Energetic characterization of zeolites using a sensor gas calorimeter

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Motivation & Targets

Zeolites are often considered as homogeneous adsorbents. However, at a molecular level the zeolite structure consists of the framework and additional cations. The cations arrange themselves on different cation sites, which have different distances to the zeolite framework. Therefore, they are energetically heterogeneous. Until now, it is largely unknown which binding sites in zeolites are preferentially occupied by adsorptive molecules, which type of interactions are formed and what the energetic contributions of the respective binding partners are. Therefore, in this project we compare adsorption isotherms and heats of adsorption with XRD analyses on systematically modified zeolites. We aim to identify the different binding sites, to clarify the predominant interactions and to gain an understanding of the adsorption mechanisms taking place.

Experimental & Methods

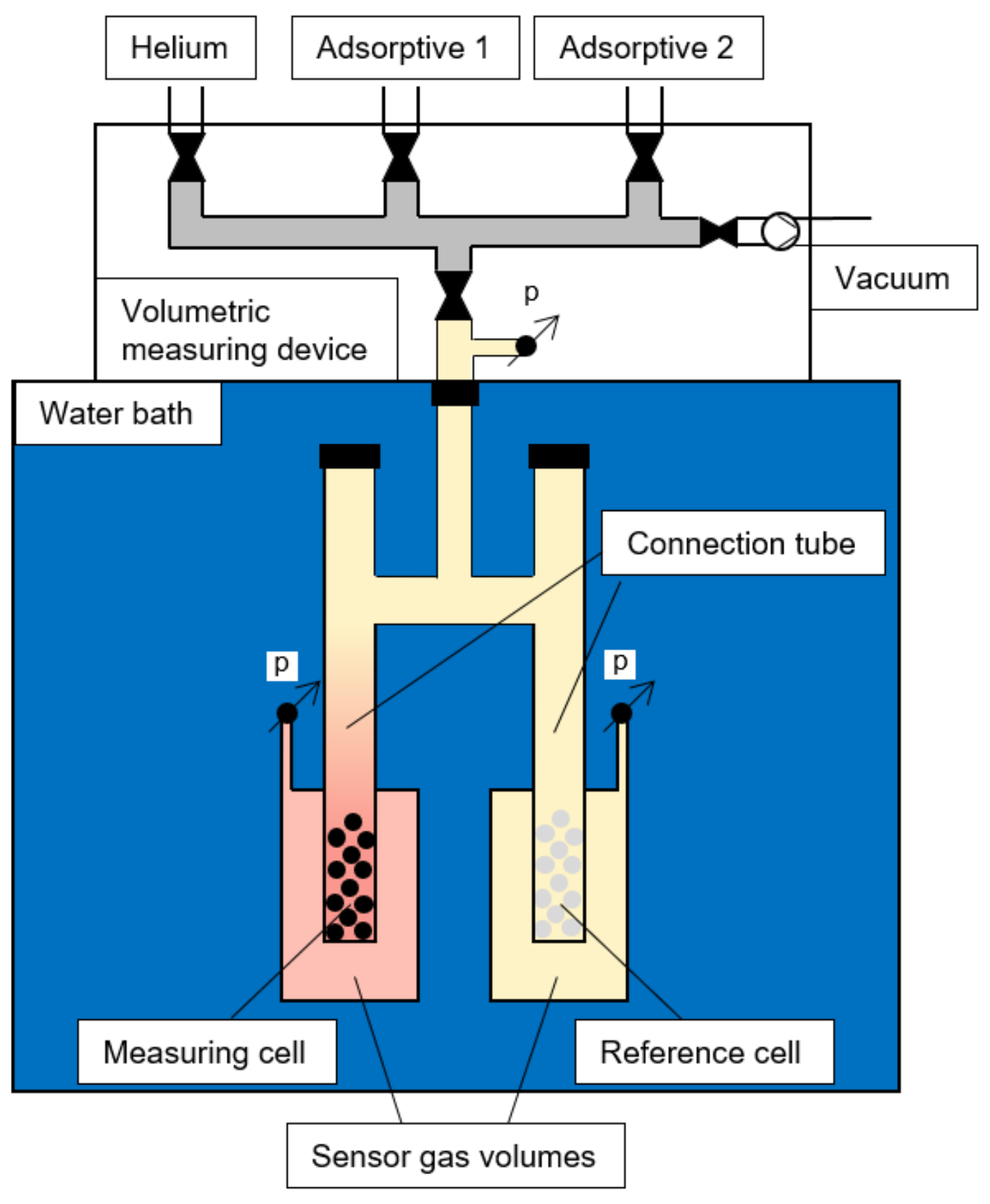


Figure 1: Schematic view of experimental setup

Isotherm:

- Volumetric adsorption measurement (autosorb iQ 3)
- Cumulative measuring principle

Load-dependent heat of adsorption:

- Combination of volumetric and calorimetric measurement
- Measurement of a time-dependent pressure difference between both sensor gas volumes
- Determination of heat of adsorption for each individual adsorption step

Linde Type A (LTA) zeolites:

- Sodalite cages linked via D4R
- Zeolite framework consists of Si-, Al- and O-atoms
- Al-tetrahedra introduce negative charge
- Charge balancing through additional cations
- Cations are exchangeable (e.g. Na^+ was exchanged for Ca^{2+})

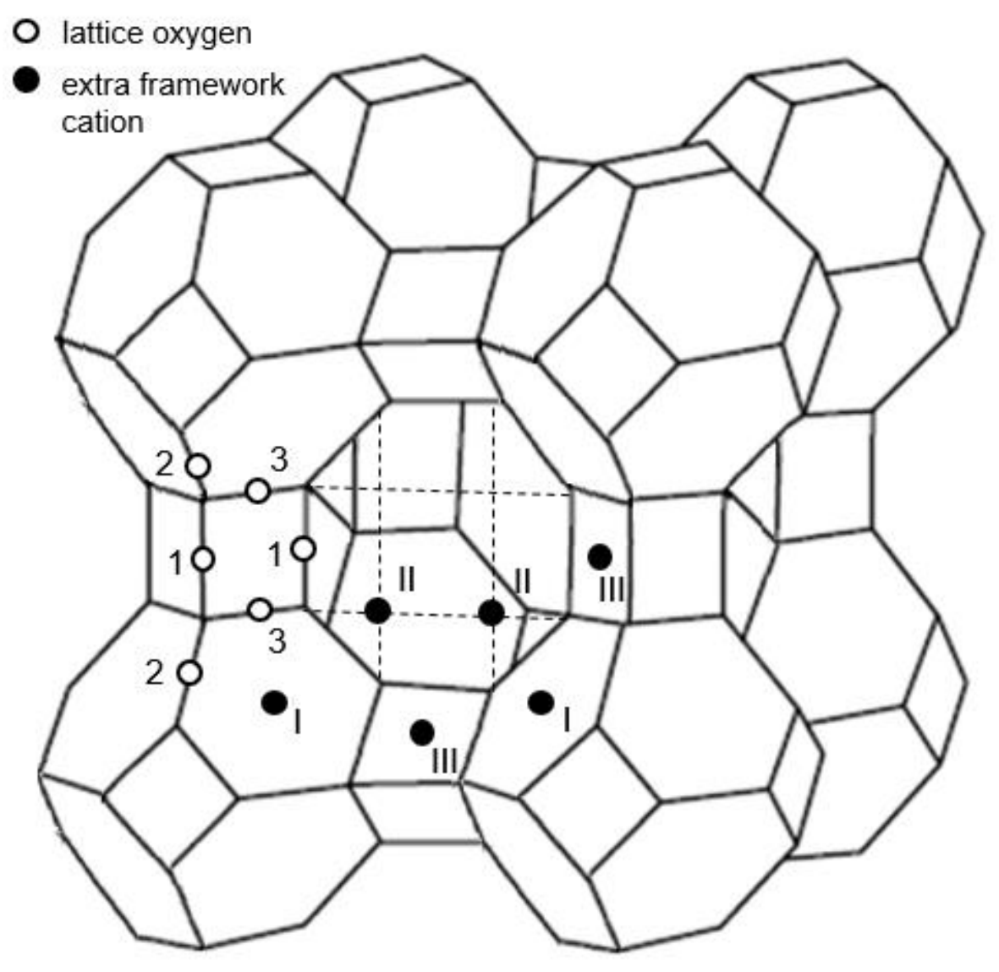


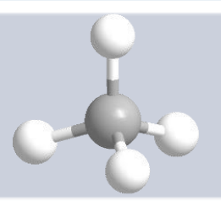
Figure 2: Structure of LTA zeolite

3 preferred cation positions

- Site I: In the α-cage on the surface of the 6-rings
- Site II: In the 8-ring of the α-cage
- Site III: In the α-cage on the surface of the 4-rings

All cation sites are accessible

Table 1: Thermodynamic and structural properties of methane

	Structure	Critical diameter	Dipole moment	Polarizability	Interactions
Methane		0.4 nm	0 D	$2.59 \cdot 10^{-30}$ m³	Induction Dispersion

Results & Discussion

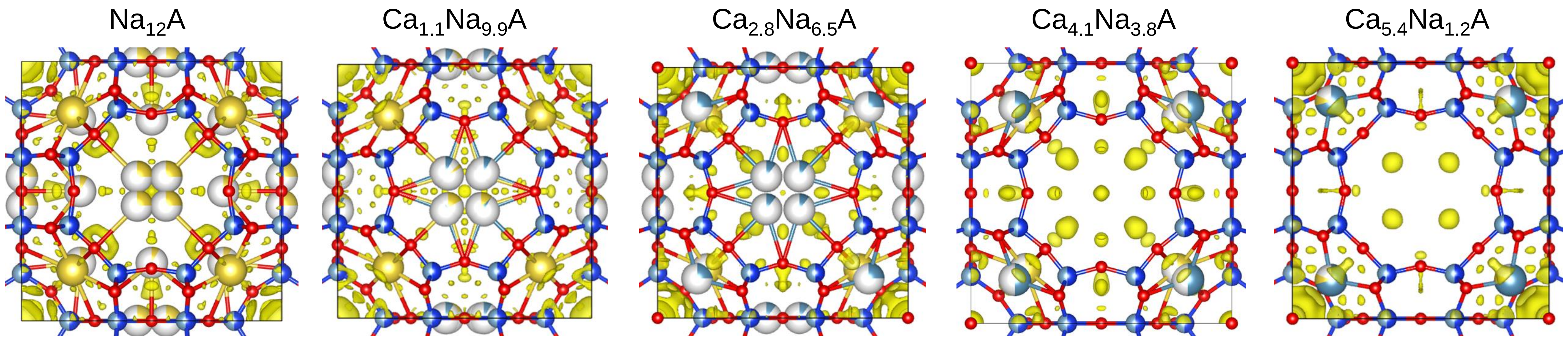


Figure 3: Results of XRD analyses – unit cell of LTA zeolite

blue: Si or Al, red: O, yellow: Na^+, turquoise: Ca^{2+}

Table 2: Calculated cation distribution in CaNaA zeolites

Zeolite	Cation sites						Total number
	Na1	Ca1	Na2	Ca2	Na3	Ca3	
$Na_{12}A$	8	0	3	0	1	0	12
$Ca_{0.5}Na_{11.0}A$	8	0	2.5	0.5	0.5	0	11.5
$Ca_{1.1}Na_{9.9}A$	8	0	2	1	0	0	11
$Ca_{2.1}Na_{7.7}A$	8	0.5	0	1.5	0	0	10
$Ca_{2.8}Na_{6.5}A$	6	2	0	1	0	0	9
$Ca_{4.1}Na_{3.8}A$	4	4	0	0	0	0	8
$Ca_{5.4}Na_{1.2}A$	1	5.5	0	0	0	0	6.5

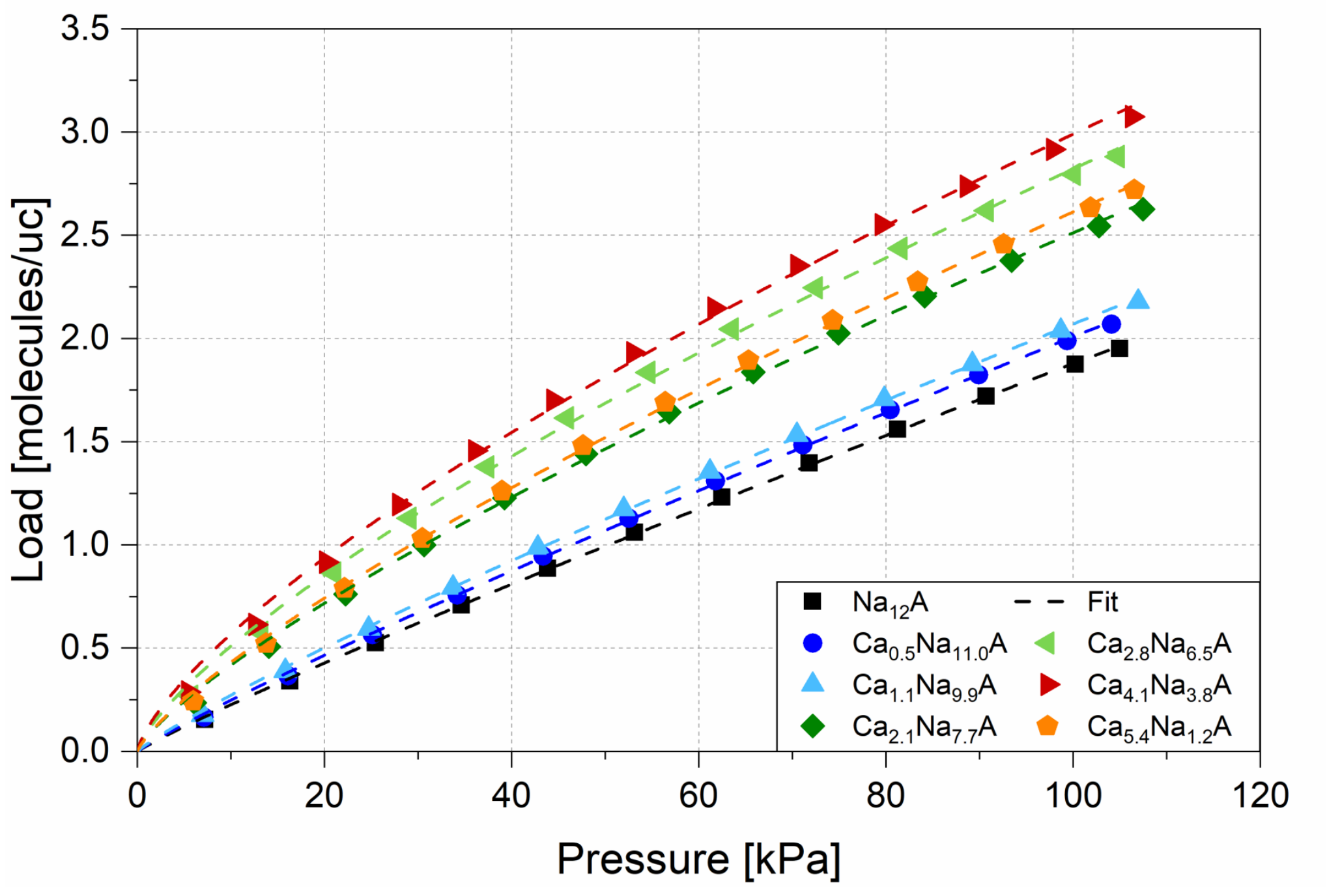


Figure 4: Adsorption isotherms of methane on CaNaA zeolites at 25 °C

- Freundlich isotherm at CaNaA zeolites
- Higher loading and curvature with higher Ca^{2+} content
- Maximium in loading at a exchange rate of 69%

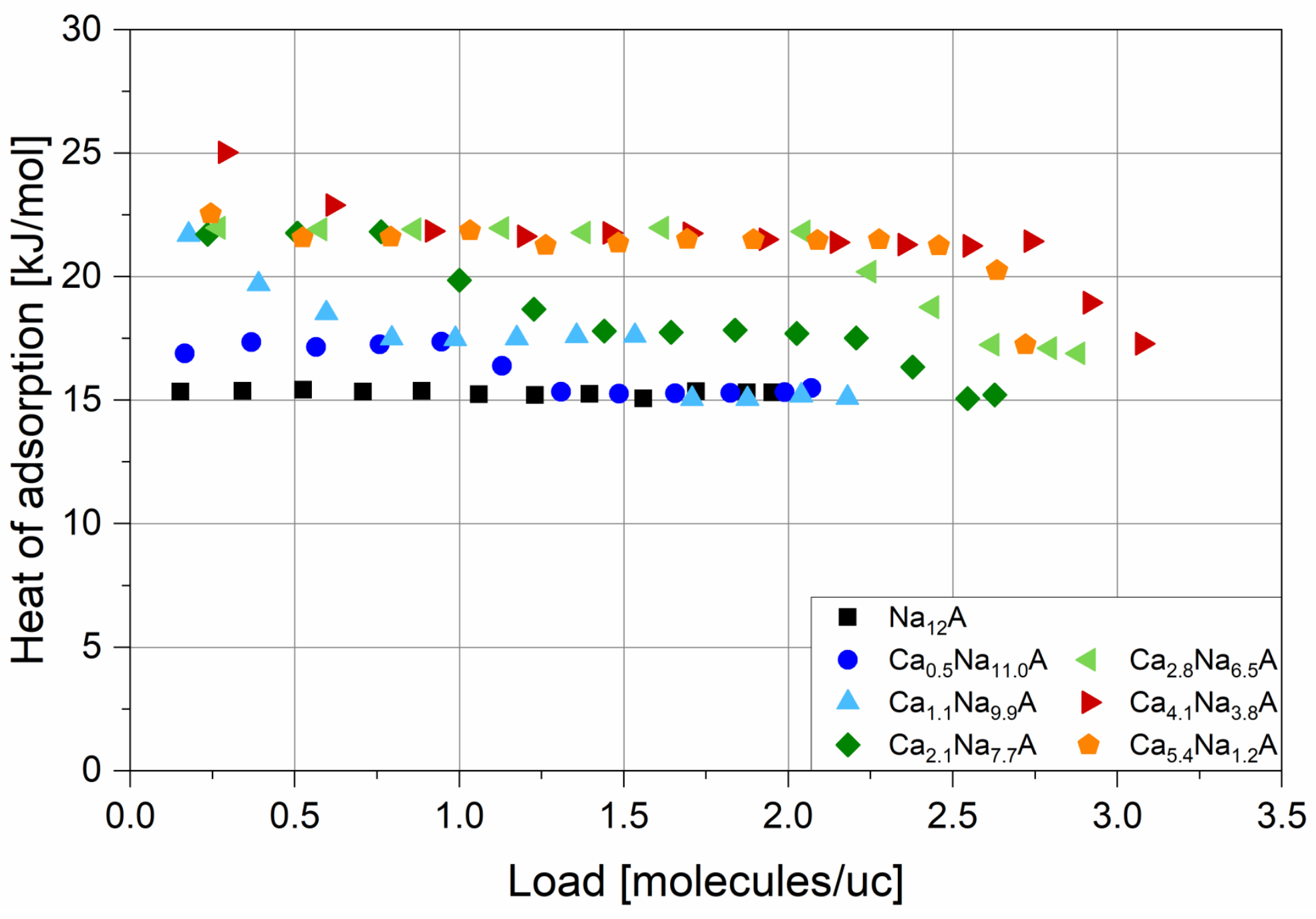


Figure 5: Load-dependent heats of adsorption of methane on CaNaA zeolites at 25 °C

- NaA: Constant heat of adsorption (HoA)
- CaNaA: Increasing HoA with increasing Ca^{2+} content
- Calcium represent energetically higher adsorption sites

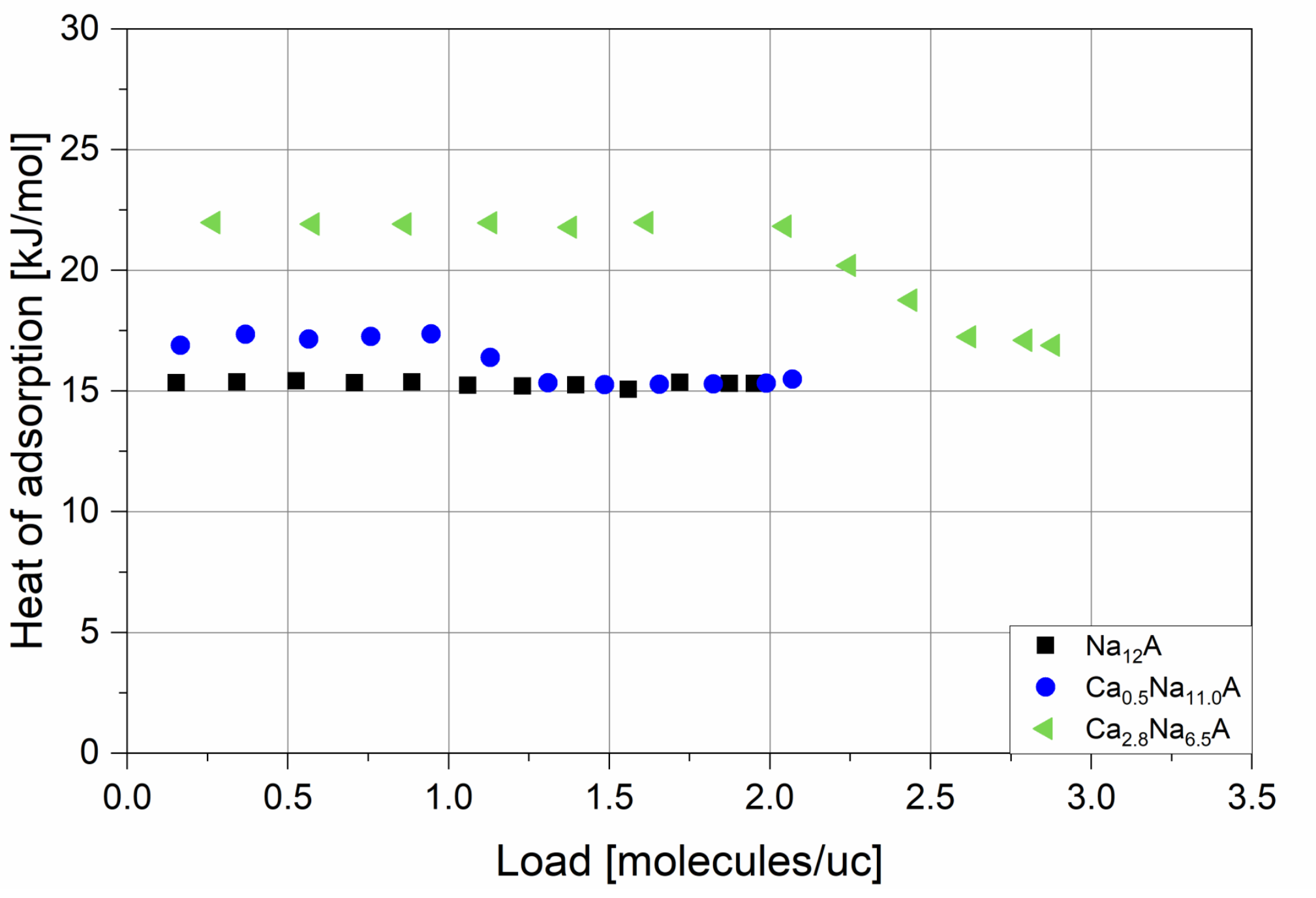


Figure 6: Load-dependent heats of adsorption of methane on selected CaNaA zeolites at 25 °C

- Plateau 15 kJ/mol: Na^+ cations on site I
- Plateau 17.5 kJ/mol: Ca^{2+} cations on site II
- Plateau 22.5 kJ/mol: Ca^{2+} cations on site I

Estimation of energetic contributions

- Thermal induction interaction energy

$$\Phi_{Ind} = -\frac{q^2 \cdot \alpha}{2 \cdot 4\pi\varepsilon_0 \cdot r^4}$$

q = charge, α = polarizability
r = distance of interaction partners

- Assumptions
  - Ca^{2+} has twice the charge of Na^+
  - Polarizability remains constant
  - Ionic radii of Ca^{2+} and Na^+ are similar

- System of equations

$$(1)\quad \Phi_{Ca^{2+}} = 4 \cdot \Phi_{Na^+}$$
$$(2)\quad \Phi_{Na^+,I} + \Phi_{FW} = 15\ \mathrm{kJ/mol}$$
$$(3)\quad \Phi_{Ca^{2+},I} + \Phi_{FW} = 22.5\ \mathrm{kJ/mol}$$
$$(4)\quad \Phi_{Ca^{2+},II} + \Phi_{FW} = 17.5\ \mathrm{kJ/mol}$$

Table 3: Energetic contributions of adsorption sites

Energetic contribution	kJ/mol
Zeolite framework	≈ 12.5
Na^+ on site I	≈ 2.5
Ca^{2+} on site I	≈ 10.0
Ca^{2+} on site II	≈ 5.0

Summary & Outlook

For the energetic characterization of zeolites, adsorption isotherms and heats of adsorption were measured simultaneously. Additionally, XRD analyses were performed. The results on differently modified zeolites show significant differences in the loadings and heats of adsorption depending on the type and number of cations. For example, three different heat plateaus can be determined for the adsorption of methane on zeolite $Ca_{2.8}Na_{6.5}A$. These indicate interactions with different cation sites. The XRD analyses show that Ca^{2+} cations occupy cation site II ahead of site I. A combination of XRD results and heats of adsorption allows an estimation of the energetic contributions. It was found that the zeolite framework provides the largest energetic contribution. In future work, the influence of divalent cations, e.g. Mg^{2+} or Ba^{2+}, on adsorption will be further investigated.

Acknowledgements

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Weil die Chemie stimmt.