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Studies on the equilibrated thermodesorption of *n*-hexane from ZSM-5 zeolite

The influence of the extraframework cations

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Abstract Equilibrated thermodesorption (TPED) and quasi-equilibrated temperature programmed desorption and adsorption (QE-TPDA) were employed as methods for studying the influence of different extraframework cations (Na^+, K^+, Li^+, Cu^{2+}, Zn^{2+}, or Mg^{2+}) on adsorption of n-hexane on ZSM-5 zeolite with high Al content (Si/Al = 15). Considerable influence of the cations on both initial adsorption in the micropores and ordering of the adsorbed molecules, occurring at high coverages, has been observed. This influence is reflected by the values of the adsorption enthalpy and entropy, determined by fitting the dual site Langmuir (DSL) adsorption function to the equilibrated thermodesorption profiles. However, no clear correlation between the determined parameters and properties of the extraframework cations could be found.

Keywords ZSM-5 · *n*-Hexane · Desorption · Adsorption · Extraframework cations

Introduction

Zeolites, crystalline microporous aluminosilicates, are of considerable practical importance because of their specific properties and large number of applications. The unique properties of zeolites result mainly from their well-defined structure, comprising microporous channels and cavities as well as from their ability of formation of catalytic or adsorption centers inside the micropores [1]. Zeolites are used in separation and catalytic technologies, and also as ion exchangers. Zeolite catalysts are employed in catalytic cracking, hydrocracking, alkylation, isomerization, and dehydroisomerisation in the refining and petrochemical industry [2–5].

Therefore, a thorough understanding of adsorption processes taking place on zeolites is crucial and many research groups have studied it in the last years [6–9]. Among the wide range of structures special attention was paid to MFI molecular sieves (ZSM-5 and silicalite-1). MFI is a medium-pore zeolite which contains straight parallel channels connected by zig-zag channels, each made of 10-membered oxygen rings [10, 11]. Molecules hosted in the narrow pores of ZSM-5 interact strongly with the force field exerted by the zeolite pore walls. This interaction leads to pronounced differences in the adsorption of molecules with different size, polarity, shape, etc. The free aperture of both channels (about 0.6 nm) is close to the size of simple aromatic and *n*-paraffin molecules. Therefore, the adsorption of light alkanes on MFI structure has been studied with a particular intention to determine the sorption capacity and the locations of adsorbed molecules within the internal pore structure [12–18]. The adsorption of *n*-hexane on ZSM-5 received especially a lot of attention because of its complex character: isotherms and isobars exhibit deviation from the typical Langmuir profile and contain a kink or a step at specific partial pressure or temperature. Since the channel dimensions in MFI framework are close to *n*-hexane kinetic diameters, this phenomenon used to be interpreted in terms of the preferential adsorption in channels (sinusoidal or linear) or in their intersections [19, 20]. Recently, the explanation based on the concept of the “commensurate freezing”—a kind of phase transition in the adsorbed hydrocarbon resulting in ordering of the molecules inside the micropores of the zeolite was generally accepted [21–23]. Complex adsorption isotherms or isobars of *n*-hexane on

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MFI molecular sieves may be fairly accurately fitted with the dual site Langmuir (DSL) model functions [24]. Such fitting results in the values of the adsorption enthalpy and entropy that are in agreement with the literature data [24].

Among numerous experimental methods that have been applied for determination of adsorption profiles of *n*-alkanes on zeolites the equilibrated thermodesorption methods were often used. In such measurements it is assumed that despite changes of temperature the extent of adsorption is controlled by the adsorption–desorption equilibrium; thus it depends only on the temperature and does not on the heating rate. Thermogravimetric measurements of desorption and adsorption of various *n*-alkanes, performed under constant partial pressure of the adsorptive, were referred to as TPE (temperature programmed equilibration) [19, 20] or TPED (temperature programmed equilibrated desorption) [23]. Another equilibrated thermodesorption technique is quasi-equilibrated temperature programmed desorption and adsorption (QE-TPDA) [25], similar to the temperature programmed desorption (TPD) used for characterization of heterogenous catalysts. In the QE-TPDA measurements a chromatographic detector (e.g., TCD) is used for monitoring changes in the composition of the carrier gas resulting from adsorption or desorption. Notwithstanding different instrumentation and principles of the measurements, the TPED and QE-TPDA techniques have been shown to yield very similar results in studies on adsorption of *n*-hexane on high silica zeolites [26].

The aim of this study was comparison of these two thermodesorption methods employed in detailed studies on the impact of different mono- and divalent extraframework cations on the adsorption of *n*-hexane on ZSM-5 zeolites with relatively large Al content (and ion-exchange capacity). Despite extensive studies focused on the sorption of *n*-hexane in the MFI structure, surprisingly small attention has been paid in the literature to the influence of the extraframework cations on this process. Ion exchange may modify the framework force field interacting with the adsorbed molecules and may also alter the effective pore sizes of the zeolite. However, for high silica zeolites such as ZSM-5 content of the extraframework cations is relatively low. Therefore, almost no differences in the adsorption properties of the ZSM-5 with Si/Al = 35 exchanged with Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, or Zn^{2+} could be observed in our earlier studies [27]. In this study, we focused on adsorption properties of ZSM-5 zeolites with relatively high Al content (Si/Al = 15), exchanged with selected mono- and divalent cations.

Experimental

The studied materials were commercial zeolites NH_4ZSM-5 (Si/Al = 15, 40 or 140, Zeolyst), NaZSM-5 (Si/Al = 35, IChP), HZSM-5 (Si/Al = 66, Akzo Nobel). Ion-exchanged samples containing Na^+, K^+, Li^+, Cu^{2+}, Zn^{2+}, or Mg^{2+} were prepared from NH_4ZSM-5 (Si/Al = 15) using wet ion-exchange procedure: zeolite was suspended in 1 M solution of the corresponding nitrate, stirred for 24 h at room temperature (RT), filtered and dried. This procedure was repeated three times to ensure complete ion exchange, which was conformed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

The QE-TPDA experiments were performed using a home-made TPD setup equipped with a thermal conductivity detector that was described in detail earlier [25, 26]. Prior the QE-TPDA experiments a sample (ca. 10 mg) was activated by heating in a flow of pure He to 500 °C at 10 K/min and then cooled down. After the activation adsorption at RT was started, by replacing He flowing through the sample cell with He/*n*-hexane mixture (0.003–0.005 bar). When the adsorption was completed and the detector signal stabilized, the QE-TPDA experiment was performed by heating the sample with the preadsorbed hydrocarbon in the flow of He/*n*-hexane mixture (7.5 cm^3/min) according to a temperature program consisting of a heating and cooling ramp ($\beta = 5$ or 10 K/min, RT-500 °C). Such desorption–adsorption cycles followed by isothermal segments (60 min at RT) were repeated several times.

The TPED experiments, previously fully described [23], were carried out in TGA/SDTA 851^e Mettler Toledo apparatus. Before the experiments the zeolites were pressed, crushed into small particles and sieved. Samples of about 10 mg of the sieve fraction 0.355–0.500 mm were placed in form of a single loose layer on the bottom of the 0.9 ml Al_2O_3 crucible. Prior each experiment the zeolite sample was activated in situ by heating in a flow of pure Ar (80 ml/min) using the temperature program: RT-400 °C, $\beta = 30$ K/min and 30 min at 400 °C.

After cooling down to the RT the in situ adsorption of *n*-hexane (analytical pure, POCh) was performed: the carrier gas flowing above the sample was saturated with the vapor of the hydrocarbon at 0 °C using a glass saturator filled with the liquid alkane and cooled with water–ice mixture. The partial pressure of the vapor determined from the Antoine equation was 0.06 bar [28]. When the adsorption was completed, and the mass of the sample stabilized, a TG measurement with a linear temperature program (RT-400 °C-RT, $\beta = 5$ K/min) was performed with the flow of the carried gas through the saturator switched on. The chosen program gives as a result not only desorption but also adsorption profiles and may confirm the equilibrium between these processes.

Precisely speaking both techniques compared in this work are quasi-equilibrated. Thermogravimetric thermodesorption measurements may be performed under true equilibrium control, keeping constant the partial pressure of the adsorptive and using the stepwise temperature program, ensuring that the sample mass stabilizes for each preset temperature value. However, in our previous studies on adsorption of *n*-hexane on zeolites [21] we have shown that such measurements give practically the same results, as those with temperature changing linearly with time, therefore both these modes of TGA measurements were included into TPED method.

Results and discussion

Examples of raw thermodesorption data obtained for NaZSM-5 (Si/Al = 35) in the TPED and QE-TPDA measurements as well as the resulting integral desorption profiles are compared in the Fig. 1. While the integral TPED profiles are calculated by simple averaging of the desorption and adsorption curve normalized to one, the QE-TPDA profiles result from more complex transformation involving integration of the desorption and adsorption peaks, followed by normalization and averaging of the results [29]. It may be noticed that the final integral and differential thermodesorption profiles (i.e., the adsorption isobars and their temperature derivatives) are very much alike. The fact that the peaks minima in the differential TPED profile appear at higher temperatures than in the QE-TPDA profiles results from the higher partial pressure of the adsorptive used in the TPED measurements.

This difference in the partial pressure results mainly from technical reasons. The TCD detector used in the QE-TPDA measurements works well for relatively low concentrations of any admixtures in the carrier gas (below 1%). Moreover, in the QE-TPDA experiments the carrier gas containing the adsorptive flows through the sample, ensuring fast equilibration. In TPED measurements the carrier gas mixture flows only above the sample layer and low concentration of the adsorptive may result in too long equilibration time.

The QE-TPDA profiles of *n*-hexane observed for the ZSM-5 zeolite (Si/Al = 15) containing different extraframework cations (Fig. 2) exhibit remarkable diversity. Although all the profiles consist of two major peaks, their widths, positions and relative intensities depend on the type of the cation. However, this dependence is not clear. For the Li-, Na- and K-containing zeolites intensity gradual increase of the intensity of the high temperature peaks with the ion radius may be noticed, accompanied by their narrowing and a shift to low temperatures. The low temperature peaks show the highest intensity for NaZSM-5—they are more than two times larger than those for KZSM-5. The profiles observed for the zeolites containing divalent cations are more uniform. In the case of CuZSM-5 and ZnZSM-5 the profiles are distorted in the high temperature region (>300 °C) due to cracking of hexane. Similar effects were observed for the acidic HZSM-5 (Si/Al = 15) [26]. Most probably the transition extraframework cations form acid sites activating the hydrocarbon molecules.

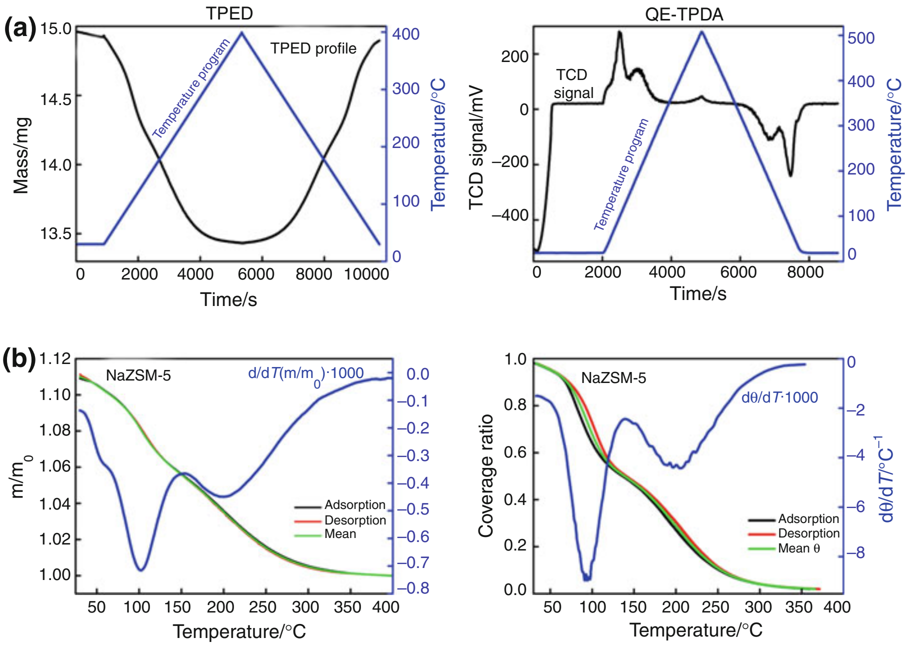
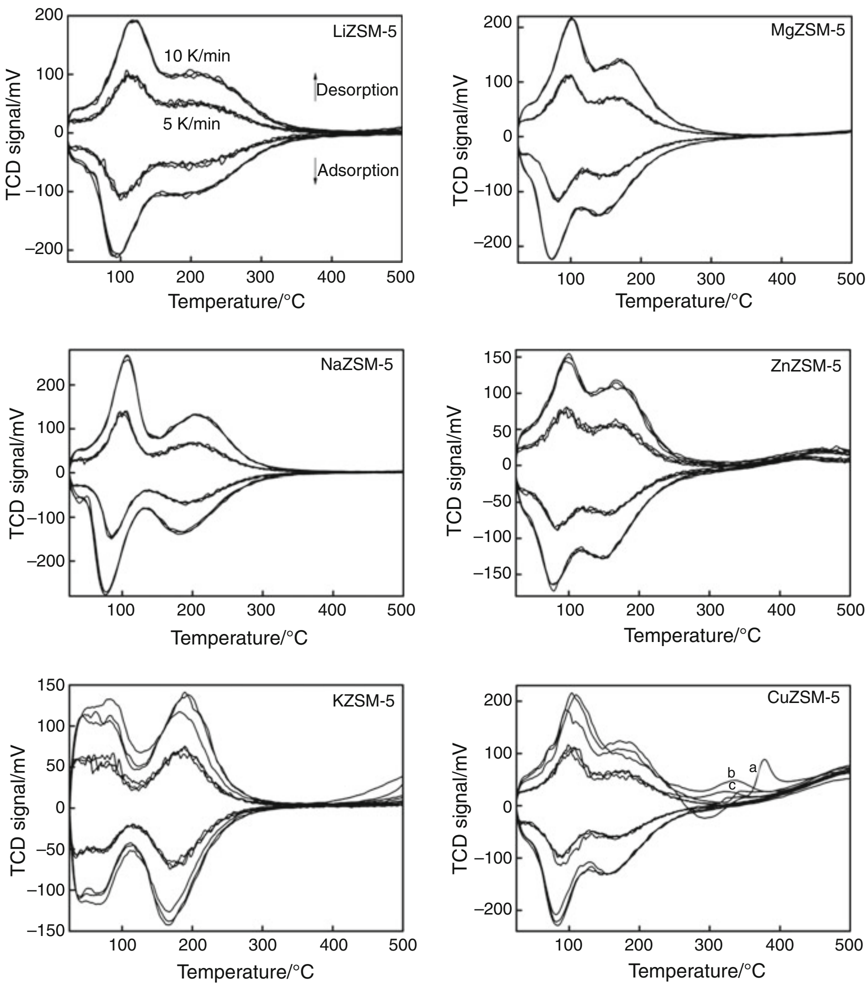


Fig. 1 Comparison of the raw experimental data obtained for NaZSM-5 (Si/Al = 35) in the TPED and QE-TPDA measurements (**a**) and the resulting integral and differential desorption profiles (**b**)

Fig. 2 The QE-TPDA profiles of *n*-hexane for the ZSM-5 zeolites (Si/Al = 15) containing different extraframework cations, measured at 10 and 5 K/min



The normalized differential QE-TPDA profiles (Fig. 3) were calculated according the procedure discussed in detail earlier [29]. They were fitted with the DSL model function, i.e., linear combination of two temperature derivatives of the Langmuir isobar (Eq. 1):

$$\frac{\mathrm{d}\theta}{\mathrm{d}T} = a_1 f_1 + a_2 f_2 \tag{1}$$

$$f = \frac{p\Delta H_{\mathrm{ads}} \exp\left(\frac{\Delta_{\mathrm{ads}}S}{R}\right) \exp\left(-\frac{\Delta_{\mathrm{ads}}H}{RT}\right)}{\left[p\exp\left(\frac{\Delta_{\mathrm{ads}}S}{R}\right)\exp\left(-\frac{\Delta_{\mathrm{ads}}H}{RT}\right)+1\right]^2 RT^2} \tag{2}$$

where θ denotes the fractional adsorption degree, a fractional contribution of each adsorption step, p the partial pressure of the adsorptive, $\Delta_{\mathrm{ads}}H$ and $\Delta_{\mathrm{ads}}S$ the adsorption enthalpy and entropy.

It may be noticed that apart from the low temperature region (<70 °C), very good agreement between the experimental data and the model function was obtained. Values of the adsorption enthalpy and entropy determined as the model parameters are listed in Table 1. Index 1 refers to the low temperature (LT) adsorption step, index 2—to the high temperature (HT) adsorption step. In Table 1 values of the saturation sorption capacity and the micropore volume as well as fractional contributions of the LT (a_1) and HT (a_2) adsorption steps in normalized total adsorption are shown.

The same adsorption data were use to the derivation of a micropore volume. Using the adsorption function based on the Langmuir model does not imply assuming chemisorption on some specific active sites. *n*-Alkanes are actually physisorbed in the micropores of zeolites and the adsorption sites are positions within the channels or cages of the zeolite framework. Thus, the maximum sorption capacity (or the total number of the adsorption "sites") is a measure of the micropore volume available for adsorption.

Differences in the pore volumes (calculated from the saturated sorption capacity data assuming that density of the adsorbed hexane is the same as that of the liquid) differ considerably. The lowest pore volumes were found for ZnZSM-5 (0.10 cm^3/g) and KZSM-5 (0.12 cm^3/g). The latter value may result from the size of the K^+ ions occupying large part of the extraframework space. In the

Fig. 3 Normalized differential QE-TPDA profiles of *n*-hexane for the ion-exchange ZSM-5 zeolites, fitted with the DSL function

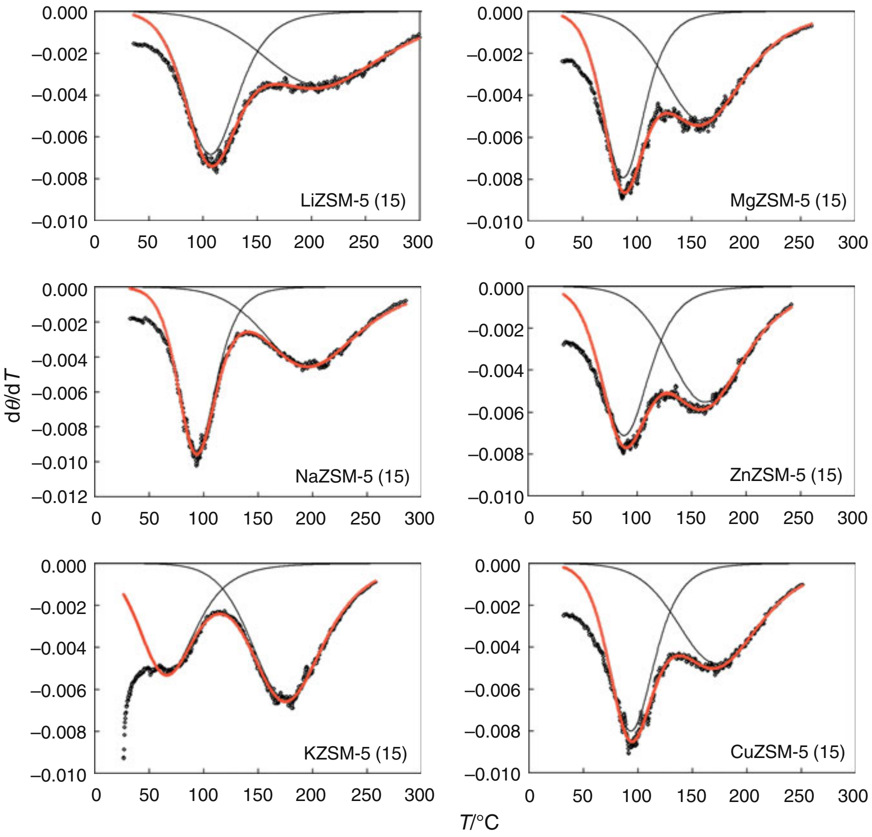


Table 1 Values of the parameters determined for ion-exchange ZSM-5 zeolite from TPED and QE-TPDA profiles

Ion	TPED		QE-TPDE							
	Sorption capacity (mmol/g)	Pore volume (cm^3/g)	Sorption capacity (mmol/g)	Pore volume (cm^3/g)	LT adsorption step			HT adsorption step		
					a_1	$-\Delta_{\mathrm{ads1}}H$ (kJ/mol)	$-\Delta_{\mathrm{ads1}}S$ (J/(mol K))	a_2	$-\Delta_{\mathrm{ads2}}H$ (kJ/mol)	$-\Delta_{\mathrm{ads2}}S$ (J/(mol K))
Li	1.10	0.15	1.07	0.14	0.44	74	153	0.55	51	62
Na	1.06	0.14	1.12	0.15	0.43	97	221	0.52	65	96
K	1.00	0.13	0.92	0.12	0.37	56	122	0.56	77	128
Mg	1.27	0.17	1.14	0.15	0.40	86	195	0.52	64	103
Zn	1.13	0.15	0.77	0.10	0.42	74	161	0.52	66	109
Cu	0.98	0.13	1.07	0.14	0.44	82	180	0.49	64	101

case of ZnZSM-5 zeolite formation of amorphous zinc hydroxide within the micropores may be expected. Other values of the micropore volume are only slightly lower than the result of low temperature N_2 adsorption measurements (0.16 cm^3/g [23]). The fact that the sum of a_1 and a_2 is always slightly below one accounts for the adsorption at temperatures below 70, where the experimental profiles deviate from the model ones. It should be pointed out that the contributions of HT adsorption steps are always greater those of the LT step, thus contradicting the widely accepted opinion that each step in adsorption of *n*-hexane in MFI structure corresponds to 4 molecules per unit cell. This difference is the highest for KZSM-5, probably due to negative effect of large potassium ions on ordering of the adsorbed molecules within the micropores.

Values of the adsorption enthalpy and entropy determined by fitting of the DSL function to the QE-TPDA profiles reflect their diversity. The adsorption enthalpies ($-\Delta_{\mathrm{ads}}H$) obtained for the HT adsorption step are close to 64–70 kJ/mol reported for ZSM-5 (Si/Al = 140) and to 60 kJ/mol—for HZSM-5 (Si/Al = 15) [26]. Values of the adsorption enthalpy of the LT step are smaller than those found for the high silica zeolite (104–110 kJ/mol) and closer to that obtained for the acidic zeolite (79 kJ/mol) [26]. The adsorption entropies ($-\Delta_{\mathrm{ads}}S$) are close to those observed for HZSM-5 (Si/Al = 15) − 172 J/(mol K) for the LT adsorption step and 88 J/(mol K) HT adsorption step [26]. However, they are more diverse than the adsorption enthalpies.

It is not possible to find a clear correlation between the values of the adsorption enthalpy and entropy determined for the ion-exchanged zeolites ZSM-5 (Si/Al = 15) and properties of the extraframework cations. The absolute values of $\Delta_{ads}H$ and $\Delta_{ads}S$ for the HT step seem to increase with the increasing size of the alkali ions. The highest value of $(-\Delta_{ads}S)$ for the LT step found for NaZSM-5 (Si/Al = 15) may indicate that the Na^+ ions within the zeolite channels may facilitate ordering of the adsorbed molecule. This concept is supported by the largest value of the micropore volume found for this zeolite.

The TPED curves of *n*-hexane desorption and adsorption on the ion-exchanged ZSM-5 zeolites measured gravimetrically are plotted in the Fig. 4. Contrary to the convention usually accepted in thermal analysis, the desorption peaks (corresponding to decrease of mass) are positive and the adsorption peaks are negative, in order to represent these results in a similar way as the QE-TPDA profiles (Fig. 2).

All the TPED profiles exhibit two main peaks characteristic for two step adsorption of *n*-hexane on MFI. The desorption and adsorption profiles for all studied samples differ one from another. This leads to the conclusion that the most important condition of TPED experiments—the equilibrium control between adsorption and desorption processes—was not satisfied and that extent of adsorption was affected by diffusion or catalytic reaction. In consequence, the DSL model could not be fitted and the adsorption enthalpy and entropy were not determined. Even so, taking into consideration only the desorption profiles, measured first, just after in situ adsorption in 25 °C, some observations can be made.

The values of sorption capacity and microporous volume determined from TPED experiments (Table 1) are generally similar to those obtained from QE-TPED results. The main difference is observed for ZnZSM-5 sample.

Before the peaks at about 115 and 210 °C additional low temperature peak was observed between 50 and 80 °C. It probably originates from hydrocarbon desorbing from the external surface, enriched by the exchange cations, which were not removed completely after ion-exchange

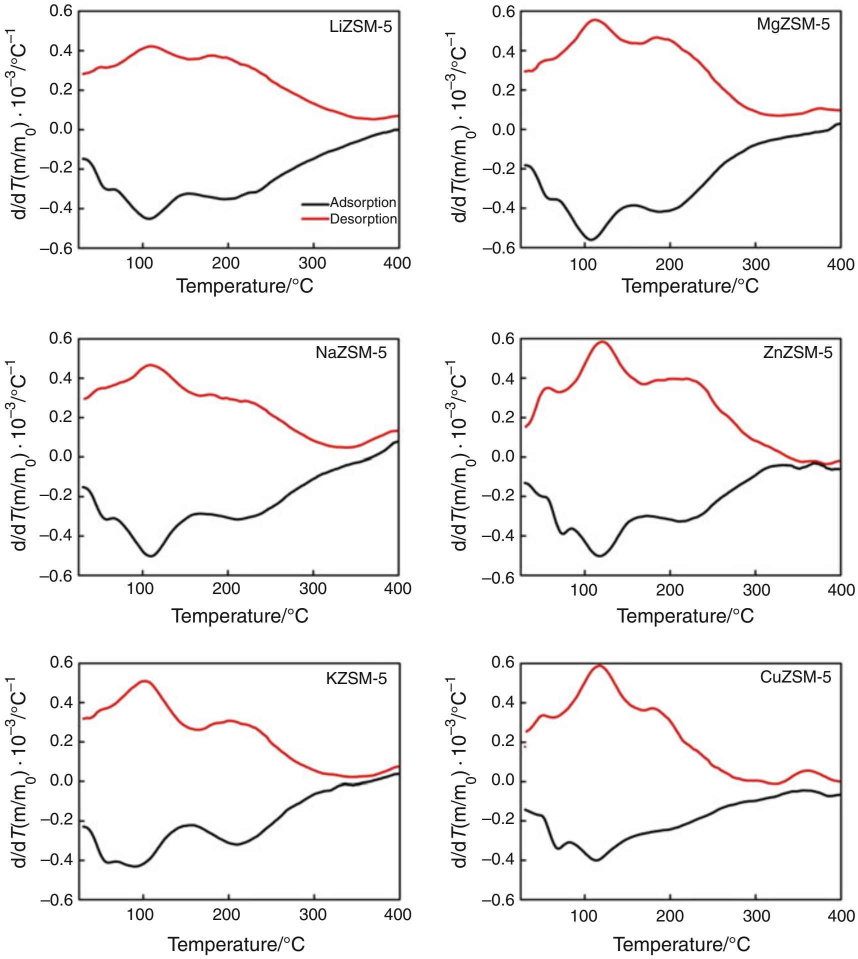


Fig. 4 The TPED profiles of *n*-hexane for the ion-exchanged ZSM-5 zeolites (Si/Al = 15), measured at 10 K/min

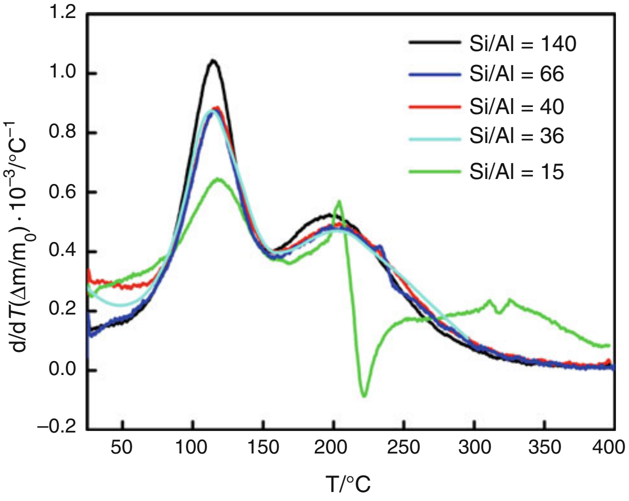


Fig. 5 The TPED profiles of *n*-hexane for HZSM-5 zeolites, differing in Si/Al ratio

procedure and could act as the additional adsorption centers. This effect was not observed in the QE-TPDA experiments most probably because of much smaller partial pressure of the adsorptive, equal to 0.005–0.01 bar (vs. 0.06 bar used in the TPED).

Above temperature 300 °C the TPED signal for all studied samples increase insignificantly. This decrease in mass should be attributed to desorption of the carbonaceous intermediates of the catalytic cracking of *n*-hexane. This effect was especially noticeable in the case of CuZSM-5—the corresponding TPED profile exhibited the additional peak at 350 °C. During the experiments the CuZSM-5 samples changed color from whitish to dark green. Such changes of color indicate coke formation that might have additionally constricted the pore volume and made it less accessible for *n*-hexane molecules in following adsorption process. It has been reported that introduction of transition metal ions into cationic positions may cause not only decrease the number of Brönsted acid sites but also generation of quite strong Lewis sites [30], which might also be responsible for catalytic cracking of *n*-hexane [31].

The concept that cracking of *n*-hexane and coking of the zeolite take place during the TPED measurements is supported by the results of the additional TPED experiments performed on HZSM-5 zeolite differing in the Si/Al ratio and thus in acidity (Fig. 5). The plots obtained for HZSM-5 with Si/Al = 66, 40 and 36 are almost identical. They are in agreement with previous results [26] and exhibit two peaks—at about 115 and 200 °C—with almost the same intensity. There profiles reflect interactions of *n*-hexane molecules with the MFI framework, which are practically not affected by relatively small number of the framework Al atoms and balancing them the extraframework protons. Major differences in the intensity of the desorption peaks are observed for the zeolites with high (140) and small (15) Si/Al ratio. In the first case they may originated from the fact that the structure of high silica zeolite is less defected. In the second case the intensity of the low temperature peak is very small and at 210 °C the sharp decrease of the differential TPED profile below zero, i.e., increase of the sample mass, was observed. This is a direct evidence of formation of the carbonaceous reaction intermediates in catalytic cracking of *n*-hexane. While the temperature increases, the sample mass quickly starts to decrease again, due to decomposition and desorption of the carbonaceous deposits. These results show that under the conditions applied cracking of *n*-hexane on Brönsted acid sites takes place about 210 °C only on highly acidic HZSM-5 (Si/Al = 15). None of TPED profiles for the ion-exchanged samples contains similar effects of the catalytic cracking of *n*-hexane at 210 °C, indicating that introduced ions were effective in poisoning Brönsted acid sites.

It is surprising that, contrary to the previous results [26, 27], the TPED measurements yielded data of much lower quality than the QE-TPDA experiments. The thermogravimetric method TPED certainly offers higher accuracy. In the QE-TPDA there are three major sources of uncertainty of the results which are not present in TPED: integration of the desorption or adsorption peaks with the arbitrary choice of the baseline, transfer of the weighted sample to the sample tube and calibration of the detector signal. The reason why the results from TPED experiments are of low quality is unclear. It is possible that the extra-framework cation change the morphology of the ZSM-5 (Si/Al = 15) zeolite crystals used in this study resulted in greater diffusion limitations.

On the other hand the high quality QE-TPDA results confirm great potential of this novel thermodesorption technique. The carrier gas containing small admixture of the adsorptive flowing through the very small sample bed ensures fast attaining of quasi-equilibrium control. Simple, flexible and inexpensive instrumentation allows application of this technique as a method of porosity characterization, combined with catalytic screening or thermal stability studies.

Conclusions

It has been shown that different extraframework cations in ZSM-5 (Si/Al = 15) zeolites have considerable influence on the two-step adsorption profiles of *n*-hexane in the MFI structure, affecting both the initial adsorption in the micropores as well as ordering of the adsorbed molecules, occurring at high coverages. This influence is reflected by the values of the adsorption enthalpy and entropy, determined by fitting the DSL adsorption function to the equilibrated thermodesorption profiles. However, no clear correlation between the determined parameters and properties of the extraframework cations could be found.

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