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ROOM-TEMPERATURE INTERACTION OF *n*-HEXANE WITH ZSM-5 ZEOLITES
Microcalorimetric and temperature-programmed desorption studies

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In this work, room temperature interaction of *n*-hexane with HZSM-5 (Si/Al=20) and ion-exchanged samples containing one (CuZSM-5, FeZSM-5 and MnZSM-5) or two transition-metal cations (Fe,CuZSM-5; Cu,MnZSM-5 and Fe,MnZSM-5) was studied by microcalorimetry and TPD methods. Both differential heats and the amounts of *n*-hexane adsorbed per one unit cell were quantitatively determined. Higher heats of adsorption and higher amounts of adsorbed gas were found for ion-exchanged samples than for HZSM-5. The experiments of *n*-hexane adsorption on hydrated samples were also performed. The amounts of *n*-hexane adsorbed on hydrated ZSM-5 were lower in comparison with dehydrated samples, while the energies of interaction were similar.

Keywords: *microcalorimetry, n-hexane, temperature-programmed desorption, ZSM-5*

Introduction

Zeolites are extensively used in chemical industry as catalysts and for gas separations [1–3]; these applications are related with their adsorption capabilities. Therefore, a widespread work has been done in studying the adsorption of many different adsorbates on molecular sieves. Since zeolites are used in separation of hydrocarbons and in catalytic processes involving them, the adsorption of *n*-alkanes has been widely studied [4–9]. Special attention was paid to the adsorption on MFI type zeolites (ZSM-5 and silicalite-1) because of their shape selective properties. ZSM-5 is a medium-pore zeolite which contains straight parallel channels interconnected by zig-zag channels, each made of 10-membered oxygen rings [10]. The free aperture of both channels is about 0.6 nm, what is similar in size to simple aromatics and *n*-paraffin molecules. Therefore, the adsorption of light alkanes on MFI structure has been studied with a particular intention to determine the amount of adsorbed gas and the locations of adsorbed molecules within the internal pore structure [8, 9, 11–13]. For those purposes, different techniques such are: calorimetric and adsorption measurements [8, 9, 11, 12], temperature programmed desorption [14, 15], NMR [16], FT-Raman [17–19] or neutron scattering spectroscopy [16] have been applied. There have also been a number of computer simulations of *n*-alkanes adsorption in silicalite [20–23]. In the respect of *n*-hexane adsorption on MFI structure, different numbers of molecules adsorbed per unit cell (from 2 to 8) have been reported [8, 9, 11], both number and locations have been found to be dependent on gas loading [11–14]. Importantly, it has been inferred that guest molecules can interact with zeolite lattice (pore walls), acid sites and other adsorbed molecules. Since MFI framework is mainly composed of Si atoms and since the channel dimensions are close to *n*-hexane kinetic diameters, the adsorption is found to origin generally from nonspecific, mainly dispersion interactions with the channels walls [14, 20]. However, there is not available literature sources concerning the influence of charge balancing cation incorporated in MFI structure.

In this work we report microcalorimetric (MC) and temperature programmed desorption (TPD) evidence for *n*-hexane adsorption on HZSM-5 zeolite (Si/Al=20) containing one or two transition metal divalent cations: copper, iron or manganese. The adsorption of *n*-hexane was investigated both in a vacuum system and in a flow of helium. Importantly, *n*-hexane adsorption from a gas flow is investigated on both dehydrated and hydrated samples. It is well known that water is commonly present in zeolite channels [24]. Besides, water is a common constituent in industrial gas streams; therefore, particular interest was devoted to the adsorption of *n*-hexane on hydrated ZSM-5 samples.

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Experimental

A parent home-produced NaZSM-5 was synthesized hydrothermally. HZSM-5 was derived by ion-exchange with ammonium chloride at 90°C and subsequent calcinations in air at 793 K, for 5 h. Under-exchanged samples containing Cu^{2+}, Fe^{2+} or Mn^{2+} were prepared using common wet ion-exchanged procedures: HZSM-5 was suspended in 0.01 M solution of corresponding divalent salt and stirred for 24 h, followed by filtering, washing with de-ionized water and drying. For bimetallic samples, consecutive ion exchange has been applied. The samples were denoted as MZSM-5, or M,NZSM-5; M and N denote cations, cation N was exchanged firstly. CuZSM-5 was obtained at 298 K using an aqueous solution of copper acetate, as described previously [25]. FeZSM-5 was obtained by aqueous ion exchange with $FeCl_2\cdot4H_2O$, at 298 K, in the flow of N_2. MnZSM-5 samples were prepared at 353 K, from a solution of manganese acetate.

The crystallinity of parent NaZSM-5, HZSM-5 and ion-exchanged forms was checked by X-ray diffraction. Powder X-ray diffraction patterns were recorded on a Bruker (Siemens) D5005 diffractometer at room temperature using CuK_α (radiation, 0.154 nm) from 3–80 2θ in a 0.02° steps with 1 s per step. XRD measurements have shown that the structure of ZSM-5 zeolite remains unaffected by ion-exchange procedure. HZSM-5 was additionally analysed using ^{29}Si and ^{27}Al magic angle spinning NMR technique. MAS NMR measurements were performed on a Bruker MSL 400 at 9.4 T at room temperature, MAS spinning rate of 10 KHz was used. Surface areas were determined by the BET method from the adsorption of nitrogen at 77 K after pretreatment for 4.0 h at 673 K under vacuum. The cation contents were determined by AES-ICP in a Spectroflame-ICP instrument. The samples were additionally characterized by ammonia adsorption examined by microcalorimetry.

The heats of ammonia and *n*-hexane adsorption were measured in a heat-flow calorimeter of the Tian-Calvet type from Setaram, linked to a glass volumetric line; both thermal effects and volumetric isotherms were detected. A well-established stepwise procedure, previously fully described [26] was followed. The samples were pretreated under vacuum at 673 K prior to adsorption of ammonia or *n*-hexane in the calorimetric cell maintained at 423 and 303 K respectively. Successive small doses of NH_3 or *n*-hexane were introduced onto the samples until a final equilibrium pressure of 66 Pa was achieved. The equilibrium pressure corresponding to each adsorbed amount was measured by means of a differential pressure gauge from Datametrics. Subsequently, the sample was pumped, desorption peak was recorded and a readsorption was performed at the temperature of adsorption. The irreversibly adsorbed amount of a chemisorbed gas was calculated from difference between primary and secondary isotherms.

TPD of NH_3 and *n*-hexane were performed on a TG/DSC 111 from Setaram consisting of a quartz micro-reactor, heated in a vertical furnace. An on-line mass spectrometer (MS, Thermostar from Pfeifer) was used as the detector; capillary-coupling system was used. All experiments were carried out in a helium flow (15 mL min^{-1}), ca. 15 mg of sample was placed in a DSC furnace. For TPD of NH_3, a sample with a gas previously adsorbed in a microcalorimetric experiment was used. The samples were purged with helium at 383 K for 30 min and then heated at 5 K min^{-1} in helium up to 823 K, the mass spectrometer was set at m/e=15 in order to avoid the interference of water fragmentation masses. Prior the TPD experiment, *n*-hexane was adsorbed in situ, from the He flow saturated with the vapor of *n*-hexane (HPLC grade, Aldrich). A simple glass saturator filled with the liquid hydrocarbon and cooled using water–ice mixture was used, the adsorption was done at 293 K. TPD experiments were carried out with or without previous pretreatment of the sample (673 K, 2 h in a helium flow). For *n*-hexane TPD, the common mass fragmentation of this molecule (86, 57, 56, 55, 43, 42, 41, 27, 39) were recorded.

Results and discussion

Chemical composition, surface areas and the amounts of ammonia adsorbed on the investigated samples are presented in Table 1. It can be seen that all the samples are under-exchanged; and that surface areas of ion-exchanged samples are not changed in comparison with HZSM-5. Differential heats (Q_{dif}) of ammonia adsorption and TPD profiles of ammonia are presented in Fig. 1. As it can be seen, the whole acidity of ion-exchanged samples was not significantly changed. However, a change of profiles Q_{dif} *vs.* ammonia uptake, particularly in their middle parts; indicate that a distribution of strength of acid sites was changed as a result of ion-exchange.

Figure 2 presents results concerning *n*-hexane adsorption, obtained from MC experiments. A brief insight in the profiles of volumetric isotherms reveals that importantly higher amounts of *n*-hexane were adsorbed on ion-exchanged samples then on HZSM-5 (Fig. 2a). In addition, *n*-hexane was adsorbed with higher heats of adsorption on these samples (Fig. 2b). In the case of bimetallic samples, the heats of adsorption similar to those found in the case of monometallic forms were detected. As an example, Q_{dif} *vs.* gas uptake profiles obtained for CuZSM-5, FeZSM-5 and Fe,CuZSM-5 are compared on Fig. 2c.

Table 1 Chemical composition, surface area and quantitative amounts of adsorbed ammonia

ZSM-5, Si/Al=20	The amount of metal/ mass%	S_{BET}/m^2 g^{-1}	NH_3 adsorbed/ mmol g^{-1*}	n_1, NH_3 molecules/ u. c.
HZ	–	322	0.348	2.1
CuZ	1.5	310	0.423	2.5
FeZ	0.3	336	0.370	2.2
MnZ	0.78	337	0.403	2.4
Fe,CuZ	Fe 0.87 Cu 0.48	325	0.397	2.4
Fe,MnZ	Fe 0.15 Mn 0.28	325	0.379	2.3
Cu,MnZ	Cu 1.2 Mn 0.13	340	0.462	2.8

*the amount of irreversibly adsorbed NH_3, obtained from the difference between primary and secondary isotherm; n_1 – the number of NH_3 molecules adsorbed per one unit cell

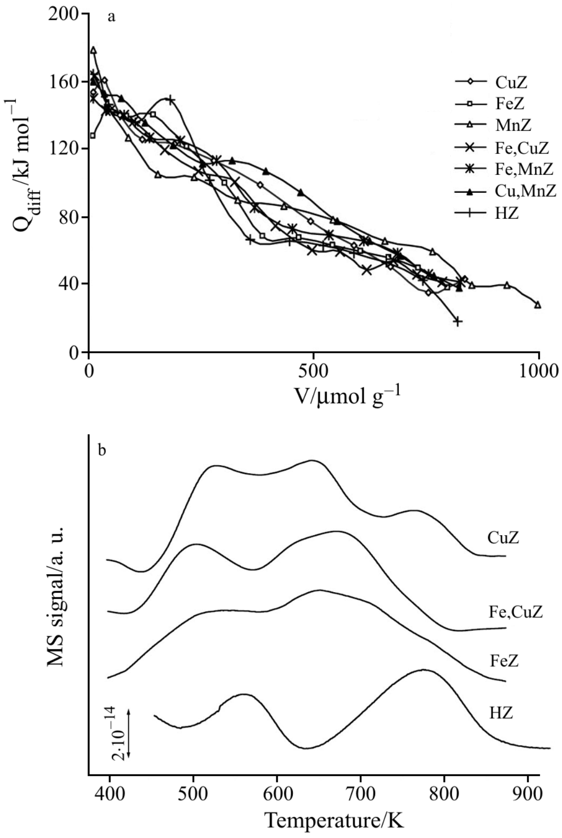

Fig. 1 a – Differential heats of NH_3 adsorption on the ZSM-5 samples investigated in this work, b – TPD profiles of NH_3 obtained from the samples containing one or two transition-metal cations. For comparison, TPD profile of NH_3 obtained for HZSM-5 is presented

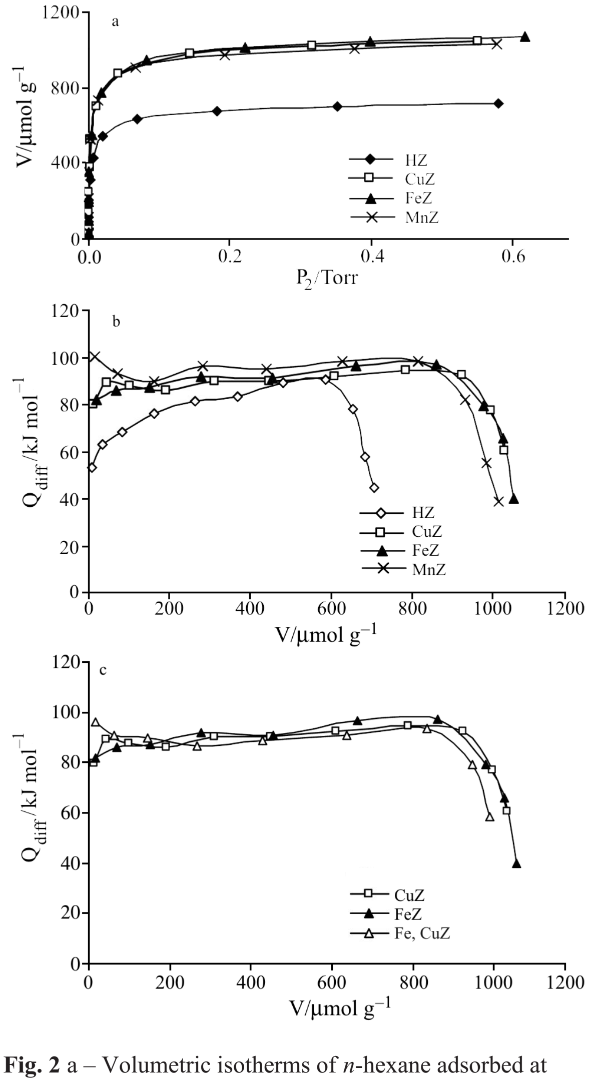

Fig. 2 a – Volumetric isotherms of *n*-hexane adsorbed at 303 K on monometallic samples, b – differential heats *vs*. gas uptake profiles obtained for *n*-hexane adsorption on the same samples, c – differential heats *vs*. gas uptake profiles obtained for *n*-hexane adsorption on two monometallic and one bimetallic sample

A profile: Q_{dif} *vs*. *n*-hexane uptake obtained for HZMS-5 is different from those reported for *n*-hexane adsorption on silicalite [8, 13], where a homogeneous surface for this interaction was found. Here, a profile similar to that one found in the case of FAU structure [13] was monitored. At low loadings Q_{dif} are lower and increase with increasing of gas uptake. The obtained profiles of Q_{dif} could be resulted of the interaction of *n*-hexane molecules with specific local electrostatic field inside zeolite structure which is more 'ionic' in comparison with silicalite structure, because of a higher content of AlO^{2-} units. It is important to notice that ^{27}Al MAS NMR experiments have shown that HZSM-5 investigated in this work does not contain extraframework Al, what means that some steric hindrances for *n*-hexane adsorption could not be expected. A fact that ion-exchange gives one energetically homogeneous surface for *n*-hexane adsorption (Figs 2b and c) is one additional indication that local electrostatic field is important for interaction. It is also worth noticing that the highest differential heats are found in the case of samples containing manganese ions. Having 3 unpaired electrons in 3d level, in comparison with 2 unpaired electrons in the case of Fe^{2+} and 1 unpaired electron for Cu^{2+}, Mn^{2+} ions express higher polarization abilities.

Besides the adsorption done in MC volumetric line, *n*-hexane was also adsorbed from a flow. In this case, the amounts of adsorbed gas were determined from TG signal. Importantly, *n*-hexane was adsorbed on previously thermally treated samples but also on non-pretreated samples containing about 7% of water. As an example, TG profiles obtained during *n*-hexane adsorption on FeZSM-5 from a flow are presented on Fig. 3a. As it could be expected, lower amount of *n*-hexane was adsorbed on unpretreated sample. Figure 3b presents TPD profiles of water and *n*-hexane collected from the unpretreated FeZSM-5 sample, on which *n*-hexane was adsorbed from the flow. Importantly, desorption profiles of water and *n*-hexane are detected in the same temperature region from 300 to 550 K, indicating that both molecules were adsorbed with similar energies of interactions. In addition, in Fig. 3c, two TPD profiles of *n*-hexane obtained from FeZSM-5 sample are compared. Desorption profiles obtained from dehydrated and hydrated samples are similar and have almost identical temperature of maxima. Evidently, *n*-hexane interacts with the same energies with dehydrated and hydrated ZSM-5 structure.

Figure 4 presents TPD spectra of *n*-hexane obtained from previously pretreated ion-exchanged samples and after a gas was adsorbed from a flow at 298 K. Evidently, all TPD spectra are similar. Double peak desorption profiles reveal that two possible sites for the interaction with *n*-hexane exist in the investigated structures. As a result of ion-exchange with one or two transition metal cations, only the changes of relative intensities of two overlapped peaks, and small changes in temperatures of maxima (T_M) are found.

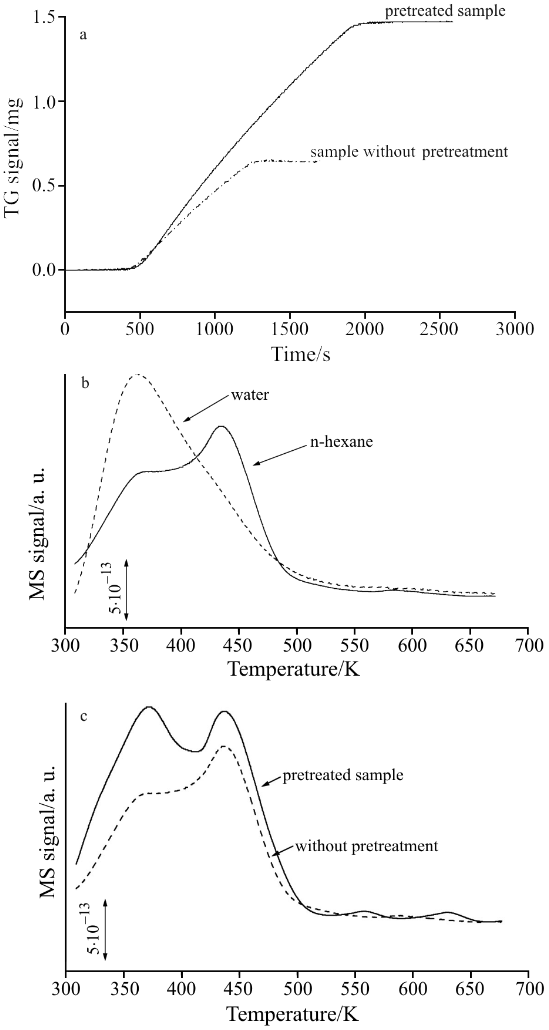

Fig. 3 a – TG signals recorded during *n*-hexane adsorption on FeZSM-5 from a flow at 298 K, b – TPD profiles of water and *n*-hexane collected from unpretreated FeZSM-5, c – TPD of *n*-hexane from pretreated and unpretreated FeZSM-5

Table 2 compiles all quantitative data obtained in this work: the amounts of *n*-hexane adsorbed in MC experiments and the amounts of *n*-hexane adsorbed and desorbed in a flow, for both thermally pretreated and unpretreated samples. It is known that *n*-hexane can completely fill the ZSM-5 channel system with 8 molecules per unit cell [11, 12, 14]. However, it is now widely accepted that at low loadings, up to 4 molecules per unit cell can be adsorbed [8, 20]. Quantitative amounts obtained in this work are in agreement with these literature data: the numbers of chemisorbed *n*-hexane molecules are lower than 4 molecules per unit cell. Importantly, these amounts, obtained from the difference between two adsorption runs in MC experiments (n_2, Table 2) are higher in the case of the samples containing manganese ions, in comparison with other samples investigated here.

Table 2 Quantitative amounts of *n*-hexane adsorbed in microcalorimeric experiment and in a flow *n*-hexane/helium

Sample	A_1/ mmol g^{-1}	n_1/molecules per u. c.	A_2/ mmol g^{-1}	n_2/molecules per u. c.	A_3/ mmol g^{-1}	n_3/molecules per u. c.	A_4/ mmol g^{-1}	n_4/molecules per u. c.	A_5/ mmol g^{-1}	n_5/molecules per u. c.
HZ	0.700	4.2	0.393	2.4	1.08	6.35	1.0	6.0	0.400	2.2
CuZ	1.038	6.2	0.438	2.6	1.21	7.25	1.1	6.35	0.420	2.45
FeZ	1.040	6.2	0.435	2.6	1.14	6.8	1.0	6.0	0.440	2.6
MnZ	1.020	6.1	0.480	2.9	1.10	6.0	1.0	6.0	0.451	2.7
Fe,CuZ	1.020	6.1	0.430	2.6	1.14	6.8	1.0	6.2	0.654	3.85
Cu,MnZ	1.048	6.3	0.540	3.2	1.15	6.85	1.0	6.2	0.487	2.8
Fe,MnZ	1.040	6.2	0.590	3.5	1.26	7.55	1.05	6.3	0.630	3.7

A_1 – the amount of *n*-hexane adsorbed in microcalorimetric experiment, up to equilibrium pressure of 66 Pa; n_1 is corresponding number of molecules per unit cell, A_2 – the amount of irreversibly adsorbed *n*-hexane (chemisorbed *n*-hexane), obtained from the difference between first and second adsorption in microcalorimetric experiment; n_2 is corresponding number of molecules per unit cell, A_3 – the amount of *n*-hexane adsorbed from a flow. Activation and adsorption done in situ in a TG/DSC cell (calculated from a change of TG signal); n_3 is corresponding number of molecules per unit cell, A_4 – the amount desorbed in TG/TPD experiment, after the adsorption of *n*-hexane on the activated sample. TPD done in temperature interval 298–673 K (calculated from a change of TG signal); n_4 is corresponding number of molecules per unit cell, A_5 – the amount of *n*-hexane adsorbed from a flow, on non-activated samples containing water (calculated from a change of TG signal); n_5 is corresponding number of molecules per unit cell

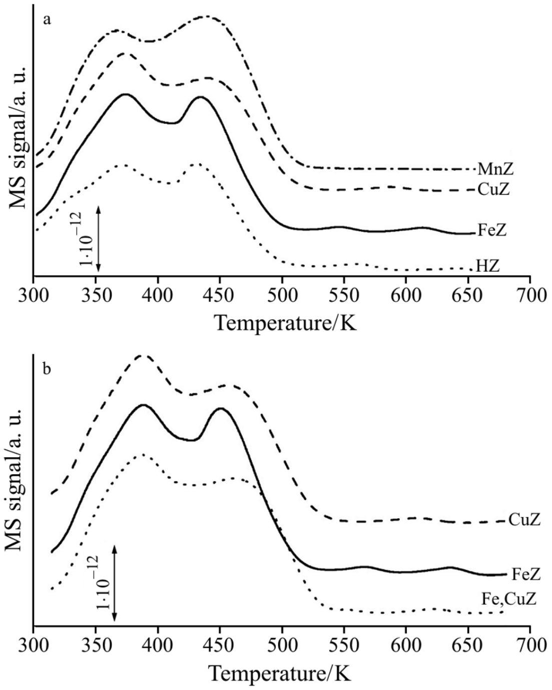

Fig. 4 TPD profiles of *n*-hexane obtained for mono- and bimetallic forms of ZSM-5

At higher loadings, achieved during the adsorption at atmospheric pressure from a flow, up to 7 molecules per unit cell were adsorbed. It can be inferred that one part is weakly adsorbed and can be easily expelled from the surface at room temperature in a helium flow (Table 2, columns A_3 and A_4). It is worth noticing that a number of *n*-hexane molecules adsorbed on hydrated samples are not negligible (columns A_5 and n_5, Table 2) thus proving that adsorption of *n*-hexane is possible even in hydrated ZSM-5 structures.

Conclusions

Ion-exchange of high-aluminum HZSM-5 with transition metal cations gave as a result only a small change of its whole acidity. However, this ion-exchange had the influence on the ability of ZSM-5 structure to adsorb *n*-hexane. Higher differential heats and higher amounts of adsorbed gas were found for ion-exchanged samples, in comparison with parent HZSM-5, this effect could be possibly assigned to the change of local electrostatic fields inside the channels, and to enhanced ability of zeolite to polarize *n*-hexane molecule. Among the investigated systems, it seems that Mn^{2+} cations express the highest ability to influence on the interaction of *n*-hexane with ZSM-5 structure, what could be related with its electronic configuration. The addition of second transition metal cation does not influence importantly *n*-hexane adsorption ability.

TPD profiles of *n*-hexane, composed of two overlapped peaks and placed in temperature region from 300 to 550 K, indicate that in the case of ion-exchanged ZSM-5, a model of two adsorption sites with no interaction between adsorbed molecules, already established for H-silicalite, can be accepted. Having in mind that the positions in zig-zag and straight channels are more favorable than in the intersections [20, 22, 23], quantitatively determined numbers of adsorbed molecules per unit cell, calculated from MC experiments performed in this work indicate that these molecules are adsorbed in the channels and not in the channel intersections. Importantly, it has been clearly shown in this work that *n*-hexane can be adsorbed on the samples partly covered with water molecules. As in the case of dehydrated samples, higher amounts were adsorbed on cation-exchanged samples then on HZSM-5. The fact that both *n*-hexane and water desorptions happen in the same temperature region indicates similar energies of interactions for both molecules. Finally, this fact reveals that in the case of possible adsorption from a mixture of water and *n*-hexane, a competitive adsorption of two gases could happen.

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