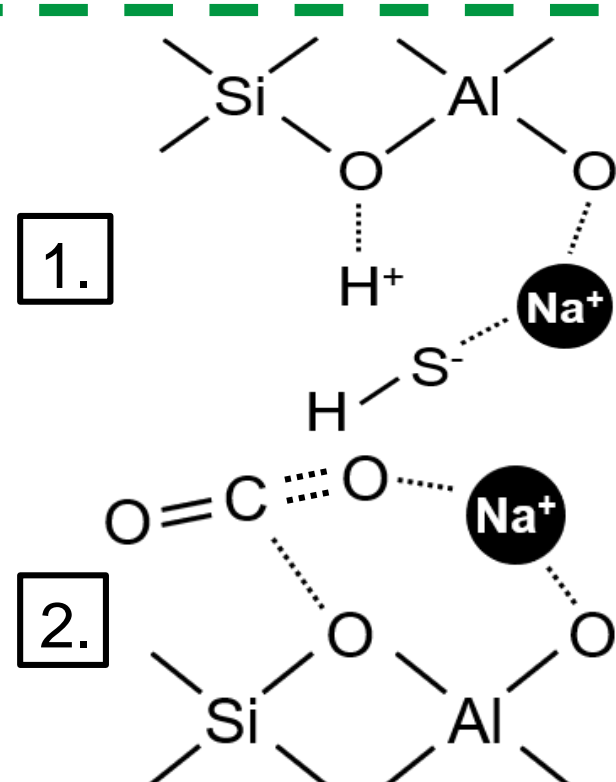
After desorption, the COS enters the product gas stream as a polluting component. For design and optimization of such processes a deep knowledge of the adsorption of all components and the COS formation is required. Furthermore, the adsorption properties of the adsorbents must be well known. The aim of this research project is to systematically investigate adsorption and desorption behavior as well as catalytic activity of commercial and newly developed zeolites.

Methods and Materials

Methods:

COS formation: catalysis on the zeolite

1. Chemisorption of H₂S with the zeolite framework.
2. Adsorption of CO₂ with the zeolite framework.
3. Catalytic reaction: $\text{H}_2\text{S} + \text{CO}_2 \rightarrow \text{COS} + \text{H}_2\text{O}$ ($\Delta H_R > 0$)
4. Adsorption of H₂O on catalytic adsorption sites. → Termination of the catalytic reaction.



Measurement of multi-component breakthrough curves (BTC) with catalytic reaction:

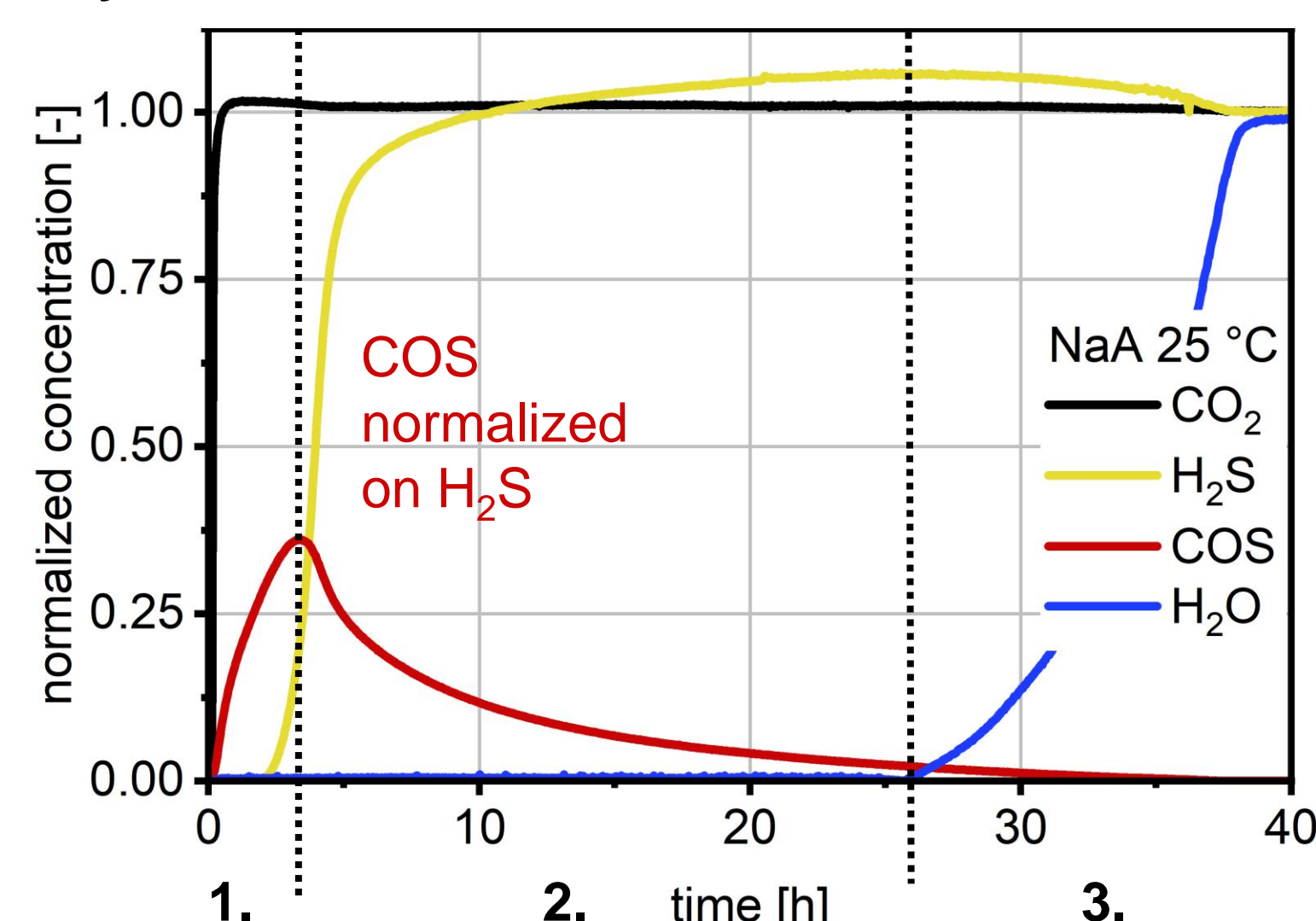


Fig. 3: BTCs on binderfree Linde Typ-A zeolite at 25 °C

1. **Kinetically controlled COS formation:**
 - No deactivation of catalytically active sites.
 - H₂S is adsorbed and consumed by the reaction.
2. **Reduction of the catalytic reaction:**
 - Occupation of catalytically active sites by water adsorption.
3. **All catalytically active sites are deactivated:**
 - COS formation comes to a standstill.

Experimental setup:

Adsorption and Desorption:
- T: 0 °C to 300 °C
- p: 1.3 bar

Analytics

to vent → EPC
to vent → μ-GC

Gas mixing section

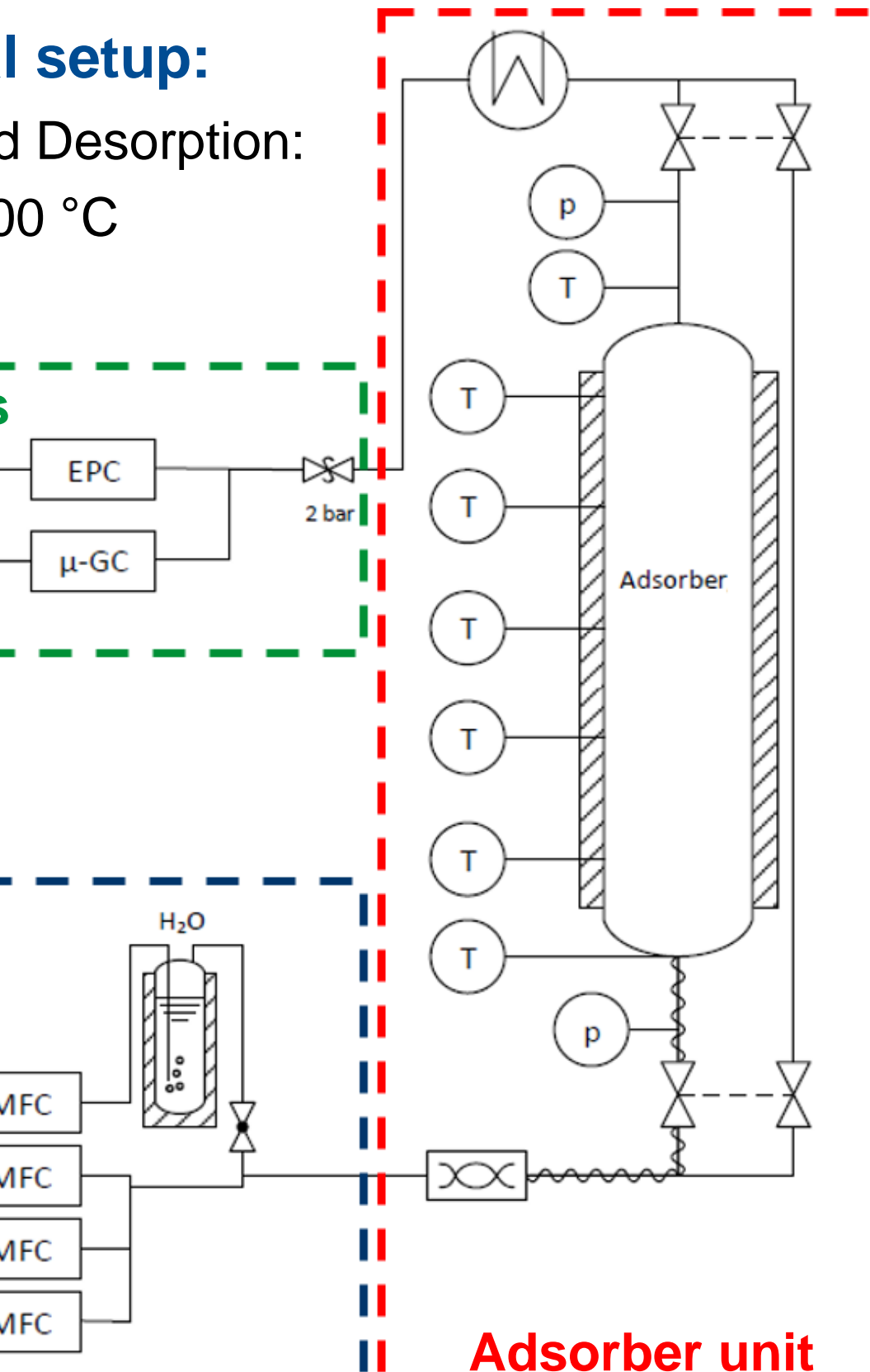
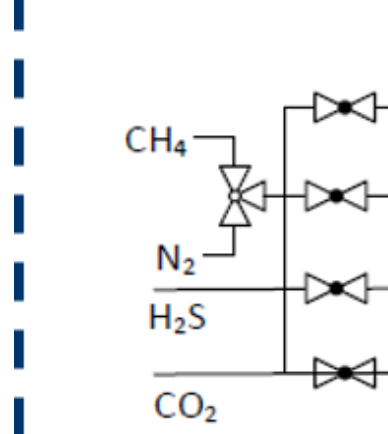
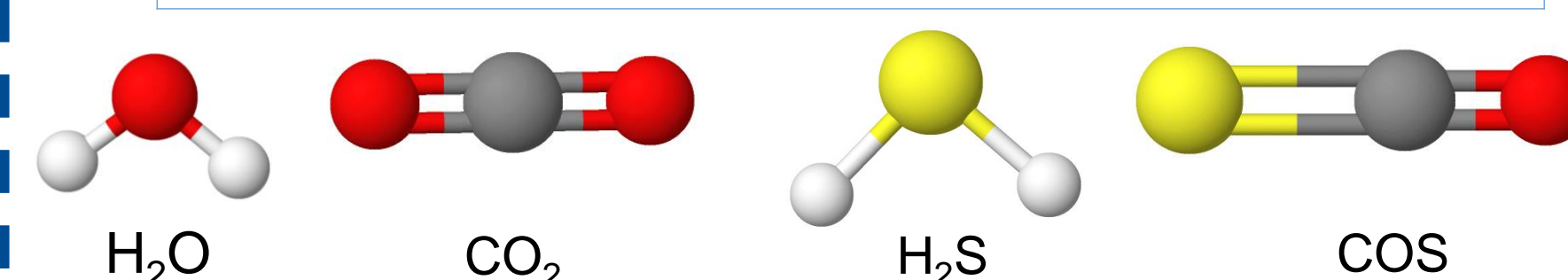


Fig. 1: Experimental setup

Adsorptives:

Tab. 1: Selected properties of the adsorptives

	Crit. diameter [Å]	Polarizability [10 ⁻³⁰ m ³]	Dipole moment [10 ⁻³⁰ Cm]
H ₂ O	2.60	1.48	6.17
CO ₂	2.80	2.63	0.00
H ₂ S	3.60	3.80	0.98
COS	2.80	5.20	0.72



Adsorbents:

Binder-free Linde Typ-A zeolite (NaA)

- Polar surface caused by cations on positions I, II, III.
- Increasing catalytic activity: I → II → III

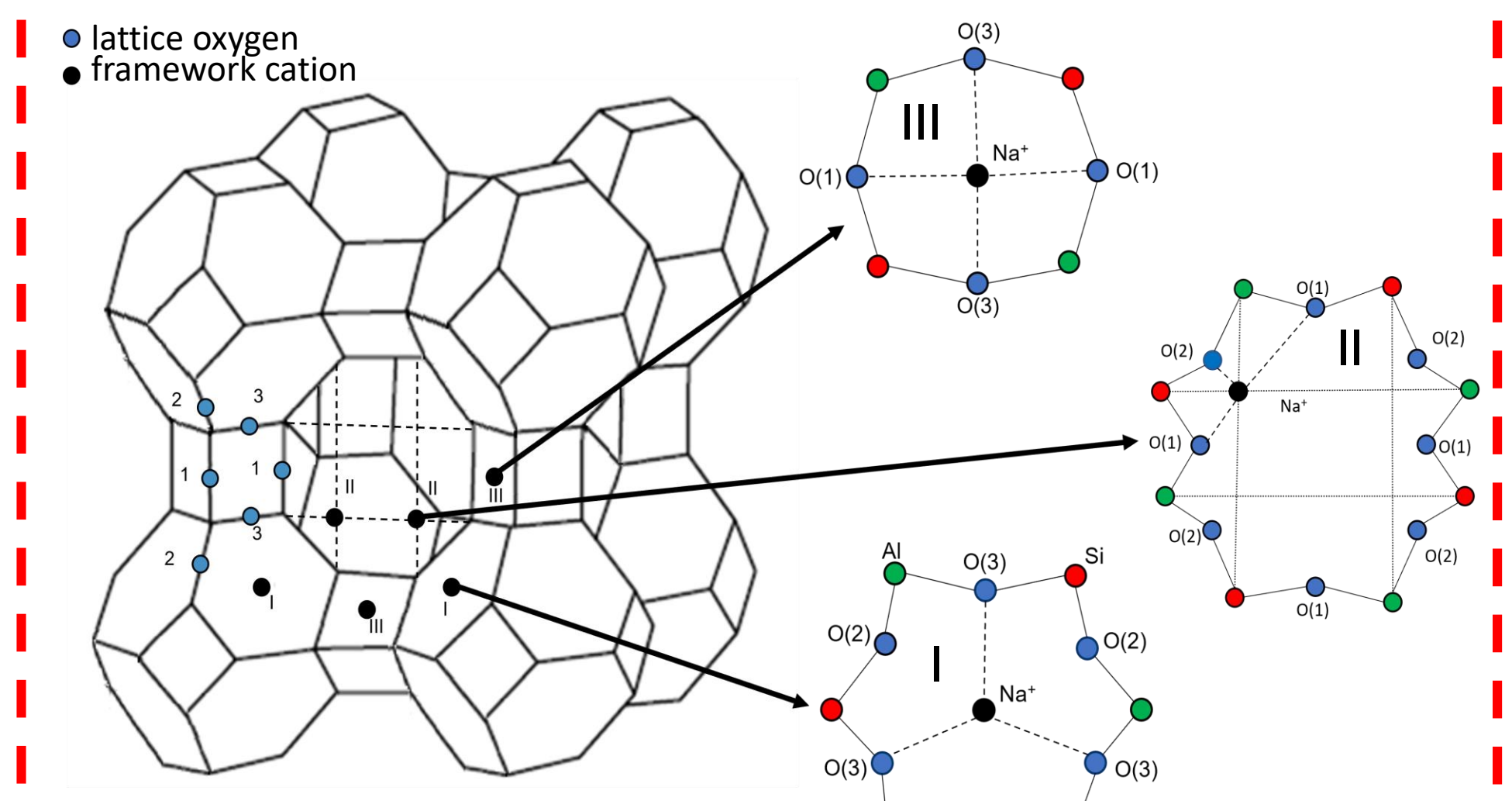


Fig. 2: Structure of a Linde Typ-A zeolite

Modification by ion exchange

- 1 divalent cation (Ca²⁺) for 2 monovalent (Na⁺). → Decreasing number of adsorption sites.
- Exchange ratio is the percentage of removed Na⁺ cations.
- Ion exchange order: III → II → I

Tab. 2: Ion exchange depending on exchange ratio

Exchange ratio	Ion exchange
0 – 8 %	Exchange of Na ⁺ on III and II for Ca ²⁺ on II.
8 – 30 %	Exchange of Na ⁺ on II and I for Ca ²⁺ on II.
30 – 100 %	Exchange of Na ⁺ on I for Ca ²⁺ on I.
55 – 90 %	Cation redistribution Ca ²⁺ from II to I.

Results and Discussion

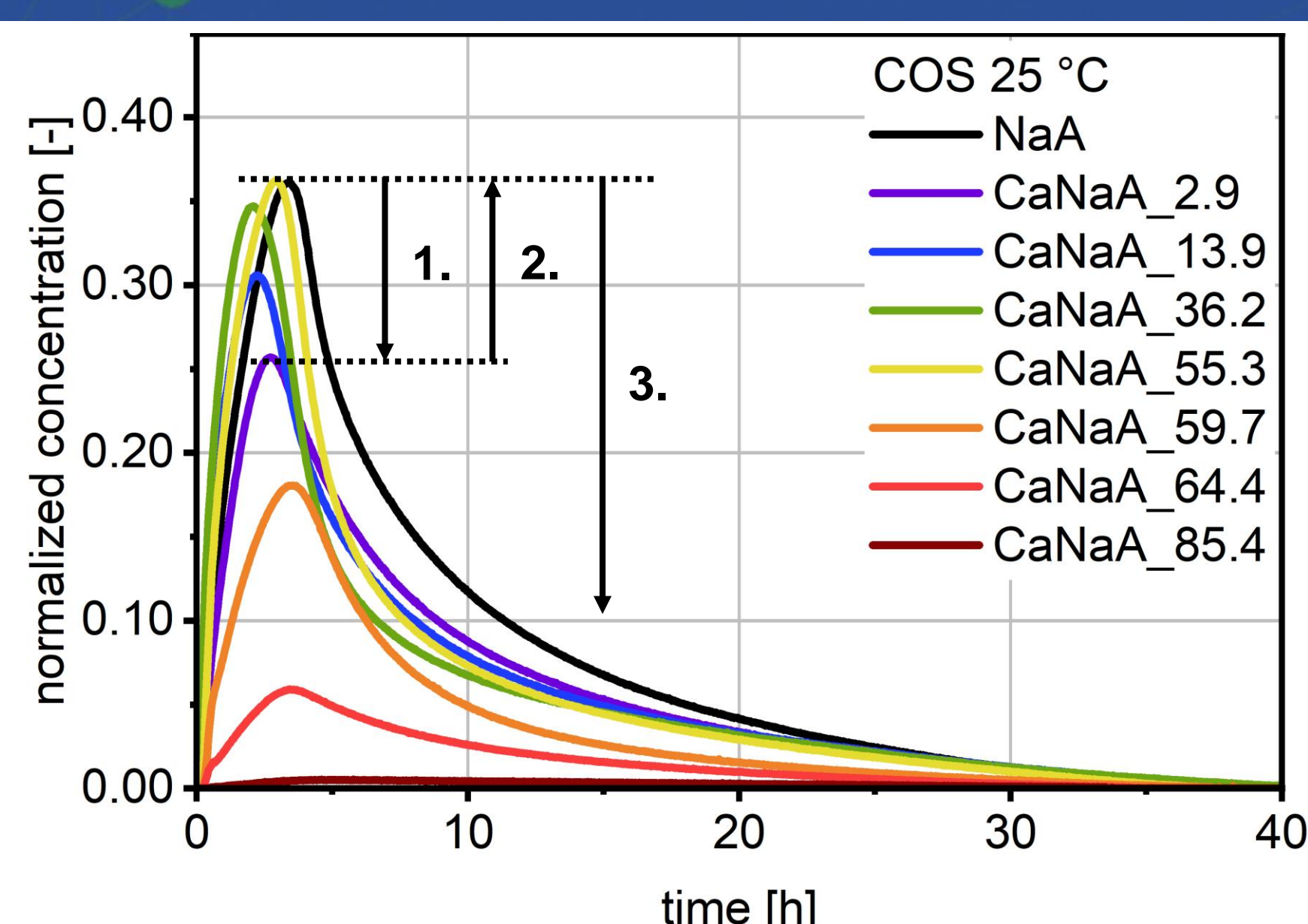


Fig. 4: COS-BTCs on CaNaA-BF zeolites at 25 °C

1. **Decreasing number of cations on position III.**
 - From 0 % to 2.9 % decreasing reaction rate.
2. **Cation position III is unoccupied.**
 - Cation position II occupied by Ca²⁺.
 - Decreasing total number of cations, but Ca²⁺ more active than Na⁺.
 - From 2.9 % to 55.3 % increasing reaction rate.
3. **Cation redistribution Ca²⁺ from II to I.**
 - From 55.3 % to 85.4 % continuously decreasing reaction rate.

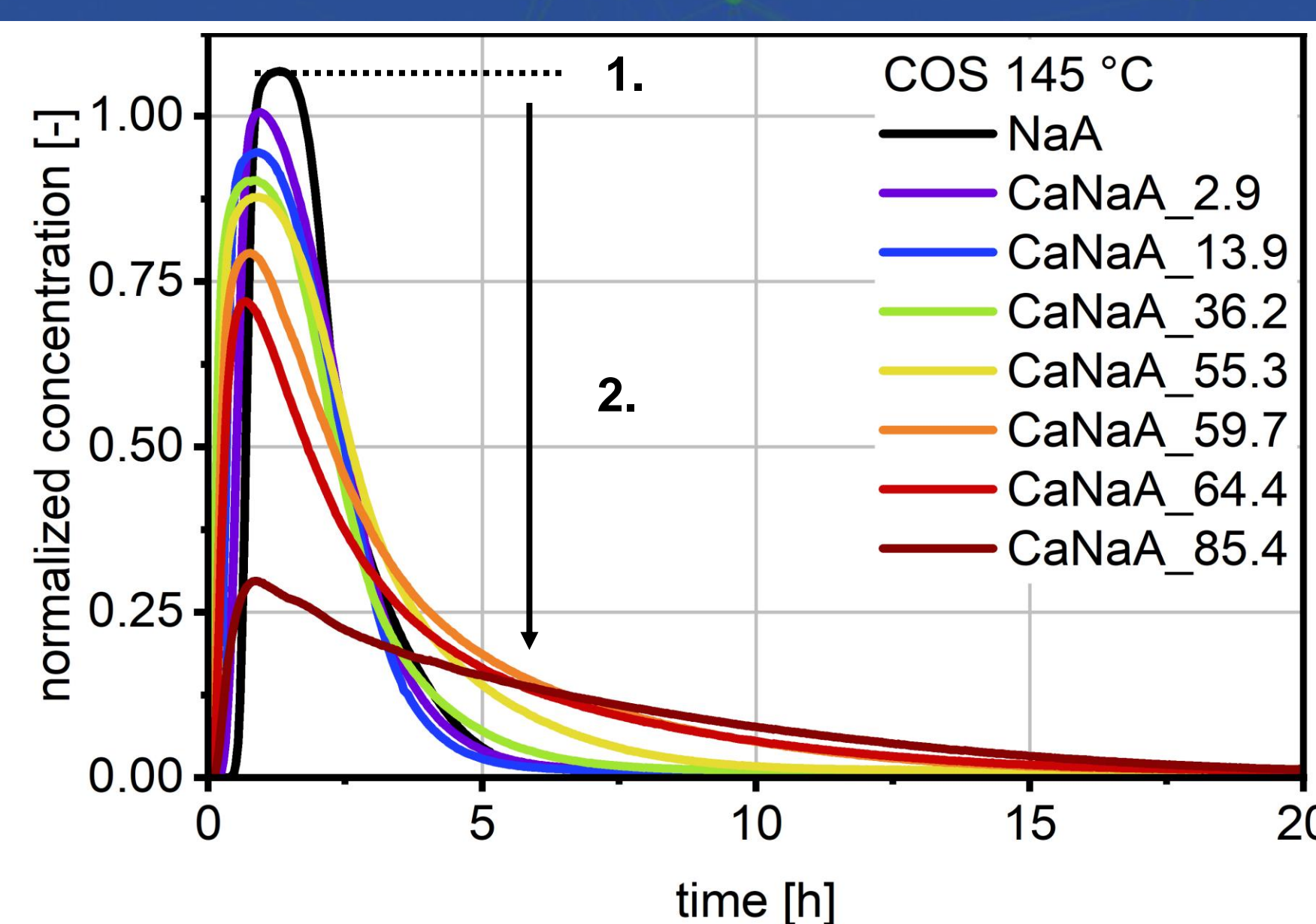


Fig. 5: COS-BTCs on CaNaA-BF zeolites at 145 °C

1. **The zeolite NaA shows the highest rate.**
 - At maximum reaction rate > 1.
2. **Continuously decreasing reaction rate.**
 - Roll-up of H₂S/COS, also at 145 °C high activity of H₂S.
 - Decreasing number of cations on position III.
 - Cation position II occupied by Ca²⁺.
 - Cation redistribution Ca²⁺ from II to I.
 - Strong decreasing reaction rate.

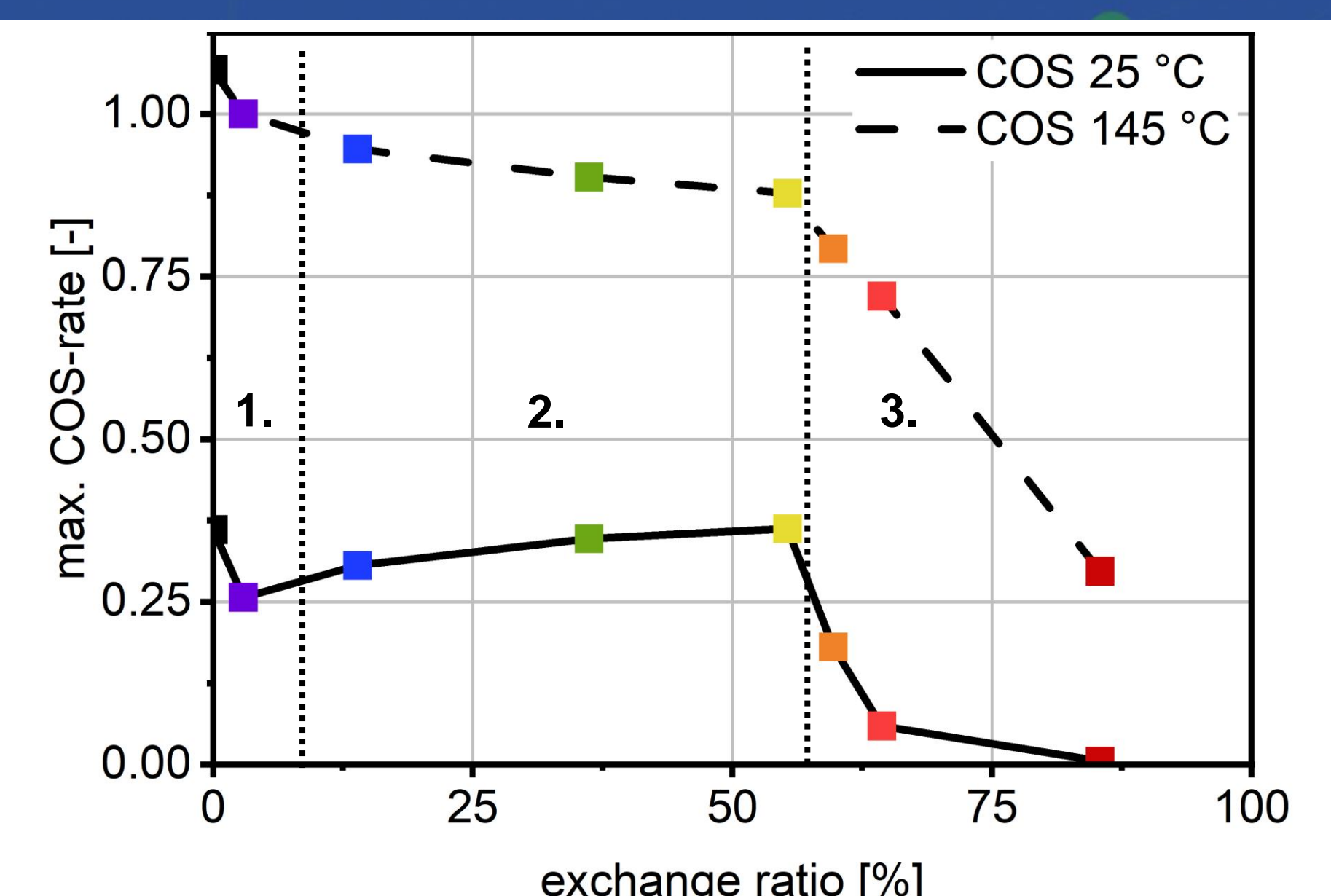


Fig. 6: Maximum COS-rate as a function of exchange ratio

- The reaction rate increases with temperature.
- With temperature the kinetics of adsorption and reaction increase.
1. **With decreasing temperature the cation position III is more important for COS formation.**
 2. **With decreasing temperature greater difference in catalytic activity between Ca²⁺ and Na⁺.**
 3. **Compared to section 1 and 2: similar reaction rates**
 - For both adsorption and desorption high exchange ratios are recommended for industrial processes.

Summary and Outlook

To investigate the catalytic activity of commercial and newly developed zeolites, multicomponent breakthrough curves were measured in a fixed-bed adsorber on eight Linde Type-A zeolites at 25 °C and 145 °C. The BTCs of the COS formed were compared to evaluate the catalytic activity. With increasing exchange ratio the reaction rate decreases. During ion exchange, the Na⁺ cations are first removed from the most catalytically active position III. At high exchange ratios, an additional redistribution of the Ca²⁺ cations from position II to I reduces the catalytic activity. With increasing temperature the reaction rate

and thus the catalytic activity increases due to the accelerating kinetics of adsorption and reaction. In addition, the positive contribution of the higher catalytic activity of cation position III and the Ca²⁺ cations to the COS formation increases with decreasing temperature.

In further work the influence of zeolite structure and ion exchange will be investigated in more detail by multicomponent adsorption experiments on zeolites NaA systematically exchanged with potassium cations.