Adsorption and separation of the C3 hydrocarbons on cationic FER zeolites: effect of dual sites existence

Eva Koudelková, Yosra Ghrib, Francisca Solanea de Oliveira Ramos, Pavel Čičmanec, Roman Bulánek*

Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic *Corresponding author, e-mail: roman.bulánek@upce.cz

Abstract

Adsorption and co-adsorption of propane and propene were investigated by combination of calorimetric-volumetric measurements with breakthrough experiments on alkali metal exchanged (Li, Na-, K-) **FER** zeolites with different Si/Al ratio. Effect of cation type and their concentration in the zeolite on adsorption selectivity was evaluated and discussed. Based on determined adsorption heats at zero coverage limit, the bridged complexes of propene were confirmed only in the case of K-**FER** zeolites. Presence of bridged complexes between two nearby K^+ cations in dual cationic sites, described in details previously (Rubes et al. J. Phys. Chem. C 122 (2018) 6128), results in significant increase in adsorption selectivity while adsorption capacity of the zeolite is not influenced and is comparable with other M-**FER** zeolites. On the other hand, Na-**FER** zeolites exhibited the lowest propene/propane selectivity (at least six-times lower than K-**FER**-8.6 zeolite).

Keywords

zeolite, bridged complexes, IAST selectivity, propane, propene,

Introduction

Zeolites play important role in industry as catalysts, adsorbents and ion exchangers.[1-5] Extra-framework cations compensating the negative charge of the zeolite framework have unsaturated coordination sphere and they act as specific adsorption sites, whose properties are controlled by location within the zeolite channels and cavities and their coordination to the framework oxygen atoms. Adsorption performance of the zeolites was usually interpreted on the basis of the idea of extra-framework cations as specific and isolated adsorption centers. However, combined experimental and theoretical studies carried out in past decade showed that even small molecules such as CO [6-16] or CO_2 [17-20] could interact with more than only one extra-framework cation due to existence of confined space in zeolite channels and cavities and specific spatial distribution of the cations within this confined space.[21]

Molecules bridging nearby cations in so called dual-cation sites (or even multiple-cation sites) were characterized by specific shifts of vibrational frequencies of bonds in the adsorbed molecules, and a stronger interaction with the zeolite than complexes formed on isolated extra-framework cations (so called single-cation sites). The pioneering work on CO adsorption on K-FER zeolites [12] started further systematic research. Subsequently, possibility to form CO bridging complexes was also investigated on other alkali metal cations not only in **FER** zeolites [8, 13-15, 22, 23], but also in **MFI** [6, 8], **BEA** [7], **LTA** [24], **FAU** [25], and **LTL** [26] zeolite frameworks. It was proved that also other small molecules like CO_2, O_2, N_2, NO and C_2H_2 can be adsorbed in the zeolites with exchanged alkali metal cations, alkaline earth metal cations and monovalent copper cations in a similar way and can form bridged complexes.[19, 27-37] Very recently, propene bridging two nearby K^+ cations in dual-cation sites in K-**FER** zeolites was identified and characterized by IR $\nu_{C=C}$ vibrational band at 1633 cm^{-1} and adsorption heat of 77 kJ/mol.[38] Such complexes were stabilized by 14 kJ/mol with respect to the adsorption complex at the isolated potassium cation. This finding arose the question how the existence of such bridged complexes influences co-adsorption of propane and propene, selectivity of adsorption and adsorption capacity of zeolitic adsorbents. It is well know that separation of propene and propane is a very energy intensive process in petrochemical industry. Currently, separation is carried out by cryogenic or high pressure distillation due to low relative volatility of propane with regard to propene (about 85 % of energy for production of propene is consumed by separation processes).[39] Thus, the searching for an alternative separation process is highly desirable. The adsorptive separation using zeolites is one of the promising way and thus to gain knowledge of the factors influencing the co-adsorption equilibrium and separation efficiency is necessary for targeting research and optimization of the adsorbent structure and composition.

In this paper, we report on study of propane and propene adsorption on alkali metal (Li-, Na- and K-) exchanged **FER** zeolites having Si/Al ratio 8.6 and 27.5. The set of materials investigated contains materials from those exhibiting significant amount of dual-cation sites for propene (previously studied and characterized in details in ref.[38]) to adsorbents having only isolated single-cation sites. The adsorption isotherms and heats of adsorption of pure components were experimentally determined by using volumetric adsorption apparatus combined with microcalorimeter, real co-adsorption of propane and propene from equimolar gas mixture was studied by transient breakthrough experiments. Experimental data from single compound adsorption isotherms were used for calculation of IAST adsorption selectivities which were compared and discussed with those obtained from breakthrough experiments. Obtained results clearly show that presence of dual-cation sites in the zeolite results in significant increase in adsorption selectivity while adsorption capacity of the zeolite is not influenced and is almost constant for all M-**FER** zeolites with the same Si/Al ratio.

Experimental part

Materials

The parent NH$_4$-**FER** zeolite with nominal Si/Al ratio 8.6 was supplied by Research Institute of Inorganic Chemistry Ústí nad Labem (Czech Republic), while NH$_4$-FER zeolite with Si/Al ratio 27.5 was supplied by Zeolyst International Inc. (USA). The ion-exchange of parent zeolites into lithium, sodium and potassium forms was performed with a 0.5 M solution of the appropriate alkali metal nitrate at 45°C. Zeolite weighing 1 g was suspended in 100 ml of salt solution and stirred with a magnetic stirrer for five days. The zeolites obtained were characterized by XRD, SEM, FTIR spectroscopy and N$_2$ adsorption/desorption isotherms measurement. For sake of brevity, details of the instruments used and the measurement conditions as well as the data obtained and the summary of the characterization results are detailed in the ESI. The samples were labelled as M-**FER**-x, where M denotes type of cation and x the zeolite Si/Al ratio.

Adsorption microcalorimetry measurement

The adsorption microcalorimetry experiments were carried out using an isothermal Tian-Calvet type of microcalorimeter (BT 2.15, SETARAM, France) combined with a homemade volumetric/manometric apparatus equipped with precise capacitance pressure transducers (Pfeiffer vacuum, Austria). Both microcalorimeter and volumetric device were kept at 30°C. Prior to adsorption experiment, all the samples (ca. 400 mg) were degassed by slow increase of temperature (with the heating rate 2 °C/min) to 420°C and kept at this temperature for 5 h under dynamic vacuum generated by turbomolecular pump (HiCube 80, Pfeiffer) (residual pressure lower than 10^{-5} mbar). The adsorption experiments were carried out at 30°C by the step-by-step dosing of small known amounts of propane (purity of 99.995% supplier - GHC Germany) or propene (purity of 99.995% supplier – GHC Germany) to the calorimetric cell until the equilibrium pressure of 900 mbar was reached. Each dose was equilibrated for at least 60 min.

IAST selectivity

The adsorption selectivity for C$_3$H$_6$/C$_3$H$_8$ separation is defined by the equation

$$\alpha_{ads} = \frac{x_{propene}/y_{propene}}{x_{propane}/y_{propane}} = \frac{p^0_{propane}}{p^0_{propene}}$$

where x$_i$ is i-th component molar fraction in the adsorbed phase, y$_i$ is i-th component molar fraction in the gas phase and p$_i^0$ is pressure of pure i-th component necessary for achieving the spreading pressure in adsorbed phase as is in considered binary mixture predicted by ideal adsorption solution theory (IAST). In general, IAST cannot be solved in close form and solution must be found numerically. For this purpose, we use our own software employing a Scilab package. The pure component adsorption isotherms were fitted with Sips (Langmuir-Freundlich) model for the purpose of IAST selectivity calculations.

$$n_{ads} = n_{max} \frac{(bp)^{1/s}}{1 + (bp)^{1/s}}$$

where p (in mbar) is the pressure of the bulk gas at equilibrium with adsorbed phase, b (in mbar^{-1}) is the affinity coefficient, n_{max} (in mmol/g) is saturation capacity of the adsorbent, s is an empirical constant and n_{ads} (in mmol/g) is amount adsorbed.

Sips adsorption isotherm allows to derive an analytic expression for the calculation of adsorption potential z as function of pressure p^0_i and the analytic expression for its inversion $p^0_i(z)$.

$$z = \frac{\phi}{RT} = \frac{\phi^0_i}{RT} = -\int_0^{p^0_i} \frac{n_i(p_i)}{p_i} dp_i = -n_{max,i} \cdot s \cdot \ln\left(1 + \left(bp^0_i\right)^{\frac{1}{s}}\right)$$

Obtained expressions can be used straightforwardly for the numeric solution of unique z value for which the following equation holds.

$$\sum_{i=1}^{N} \frac{p_i}{p_i^0(z)} - 1 = 0$$

where p_i are true partial pressures of components in the mixture. Described calculation scheme was more detailed described in Refs [40, 41].

Breakthrough adsorption experiments

The breakthrough experiments were carried out in a breakthrough set-up schematically illustrated in Fig. S1 in ESI. A glass column with diameter of 5 mm and a length of 50 mm was charged by 200 mg (in grains of 0.25-0.315 mm) of samples investigated. Before the breakthrough experiment, the samples were pre-treated by slow heating (heating rate 5°C/min) in the flow of oxygen (flow rate of 20 ml/min) to 400°C and by calcination at this temperature for 2 h. Then the samples were cooled down to RT freely in oxygen (flow rate of 5 ml/min). For the breakthrough experiments, the gas mixture with flow rate of 20 ml/min, consisting of propane, propene, and helium in molar ratio 9 : 9 : 2, was prepared in gas line by mixing pure gases flows controlled the mass flow controller (Bronkhorst, El-flow) and fed to the adsorbent column at 30°C controlled by high precision custom-made cryostat (E-lab services, Czech Republic). The gas composition at the column outlet was monitored by mass spectrometer (Omnistar GDS 310, Pfeiffer vacuum). The mass intensities at 4, 29, 32, 41 and 44 m/e were measured every second of the experiment. Concentration of propane in outlet gas was obtained from the signal at 29 m/e. Propene content was determined from line at 41 m/e after subtraction propane contribution to this line (determined from the intensity of the line at 29m/e multiplied by the intensity ratio of 41/29 masses in the pure propane mass spectrum determined in separate experiment).

Results and Discussion

Successful ion exchange of the original ammonium cations of parent **FER** zeolites for alkali metal cations (Li, Na, K) was checked by FT-IR spectroscopy. The IR spectra of the outgassed samples (by slow heating of the sample to 420 °C under vacuum generated by turbomolecular pump) are shown in Fig. S2 in the ESI. The absence of IR absorption bands corresponding to the Brønsted Si(OH)Al groups at 3603 cm^{-1}, which are generated by thermal decomposition of the ammonium ions, in the IR spectra

was considered to be evidence of the complete ion exchange. The diffraction patterns of samples (Fig. S3 ESI) contain only diffraction lines characteristic of the **FER** structure. Sharp and well resolved diffraction lines, especially in the 22-30° 2θ range, prove the well-developed crystalline phase of all M-**FER** samples. After ion-exchange with alkali metal cations, the frameworks of both **FER** zeolites are completely preserved. The morphology of the parent zeolites is shown on SEM micrographs (Fig. S4 ESI). SEM images display agglomerates of typical plate-like microcrystals with sizes from several hundreds of nanometers to several micrometers and thickness about 100-200 nm.

Porosity and textural properties of zeolites were studied by N_2 physisorption (Fig. S5 ESI). The typical type I isotherms indicate the microporous character of the M-**FER** samples. BET surface area and micropore volume of all zeolites prepared are in narrow range from 369 to 343 m^2/g for the BET specific surface areas and from 0.138 to 0.127 cm^3/g for micropore volumes (cf. data in Table S1 ESI). The only exception is K-**FER**-8.6 sample, which has a BET specific surface area and volume of micropores reduced to ca. 42% of the other samples despite the fact that crystallinity of K-**FER**-8.6 sample is comparatively good with other samples. This reduction of BET area and micropore volume is probably the consequence of high population of K^+ sites in the centre of the entrance window to the perpendicular channel cavity (intersection sites in the vicinity of T_1 and T_2 position of Al) [12, 38] where potassium cations prevent diffusion of dinitrogen molecules into perpendicular channel cavity. This hypothesis is indirectly supported by our previous study of CO_2 adsorption in these materials revealing similar capacity for both K-**FER** zeolites (capacity was even slightly higher for K-**FER**-8.6 sample).[20] We interpret this as an interplay of smaller kinetic diameter of CO_2 molecule compared to dinitrogen and significantly higher temperature of adsorption in the case of CO_2 (34°C for CO_2 adsorption vs. -196 °C for dinitrogen) and thus enhanced vibration of the skeleton and more flexibility of the framework. The external surface areas, determined by the t-plot method, are independent of cation type, but differ slightly for the individual zeolites (ca. 10 m^2/g for **FER**-8.6 and 15 m^2/g for **FER**-27.5), which can be explained by differences in particle sizes (see SEM images in Fig. S4 ESI).

Adsorption of individual pure hydrocarbons was investigated using a combined calorimetric-volumetric apparatus, allowing simultaneous assessment of the adsorbed amount and released adsorption heat. Figure 1 shows adsorption isotherms of propane and propene at 30°C on all **FER** zeolites investigated. Apparently, propene is adsorbed slightly more than propane on the same sample. It is given by stronger interaction of propene with the adsorbent, differences in sizes of both hydrocarbons (propane size is 0.45 nm, while propene size 0.43 nm [42] and thus variation in density of liquid-like phases. All the isotherms are well fitted by using of Sips (Langmuir-Freundlich) model. The fitting parameters are summarized in Table 1. The adsorption capacity of the zeolites seems to be almost independent on type of cation for **FER**-8.6 and only slightly decreasing with the increasing size of the cations in the case of **FER**-27.5 zeolite. It is noteworthy that adsorption capacity of the K-**FER**-8.6 does not differ from adsorption capacities of the other **FER**-8.6 samples, even though the sample exhibited significantly lower specific surface area and micropore volume in the nitrogen adsorption isotherm (cf. Table S1 and Fig. S5 in the ESI). It could be explained by the thermal vibration of the framework and its larger flexibility at 30°C compared with the behaviour of framework at liquid nitrogen temperature (at which N_2 physisorption is measured) that allows the hydrocarbon molecules to penetrate/diffuse to the perpendicular channel cavity through 8-membered ring occupied by potassium cation, while dinitrogen molecule at low temperature and small thermal vibration of framework cannot diffuse through this window. Taking into account the micropore volume estimated from N_2 adsorption isotherms and saturation capacity of the zeolites investigated for individual

hydrocarbons, resulting densities of adsorbed state (calculated from adsorption capacity and volume of micropores of individual zeolites) in micropores reach 85-99% density of the liquid state of bulky hydrocarbon at 30°C and atmospheric pressure (0.501 g/cm^3 for propane and 0.515 g/cm^3 for propene). In the case of K-**FER**-8.6 zeolite, the use of a micropore volume determined from the nitrogen isotherm leads to a physically meaningless (strongly overestimated) density value of the adsorbed phase. It can be understood as another indirect evidence that propene also occupies spaces in the channel system inaccessible for the nitrogen molecules at -196 ° C. It should be noted that using of average value of micropore volume calculated from textural parameters of other M-**FER**-8.6 zeolites, led to density of adsorbed state of 86 % of bulky propene liquid phase.

From the data in Tab. 1, it is clear that propene interacts with K-**FER**-8.6 significantly differently than in other zeolites (the affinity coefficient (b) for propene/K-**FER**-8.6 is more than one order of magnitude higher compared with others). Recently, the bridged complexes, where propene molecule interacts with two adjacent potassium cations, were described for this zeolite.[38] From previous studies [6, 9, 12, 14, 16, 20, 24, 27] of dual cation sites in zeolites and interaction of small probe molecules with this type of is evident that presence of such sites and bridged complexes formed upon adsorption on them is reflected in larger heat of adsorption at low amounts adsorbed (low coverages) relative to the same zeolite type with low concentration of cations (high Si/Al ratio) significantly suppressing probability of existence dual cationic sites. Thus, heats of adsorption (HOA) of both hydrocarbons at amount adsorbed limiting to zero were carefully measured and analysed (Table 2). The propane adsorption heats are significantly smaller compared to propene. It is caused by differences in interactions of both hydrocarbons with cationic zeolites. While propene interacts specifically with cations via its double bond, propane interacts mainly by dispersive interactions and cationic sites does not act as distinct specific adsorption sites as can be documented by shape of low-pressure region of adsorption isotherms. Fig. 2 shows adsorption isotherms of propane and propene on Li-**FER**-27.5 in semi-logarithmic scale, where typical sigmoidal shape of adsorption isotherm beginning is clearly visible in propene isotherm while propane isotherm does not show such character. It is caused by preferential binding of propene on cationic sites. It worth to note that this sigmoidal low-pressure part of isotherm ends at amount adsorbed of ca. 0.35 mmol/g which correspond well with content of extra-framework cation in Li-**FER**-27.5. The same artefact is observable also for sodium and potassium form of **FER** zeolite (cf. Fig. S6). It should be note that upper limits of amount adsorbed for these cations correspond well with value for Li-**FER**-27.5 and thus with content of cations in the zeolite samples. Propane heat of adsorption is insensitive to the cation concentration (Si/Al ratio) as is reflected in differences in HOA being ± 1 kJ/mol and it only slightly increases with decreasing size of cations (increase in polarizing force given by increasing intensity of electrostatic field) in order K < Na < Li. Presence of cations in zeolite increases propane HOA only by 1.3 – 8.1 kJ/mol compared to heat of adsorption of propane on pure silica **FER (**53.3 kJ/mol [43]). On the contrary, presence of cations increases propene heat of adsorption by 15.8-30.3 kJ/mol relative to pure silica **FER** (it exhibits propene HOA of 50.6 kJ/mol [38]). For **FER**-27.5, values of adsorption heat increase in order K-**FER** (66.1 kJ/mol) < Na-**FER** (76.8 kJ/mol) < Li-**FER** (80.9). Effect of Si/Al ratio is negligible for Li-**FER** (difference between Si/Al 8.6 and 27.5 is -1.1 kJ/mol), only small for Na-**FER** (difference is 3.6 kJ/mol), but distinctive for K-**FER** (11.5 kJ/mol). Thus presence of dual cationic sites in Li-**FER** is not expected in agreement with previous findings in studies of CO and CO$_2$ adsorption on this zeolitic material. [13, 15, 20] It is related to small size of cation, short distance from skeletal oxygen atoms and the shortest distance of cation from each other (from alkali metals) necessary for generation of dual cationic site. Even in the case of

Na-**FER**, the difference in adsorption heat is insignificant, so it can be assumed that the number of dual centers will be insignificant in this zeolite system. The only zeolite from all investigated ones exhibiting significant amount of dual cationic sites for adsorption of propene is K-**FER** zeolite. Existence and detailed characterization of bridged complexes in this zeolite was reported recently by us.[38] The relevant data on the adsorption heats of propane and propene are rather scarce in the literature due to fact that majority of the reported studies concern aluminium rich zeolites (LTA, FAU) with sodium as extraframework cation. So direct comparison of our data with those in literature is not absolutely correct due to different framework densities and thus different contributions of dispersion forces. The most relevant are propane heats measured on H-FER zeolites by Yoda et al. (52 kJ/mol)[44] and by Eder and Lercher (49 kJ/mol) [45, 46]. On sodium form of zeolites, reported propane and propene heats of adsorption were 43.1 kJ/mol for propane and 51.9 kJ/mol for propene on Na-X zeolite [47] and 35 kJ/mol for propane and 39.6 kJ/mol for propene on Na-FAU zeolite [48]. These values are lower than our data measured on FER zeolites due to significant difference in framework density and size of channels and cavities affected dispersion interaction pronouncedly. Anyway, propene heat of adsorption is always larger compared to propane in line with our data obtained on M-**FER** zeolites.

To study, how the nature of cation balancing the negative charge of the zeolite framework and existence of dual cationic sites influence ability to adsorb and separate propane/propene mixture, the IAST approach was used to predict the composition of the adsorbed phase in the presence of gas mixture. The IAST selectivities were obtained from single component Sips fits (Table 1, lines in Fig. 1) and calculated selectivity values for equimolar propane/propene mixture at 30°C and atmospheric pressure are summarized in Table 3. This qualitative comparison confirms that all of these zeolites selectively adsorb propene over propane. The IAST selectivity values for Li- and Na-**FER** zeolites are very similar. Selectivity values are slightly higher for M-**FER**-8.6 zeolite than for zeolites with Si/Al 27.5 (2.6 vs. 2.3). The existence of dual cationic sites, as in K-**FER** zeolites, significantly increases propene/propane selectivity. In the case of K-**FER**-27.5, where only small amount of propene bridged complexes was detected previously by FT-IR spectroscopy [38], IAST selectivity increased by 50 rel. % compared with selectivity of Li- or Na-**FER** zeolites. For K-**FER**-8.6 zeolite, exhibiting huge amount of bridged complexes characterized by IR band at 1633 cm^{-1} [38], the IAST selectivity increases 27-times (α_{ads} = 71.2). IAST selectivity reported in the literature for the most frequently investigated cationic zeolites are 2.1-2.9 for 5A zeolite[49] and 11-21 for Na-X [47, 50]. Selectivity of low-silica zeolites is comparable with M-**FER** zeolites, except K-**FER**-8.6 zeolite exhibiting significantly larger value. Such high selectivity (71.2) corresponds to composition in an adsorbed phase of 98.6% propene in equilibrium with the equimolar gas phase and thus could act as very efficient adsorbent for separation and purification of propene.

To test behaviour of adsorbents under realistic conditions, all of them were tested in a breakthrough experiments. The experimental breakthrough curves are shown in the Fig. 3. For all adsorbents, the propane breaks through the adsorbent bed first. The delay of propene break varied for various zeolites. From break times and composition of outlet gas, the adsorbed amount of both propane and propene can be determined and used for calculation of separation selectivity (see Table. 3). The Na-**FER** zeolites are the least selective adsorbents of all, having selectivity only slightly above unity. Li-**FER** zeolites exhibit selectivity of 2.8 and 4.8 for Li-**FER** with Si/Al of 8.6 and 27.5, respectively. K-**FER**-27.5 exhibits selectivity of 2.3, while K-**FER**-8.6 showed the highest selectivity of all (6.2). It should be noted, that IAST selectivity, predicted from single component adsorption isotherms, is in all cases higher than selectivity obtained from real co-adsorption of propane and propene investigated

by breakthrough experiments. Even under breakthrough experiment conditions, K-**FER**-8.6 zeolite exhibits the highest selectivity from all the tested zeolites, but the value is ten-times lower compared with IAST selectivity (6.2 vs. 71.2). It is not extraordinary that the IAST prediction is not fully in line with real selectivity. A similar difference was also observed for the Na-X zeolite [47], which exhibited a real selectivity value determined by transient breakthrough experiment of 7, while the IAST prediction led to value of 21. The reasons for these differences can be the fact that IAS theory is based on several assumptions (ideal behaviour of adsorbed phase, adsorbate molecules interact with adsorbent with similar strength, and adsorbent is homogeneous) that are not fully met for cationic zeolites (especially heterogeneity of adsorbent and significantly different interaction of individual adsorbates).[40, 51] Even if the real selectivity of K-**FER**-8.6 zeolite is taken into account, adsorbed phase on this zeolite under breakthrough conditions consisted of 86% propene in equilibrium. Two-stage process employing this adsorbent would be able to generate propene purity of 99.7% (value close to required polypropylene grade). Based on the results obtained, it can be stated that presence of dual cationic sites enhances selectivity of propene/propane mixture separation while adsorption capacity of the zeolite is preserved. Due to very steep shape of hydrocarbons isotherms at 30°C vacuum swing adsorption or temperature swing adsorption processes could be appropriate for propene/propane separation.

Conclusion

Interaction of propane and propene with alkali metal exchanged **FER** zeolites with different Si/Al ratio and their co-adsorption on these adsorbents were investigated by combination of calorimetric-volumetric measurements with breakthrough experiments. The above discussed results allow us to draw the following conclusions:

- The propene molecule is adsorbed more strongly than propane due to specific interaction of propene double bond with electrostatic field of charge compensating cations. Adsorption heats range from 66.1 to 80.9 kJ/mol, which differ significantly from interaction with pure silica **FER** zeolite (50.6 kJ/mol), which indicates significant contribution of electrostatic interaction.

- Propane adsorption heats are in the range from 54.5 to 62.7 kJ/mol. They are not very different from dispersive interaction of propane with pure silica **FER** (51.6 kJ/mol) indicating almost nonspecific interaction of propane molecule with zeolite framework.

- All M-**FER** zeolites selectively adsorb propene over propane. This separation does not rely on size exclusion (adsorption capacity of both hydrocarbons are similar), but it arises from differences in adsorption heats between propane and propene.

- The least effective adsorbent for separation of propene/propane mixture is Na-**FER** with breakthrough selectivity being unity.

- In the case of potassium form of **FER** zeolite with Si/Al ratio 8.6, presence of significant amount of bridged complexes formed on so-called dual adsorption sites described previously[38], results in significant increase in adsorption selectivity while adsorption capacity of the adsorbent is comparable with other M-**FER** adsorbents. Thus, dual cationic sites have a positive effect on selectivity of propene/propane separation.

Acknowledgement

References

[1] J. Prech, Catalytic performance of advanced titanosilicate selective oxidation catalysts - a review, Catal. Rev.-Sci. Eng., 60 (2018) 71-131.

[2] D.P. Serrano, J.A. Melero, G. Morales, J. Iglesias, P. Pizarro, Progress in the design of zeolite catalysts for biomass conversion into biofuels and bio-based chemicals, Catal. Rev.-Sci. Eng., 60 (2018) 1-70.

[3] A. Burton, Recent trends in the synthesis of high-silica zeolites, Catal. Rev.-Sci. Eng., 60 (2018) 132-175.

[4] J. Cejka, A. Corma, S. Zones, Zeolites and Catalysis. Synthesis, Reactions and Applications, Wiley-VCH Verlag GmbH, Weinheim, 2010.

[5] J. Cejka, R.E. Morris, P. Nachtigall, Zeolites in Catalysis: Properties and Applications, Royal Society of Chemistry, Cambridge, 2017.

[6] C.O. Arean, M.R. Delgado, K. Frolich, R. Bulanek, A. Pulido, G.F. Bibiloni, P. Nachtigall, Computational and Fourier transform infrared spectroscopic studies on carbon monoxide adsorption on the zeolites Na-ZSM-5 and K-ZSM-5: Evidence of dual-cation sites, J. Phys. Chem. C, 112 (2008) 4658-4666.

[7] R. Bulanek, E. Koudelkova, Carbon monoxide adsorption on alkali-metal exchanged BEA zeolite: IR and thermodynamics study, Micropor. Mesopor. Mater., 151 (2012) 149-156.

[8] R. Bulanek, E. Koudelkova, Quantitative analysis of IR spectra of carbonylic species in alkali-metal exchanged ZSM-5 and FER zeolites, Catal. Today, 243 (2015) 62-68.

[9] R. Bulanek, E. Koudelkova, Determination of adsorption heats of individual adsorption complex by combination of microcalorimetry and FTIR spectroscopy, J. Therm. Anal. Calorim., 113 (2013) 97-103.

[10] P. Cicmanec, R. Bulanek, K. Frolich, Thermodynamics of CO probe molecule adsorption on Cu-FER-zeolite comparison of TPD, FTIR, and microcalorimetry results, J. Therm. Anal. Calorim., 105 (2011) 837-844.

[11] K. Frolich, E. Koudelkova, E. Frydova, R. Bulanek, The quantity of Cu+ ions forming isolated and bridged carbonyl complexes in FER zeolites determined by IR spectroscopy, Vib. Spectrosc., 58 (2012) 146-152.

[12] E. Garrone, R. Bulanek, K. Frolich, C.O. Arean, M.R. Delgado, G.T. Palomino, D. Nachtigallova, P. Nachtigall, Single and dual cation sites in zeolites: Theoretical calculations and FTIR spectroscopic studies on CO adsorption on K-FER, J. Phys. Chem. B, 110 (2006) 22542-22550.

[13] P. Nachtigall, R. Bulanek, Theoretical investigation of site-specific characteristics of CO adsorption complexes in the Li+-FER zeolite, Appl. Catal. A-Gen., 307 (2006) 118-127.

[14] P. Nachtigall, M.R. Delgado, K. Frolich, R. Bulanek, G.T. Palomino, C.L. Bauca, C.O. Arean, Periodic density functional and FTIR spectroscopic studies on CO adsorption on the zeolite Na-FER, Micropor. Mesopor. Mater., 106 (2007) 162-173.

[15] P. Nachtigall, K. Frolich, H. Drobna, O. Bludsky, D. Nachtigallova, R. Bulanek, FTIR study of CO interactions with Li+ ions in micro- and mesoporous matrices: Coordination and localization of Li+ ions, J. Phys. Chem. C, 111 (2007) 11353-11362.

[16] D. Nachtigallova, O. Bludsky, C.O. Arean, R. Bulanek, P. Nachtigall, The vibrational dynamics of carbon monoxide in a confined space - CO in zeolites, Phys. Chem. Chem. Phys., 8 (2006) 4849-4852.

[17] L. Grajciar, J. Cejka, A. Zukal, C.O. Arean, G.T. Palomino, P. Nachtigall, Controlling the Adsorption Enthalpy of CO2 in Zeolites by Framework Topology and Composition, ChemSusChem, 5 (2012) 2011-2022.

[18] P. Nachtigall, L. Grajciar, J. Perez-Pariente, A.B. Pinar, A. Zukal, J. Cejka, Control of CO2 adsorption heats by the Al distribution in FER zeolites: effect of synthesis conditions, Phys. Chem. Chem. Phys., 14 (2012) 1117-1120.

[19] R. Bulanek, K. Frolich, E. Frydova, P. Cicmanec, Study of adsorption sites heterogeneity in zeolites by means of coupled microcalorimetry with volumetry, J. Therm. Anal. Calorim., 105 (2011) 443-449.

[20] R. Bulanek, K. Frolich, E. Frydova, P. Cicmanec, Microcalorimetric and FTIR Study of the Adsorption of Carbon Dioxide on Alkali-Metal Exchanged FER Zeolites, Top. Catal., 53 (2010) 1349-1360.

[21] P. Nachtigall, M.R. Delgado, D. Nachtigallova, C.O. Arean, The nature of cationic adsorption sites in alkaline zeolites-single, dual and multiple cation sites, Phys. Chem. Chem. Phys., 14 (2012) 1552-1569.

[22] R. Bulanek, K. Frolich, P. Cicmanec, D. Nachtigallova, A. Pulido, P. Nachtigall, Combined Experimental and Theoretical Investigations of Heterogeneous Dual Cation Sites in Cu,M-FER Zeolites, J. Phys. Chem. C, 115 (2011) 13312-13321.

[23] I. Voleska, P. Nachtigall, E. Ivanova, K. Hadjiivanov, R. Bulanek, Theoretical and experimental study of CO adsorption on Ca-FER zeolite, Catal. Today, 243 (2015) 53-61.

[24] C.O. Arean, M.R. Delgado, C.L. Bauca, L. Vrbka, P. Nachtigall, Carbon monoxide adsorption on low-silica zeolites-from single to dual and to multiple cation sites, Phys. Chem. Chem. Phys., 9 (2007) 4657-4661.

[25] Z. Nour, D. Berthomieu, Multiple adsorption of CO on Na-exchanged Y faujasite: a DFT investigation, Mol. Simul., 40 (2014) 33-44.

[26] M.R. Delgado, A.M. de Yuso, R. Bulanek, C.O. Arean, Infrared spectroscopic and thermodynamic assessment of extraframework cationic adsorption sites in the zeolite K-L by using CO as probe molecule, Chem. Phys. Lett., 639 (2015) 195-198.

[27] A. Zukal, C.O. Arean, M.R. Delgado, P. Nachtigall, A. Pulido, J. Mayerova, J. Cejka, Combined volumetric, infrared spectroscopic and theoretical investigation of CO2 adsorption on Na-A zeolite, Micropor. Mesopor. Mater., 146 (2011) 97-105.

[28] H.V. Thang, L. Grajciar, P. Nachtigall, O. Bludsky, C.O. Arean, E. Frydova, R. Bulanek, Adsorption of CO2 in FAU zeolites: Effect of zeolite composition, Catal. Today, 227 (2014) 50-56.

[29] A.I. Serykh, M.D. Amiridis, DRIFTS evidence for the formation of binuclear Cu(I)-dinitrogen complexes upon adsorption of N-2 on CuZSM-5, Micropor. Mesopor. Mater., 94 (2006) 320-324.

[30] S. Recchia, C. Dossi, A. Fusi, R. Psaro, R. Ugo, G. Moretti, Irreversible dinitrogen adsorption on Cn-ZSM-5 catalysts and in situ IR identification of the NO decomposition sites, Chem. Commun., (1997) 1909-1910.

[31] G. Moretti, G. Ferraris, G. Fierro, M. Lo Jacono, S. Morpurgo, M. Faticanti, Dimeric Cu(I) species in Cu-ZSM-5 catalysts: the active sites for the NO decomposition, J. Catal., 232 (2005) 476-487.

[32] S. Morpurgo, G. Moretti, M. Bossa, A computational study on N-2 adsorption in Cu-ZSM-5, Phys. Chem. Chem. Phys., 9 (2007) 417-424.

[33] S. Morpurgo, G. Moretti, M. Bossa, A computational study on the mechanism of NO decomposition catalyzed by Cu-ZSM-5: A comparison between single and dimeric Cu+ active sites, J. Mol. Catal. A-Chem., 358 (2012) 134-144.

[34] A. Itadani, Y. Sogawa, A. Oda, H. Torigoe, T. Ohkubo, Y. Kuroda, Further Evidence for the Existence of a Dual-Cu+ Site in MFI Working as the Efficient Site for C2H6 Adsorption at Room Temperature, Langmuir, 29 (2013) 9727-9733.

[35] A. Itadani, M. Tanaka, T. Mori, H. Torigoe, H. Kobayashi, Y. Kuroda, Potential for Fixation of N-2 at Room Temperature Utilizing a Copper-Ion-Exchanged MFI-Type Zeolite As an Adsorbent: Evaluation of the Bond Dissociation Energy of Adsorbed N N and the Bond Strength of the Cu+-N(N) Species, J. Phys. Chem. Lett., 1 (2010) 2385-2390.

[36] A. Itadani, H. Torigoe, T. Yumura, T. Ohkubo, H. Kobayashi, Y. Kuroda, Dual-Copper Catalytic Site Formed in CuMFI Zeolite Makes Effective Activation of Ethane Possible Even at Room Temperature, J. Phys. Chem. C, 116 (2012) 10680-10691.

[37] A. Itadani, T. Yumura, T. Ohkubo, H. Kobayashi, Y. Kuroda, Existence of dual species composed of Cu+ in CuMFI being bridged by C2H2, Phys. Chem. Chem. Phys., 12 (2010) 6455-6465.

[38] M. Rubes, E. Koudelkova, F.S.D. Ramos, M. Trachta, O. Bludsky, R. Bulanek, Experimental and Theoretical Study of Propene Adsorption on K-FER Zeolites: New Evidence of Bridged Complex Formation, J. Phys. Chem. C, 122 (2018) 6128-6136.

[39] P.F. Bryan, Removal of propylene from fuel-grade propane, Sep. Purif. Rev., 33 (2004) 157-182.

[40] A.L. Myers, J.M. Prausnitz, Thermodynamics of mixed-gas adsorption, Aiche J., 11 (1965) 121-+.

[41] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press1998.

[42] W. Zhu, F. Kapteijn, J.A. Moulijn, M.C. den Exter, J.C. Jansen, Shape selectivity in adsorption on the all-silica DD3R, Langmuir, 16 (2000) 3322-3329.

[43] S. Savitz, F. Siperstein, R.J. Gorte, A.L. Myers, Calorimetric study of adsorption of alkanes in high-silica zeolites, J. Phys. Chem. B, 102 (1998) 6865-6872.

[44] E. Yoda, J.N. Kondo, K. Domen, Detailed process of adsorption of alkanes and alkenes on zeolites, J. Phys. Chem. B, 109 (2005) 1464-1472.

[45] F. Eder, J.A. Lercher, On the role of the pore size and tortuosity for sorption of alkanes in molecular sieves, J. Phys. Chem. B, 101 (1997) 1273-1278.

[46] F. Eder, J.A. Lercher, Alkane sorption in molecular sieves: The contribution of ordering, intermolecular interactions, and sorption on Bronsted acid sites, Zeolites, 18 (1997) 75-81.

[47] A. van Miltenburg, J. Gascon, W. Zhu, F. Kapteijn, J.A. Moulijn, Propylene/propane mixture adsorption on faujasite sorbents, Adsorpt.-J. Int. Adsorpt. Soc., 14 (2008) 309-321.

[48] M.A. Granato, T.J.H. Vlugt, A.E. Rodrigues, Molecular simulation of propane-propylene binary adsorption equilibrium in zeolite 13X, Ind. Eng. Chem. Res., 46 (2007) 7239-7245.

[49] S. Divekar, A. Nanoti, S. Dasgupta, Aarti, R. Chauhan, P. Gupta, M.O. Garg, S.P. Singh, I.M. Mishra, Adsorption Equilibria of Propylene and Propane on Zeolites and Prediction of Their Binary Adsorption with the Ideal Adsorbed Solution Theory, J. Chem. Eng. Data, 61 (2016) 2629-2637.

[50] Y.H. Huang, J.W. Johnson, A.I. Liapis, O.K. Crosser, Experimental-determination of the binary equilibrium adsorption and desorption of propane propylene mixtures on 13X molecular-sieves by a differential sorption bed system and investigation of their equilibrium expressions, Sep. Technol., 4 (1994) 156-166.

[51] K.S. Walton, D.S. Sholl, Predicting multicomponent adsorption: 50 years of the ideal adsorbed solution theory, Aiche J., 61 (2015) 2757-2762.