TEMPERATURE-PROGRAMMED DESORPTION OF *n*-HEXANE FROM HYDRATED HZSM-5 AND NH₄ZSM-5 ZEOLITES

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Temperature-programmed desorption coupled with mass spectrometer as a detector (TPD), IR and ^{13}C NMR measurements are used to study the adsorption of *n*-hexane on hydrated HZSM-5 and NH₄ZSM-5 zeolites. The ^{13}C NMR measurements show that *n*-hexane can access the pore structure of ZSM-5 zeolites previously saturated with water. TPD spectra of *n*-hexane are monitored in the temperature region 50–300°C, in the case of fully or partially hydrated samples; two-stage desorption of *n*-hexane is found. Simultaneous desorption of water and *n*-hexane in the same temperature region are found, in all investigated samples.

Introduction

Zeolites are used extensively in the chemical industry for gas separations and as catalysts. Both applications are influenced by adsorption and diffusion of adsorbate molecules within the microporous structures. Therefore, considerable experimental and theoretical work has been devoted to these processes and to their relations with framework topologies and characteristics [1–20]. Some important separation procedures, such are differentiating between olefins and alkanes; and between branched and linear hydrocarbons are based upon differences in adsorption processes and molecule sizes.

Among the other structures, ZSM-5 zeolite and its microporous silica polymorph, silicalite, are widely investigated. The framework topology of ZSM-5 zeolite is composed of a three-dimensional network of straight and zigzag channels, with channels apertures close to the *n*-alkanes kinetic diameters [8]. A separation of *n*-alkanes from isoalkanes on this zeolite has been established. The length of *n*-hexane molecule (10.3 Å) is comparable to the length of ZSM-5 channels [8, 13, 20], which enables a shape-selective adsorption. Many investigations have therefore been devoted to the interaction of *n*-hexane and ZSM-5 and silicalite structures [1–19].

The interaction of *n*-hexane with ZSM-5 zeolite, its location and dynamics in this structure, has been investigated by temperature programmed desorption [13–16], neutron scattering [7, 10], solid-state NMR [12, 17–19] and XRD [12] techniques. Typically, TPD profiles with few overlapped peaks were obtained, indicating heterogeneity of a ZSM-5 zeolite for the adsorption of *n*-hexane. The location of *n*-hexane molecules in the ZSM-5 zeolite has been under discussion in the past years. NMR, neutron scattering and XRD investigation, as well as molecular modeling, led to the conclusion that the sorption sites of the *n*-hexane molecules are well-defined within the channel system, being located only in the straight and sinusoidal channels, leaving the intersections unoccupied [12].

It is important to point out that the interaction of *n*-alkane and ZSM-5 zeolite was investigated on dehydrated samples. However, the adsorption on partially or fully hydrated solids is becoming an important subject. Gas streams which are subjected to separation processes often contain water. Environmentally and economically beneficial catalytic processes of alkanes' and other molecules' oxidation in aqueous solutions have recently attracted vast attention [21]. Many steps in such catalytic processes in a general sense can depend on water co-adsorption on the adsorption sites. Several literature sources concerning the adsorption of organic molecules in the presence of water are available [22–24]. The influence of a small quantity of preadsorbed water on the kinetics of hydrocarbons in NaX zeolite has been noticed [23]. It has been found that water reduces the adsorption capacity especially at low adsorbate concentration. Recently [24], we have performed TPD studies, which provided relevant qualitative insight in this area. It was shown that *n*-hexane is adsorbed on fully hy-

drated hydrogen and cation exchanged forms of Y and ZSM-5 type zeolites. Our results support the idea of a subdivision of the pore space for adsorption of water and *n*-hexane.

The major objective of this work is the investigation of *n*-hexane interaction with fully hydrated HZSM-5 zeolites as a function of their compositions. It is well known that ion exchange capacity, catalytic activity and hydrophobicity of zeolites depend linearly on the amount of Al present in the framework [25, 26]. It is also known that Al-rich zeolites are suitable for the separation of water-organic mixtures, while Al-free silicalite is the best shape selective adsorbent [27]. Therefore, in this work we investigated the adsorption of *n*-hexane on a series of hydrated HZSM-5 samples with different Si/Al ratio. To study these interactions, we used temperature-programmed desorption method. ^{13}C NMR and IR spectroscopies have been used for additional investigation of *n*-hexane adsorption on these systems.

Experimental

NH$_4$ZSM-5 and HZSM-5 zeolites investigated in this work were purchased from Zeolyst. Two sets of ZSM-5 samples investigated in this work are denoted as HZSM-5(x) and NH$_4$ZSM-5(x), where *x* indicates the Si/Al ratio (15, 25, 40 or 140).

The adsorption of *n*-hexane on fully hydrated samples was performed using a procedure similar to those applied by Millot [15] and Makowski [16]: the samples were stored for 24 h in a desiccator containing liquid *n*-hexane in an open vessel, at room temperature. Spectroscopic grade *n*-hexane obtained from Merck was used without further purification. In this way obtained samples were characterized using NMR and IR spectroscopies.

The ^{13}C cross-polarized (CP) magic angle spinning (MAS) NMR measurements were performed on a Bruker DSX 400 spectrometer at room temperature, with a spinning rate of 5 KHz. The contact time for cross polarization was 1 ms, while the repetition delay was 6 ms. Number of scans accumulated were 7000. Tetramethylsilane was used as an external reference.

The free induction decays (FID) were weighted with a line broadening of 30 Hz prior to Fourier transformation; the resulting spectra were simulated using the WINFIT program of Bruker. The infrared (IR) spectra of self-supported solid HZSM-5 samples were recorded in the range of 4000–400 cm^{-1} on a Nicolet 370 FTIR spectrometer.

Desorption of water and *n*-hexane was studied using the temperature-programmed desorption technique (TPD), carried out in a flow of helium, in the temperature range 20–400°C. Setaram DSC/TG 111 differential scanning calorimeter consisted of a quartz micro-reactor heated in a vertical furnace and capillary coupled with an on-line Pfeiffer Thermostar mass spectrometer as a detector, was used. Prior to TPD procedure, the sample was flushed with helium for 30 min, in order to ensure complete removal of physisorbed species. Desorption of water and *n*-hexane was then carried out from 25 to 300°C, using a temperature ramp of 10°C min^{-1}. The masses corresponding to water (m/e=18, 17) and *n*-hexane (m/e= 57, 43, 41 and 29) were recorded in each experiment. For each experiment, ca 20 mg of a sample was used. The flow of helium was kept at 40 mL min^{-1}.

On dehydrated samples, *n*-hexane was adsorbed as follows: the sample was activated at 400°C for 2 h under a helium flow, in DSC furnace. Subsequently, the sample was cooled to the room temperature, and *n*-hexane was admitted by circulation of helium through a cell containing liquid *n*-hexane. TPD was performed afterwards, in situ.

Results and discussion

Quantitative data concerning the amounts of water present in the investigated systems, and the amounts *n*-hexane adsorbed on these hydrated samples at room temperature, are obtained by thermogravimetry, performed up to 400°C. Table 1 compiles the data obtained for HZSM-5 zeolite samples before (columns 2 and 3) and after the same samples were exposed to *n*-hexane (columns 4–6). It is obvious that the amounts of water desorbed up to 400°C are decreasing with the increase of Si/Al ratio. Quite contrary, the amounts of *n*-hexane

Table 1 Quantitative data obtained by thermogravimetric analysis

Sample	Δm_1/%	n_1, H$_2$O molecules per unit cell	Δm_2/%	$m_{hexane}=\Delta m_2-\Delta m_1$/%	n_2, C$_6$H$_{14}$ molecules per unit cell
HZSM-5(15)	7.25	24	8.55	1.3	0.9
HZSM-5(25)	6.65	22	9.0	2.35	1.65
HZSM-5(40)	4.90	16.3	10.3	5.35	3.7
HZSM-5(140)	1.80	5.9	8.75	6.95	4.8

Δm_1 – mass loss obtained from fully hydrated HZSM-5 zeolite samples. Δm_2 – mass loss obtained from fully hydrated HZSM-5 zeolite samples exposed to *n*-hexane vapour
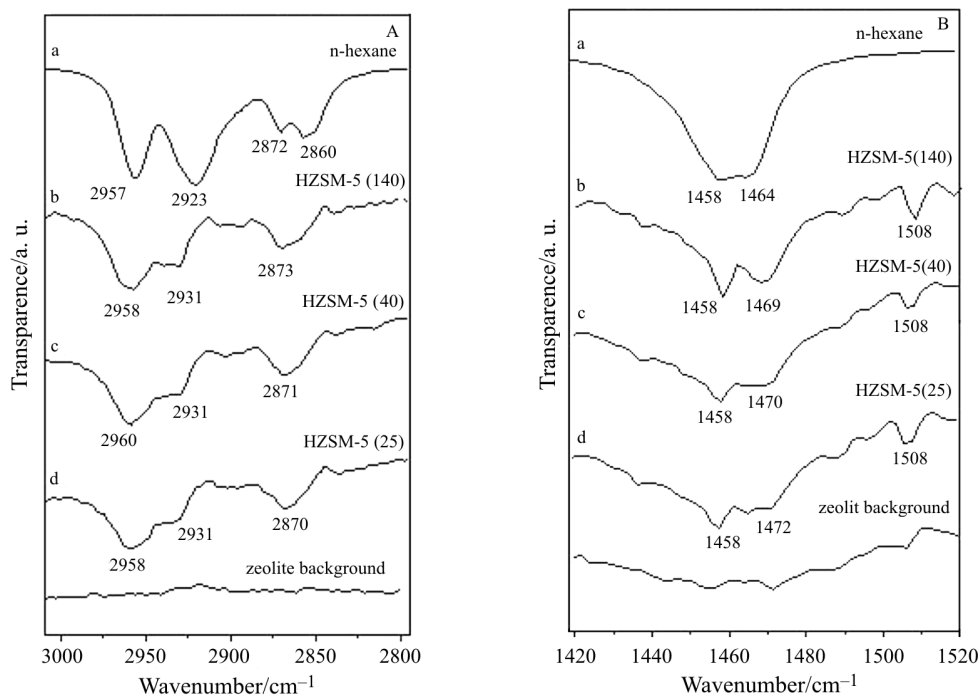
Fig. 1 FTIR spectra of *n*-hexane in the region of the stretching (A) and bending (B) C–H vibrations. Spectra: a – pure *n*-hexane in liquid phase; b – d *n*-hexane in HZSM-5(140), HZSM-5(40) and HZSM-5(25) zeolites, respectively

desorbed from the same samples are higher for more siliceous HZSM-5 samples, as expected from already known literature data [3, 8].

The results presented in Table 1 indicate the interaction of *n*-hexane with fully hydrated ZSM-5 structures, as a result of their exposure to *n*-hexane vapour. In order to characterize the samples after their exposure to *n*-hexane, IR and ^{13}C NMR spectra were collected. Figure 1 presents IR spectra recorded after the exposure of these fully hydrated samples to *n*-hexane. The bands characteristic for stretching and bending vibrations of C–H bonds are apparent, in the case of all investigated samples, which is evidence of established interaction between *n*-hexane and zeolite host.

Figure 2. displays the ^{13}C NMR spectra of *n*-hexane adsorbed in fully hydrated HZSM-5 zeolites with different Si/Al ratio. Adsorption of *n*-hexane in all investigated HZSM-5 samples leads to three signals in the NMR spectra: one signal originating from the methyl group, around 13 ppm, and two signals originating from the methylene group, around 22 and 32 ppm. All three signals are in accordance with the signals obtained for *n*-hexane adsorbed in channels of dehydrated zeolites, previously reported in the literature [19]. Hence, these results confirm that during exposure of fully hydrated HZSM-5 samples at room temperature to *n*-hexane vapour, *n*-hexane molecules have been adsorbed in the channels of all investigated ZSM-5 zeolites.

The results presented so far show that *n*-hexane was adsorbed on all investigated fully hydrated

HZSM-5 zeolite samples. The estimation of the strength of this interaction was done by studying desorption processes, performed by TPD technique. The TPD profiles obtained for *n*-hexane desorption from HZSM-5 samples with different Si/Al ratio are shown in Fig. 3. It is worth noticing that during the TPD procedure, the masses which are originating from the fragmentation of the *n*-hexane molecules in the chamber of the spectrometer (*m/e*=57, 43, 41, 29) were monitored. The
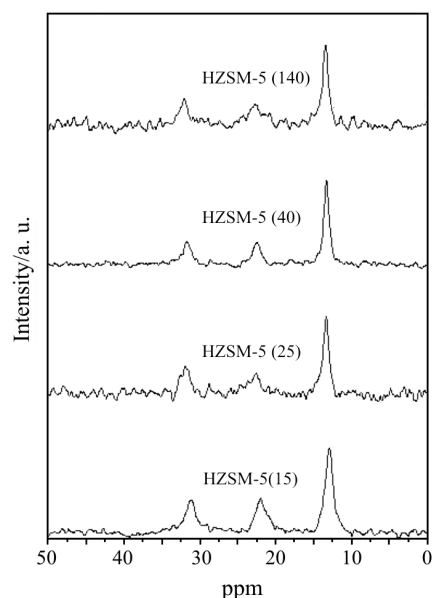

Fig. 2 ^{13}C NMR spectra of *n*-hexane in HZSM-5 with different Si/Al ratio, indicated in the spectra
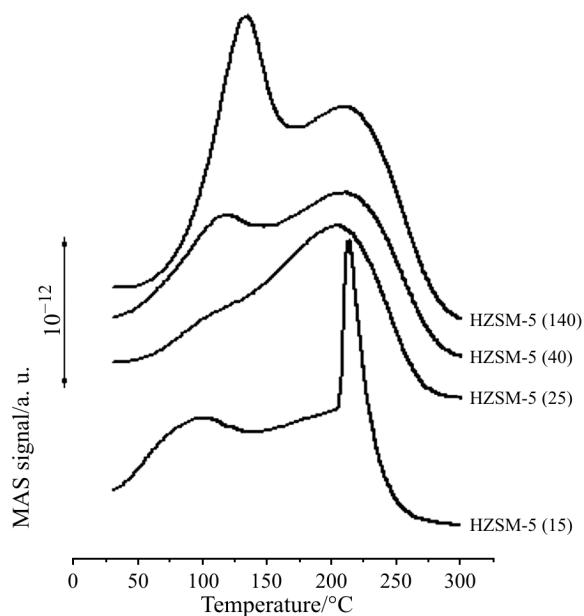
Fig. 3 TPD spectra of *n*-hexane (*m/e* = 41) from hydrated HZSM-5 zeolites with different Si/Al ratio

desorption curves found for all *n*-hexane fractions expressed the same profiles, what is a clear indication of molecular desorption of *n*-hexane.

All TPD spectra presented in Fig. 3 are complex, composed of two overlapped, *l*- and *h*- (low and high temperature) peaks, both peaks being broad. The exception is a very sharp *h*-peak centered at 210°C which is present in the TPD spectrum of *n*-hexane desorbed from HZSM-5(15) zeolite. It is evident that all investigated hydrated samples have the sites accessible for *n*-hexane adsorption. It is also clear that these sites could be classified in two main types: weak and strong. A brief insight in the results presented in Fig. 3 reveals evidence that the *l*-peak which originate from weakly held *n*-hexane is strongly related to the Si/Al ratio. With increase of Si/Al ratio from 15 to 140, the temperature of maxima (T_m) of the *l*-temperature peak increases from 70°C, in the case of HZSM-5(15), up to 130°C found for HZSM-5(140). On the contrary, the *h*-peak which is due to the strongly bonded *n*-hexane is not related to the change in Si/Al ratio of the zeolite: all *h*-temperature peaks have the same T_m. The relative intensities of *l*- and *h*-peaks differ with the composition of HZSM-5 zeolites, indicating the change of coverage of two possible sites for *n*-hexane adsorption, as a result of change in Si content in the investigated samples.

TPD spectra of water is also recorded in the course of *n*-hexane desorption. The obtained results are presented in Fig. 4.

Besides the TPD spectra of water recorded from the hydrated samples exposed to *n*-hexane vapour (dashed lines), the signal of water was also monitored
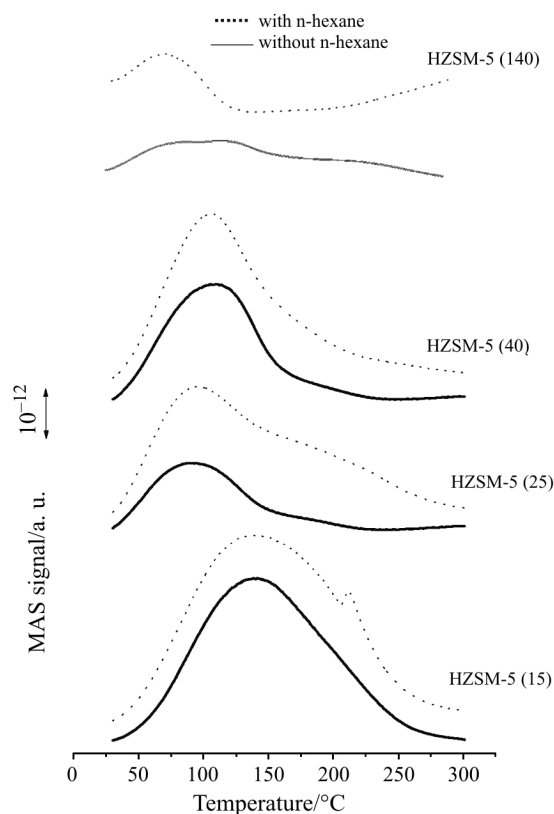

Fig. 4 TPD spectra of water (*m/e* = 18) from HZSM-5 zeolites with different Si/Al ratio. Solid lines – before exposure to *n*-hexane, dashed lines – after exposure to *n*-hexane

in the course of temperature programmed heating of fully hydrated HZSM-5 zeolite samples, before the exposure to *n*-hexane. As it can be seen from Fig. 4, TPD profiles of water are similar; nevertheless the water comes from the samples with or without adsorbed *n*-hexane. This fact refers to the conclusion that the desorptions of water and *n*-hexane are possibly independent processes. The decrease of water peaks intensities with increasing Si/Al ratio is also noticeable, and most prominent in the case of HZSM-5(140) sample, what is in accordance with already known fact that silica rich ZSM-5 zeolites express high hydrophobic/organophilic character.

The adsorption of *n*-hexane was also performed on activated samples. Before adsorption which was done at 20°C from the flow of helium saturated with *n*-hexane vapour, the sample was kept at 400°C for 2 h. Mass loss and TPD profile of *n*-hexane, obtained in the temperature range 20-400°C for HZSM-5(15) are presented in Fig. 5. The obtained TPD result shows again two-stage desorption. Like in the case of *n*-hexane adsorption in fully hydrated samples, this result indicates again that *n*-hexane molecules are adsorbed on two main types of positions in the HZSM-5 zeolite structure. The analysis of TPD profile of *n*-hexane recorded after adsorption performed under these particular conditions (from the flow, in the pres-
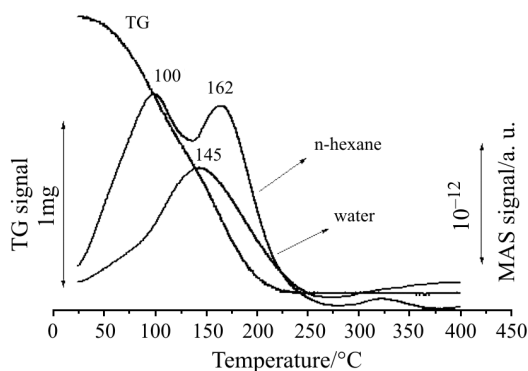
Fig. 5 TG and TPD profiles of *n*-hexane (*m/e* = 41) and water
(*m/e* = 18) recorded during desorption from
HZSM-5(15), after this sample was activated at 400°C,
and subsequently *n*-hexane was adsorbed at 20°C, in situ

ence of small amount of water) reveals that this profile is somehow different in comparison with that one obtained from fully hydrated sample. Namely, the position of *l*- peak is the same, while the T_m of *h*- peak is changed in comparison with TPD profile obtained for fully hydrated HZSM-5(15) zeolite.

TPD profile of water recorded in the course of same experiment is also presented in the same Figure. The appearance of water adsorbed on previously activated sample comes, most probably, from the experimental difficulties to isolate a flow system from the atmosphere. The amount of water desorbed in this experiment is calculated as follows: having in mind that MS signal for both *n*-hexane and water are of the same magnitude, the sum of the integrated areas under both TPD curves are assigned to the total mass loss, obtained from TG. A part of this total area which can be assigned to the area found under the water signal, and expressed in percentages, has been taken as a percentage of total mass loss (TG signal) which comes from water desorption. The amount of desorbed water is much lower (~ 4 molecules per unit cell) in comparison with that one found for fully hydrated HZSM-5(15) sample (24 molecules per unit cell). Besides, the profile of water desorption is almost identical to that one recorded from fully hydrated HZSM-5(15) (T_m=145°C, Figs 4 and 5). Importantly, the amount of adsorbed *n*-hexane, calculated in the same previously explained way, is 3.5 molecules per unit cell; this is much higher value in comparison with the one obtained in the case of fully hydrated sample (0.9 molecules per unit cell, Table 1). As it could be expected, it is easier for *n*-hexane molecules to reach empty channels of HZSM-5 zeolite, in comparison with those filled with water. These results can be interpreted as another indication of independency of two processes: water and *n*-hexane interactions with investigated structure.

In order to check the effect of the acidity of the zeolite on the adsorption of *n*-hexane, the TPD pro-
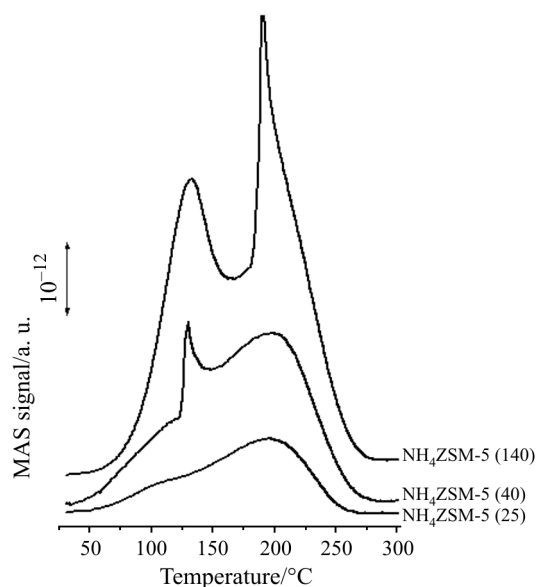

Fig. 6 TPD spectra of *n*-hexane (*m/e* = 41) from hydrated
NH₄ZSM-5 zeolites with different Si/Al ratio

files recorded after its adsorption on fully hydrated hydrogen and ammonium exchanged zeolites were compared (Figs 3 and 6). In the hydrogen form of zeolites Lewis and Brønsted sites are present, while in ammonia form only Lewis sites are accessible for adsorption of water or *n*-hexane. TPD profiles found for ammonium exchanged samples are similar in shape with those found for HZSM-5 zeolites: they are also complex and composed of two overlapped peaks. The intensities of the desorption peaks in the case of ammonia forms are systematically higher than in hydrogen forms of investigated samples, thus indicating that higher amounts of *n*-hexane are adsorbed on ammonium exchanged samples.

All TPD results presented so far clearly demonstrate two-stage desorption of *n*-hexane found in the case of investigated zeolites, partially or fully hydrated. These results are comparable with those published in the literature for dehydrated HZSM-5 and silicalite structures [13–16]. Two well defined TPD peaks, overlapped in the same temperature region as in the case of dehydrated systems, suggest that the same positions for adsorption on partially or fully hydrated samples could be active. In the case of dehydrated systems, combined results obtained from experiments and molecular modeling have shown that 4 *n*-hexane molecules adsorbed per unit cell can occupy only the straight and sinusoidal channels, leaving the intersections free. The location and dynamics of *n*-hexane molecules could be determined by their interaction with zeolite framework and by the presence of water molecules. Therefore, precise insight into the problem of *n*-hexane adsorption on hydrated systems should be obtained from multidisciplinary experi-

mental and molecular modeling approach. Neverthe-less, the adsorption of *n*-hexane on hydrated zeolites seems to be an important finding for designing new environmentally friendly catalytic processes.

Acknowledgements

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