UNIVERSITY OF PARDUBICE

FACULTY OF CHEMICAL TECHNOLOGY

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Adsorptive Separation of Small Molecules on Zeolitic Materials

Theses of the Doctoral Dissertation

Pardubice 2025

Study program: **Physical Chemistry**
Study field: **Physical Chemistry**

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Year of the defense: **2025**

References

HALAMEK, Jakub. *Adsorptive Separation of Small Molecules on Zeolitic Materials*. Pardubice 2025. 71 pages + attachments. Dissertation thesis (Ph.D.). University of Pardubice, Faculty of Chemical Technology, Department of Physical Chemistry, Supervisor prof. Ing. Roman Bulánek, Ph.D.

Abstract

This doctoral thesis investigates various phenomena influencing the capacity of zeolite structures to perform the adsorptive separation of CO_2/CH_4 and light hydrocarbon (C_2 – C_4) mixtures, two of the most important contemporary research problems in the development of adsorptive separation processes. A large variety of zeolite materials is investigated within the scope of this thesis - particularly those possessing the chabazite (**CHA)** and Linde type-A (**LTA**) framework, as well as a set of materials recently synthesized by the so-called ADOR process from the **UTL** and **UOV** precursors. More specifically, this doctoral thesis aims to gain deeper insights into the influence of the chemical composition of the zeolite framework, the nature and quantity of the charge-compensating extra-framework cations, and the zeolite framework topology (influencing the pore size and shape), on the adsorption of CO_2 and light hydrocarbons in well selected zeolite systems, as well as to explain hitherto unexplained adsorption phenomena, observed in some specific zeolites, related to the presence of structural imperfections in the zeolite structure. The presented research was carried out using a combination of quantitative experiments, performed on volumetric and gravimetric devices, designed to investigate both the adsorption equilibria and kinetics, coupled with advanced characterization methods (adsorption microcalorimetry, in-situ FTIR employing probe molecules, MAS NMR, PXRD) and computational methods (performed by the collaborators - Dr. Ota Bludský et al.).

Keywords

zeolite, adsorption, separation, carbon dioxide, hydrocarbon, extra-framework cation

Anotace

Tato disertační práce se zabývá různými jevy ovlivňujícími schopnost zeolitových struktur provádět adsorpční separaci směsí CO_2/CH_4 a lehkých uhlovodíků (C_2 – C_4), v současnosti jedny z dvou nejdůležitějších výzkumných problémů v oblasti vývoje adsorpčních separačních procesů. V rámci této práce je zkoumána široká škála zeolitových materiálů – zejména materiály na bázi chabazitové (**CHA**) a **LTA** mřížky, a také soubor materiálů nedávno syntetizovaných tzv. ADOR procesem z **UTL**, resp. **UOV** prekurzorů. Konkrétním cílem této disertační práce je získání hlubšího vhledu do vlivu chemického složení zeolitové mřížky, charakteru a množství mimomřížkových kationtů a topologie mřížky (ovlivňující velikost a tvar pórů) na adsorpci CO_2 a lehkých uhlovodíků ve specificky vybraných zeolitových systémech, a dále vysvětlit dosud neobjasněné adsorpční chování některých specifických systémů, související s přítomností strukturních nedokonalostí ve struktuře zeolitu. Prezentovaný výzkum byl proveden na základě kombinace kvantitativních experimentů, prováděných na volumetrických a gravimetrických aparaturách, určených ke zkoumání adsorpčních rovnováh i kinetiky, ve spojení s pokročilými charakterizačními metodami (adsorpční mikrokalorimetrie, in-situ FTIR s využitím zkušebních molekul, MAS NMR, PXRD) a výpočetními metodami (provedenými spolupracovníky – Dr. Otou Bludským a kol.).

Klíčová slova

zeolit, adsorpce, separace, oxid uhličitý, uhlovodík, mimomřížkový kationt

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1. Introduction

Gas separation processes are of paramount importance across numerous industrial sectors, encompassing applications from air purification and natural gas processing to the isolation of critical components from flue gases and hydrocarbon mixtures. Traditionally, these separations have relied heavily on energy-intensive methods such as fractional distillation and gas absorption (scrubbing). Distillation often necessitates high pressures and extremely low temperatures, particularly for gases with similar boiling points, leading to significant energy consumption and high operational costs. Similarly, gas absorption processes, frequently employed for acid gas removal like CO_2 or H_2S, involve energy-intensive regeneration cycles, often relying on hazardous amine absorbents. The substantial environmental and economic burdens associated with these conventional techniques highlight an urgent need for more sustainable and cost-effective alternatives.

In this context, adsorptive separations have emerged as a highly promising alternative, offering distinct advantages over traditional methods. Adsorption processes leverage materials with high specific surface areas, known as adsorbents, which selectively interact with different components of a gas mixture. Unlike distillation or absorption, these processes can often operate at ambient temperatures, and their regeneration, typically achieved via pressure swing adsorption (PSA), vacuum swing adsorption (VSA), or temperature swing adsorption (TSA), generally requires significantly less energy than for example gas absorption procedures in liquid solvents as it avoids the heating of large quantities of liquid water. This reduction in energy demand translates directly into lower operational costs and a smaller carbon footprint, aligning with global efforts towards energy efficiency and environmental sustainability.

The efficiency and selectivity of adsorption-based separations are critically dependent on the tailored properties of the adsorbent materials. Recent advancements in materials science have driven an intense focus on developing novel adsorbents capable of addressing some of the most challenging contemporary separation problems. Two particularly critical areas of research are the selective adsorption of CO_2 (for carbon capture and purification of industrial gas streams) and the separation of light hydrocarbon mixtures (e.g., olefin/paraffin separations - which are notoriously difficult and costly to achieve via conventional means due to the similar physical properties of the components). The last decades have seen an enormous body of scientific literature on zeolites as adsorbents, with a particularly intense focus on these two application areas, as evidenced by numerous recent review papers[1-6].

Historically, research efforts have concentrated on readily available, low-silica zeolites with, e.g., **FAU**, **LTA**, or ***BEA** frameworks, or higher silica **MFI** materials. However, recent breakthroughs in zeolite synthesis, including the development of the ADOR (Assembly-Disassembly-Organization-Reassembly) process, have expanded the repertoire of available zeolitic materials with unprecedented control over their morphology, chemical composition, and framework topology[7-11]. This new generation of zeolites offers exciting opportunities to engineer adsorbents with enhanced selectivity and lower regeneration costs. For instance, while cation-rich low-silica zeolites perform well in CO_2 adsorption, their high polarity often leads to undesirable moisture uptake and high regeneration costs. Consequently, current research is shifting towards lower-polarity zeolites that facilitate regeneration while maintaining high CO_2 selectivity[5]. Similarly, the separation of nonpolar hydrocarbons presents challenges for traditional low-silica zeolites, but these can be overcome by utilizing small-pore, electroneutral frameworks that enable kinetics-driven separations, offering high selectivity and reduced interaction with polar impurities like CO_2 and H_2O[7, 12-15]. This thesis contextualizes its research within these contemporary challenges, exploring how various characteristics of zeolitic materials can be precisely tuned to achieve efficient and selective gas separations.

2. Aims of the thesis

This doctoral thesis is occupied with the two research problems mentioned in the introduction, namely the selective adsorption of CO_2 and the separation of light hydrocarbon mixtures. Within the scope of this thesis, a number of phenomena important for these two fundamental research problems were investigated. The main research aims can be summarized as follows:

1) **Investigation of the influence of different types of hetero-atoms present in the framework of CHA zeolites on the CO_2 and CH_4 adsorption.** Since the vast majority of employed zeolites are aluminosilicates, materials characterized by frameworks composed of different T-atoms haven't generally been previously investigated with respect to the CO_2/CH_4 adsorption. Considering that the **CHA** framework can be synthesized with various types of T-atoms in its framework[16], it was selected as an appropriate system for the study of the direct influence of the framework chemical composition on the CO_2/CH_4 adsorption. In this work, the pure-silica Si-**CHA**, as well as hetero-substituted B-**CHA**, Al-**CHA**, and Ga-**CHA** materials, all in the H^+ form, were investigated.

2) **Investigation of the localization (based on their type and quantity) of alkali-metal EF-cations present in the CHA framework and their influence on the CO_2 and CH_4 adsorption in the CHA (and LTA) systems.** While the very cation-rich low-silica zeolites (Si/Al → 1) usually contain the EF-cations in regularly repeating positions, making them thus detectable via PXRD or other crystallographic methods, the less polar medium- or high-silica materials generally don't contain their EF-cations in such highly regular arrangements, making it necessary to employ other approaches to describe their localization in the zeolite pore – a key parameter influencing the nature of the adsorption of gas molecules on the EF-cationic active sites. In this work, the localization of the EF-cations (Li^+, Na^+, K^+) present in the high-silica **CHA** zeolites ($Si/Al > 8.0$), as well as in the low-silica **CHA** ($Si/Al = 2.1$), was investigated. The alkali-exchanged high-silica **CHA**, in addition to the medium-silica **LTA** zeolites ($Si/Al = 4.5$), were furthermore subjected to a very comprehensive investigation of their CO_2 and CH_4 adsorption behavior, which was clearly shown to be strongly influenced both by the quantity, as well as by the type of the EF-cation.

3) **Investigation of the influence of the framework topology (pore size and shape) of electroneutral zeolite frameworks (CHA and materials synthesized by the ADOR process) on the CO_2 and light hydrocarbon adsorption.** Whereas the EF-cations usually have the decisive role in the processes seeking to selectively adsorb CO_2, electroneutral frameworks characterized by their narrow channels can likewise exhibit very selective behavior towards CO_2, brought about by the maximization of the non-specific interactions. An even more pronounced influence of the framework topology on the adsorption can often be observed in the case of various light hydrocarbon molecules, where very minor structural differences in hydrocarbon isomers can lead to massively different mass-transport behavior in the channel system of a zeolite material possessing an electroneutral framework. In this thesis, a set of novel materials synthesized by the so-called ADOR process[9], characterized by different pore-

sizes while retaining a very similar general structure, was employed to study the influence of the framework topology on the CO_2 adsorption. This set of materials (along with the Si-**CHA**) was furthermore tested with respect to the propane/propene adsorption (in the case of Si-**CHA**, all C_1 – C_4 hydrocarbons).

4) **Investigation of the anomalously high selectivity towards propene in the propene/propane separation on the PCR zeolite synthesized by the ADOR process.** One of the materials studied within Aim 3) of this thesis, namely the **PCR** material (characterized by a pair of connected perpendicular 10MR and 8MR channels forming a 2D pore system), was found to exhibit an extraordinarily different adsorption behavior with respect to propene (where a sizeable amount is adsorbed at reasonable rates) and propane (where the adsorption is extremely slow). Furthermore, according to the molecular simulations, no mass-transport blocking was predicted to take place for neither of the two molecules. In this work, a thorough investigation, employing various advanced experimental approaches, was performed on a number of different **PCR** batches in order to elucidate the experimentally observed unexpected behavior of the material.

3. Methodology

The experimental methodology employed for the purpose of achieving the aims defined within the scope of this thesis consists primarily of direct quantitative measurements of both the adsorption equilibria as well as the adsorption kinetics by means of either volumetric or gravimetric methods. Depending on the specific adsorbent-adsorbate system and the research question, these quantitative measurements were further complemented by additional spectroscopic (typically FTIR spectroscopy), microcalorimetric, or diffractometric (powder X-ray diffraction) experiments (in addition to the other conventionally employed characterization methods such as various techniques for the determination of the chemical composition, SEM imaging, and measurements of nitrogen isotherms at 77.3 K for the textural properties characterization).

The **volumetric and gravimetric techniques** are primarily used to obtain the adsorption isotherms – pressure dependencies of adsorbed amount – for given adsorbate-adsorbent systems at isothermal conditions, but they can also be used to collect time-resolved uptake curves for separate doses. In addition, the data from these two methods can also be used to estimate the adsorption heat (in case the experiments are performed at multiple temperatures), or to estimate the adsorption selectivity, without the need to perform co-adsorption experiments. The setups for both techniques function largely on the same principle. In each case, a vacuum line is used that allows the sample to be exposed to a controlled pressure of the adsorptive. For gravimetry, the adsorbed amount at each dose is determined directly by a microbalance, while in the case of volumetry, it is necessary to calculate the adsorbed amount using the recorded values of pressure. The machines used in this work were two commercially available volumetric gas analyzers ASAP 2020 Physisorption by Micromeritics (USA) and a home-made vacuum line connected to a microbalance MK5 by CI Precision (UK). All the apparatuses allowed to measure adsorption in the temperature interval of 273 to 333 K (regulated by Peltier thermostat).

In addition to the devices above, a calorimetric setup was employed for some experiments presented in this thesis. This device was used for the direct determination of adsorption heats at isothermal conditions. The setup for this technique functions essentially on the same principles as the one for volumetry described above, with the exception that the sample tube is not submerged in an isothermal bath, but is instead put inside an isothermally operated calorimeter that is able to detect very small temperature changes occurring due to processes taking place in the sample tube. A BT 2.15 Tian-Calvet-type microcalorimeter by Setaram (France), allowing for measurements at both the room temperature as well as at lower temperatures (with cooling provided by the liquid nitrogen) – all experiments presented in this thesis were performed at isothermal conditions – was used for the determination of the adsorption heats.

The remaining home-made setup used for the experiments presented in this thesis is the in-situ Fourier-transform infrared spectroscopy (FTIR) device. This apparatus is conceptually very similar to the above described calorimetric setup in that it consists of a home-made vacuum-line connected to an advanced signal detector – in this case an FTIR spectrometer operating in the transmission mode (Nicolet 6700 and Nicolet iS50 FTIR spectrometers equipped with MCT/D cryo-detectors by Thermo Scientific were employed in this work). The experiments performed on this setup allow us to directly study the properties (acidity, localization, quantity, etc.) of the O–H bonds present in the material. Both the hydroxyl groups as well as other types of active sites, such as extra-framework cations, can furthermore be studied indirectly with the help of well-chosen probe molecules, such as carbon monoxide or various nitrile or other probes. The experimentally obtained FTIR spectra (as well as the interaction energies as measured by calorimetry) are of key importance when trying to model adsorbate-adsorbent systems by methods of computational chemistry, serving as a bridge between both approaches.

It should be pointed out that all throughout the work on this doctoral thesis, the results were continuously interpreted in a close collaboration with a computational chemistry group of Dr. Ota Bludský from the Institute of Organic Chemistry and Biochemistry (IOCB) of the Czech Academy of Sciences.

4. Results and Discussion

A relatively large body of interesting results was generated in the course of working on this doctoral thesis. The results are broadly classified according to the governing mechanism that drives the adsorption preference of some gas molecules over others, investigated in line with each of the four aims of the thesis, as defined in Section 4 of the main text.

4.1. Preferred adsorption due to framework composition

The first presented study, performed to achieve Aim 1 of the thesis, investigated the influence of the hetero-atom type present in the CHA framework on the adsorption of CO_2 and CH_4. The study was performed on a series of four samples of different framework compositions – a pure-silica material denoted as Si-**CHA**, and three materials containing hetero-atoms, denoted as B-**CHA** (Si/B = unknown), Al-**CHA** (Si/Al = 17), and Ga-**CHA** (Si/Ga = 26) (each possessing charge-compensating H^+ cations).

The adsorption isotherms of CO_2 and CH_4 measured on the samples can be found in Figure 1.

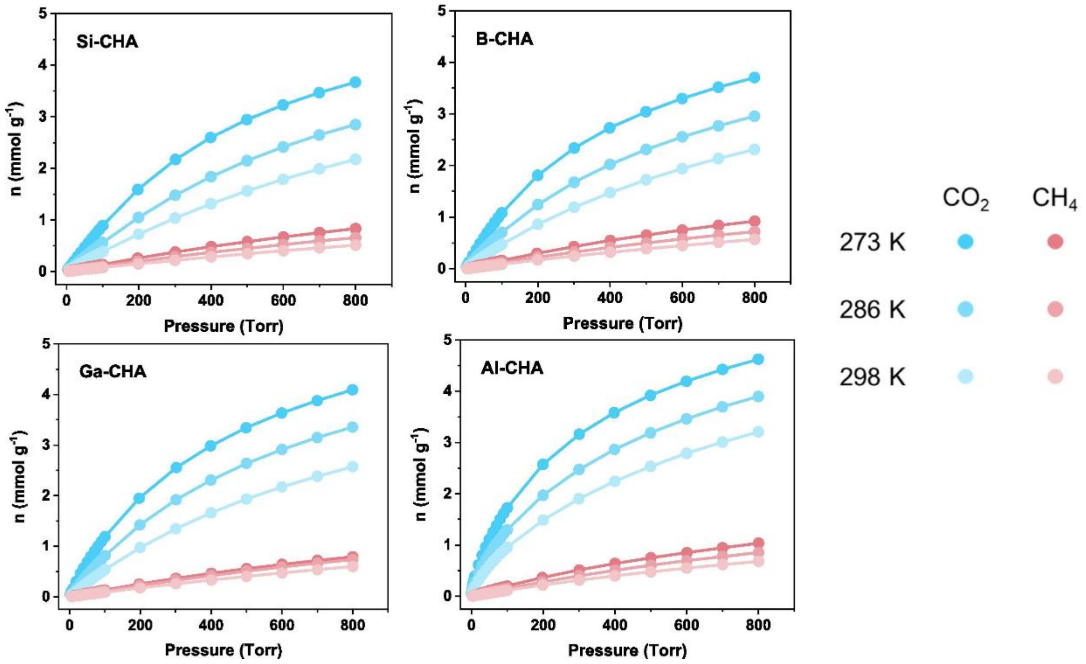

*Figure 1: Single-component adsorption isotherms of CO_2 and CH_4 at 273, 286, and 298 K on M-**CHA** (M = Si, B, Al and Ga).*

For all materials, a clear preference for CO_2 over CH_4 was observed. This preference was due to the comparably stronger interaction of CO_2 with the relatively polar framework of the zeolites due to the large quadrupole moment of CO_2. This preference was furthermore intensified in the case of the Ga-**CHA** and especially Al-**CHA** (as well as possibly in the case of B-**CHA**) due to the presence of EF H^+ cations, which further increased the electric field gradient at the surface of the material, leading to a stronger interaction with the quadrupole moment of the CO_2. These findings were supported by the analysis of the adsorption heats, calculated by the isosteric method from the adsorption data presented in Figure 1, and discussed in light of the information from literature[17, 18].

To gain further insight into the nature of the CO_2 interaction with the samples, in-situ FTIR spectra of adsorbed carbon dioxide (Figure 2) were measured. The spectra revealed three different types of behavior for the CO_2 vibration: Al-**CHA** and Ga-**CHA** samples exhibited bands at 2346 cm^{-1}, while Si−**CHA** showed a weaker band shifted to 2341 cm^{-1}. These frequencies matched those observed previously in the literature, assigned to the interaction of CO_2 with the H^+ cation[19, 20] and to its interaction with the silicate framework[21]. For B-**CHA**, the band appeared to be composed of at least two signals, indicating the presence of weaker acidic sites, likewise previously observed in literature[22].

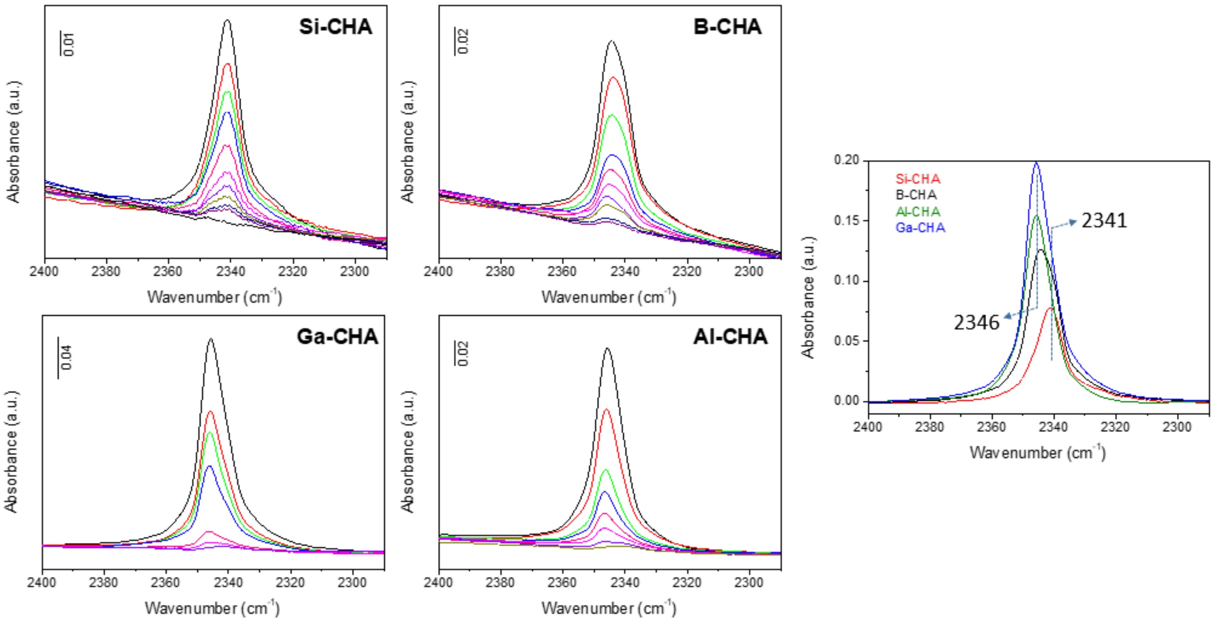

Figure 2: Representative spectra of CO_2 adsorbed on M-CHA (M = Si, B, Al and Ga) as a function of CO_2 pressure (from 0.2 to 8 Torr from bottom to top). Comparison of the adsorbed CO_2 asymmetric stretching vibration (ν_3) at 8 Torr at room temperature on all M-CHA (right)

Furthermore, diffractometric experiments revealed that the introduction of hetero-atoms in the **CHA** framework leads to slight changes in the framework topology, particularly in the entrance window dimensions, which may have also exerted some influence on the CO_2 adsorption, particularly leading to differences between the behavior of Al-**CHA** and Ga-**CHA** materials.

To achieve Aim 2, an extensive investigation of CO_2 and CH_4 adsorption on various Al-**CHA** and Al-**LTA** materials was carried out (Table 1). The study was performed on samples obtained by the ion-exchanges of four **CHA** zeolite matrices (Si/Al = 35.4, 16.3, 9.2, and 8.0) into various alkali-metal forms (Li^+, Na^+, and K^+), as well as on three UZM-9 samples (**LTA** framework with Si/Al = 4.5), likewise exchanged into the three respective alkali-metal cationic forms (Li^+, Na^+, and K^+). The presence of EF-cations leads to increased polarizability, electric field, and electric field gradients on the zeolite surfaces, resulting in stronger interactions with gas molecules. While CH_4 interaction slightly increased due to polarizability effects, CO_2 interaction saw a massive increase primarily due to its large quadrupole moment. This was particularly evident in the increased adsorption heats observed for CO_2 on all the investigated cation-exchanged samples.

Quantification of adsorption performance revealed that for **CHA** (Si/Al = 8 – ∞), uptakes generally grew with increasing EF-cation content. Despite Li^+ showing the strongest interaction with CO_2, Na-exchanged samples often exhibited larger CO_2 uptake, possibly due to better site accessibility. In the **CHA** system, the selectivity of CO_2 over CH_4 increased with growing cation polarity (in the order $K^+ < Na^+ < Li^+$), in line with the simple predictions given by the model of an alkali-metal cation interacting with a single CO_2 molecule.

Table 1: The summary of CO_2 and CH_4 adsorption data on the hetero-substituted and alkali-exchanged ***CHA*** *and* ***LTA*** *materials.*

Sample	n_{CO_2}[a] **(mmol/g)**	n_{CH_4}[a] **(mmol/g)**	S_{CO_2/CH_4}[b] **(-)**	ΔH_{CO_2}[c] **(kJ/mol)**	ΔH_{CH_4}[c] **(kJ/mol)**
Si-**CHA**	2.17	0.51	5.0	24.6 (*)	15.9 (*)
B-**CHA**	2.31	0.57	5.7	26.0 (*)	17.2 (*)
Al-**CHA** (Si/Al = 17)	3.21	0.68	21.3	30.6 (*)	16.9 (*)
Ga-**CHA** (Si/Ga = 26)	2.57	0.60	6.4	28.2 (*)	16.6 (*)
Si-**CHA** (batch 2)	2.40	0.55	4.9	23.9	17.5 (*)
K-**CHA**-35	3.00	0.68	48.1	39.7	–
K-**CHA**-16	2.95	0.71	71.1	41.2	18.7 (*)
K-**CHA**-9	3.73	0.86	89.9	–	19.2 (*)
K-**CHA**-8	3.59	0.94	100.0	45.4	20.5 (*)
Na-**CHA**-16	3.10	0.74	50.6	44.1	21.6 (*)
Na-**CHA**-9	3.95	0.98	95.8	44.3	22.1 (*)
Na-**CHA**-8	3.93	1.04	140.8	47.5	23.0 (*)
Li-**CHA**-16	2.95	0.64	140.6	53.2	–
Li-**CHA**-9	3.88	0.86	222.8	–	–
Li-**CHA**-8	3.93	0.90	241.5	56.0	–
K-**LTA**-4.5	3.63	0.58	188.2	38.0 (*)	17.1 (*)
Na-**LTA**-4.5	3.87	0.46	162.7	34.5 (*)	17.6 (*)
Li-**LTA**-4.5	4.39	0.44	60.8	34.5 (*)	17.2 (*)

[a] – uptake at 800 torr, 298 K measured volumetrically (293 K in the case of **LTA**)

[b] – selectivity at ~zero coverage (5 torr) estimated by IAST for a 1:1 mixture, 298 K (293 K for **LTA**)

[c] – zero coverage adsorption heat measured calorimetrically or by the isosteric method (*)

For the **LTA** systems, comparable CO_2 uptakes were observed (accompanied by lower adsorption heats, implying better CO_2 regenerability), but CH_4 affinity was clearly smaller. This suggested that the **LTA** framework is more appropriate for CO_2/CH_4 separation than the **CHA** framework. Furthermore, in the case of **LTA**, the basic model of a single interacting CO_2 with a cation was found to be inadequate, as the strength of CO_2 interaction increased in an inverted order of $Li^+ < Na^+ < K^+$. This behavior was explained, based on similar results obtained on related materials in the literature, by the presence of either the bridging CO_2 species interacting with two large K^+ cations, or by the creation of arrangements where CO_2 interacts with simultaneously with an exposed K^+ cation and the adjacent basic oxygens of the framework[23-25].

To understand EF-cation localization in the **CHA** system, CO was used as a probe molecule in calorimetric and in-situ FTIR experiments, interpreted with molecular simulations, performed at IOCB. The investigations revealed clearly localized cationic sites in **CHA** materials with Si/Al ratios up to ~8, with Li^+ and Na^+ preferring the position above the D6R (SII), and K^+ predominantly favoring the position in the middle of the 8MR (SIII'), confirming previous findings[26-28]. These localization preferences were not absolute and changed with increasing cation content. The CO probe generally formed mono-carbonyl or di-carbonyl complexes, with bridging carbonyls observed for the K-exchanged materials. Further investigation of low-silica **CHA** systems (K-**CHA**-2 and Na-**CHA**-2, Si/Al = 2.1) revealed a clearly different behavior from the high-silica materials. The CO adsorption experiments (at 77.3 K) revealed that for K-**CHA**-2, CO adsorption was significantly hindered, unlike Na-CHA-2, which adsorbed CO quickly. Computational results indicated that the behavior exhibited by K-**CHA**-2 was due to a gate effect, with ~90% of the characteristic **CHA** cages being completely closed off by K^+ cations, explaining the observed obstruction.

4.2. Preferred adsorption due to framework topology

Aim 3 of this thesis focused on the influence of framework topology on adsorption. Electroneutral zeolite frameworks, such as pure-silica or aluminophosphate variants with appropriate pore sizes (typically 8MR pore entrances), can be exploited for highly selective kinetically-driven adsorptive separations of light hydrocarbons[12-15]. This mechanism is advantageous because the lack of strong active sites reduces undesired chemical reactions and prevents adsorbent coking or poisoning, a common problem in hydrocarbon adsorption applications. Furthermore, the weaker electric field of the silicate framework leads to weaker interactions with impurities, commonly present in the hydrocarbon mixtures, such as water, NO_x, H_2S, or CO_2, reducing poisoning.

The light hydrocarbon (C_1 – C_4) adsorption/diffusion was extensively investigated on the Si-**CHA** material. Normalized hydrocarbon uptake curves on the Si-**CHA** sample, measured by both quantitative the volumetric and gravimetric methods, are shown in Figure 3.

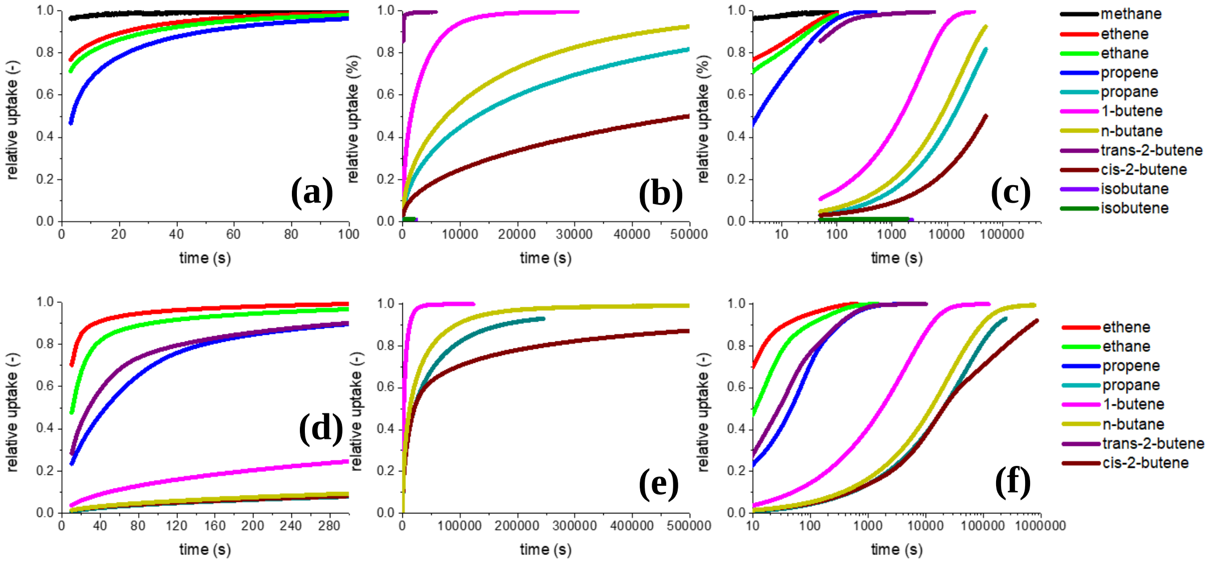

*Figure 3: The hydrocarbon uptake curves on the Si-**CHA** measured by volumetry (a-c), and by gravimetry (d-f).*

Large differences in uptake rates were observed: methane adsorbed within seconds, while ethane and ethene required hundreds of seconds. Particularly large uptake-rate differences were observed for propene and propane and for trans-2-butene and cis-2-butene respectively, confirming previous findings[13, 29]. Generally, the diffusion blocking of C_3 and C_4 hydrocarbons increased in the order: trans-2-butene ~ propene < 1-butene < n-butane < propane < cis-2-butene << isobutene ~ isobutane. Despite quantitative differences in the diffusion coefficient determination, the relative order of increasing diffusion restrictions was qualitatively in perfect agreement with the computational predictions performed by the collaborators from IOCB.

To investigate the influence of pore size on CO_2 adsorption, two germanosilicate materials (**UTL** and **UOV**) and their ADOR-derived pure-silica daughter-structures were tested. At low pressures, a clear inverse correlation between adsorption isotherm steepness and pore size was observed, particularly for the **UTL** family materials. The isosteric adsorption heats (Figure 4) also clearly correlated with the pore size – whereas the largest-pore **UTL** exhibited a zero-coverage heat of about 23.5 kJ/mol, the smaller-pore materials showed higher values, with the smallest pore IPC-9 reaching up to 32.8 kJ/mol. While for the materials of the **UTL**-family, the CO_2 adsorption heats remained largely constant with changing uptakes – demonstrating the energetically homogenous nature of their channel systems vis-à-vis CO_2 – clear changes in CO_2 adsorption heat upon increasing uptakes were observed for IPC-12 and its precursor **UOV**. This energetical heterogeneity of the pore system of the **UOV**-family materials with respect to CO_2 indicated a presence of a number of active sites exhibiting clearly different affinities for the CO_2 adsorbate

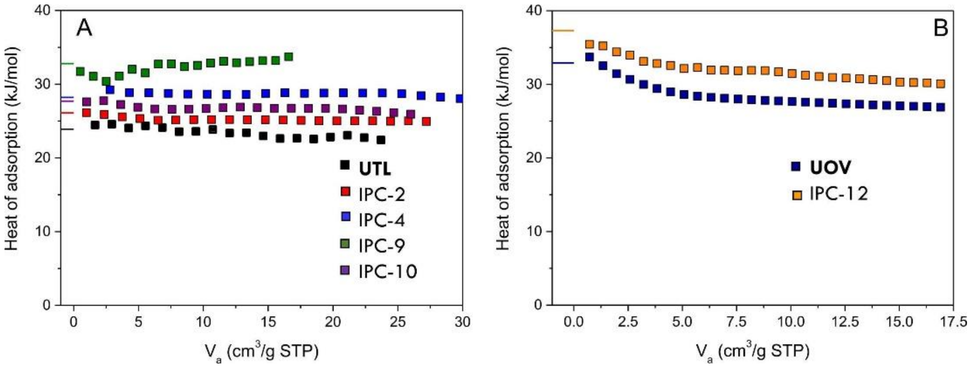

Figure 4: Isosteric heats of adsorption of CO_2 on the ADOR zeolites.

To elucidate the experimentally observed behavior, computational investigation was again performed by the collaborators at IOCB (DFT/CC simulations at 300 K). The obtained results were generally in good agreement with the experimental observations – for the **UTL**-family materials, computations systematically predicted an increase in interaction energy as pore size decreased.

The exceptional affinity of the IPC-12 material towards CO_2 was attributed to a specific structural motif (Figure 5) consisting of two elongated 8-membered rings, coupled to form an elliptically-shaped cage of ideal shape and dimensions for encapsulating a CO_2 molecule (with predicted interaction energy over 40 kJ/mol). This motif was found to incorporate previously predicted structural features which favor CO_2 adsorption[30].

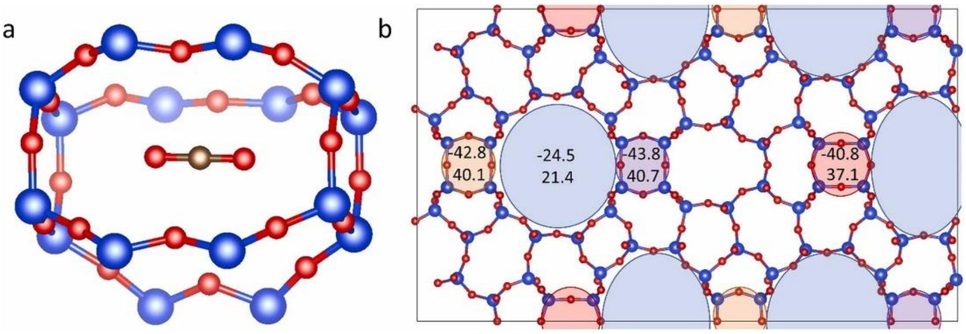

Figure 5: The CO_2 binding in IPC-12. (a) the binding motif, (b) the lowest interaction energy (negative) and the overall adsorption heat (positive) for a given space in IPC-12. Data from the 10 000 structures for which the DFT/CC energy is available (color code: Si blue, O red, C brown).

4.3. Preferred adsorption due to defects and impurities

Initial screening of propane and propene adsorption on **UTL**-family materials (Figure 6) revealed that **PCR** (IPC-4) exhibited nearly zero adsorption of propane across the studied pressure range, completely overshadowing the performance of other **UTL-family** materials (whose selectivity for the propene/propane system was, nonetheless, clearly dependent on to their pore size). The extraordinary performance of the **PCR** framework was very similar the performance of several previously studied zeolite frameworks, such as the previously studied **CHA (**Figure 3, as well as the ref[13, 29]) **DDR**[12, 13], **ITE**[13], **IHW**[14], and **RRO**[31].

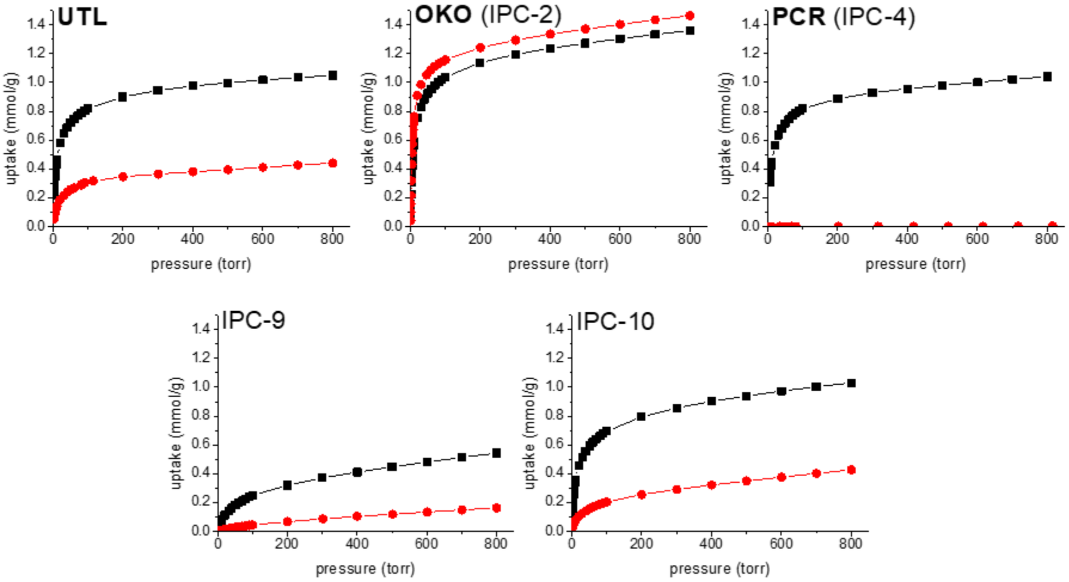

*Figure 6: The adsorption isotherms of propane (red) and propene (black) on the **UTL**-family ADOR zeolites (measured at 303 K)*

This experimentally observed absolute selectivity implied that both the 10MR and 8MR channels of the **PCR** framework must've been inaccessible to propane, while at least one type of channels remained accessible to propene. Initial computational investigations (performed by the collaborators from IOCB) revealed, however, that the **PCR** channel system should clearly be accessible to both of these hydrocarbon molecules. The Aim 4 of the presented thesis investigated this unexpectedly high selectivity towards propene in propene/propane separation on this zeolite framework.

To verify reproducibility, four additional **PCR** batches (**PCR**-1, 2, 3, 4; the original being **PCR**-0) were acquired and tested (Figure 7). While all four batches showed clear selectivity towards propene, significant differences were observed in both propene, as well as propane uptakes, with one of the batches (**PCR**-4) actually adsorbing a sizeable quantity of propane, while none of the other new batches exhibited the nearly total exclusion of propane seen in the initially studied batch. Gravimetric measurements on the best performing of the new batches (**PCR**-3) (Figure 7b) revealed a propene-to-propane diffusion coefficient ratio of about 730.

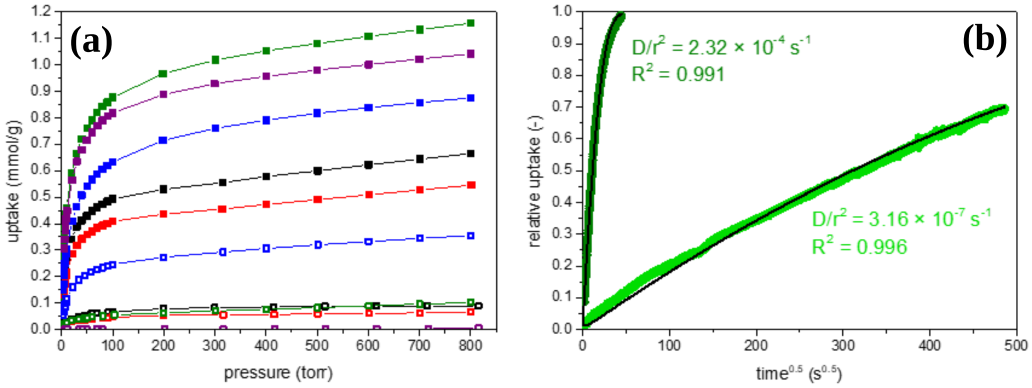

Figure 7: (a) The adsorption isotherms of propene (■) and propane (□) at 303 K on ***PCR****-0 (purple),* ***PCR****-1 (black),* ***PCR****-2 (red),* ***PCR****-3 (green) and* ***PCR****-4 (blue), (b) The propene (dark) and propane (light) uptake curves (at 303 K) on* ***PCR****-3.*

Molecular simulations (performed by the collaborators at IOCB) investigated three possible modes of transport for propene and propane – from the main channel into the side channel (m→s), from the side channel into the main channel (s→m), and along the main channel (m→m). It was found that the narrower 8MR windows should considerably hinder the transport of both hydrocarbons, with a diffusivity ratio of approximately 140 and 1200 for m→s and s→m modes of transport respectively. The simulations, however, predicted unrestricted transport along the main 10MR channel (m→m), clearly contradicting the experimental results. This difference in the experimental and computational results led to the hypothesis that the main 10MR channels had to feature regular mass-transport hindrances, forcing the adsorbing hydrocarbon molecules to diffuse through the smaller 8MR channels.

Such a mechanism could explain the observed adsorption behavior, as the 2-dimensional nature of the **PCR** channel system, combined with a unique morphology (the **PCR** forms large flat crystals with pore openings exclusively in their very narrow edges) would allow even a small number of blocking species to be sufficient to make the diffusion through the 8MR windows the rate-determining step. This hypothesis was further supported by the very close agreement between the experimentally obtained diffusion coefficients’ ratio (730) and the computationally obtained values for the transport involving the smaller 8MR channels (140 and 1200, for the m→s and s→m modes of transport respectively).

It was hypothesized that these kinetic restrictions are due to the presence of foreign species and/or impurities in the pores, either intercalated during synthesis or bound to numerous defect sites (the specific nature of these species remains unknown). The high concentration of defects was evidenced by the large quantities of silanol groups in the **PCR** materials, as demonstrated by in-situ FTIR spectra (Figure 8a).

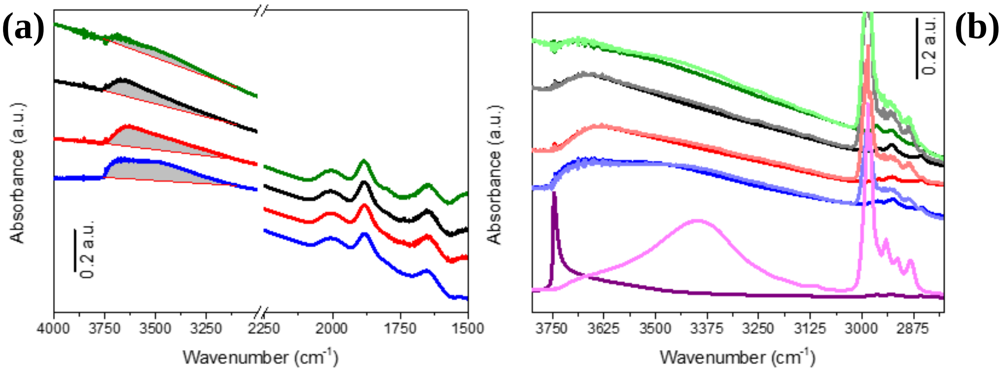

Figure 8: In-situ FTIR spectra of the evacuated (dark color) samples (a) and of the samples exposed to 6 torr of pivalonitrile (light color) for >15 minutes (b). The ***PCR*** *spectra were normalized to the same Si-O overtone intensity.* ***PCR****-1 = black,* ***PCR****-2 = red,* ***PCR****-3 = green,* ***PCR****-4 = blue and the SBA-15 standard = purple.*

The localization of the vast majority of the silanol species inside the micropores was furthermore demonstrated by the in-site FTIR experiments employing the bulky pivalonitrile probe (Figure 8b), able to only interact with the silanols present on the external surface of the zeolite, and by ^{1}H spin-echo solid-state MAS NMR experiments, employing a shift reagent d^{27}-[Eu(fod)$_3$].

5. Conclusions

Adsorptive separation employing zeolite adsorbents is an increasingly important method in a wide range of chemical, petroleum, and other large-scale industrial processes – particularly due to its capacity to replace the highly energy-intensive state-of-the-art distillation-based methods. As of now, a wider application of adsorption-based processes is limited by, among other things, the insufficient performance of established adsorbents, as well as by the lack of sufficiently deep understanding of the underlying mechanism on the molecular scale. The implementation of more affordable capture and separation methods is particularly demanded in the field of CO_2 adsorption (due to the necessity to perform carbon capture, as well as the processing of various industrial gas mixtures containing other small molecules, such as CH_4, N_2, or CO) and in the field of hydrocarbon separation (particularly due to the exceedingly high costs of performing the fractionation of the olefin/paraffin mixtures).

This doctoral thesis set out to explore four specific research questions related to the successful application of zeolitic adsorbents (particularly of the **CHA** and **LTA** frameworks, as well as the hitherto uninvestigated materials synthesized by the recently developed ADOR procedure) in these two broad fields. These research questions included the investigation of the following phenomena: 1) the influence of different types of hetero-atoms on the CO_2/CH_4 adsorption on acidic **CHA** zeolites, 2) the localization of alkali-metal extra-framework cations and their influence on the CO_2/CH_4 adsorption on **CHA** and **LTA** zeolites, 3) the influence of the framework topology on both the CO_2, as well as light hydrocarbon adsorption on the **CHA** and ADOR-synthesized zeolites, and finally, 4) the anomalously high selectivity of one of the ADOR-synthesized materials – **PCR** – for propene/propane separation.

The results obtained for each of the four research questions can be summarized as follows:

1) A clear influence of the heteroatom type (none, B, Al, Ga), present in the **CHA** framework, on the CO_2 and CH_4 adsorption was observed. The affinity of the materials towards CH_4 remained very similar, whereas their affinity towards CO_2 clearly increased in the order of Si-**CHA** < B-**CHA** < Ga-**CHA** < Al-**CHA**, as evidenced both by the adsorbed amounts, as well as the values of the CO_2 interaction energy, which nonetheless increased only modestly – making Al-**CHA** the best performing material. These changes in affinity were primarily ascribed to the changes in the acidity of the active sites present in the respective materials, although they may have also been connected to changes in the framework geometry (as evidenced by the PXRD experiments).

2) Clearly different localization preferences inside the **CHA** pore system were observed for each of the three alkali-metal cations (Li^+, Na^+, K^+), particularly with changing Si/Al. While the higher-silica frameworks (Si/Al > 8) exhibit the previously reported preferences (Li^+, Na^+ prefer the 6MR, K^+ prefers the 8MR pore entrance), the frameworks with Si/Al ≈ 2 exhibit significantly altered site occupancies (e.g., large occupancy of the 8MR pore entrance even by the Na^+ cations), resulting in observable influence on the CO diffusion into the channel system. The comprehensive investigation of CO_2/CH_4 adsorption on the high/medium-silica **CHA** and **LTA** (Si/Al = 4.5) revealed a complex influence

of the cation type on the adsorbent performance, manifesting itself differently for both the **CHA** and **LTA** frameworks. Of the studied materials, the **LTA** frameworks exhibited the best CO_2/CH_4 separation performance (identification which cationic form is optimal would require tests under real industrial conditions).

3) Both the pore size, as well as the pore shape, were identified as key factors influencing the CO_2 adsorption on the electroneutral frameworks derived from the **UTL** and **UOV** precursors by the ADOR process. Smaller channel width was found to generally result in a stronger CO_2 adsorption, albeit the CO_2 wasn't always necessarily located in the most confined parts of the channel system. The **UOV**-derived IPC-12 material was found to exhibit an exceptional affinity towards CO_2 due to the presence of characteristic structural motifs capable of strongly encapsulating the CO_2 molecules. The **UTL**-derived materials, furthermore, exhibited various capacity to adsorb propane and propene – the propene/propane selectivity increased as the pore size decreased, with the small pore PCR material capable of clearly the largest separation effect.

4) Repeated propene/propane adsorption experiments on additional **PCR** batches revealed that the observed effect was only partially reproducible – each batch was found to be clearly selective towards propene, but to differing extents. Computational investigation was further found to be unable to predict the observed behavior. A possible interpretation, which would explain the experimental observations in light of the computational results, was developed – assuming the presence of obstructing impurities in the **PCR** channels, rendering the diffusion through the smaller 8MR pores the rate-determining step. The likely presence of these foreign species was indirectly demonstrated by the use of advanced in-situ FTIR and MAS NMR experiments.

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7. List of Published Works

I) Qiudi Yue, Jakub Halamek, Daniel N. Rainer, Jin Zhang, Roman Bulánek, Russell E. Morris, Jiří Čejka, Maksym Opanasenko. Tuning the CHA framework composition by isomorphous substitution for CO_2/CH_4 separation. Chemical Engineering Journal, 429, 2022, 131277. DOI: 10.1016/j.cej.2021.131277. IF = 13.2, Q1 (WOS).

II) Michal Trachta, Tomáš Volný, Roman Bulánek, Eva Koudelková, Jakub Halamek, Miroslav Rubeš, Mariya Shamzhy, Michal Mazur, Jiří Čejka, Ota Bludský. Strong CO_2 adsorption in narrow-pore ADOR zeolites: A combined experimental and computational study on IPC-12 and related structures. Journal of CO_2 Utilization, 74, 2023, 102548. DOI: 10.1016/j.jcou.2023.102548. IF = 8.4, Q1 (WOS).

III) Jakub Halamek, Roman Bulánek, Miroslav Rubeš, Ota Bludský. Properties of multiple Lewis acid sites in alkali metal-exchanged chabazites probed by CO adsorption. Microporous and Mesoporous Materials, 374, 2024, 113152. DOI: 10.1016/j.micromeso.2024.113152. IF = 4.7, Q2 (WOS).

IV) Jakub Halamek, Martin Kubů, Branislav Koreň, Jiří Čejka, Jan Valenta, Roman Bulánek. Selective CO_2 adsorption over alkali metal cation-exchanged UZM-9 zeolites. Submitted manuscript (Journal of CO_2 Utilization).

V) Jakub Halamek, Tomáš Volný, Roman Bulánek, Jan Blahut, Jiří Čejka, Pavla Eliášová, Maksym Opanasenko, Ota Bludský. Defect-controlled adsorptive separation of propane and propene on the PCR zeolite synthesized by the ADOR process. Finalized manuscript.