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Effect of transition metal cations on the commensurate freezing of *n*-hexane confined in micropores of ZSM-5

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Abstract: Besides its importance concerning fundamental studies on gas adsorption in narrow pores, investigation of the commensurate freezing of a fluid within a zeolite is of practical importance in the application of zeolites in the processes of adsorption, separation and catalysis. In this work, the adsorption of *n*-hexane on HZSM-5 and its transition metal ion-exchanged modified forms was studied at 303 K by means of microcalorimetry. The thermal molar entropies changes of adsorption were calculated and thereby, the freezing-like behaviour of *n*-hexane inside the structure of the zeolite as a confinement media was noticed. This effect is governed by the attractive interactions between *n*-hexane molecules and the pore walls, and is influenced by the length of the pores and the nature of the charge-balancing cations. Among the investigated zeolites, a solid-like phase of *n*-hexane in the pores of zeolites with Fe(II) ions was the most similar to solid bulk *n*-hexane, while Cu(II) ions contributed to the lowest ordering of the obtained solid-like *n*-hexane phase.

Keywords: confinement media; adsorption; entropy; microcalorimetry; ZSM-5.

INTRODUCTION

The confinement of fluids in limited spaces, such as narrow pores, is a very interesting phenomenon. The behaviour of fluid confined in a pore is influenced by many factors, such as pore size and geometry, and the atomic structure of the pore surface. Consequently, its properties are distinctly different from those of bulk phase. For example, a confined fluid can have a higher density or can be in a different aggregation state from its analogue under normal conditions. There are many experimental and theoretical studies reporting that the phase behaviour of

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different fluids under extreme confinement is qualitatively different from that of the bulk.[1–13] In the confinement medium, the presence of fluid–pore wall and fluid–fluid forces can lead to interesting surface-driven phase changes. These include new types of phase transitions not found in the bulk phase and shifts in transitions. In a bulk system, freezing is considered a first-order phase transition accompanied by an infinitely sharp change in a suitable order parameter, usually density or composition. In a confinement medium, the freezing phase transition is possible but with evident effects of confinement. The freezing temperature of a fluid confined in pores is determined by the bulk freezing temperature, pore wall–solid and pore wall–fluid surface tensions, the molar volume of the liquid, the latent heat of melting in the bulk and pore width.[14] A decrease or increase in the freezing temperature due to confinement is strongly affected by the strength of the attractive forces between the fluid molecules and the pore walls.[14,15] For repulsive or weakly attractive pore walls, the shift in the freezing temperature is negative.[16,17] For highly attractive adsorbents where the adsorbate–pore wall interactions are strong compared to the adsorbate–adsorbate interactions, an increase in freezing temperature over the bulk value is observed.[15,18,19–22]

Zeolites are regular crystalline solid microporous materials with peculiar structural characteristics (a three-dimensional lattice with well defined pores, high internal surface area and curvature, high ion-exchange capacity and remarkable thermal stability). Zeolites are extensively used in the chemical industry as catalysts and for the separation of gases, particularly hydrocarbons.[23–25] Therefore, the adsorption of hydrocarbons, especially *n*-alkanes, has been widely studied.[4,6,26–29] According to the molecular dimensions of their pores, zeolites may be considered as confinement media and the effect of confinement on fluids adsorbed in zeolites may be expected. For example, investigations of hexane and heptane adsorption at room and at slightly higher temperatures on silicalite-1 and ZSM zeolite revealed anomalous behaviour of these two hydrocarbons compared to other alkanes.[2–6] An explanation was given for the first time by Smit and Maesen.[30] Their interpretation is that the adsorption of straight chain hydrocarbons on silicalite leads to a phase transition of the hydrocarbons inside the pores of the silicalite. Bearing in mind that silicalite-1 and ZSM have two types of channels, straight and zigzag (sinusoidal) connected *via* intersections, they showed that phase transition occurred when the lengths of the adsorbed molecules were similar to the length of the channels. Indeed, the length of *n*-hexane and heptane molecules are 1.03 and 1.16 nm, respectively, while the length between the centres of channel intersections of the silicalite structure is 1.2 nm, *i.e.*, they are comparable. Under the above conditions, fluid can freeze in a configuration that is commensurate with the pore structure.[30–33] Phase transitions of hexane and heptane between the gas, liquid and solid phases in the pores of silicalite-1 and ZSM are generally accepted and were the subject of many studies.[34–41]

Commensurate adsorption of hydrocarbons (*e.g.*, *p*-xylene, *n*-hexane, *n*-heptane, benzene, *etc*.) was found in several different types of zeolites, for instance, MFI, ITW, ERI, CHA, LTA, AFX and silicalites.[42–46]

Evidence for freezing of *n*-hexane molecules inside the channels of ZSM can be seen from the adsorption isotherms, which can show a step or kink when half of the maximum loading (about 4 molecules per unit) is achieved; such isotherms were obtained for adsorption measurements at temperatures above 338 K.[4,6,30,47–49] Lohse *et al.*[50] did not provide evidence for a kink at half of the loading because the temperature of adsorption (298 K) was too low. Additionally, Meansen[30] showed in a simulation that the kink becomes more pronounced with increasing temperature. The adsorption isotherms measured by Zhu *et al.*[51] showed a kink in the temperature region 338–373 K, but not at 303 K. The volumetric adsorption isotherms of *n*-hexane on HZSM-5 zeolite and its transition metal modified forms were reported,[52] but they did not show a kink since a low temperature of adsorption (303 K) was applied.

In addition to isotherms, temperature programmed desorption (TPD) profiles also gave evidence of commensurate freezing of *n*-hexane in the zigzag channels of zeolite. The TPD studies showed that among the linear alkanes, hexane and heptane behave distinctly differently.[28,32,44,45,48,53–57] While other linear alkanes showed a single desorption step, *n*-hexane and especially *n*-heptane exhibited two-step desorption profiles. The first desorption peak of *n*-hexane and *n*-heptane occurred at lower temperatures than expected based on the chain length of these two *n*-alkanes. This low temperature peak corresponds to desorption from the zigzag channels and should be caused by a relatively high gain in entropy upon desorption compared to the other *n*-alkanes. The relatively high gain in entropy upon desorption can only be the result of a low entropy value in the constrained position of the adsorbed *n*-hexane and *n*-heptane molecules at high loadings. Partial desorption then allows a rearrangement of the adsorbed *n*-hexane or *n*-heptane molecules, resulting in an ordering similar to the ordering of the other *n*-alkanes with normal entropy values. The high temperature peak corresponds to desorption from the straight channels and it occurs at temperatures that are in accordance with the chain length of the *n*-alkane. It was reported[58] that the TPD profiles of *n*-hexane sorbed on ZSM-5 were composed of two well-defined peaks in the temperature region from 300 to 550 K, consistent with the results of other researchers.[28,32,44,54,56] Accordingly, this indicated that the phase transition of freezing occurred when *n*-hexane was adsorbed on the samples of ZSM used in the present study.

In the last decade, among the transition metal ion-containing zeolites, the Fe-, Cu- and Mn-MFI zeolites have received much attention because they are catalytically active in some important reactions, such as N_2O and NO decomposition, reduction of NO_x to N_2 in the reaction with various hydrocarbons[59–61] and catalytic cracking of hydrocarbons.[62–64] Many experimental results indicate that the physical adsorption of *n*-alkane reactants contributes to the kinetics of catalytic reactions.[65–67]

In this work, the phase transition of commensurate freezing of *n*-hexane confined in microporous of HZSM-5 and in its forms modified by different charge balancing cations: Cu(II), Mn(II) and Fe(II), was investigated. It is known that attractive adsorbate–pore wall interactions in zeolite partly originate from the charge balance cation–adsorbate interactions, and hence, an influence of transition metal cations on the adsorption of *n*-hexane and on its commensurate freezing could be expected. Recently, molecular dynamics (MD) simulation studies[31] clearly showed that the behaviour of *n*-hexane at a loading of 4 mol per unit cell (u.c.) in silicalite-1 should not be ascribed to an enthalpy effect but to an entropy change of the system approaching 4 mol $(\text{u.c.})^{-1}$, which was in agreement with the results of Smit *et al.*[1] Therefore, in order to investigate the influence of the nature of the charge balancing cation on the commensurate freezing of *n*-hexane inside the zeolite structure, one physical property, thermal molar entropy, was studied, which was chosen for two reasons: first, the appearance of a low temperature peak in TPD profile, as confirmation that commensurate freezing is associated with the entropy change, and secondly, the property in relation to the molar entropy of liquid and solid *n*-hexane may cast insight into the freedom of the *n*-hexane molecules within the zeolite and thus, could provide evidence for the occurrence of commensurate freezing.

EXPERIMENTAL

The parent self-produced NaZSM-5 (Si/Al = 20) was synthesized hydrothermally. HZSM-5 and under-exchanged forms of HZSM-5 containing Cu(II), Fe(II) or Mn(II) cations (mono- or bi-metallic) were obtained by appropriate common wet ion-exchange procedures, fully described previously.[22] The crystallinity of the parent NaZSM-5, HZSM-5 and ion-exchanged forms was proved by X-ray diffraction. The measurements were performed on a Bruker (Siemens) D5005 diffractometer at room temperature using CuK_α radiation (0.154 nm), 2θ from 3 to 80°, in 0.02° steps with 1 s per step, and the results showed that the structure of the ZSM-5 zeolite remained unchanged during the ion-exchange process. XRD analysis proved that the structure was also not changed by adsorption of *n*-hexane. The differential heats and the isotherms of *n*-hexane adsorption were collected using a coupled microcalorimetric–volumetric line, using the procedure fully described elsewhere.[23] Briefly, the heats of adsorption were measured in a heat-flow microcalorimeter (C80, Setaram) linked to a glass volumetric line that permitted the admission of successive known doses of adsorbed gas, until a final equilibrium pressure of 66 Pa. Subsequently, the sample was pumped, the desorption peak was recorded and re-adsorption was performed at the same temperature. Before the adsorption, the samples were pre-treated in vacuum (10^{-3} Pa) overnight at 673 K, while the adsorption temperature was maintained at 303 K. In order to clarify the states of cation species in the investigated samples, UV–Vis diffuse reflectance spectra were recorded, in 190–1000 nm spectral region, using a Perkin Elmer Lambda 35 UV–Vis spectrometer equipped with a diffuse reflectance accessory. The powder samples were placed in the sample cup and BaSO_4 was used as a reference.

The thermal entropy of sorbed *n*-hexane was calculated from the values of the entropy change of adsorption, ΔS^0, obtained from calorimetric measurements.[52] The obtained values of entropy change of adsorption are in good agreement with the values from the literature.[44,56,68,69] The following expression was used to calculate ΔS^0 from the microcalorimetry data:

$$\Delta S^0 = R\ln\frac{p^0}{p} + \frac{\Delta H^0}{T} \tag{1}$$

where T is the adsorption temperature, p^0 is the standard pressure, p is the equilibrium pressure at temperature T and ΔH^0 is the standard enthalpy change in the adsorption process. These values were obtained from microcalorimetry as differential heats of adsorption. The entropy change accompanying the adsorption process can be expressed as:

$$\Delta S^0 = S_{\mathrm{g}}^0 - S_{\mathrm{s}}^* \tag{2}$$

where S_{g}^0 is the molar entropy of *n*-hexane vapour at standard pressure p^0 and temperature T, while S_{s}^* is the differential molar entropy of adsorbed *n*-hexane. The differential molar entropy, is a finite, positive quantity that may be separated into thermal and configurational entropy components.[70] In this case, S_{s}^* can be represented by:

$$S_{\mathrm{s}}^* = S_{\mathrm{c}} + S_{\mathrm{th}} \tag{3}$$

where S_{c} and S_{th} are the differential molar configurational and differential molar thermal entropies, respectively. When the density of the molecules adsorbed in the channels of the zeolite is high, it is generally assumed that these molecules attempt to pack closely together and take up the walls of the anion framework. With such a localized sorption process, S_{c}, may be calculated with the equation:

$$S_{\mathrm{c}} = R\ln\frac{x}{1-x} \tag{4}$$

where $x = W/W_0$ (W is the amount adsorbed at equilibrium pressure p, and W_0 is the total adsorption capacity at 303 K).[71] Subtraction of Eq. (4) from S_{s}^* gives S_{th}:

$$S_{\mathrm{th}} = S_{\mathrm{s}}^* - R\ln\frac{x}{1-x} \tag{5}$$

RESULTS AND DISCUSSION

The values of differential molar entropy, differential molar configurational and differential molar thermal entropies were calculated for the adsorption of *n*-hexane with different loadings (expressed as *N*, number of molecules adsorbed per unit cell), on both parent HZSM-5 and its cation modified forms using Eqs. (2)–(5). The profiles of differential molar thermal entropies plotted *vs*. the amount adsorbed are shown in Fig. 1.

The profiles of the S_{th} values *vs*. loading gave evidence that the differential molar thermal entropies of the *n*-hexane adsorbed on zeolite was dependent on the nature of the environment of the adsorbate molecules, *i.e.*, the porous zeolite lattice with its charge balance cations. It can be seen from Fig. 1 that the S_{th} of parent HZSM-5 was altered by the incorporation of transition metal cations in its lattice. Furthermore, the presence of transition metal cations increased the adsorption capability of HZSM-5 zeolite from 4 (obtained in the case of HZSM-5) to 6 molecules of *n*-hexane per unit cell (found for zeolites with transition metal cations). Different numbers (from 2 to 8) of sorbed *n*-hexane molecules per unit cell were reported in the literature,[4,32,72] while the theoretical loading limit for ZSM-5 was 8 hexane molecules per unit cell.[73] It could be inferred that the charge balance cations influence the values of $S_{\rm th}$ since they result from *n*-hexane attractive interactions with the zeolite pore wall, originating from the macroanion framework and extra-framework charge-balancing cations.

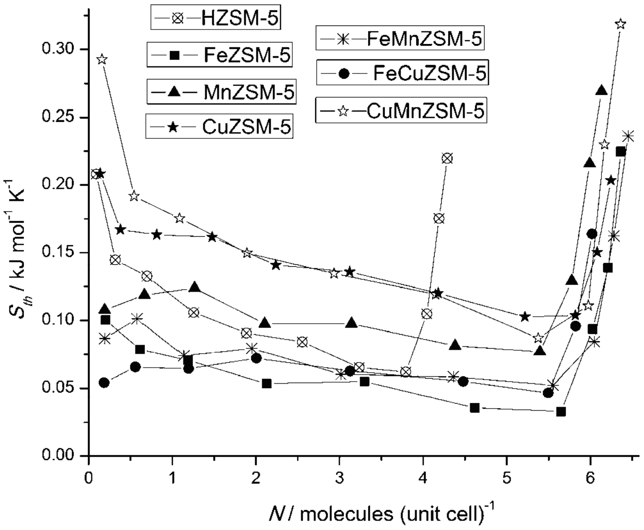

Fig. 1. Differential molar thermal entropies ($S_{\rm th}$) as a function of loading *N* (molecules per unit cell) of *n*-hexane.

In a study of *n*-hexane adsorption on ZSM, several facts must be taken into account. First, the length of the *n*-hexane molecule is almost the same as the distance between channel intersections and hence, these molecules cannot be wholly located in the channel segments and the possibility of adsorbate–adsorbate interaction at the channel intersections always exists at high surface loadings. In fact, adsorbate–adsorbate interaction are enhanced for a loading of 4 *n*-hexane molecules per unit cell; while for even higher values (4–8 molecules per unit cell), the adsorbed molecules arrange in such way that additional side-on interactions can occur; while with further increase in the *N* values, closer packing of *n*-hexane molecules occurs and thus, repulsion interactions become significant.[4,47,74,75]

For all the investigated zeolites, the $S_{\rm th}$ *vs.* loading profiles can be divided into three regions of loading. It could be seen from Fig. 1 that these regions are:

$N < 2$, $2 < N < 6$ and $N > 6$. The $S_{\rm th}$ values found for *n*-hexane adsorption on HZSM-5, CuZSM-5 and CuMnZSM-5 decreased sharply in the initial, micro-pore-filling region ($N < 2$). This is probably due to the fact that the first molecules entering the micropores occupy the most favourable sites, which results in their fast ordering and fast loss in $S_{\rm th}$. In the case of adsorption on FeZSM-5, the $S_{\rm th}$ values decreased very slowly up to $N < 2$. However, it is important to notice that in this low-surface coverage region, the $S_{\rm th}$ values measured for *n*-hexane adsorption on MnZSM-5, FeMnZSM-5 and FeCuZSM-5 showed increased values with a more or less marked maxima. Barrer *et al.*[70,76] reported that strong energetic heterogeneity is reflected in a maximum in the entropy curves against coverage for low adsorbate uptakes. Indeed, it seems that on these samples, the ordering of adsorbed molecules occurred as a result of interaction with surface active sites. After the maximum values of $S_{\rm th}$ were reached on MnZSM-5 and on the samples containing Fe(II) cations (FeZSM-5, FeMnZSM-5 and FeCuZSM-5), the $S_{\rm th}$ values remained almost constant in the medium surface coverage region ($2 < N < 6$), thus indicating highly localized adsorption. In contrast, the $S_{\rm th}$ values of HZSM-5 and the zeolites containing Cu(II) cations (CuZSM-5 and CuMnZSM-5) slightly decreased from the constant values, thus indicating that there were some deviations of the localized sorption. For high surface coverages ($N > 4$ for HMnZSM-5 and $N > 6$ for all other samples), the $S_{\rm th}$ values increased sharply as a result of repulsion interactions among the closely packed *n*-hexane molecules.

At low surface coverage, the adsorbate molecules can move freely in the zigzag channels and thus fill one part of the intersections for some time. As a consequence, further adsorption would become restricted, since the intersections are blocked while the straight channels are too short to accommodate *n*-hexane molecules. To fill the zeolite completely, the molecules adsorbed in a zigzag channel have to be confined in their position, which leads to a loss in entropy.[8] It is accepted that when a coverage of half a loading per unit cell is achieved, the intersections are blocked. Then, the adsorbed molecules in the zigzag zeolite channels undergo phase transition, which is known as commensurate freezing. The $S_{\rm th}$ values of *n*-hexane adsorbed that are achieved at half-loading (≈3 molecules per unit cell) may be compared with the entropy of liquid *n*-hexane at 303 K (300 J mol^{-1} K^{-1}) and the sum of the vaporization entropy change (94 J mol^{-1} K^{-1}) and the fusion entropy change of *n*-hexane (72 J mol^{-1} K^{-1}) at 178 K.[77] According to Eq. (3), the values of the differential molar entropy at half-loading enable the derivation the $S_{\rm th}$ part of the respective differential molar entropy since $S_{\rm c} = 0$. These values of $S_{\rm th}$ are listed in Table I.

The $S_{\rm th}$ part of the respective $S_{\rm s}^{*}$ obtained for the configurational entropy $S_{\rm c} = 0$ of *n*-hexane adsorbed within the channels of FeZSM-5, FeMnZSM-5 and FeCuZSM-5 were between 55 and 62 J mol^{-1} K^{-1}; values sufficiently lower than the sum of the vaporization entropy change and the fusion entropy change of *n*-hex-

TABLE I. The S_{th} part of respective S_s^* (for $S_c = 0$)

Zeolite	S_s^* (= S_{th}) / J mol^{-1} K^{-1} ($S_c = 0$)
CuMnZSM-5	134
CuZSM-5	136
MnZSM-5	98
FeMnZSM-5	60
FeZSM-5	55
FeCuZSM-5	62

ane at 178 K to suggest that degree of ordering of the molecules adsorbed in the pores of these zeolites was similar to that in solid *n*-hexane. Similar results were found for *n*-hexane adsorbed on MnZSM-5. In this case, the S_{th} part of the respective S_s^*, for $S_c = 0$ equalled 98 J mol^{-1} K^{-1}, which is more than the S_{th} found in the case of the zeolites containing Fe(II) cations, but still less than the sum of the vaporization entropy change and the fusion entropy change of *n*-hexane at 178 K. The S_{th} parts of the respective S_s^* obtained for $S_c = 0$ within the channels of CuMnZSM-5 and CuZSM-5 were practically equal (134 and 136 J mol^{-1} K^{-1}) and also less than the sum of the vaporization entropy change and the fusion entropy change of *n*-hexane at 178 K. Obviously, the presence of Mn(II), Cu(II) and especially Fe(II) cations changes the attractive interactions between *n*-hexane molecules and the pore walls in such a way to enable the adsorbed *n*-hexane molecules to be arranged as in a solid-like state of *n*-hexane. It is noteworthy that the S_{th} values obtained for the samples containing Fe(II) cations were about 100 J mol^{-1} K^{-1} lower than the sum of the vaporization entropy change and the fusion entropy change of *n*-hexane at 178 K, while the S_{th} values for the samples containing Cu(II) ions were only about 20 J mol^{-1} K^{-1} lower than the above mentioned sum, indicating a higher ordering of the hexane molecules in the zeolites containing Fe(II) cations than inside those containing Cu(II) cations. The general conclusion, based on the values of S_{th}, is that a phase transition from gaseous *n*-hexane to a solid-like structure of *n*-hexane, *i.e.*, commensurate freezing of *n*-hexane, occurred in the pores of ZSM-5 containing transition metal ions. The commensurate freezing occurred at 303 K, well above the temperature of the bulk freezing of *n*-hexane (178 K). Increasing of the freezing temperature is a characteristic of fluids confined in a confinement medium with highly attracting pore-walls, as is the case with the investigated zeolites.

In order to better illustrate the influence of the extra framework cations on decreasing S_{th}, the difference between S_{th} and S_g^0 was calculated and plotted as ($S_{th} - S_g^0$) *vs.* loading (Fig. 2).

At the very beginning of the sorption, the entropy loss followed the order: FeCuZSM-5 > FeMnZSM-5 > FeZSM-5 > MnZSM-5 > HZSM-5 > CuZSM-5 > CuMnZSM-5. At half of the maximum loading, the entropy loss followed the order: FeZSM-5 > FeCuZSM-5 = FeMnZSM-5 > HZSM-5 > MnZSM-5 >

CuZSM-5 = CuMnZSM-5, while at the maximum loading ($N = 6$), the entropy loss followed the order: FeZSM-5 > FeCuZSM-5 > FeMnZSM-5 > MnZSM-5 > CuMnZSM-5 > CuZSM-5.

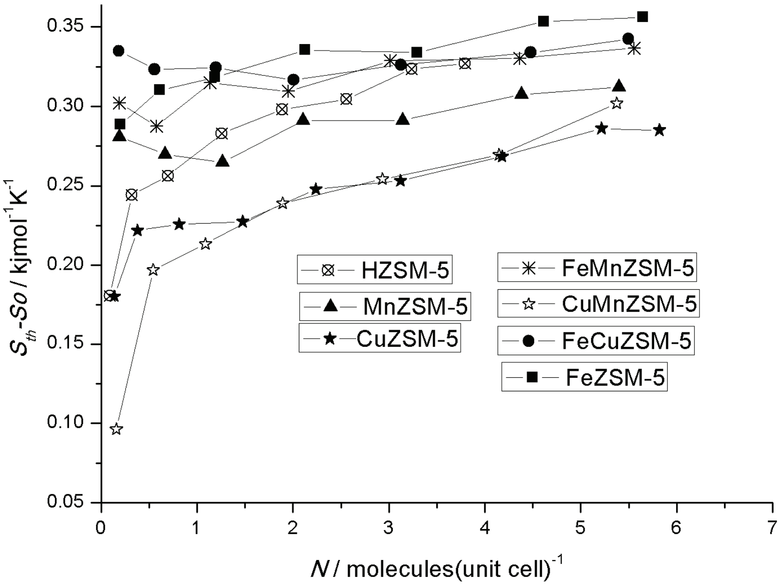

Fig. 2. Dependence of the entropy loss $(S_{\text{th}} - S_{\text{g}}^{0})$ of adsorbed *n*-hexane on loading *N*.

The maximum entropy loss was achieved for *n*-hexane adsorption in the zeolites with Fe(II) cations and the minimum entropy loss was found for *n*-hexane adsorption in zeolites with Cu(II) cations. The rigid zeolite structure is the same in all these samples, which means that the presence of the charge-balancing cations influences the distribution and ordering of *n*-hexane molecules inside the zeolite channels, and thus the S_{th} values. It is important to note that[27] Al MAS NMR experiments showed that the HZSM-5 investigated in this work does not contain extra framework Al, which means that some steric hindrance for *n*-hexane adsorption was not to be expected.[78] The different values of the S_{th} part of respective S_{s}^{*} (for $S_{\text{c}} = 0$) of the samples with different charge balancing cations indicate that the created solid-like phase was not always the same and depended on the type of the extra framework cations. Cu(II), Mn(II) and Fe(II) have the same charge, but different ion radii (Cu: 0.73 nm, Mn: 0.82 nm and Fe: 0.78 nm) and hence, they create different electrostatic interactions with *n*-hexane molecules. In addition, Cu(II), Mn(II) and Fe(II) have different electron configurations, *i.e.*, (Mn(II) possesses five and Fe(II) four incomplete d-orbitals, while Cu(II) has only one unpaired electron in the $4s^1$ orbital). The electrons of uncompleted orbitals can form bonds with oxygen atoms from the lattice, as well with adsorbed *n*-hexane molecules. If these electrons "react" with the oxygen of the lattice, the reaction of *n*-hexane with oxygen atoms is reduced, while the cations partly lose the possibility of interaction with *n*-hexane. Both effects cause an increase in S_{th}. However, the interaction of spin unpaired electrons with *n*-hexane molecules produce the opposite effect, *i.e.*, a decrease in S_{th}. The low S_{th} obtained for samples with Mn(II) and Fe(II) cations shows that Mn(II) and Fe(II) present in zeolite lattice coordinated the electrons of adsorbed *n*-hexane easier than the electrons of the oxygen atoms from the lattice. Therefore, the S_{th} of the samples containing Mn(II) and Fe(II) ions are influenced both by ion-induced dipole interactions, while the additional interactions originate from the possibility of Mn(II) and Fe(II) to behave as electron acceptors. On the contrary, considering that Cu(II) ions have only one unpaired electron in the $4s^1$ orbital, the S_{th} value of samples possessing Cu(II) ions is mostly determined by ion-induced dipole interactions through electrostatic and dispersive forces. If all the interactions achieved between *n*-hexane molecules and the samples possessing Fe(II) and Mn(II) ions are compared, it could be concluded that Fe(II) ions can achieve stronger electrostatic (its ionic radius is smaller), but weaker additional interactions (Fe(II) possesses four uncompleted d-orbitals, Mn(II) five). Based on the values of S_{th}, it seems that both these interactions are stronger in the samples containing Fe(II) cations, which led to better ordering of the adsorbate and finally to the formation of a solid-like phase in the course of a phase transition known as commensurate freezing.

CONCLUSIONS

The results obtained in this work show that the phase transition of commensurate freezing of *n*-hexane occurred during the adsorption of *n*-hexane into the parent HZSM-5 and its transition metal modified forms: CuZSM-5, MnZSM-5, FeZSM-5, CuMnZSM-5, FeMnZSM-5 and FeCuZSM-5. Freezing of *n*-hexane, the molecules of which "fit" the zigzag channels of ZSM-5, occurred at 303 K, which is well above the freezing temperature of bulk *n*-hexane (178 K). The positive shift in the freezing temperature was affected by the strong attractive forces between the *n*-hexane molecules and pore walls of the zeolite, originating from the presence of charge balancing cations. The results showed that above the circumstances of reduced dimensionality, such is in the case of zeolite lattice, the type (size and charge) and nature (electron configuration) of the charge balancing cation determine the ordering of the solid like phase of *n*-hexane obtained in the phase transition of commensurate freezing. Among the investigated zeolites, the solid-like phases obtained in zeolites possessing Fe(II) cations (FeZSM-5, FeMnZSM-5 and FeCuZSM-5) were the most similar to the solid *n*-hexane phase. Obviously, the presence of Fe(II) as the charge balancing cation facilitated the ordering of the adsorbed *n*-hexane molecules inside the zeolite. The smallest ordering of the solid like phase of *n*-hexane obtained in the process of commensurate freezing was in the zeolites with Cu(II) as the charge balancing cations (CuMnZSM-5 and CuZSM-5).

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ИЗВОД

УТИЦАЈ КАТЈОНА ПРЕЛАЗНИХ МЕТАЛА НА “МРЖЊЕЊЕ” ХЕКСАНА У ОГРАНИЧЕНОМ ПРОСТОРУ МИКРОПОРА ZSM-5 ЗЕОЛИТА

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Commensurate freezing је назив за појаву фазног прелаза првог реда (мржњења) гасова на температурама које су знатно изнад температуре сублимације слободног гаса, у условима када се гас адсорбује у уским порама чије димензије одговарају димензијама молекула гаса. Поред значаја у основним испитивањима адсорпције гасова, испитивање “мржњења” флуида унутар зеолита као микропорозног материјала је од практичног значаја у примени зеолита у процесима адсорпције, раздвајања компонената и катализи. У овом раду је проучавана адсорпција *n*-хексана из гасне фазе на ZSM-5 зеолиту, као и његовим облицима модификованим јонима прелазних метала, применом микрокалориметрије на температури од 303 K. ZSM-5 зеолит има два типа канала, праве и синусоидалне (цик-цак) који се међусобно секу. Дужина молекула *n*-хексана (1,03 nm) одговара растојању између центара пресека правих и цик-цак канала зеолита (1,2 nm), тако да под овим условима *n*-хексан може да се адсорбује на такав начин да је његово кретање толико ограничено да може да се схвати као замрзавање у каналима зеолита. Ова појава је у литаратури названа *commensurate freezing* и повезана је са променом ентропије система, па је у раду на основу израчунатих вредности промене термалне моларне ентропије адсорпције потврђено да је дошло до формирања структуре *n*-хексана која личи на чврсти *n*-хексан. Такође је показано да наведена фазна промена *n*-хексана зависи од природе катјона прелазних метала (електронске конфигурације, димензија и наелектрисања) који компензују негативно наелектрисање решетке. Међу испитиваним зеолитима, у оном са Fe(II) јонима је постигнут највећи степен уређености молекула *n*-хексана тако да је у том случају он у стању које је најсличније чврстом док је у зеолиту са Cu(II) јонима постигнута његова најмања уређеност.

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REFERENCES

1. B. Smit, T. Maesen, *Chem. Rev.* **108** (2008) 4125
2. G. Rakhmatkariev, K. Zhalalov, K. Akhmedov, *Uzb. Khim. Zh.* **3** (1998) 68
3. M. Dubinin, G. Rakhmatkariev, A. Isirikyan, *Izv. Akad. Nauk. SSSR Ser. Khim.* **10** (1989) 2333
4. F. Eder, J. Lercher, *Zeolites* **8** (1997) 75
5. F. Eder, J. Lercher, *J. Phys. Chem., B* **101** (1997) 1273

6. H. Zhang, S. Peng, L. Mao, X. Zhou, J. Liang, C. Wan, J. Zheng, X. Ju, *Phys. Rev., E* **89** (2014) 89
7. C. Malheiro, B. Mendiboure, J. Miguez, M. Pineiro, C. Miqueu, *J. Phys. Chem., C* **118** **(**2014) 24905
8. C. Bilgic, A. Askin, *J. Chromatogr., A* **1006** (2003) 281
9. A. Chica, A. Corma, P. Miguel, *Catal. Today* **65** (2001) 101
10. J. Delgado, T. Nijhuis, F. Kapteijn, J. Moulijn, *Chem. Eng. Sci.* **59** **(**2004) 2477
11. J. Denayer, G. Baron, J. Martens, P. Jacobs, *J. Phys. Chem., B* **102** (1998)3077
12. L. Domokos, L. Lefferts, K. Seshan, J. Lercher, *J. Catal.* **203** (2001) 351
13. J. Ndjaka, G. Zwanenburg, B. Smit, M. Schenk, *Micropor. Mesopor. Mat.* **68** (2004)37
14. M. Pera-Titus, *J. Phys. Chem., C* **115** (2011) 3346
15. M. Miyahara, K. Gubbins, *J. Chem. Phys.* **106** (1997) 2865
16. K. Morishige, K. Kawano, *J. Chem. Phys.* **110** (1999) 4867
17. M. Sliwinska-Bartkowiak, J. Gras, R. Sikorski, R. Radhakrishnan, L. Gelb, K. Gubbins, *Langmuir* **15** (1999) 6060
18. J. Klein, E. Kumacheva, *Science* **269** (1995) 816
19. J. Klein, E. Kumacheva, *J. Chem. Phys.* **108** (1998) 6996
20. M. Miyahara, M. Sakamoto, H. Kanda, K. Higashitani, *Stud. Surf. Sci. Catal.* **14** (2002) 411
21. U. Raviv, P. Laurat, P. Klein, *Nature* **413** (2001) 51
22. R. Radhakrishnan, K. Gubbins, A. Watanabe, K. Kaneko, *J. Chem. Phys.* **111** (1999) 9058
23. K. Sirkar, *Chem. Eng. Commun.* **157** (1997) 145
24. S. Bates, R. Van Santen, *Adv. Catal.* **42** (1998) 1
25. B. Newalkar, N. Choudary, U. Turaga, R. Vijayalakshmi, P. Kumar, S. Komarneni, T. Bhat, *Chem. Mater.* **15** (2003) 1474
26. R. Kolvenbach, L. Gonzalez-Pena, F. Luis, A. Jentys, J. Lercher, *Catal. Lett.* **143** **(**2013) 1116
27. T. Vlugt, M. Schenk, *J. Phys. Chem., B* **106** (2002) 12757
28. S. Bates, M. Gillan, G. Kresse, *J. Phys. Chem., B* **102** (1998) 2017
29. P. Jacobs, H. Beyer, J. Valyon, *Zeolites* **1** (1981) 161
30. B. Smit, T. Maesen, *Nature* **337** (1995) 42
31. N. Floquet, J. Simon, J. Coulomb, J. Bellat, G. Weber, G. Andre, *Micropor. Mesopor. Mater.* **122** (2009) 61
32. D. Olson, P. Reischman, *Zeolites* **17** **(**1996) 434
33. W. Well, J. Wolthuizen, B. Smit, J. Hooff, R. Santen, *Stud. Surf. Sci. Catal.* **105** (1997) 2347
34. M. Henri, H. Loven, *Phys. Rev. Lett.* **85** (2000) 366 8
35. D. Majda, W. Makowski, *J. Therm. Anal. Calorim.* **101** (2010) 519
36. H. Morell, K. Angermund, A. Lewis, D. Brouwer, C. Fyfe, H. Gies, *Chem. Mater.* **14** **(**2002) 2192
37. J. Coulomb, P. Llewellyn, Y. Grillet, J. Rouquerol, *Stud. Surf. Sci. Catal.* **87** (1994) 535
38. U. Müller, H. Reichert, E. Robens, K. Unger, Y. Grillet, *Anal. Chem.* 3**33** (1989) 433
39. P. Llewellyn, J. Coulomb, Y. Grillet, J. Patarin, H. Lauter, H. Reichert, J. Rouquerol, *Langmuir* **9** (1993) 1846
40. D. Dubbeldam, S. Calero, T. Maesen, B. Smit, *Phys. Rev. Lett.* **90** (2003) 245901
41. G. Manos, L. Dunne, M. Chaplin, Z. Du, *Chem. Phys. Lett.* **335** (2001) 77
42. R. Krishna, S. Calero, B. Smit, *Chem. Eng.* **88** (2002) 81

43. W. Makowski, D. Majda, *Thermochim. Acta* **412** (2004) 31
44. W. Makowski, D. Majda, *Appl. Surf. Sci.* **252** (2005) 707
45. W. Haohan, Q. Gong, D. Olson, J. Li, *Chem. Rev.* **112** (2012) 836
46. D. Olson, A. Lan, J. Seidel, K. Li, J. Li, *Adsorption* **16** (2010) 559
47. R. Richards, L. Rees, *Langmuir* **3** (1987) 35
48. R. Marguta, S. Khatib, J. Guil, E. Lomba, E. Noya, J. Perdigon-Melon, S. Valencia, *Micropor. Mesopor. Mater.* **142** (2011) 258
49. T. Vlugt, R. Krishna, B. Smit, *J. Phys. Chem., B* **103** (1999) 1102
50. U. Lohse, H. Thamm, M. Noack, B. Fahlke, *J. Incl. Phenom.* 5 (1987) 307
51. W. Zhu, F. Kapteijn, B. Linden, A. Moulijn, *Phys. Chem. Chem. Phys.* **3** (2001) 1755
52. R. Hercigonja, V. Rac, V. Rakic, A. Auroux, *J. Chem. Thermodyn.* **48** (2012) 112
53. S. Ashtekar, A. McLeod, M. Mantle, P. Barrie, L. Gladden, J. Hastings, *J. Phys. Chem., B* **104** (2000) 5281
54. Y. Yang, C. Rees, *Micropor. Matter.* **12** (1997) 117
55. B. Millot, A. Methivier, H. Jobic, *J .Phys. Chem., B* **102** (1998) 3210
56. D. Majda, W. Makowski, *J. Therm. Anal. Calorim.* **101** (2010) 519
57. W. Makowski, L. Ogorzale, *Thermochim. Acta* **465** (2007) 30
58. V. Rac, V. Rakic, S. Gajinov, V. Dondur, A. Auroux, *J. Therm. Anal. Calorim.* **84** (2006) 239
59. J. Pieterse, S. Booneveld, R. van den Brink, *Appl. Catal., B-Environ.* **51** (2004) 215
60. R. Burch, P. Millington, *Appl. Catal., B-Environ.* **2** (1993) 101
61. S. Yashnik, Z. Ismagilov, V. Anufrienko, *Catal. Today* **110** (2005) 310
62. X. Li, B. Shen, C. Xu, *Appl. Catal., A-Gen.* **375** (2010) 222
63. O. Bortnovsky, P. Sazama, B. Wichterlova, *Appl. Catal., A-Gen.* **287** (2005) 203
64. K. Kohei, I. Hajime, N. Seitaro, I. Akira, *Catal. Commun.* **29** (2012) 162
65. W. Haag, R. Dessau, R. Lago, *Stud. Surf. Sci. Catal.* **60** (1991) 255
66. T. Narbeshuber, H. Vinek, J. Lercher, *J. Catal.* **157** (1995) 388
67. W. Haag, *Stud. Surf. Sci. Catal.* **84** (1994) 1375
68. W. Makowski, B. Gil, D. Majda, *Catal. Lett.* **120** (2008) 154
69. J. Janchen, H. Stach, L. Uytterhoven , W. Mortier, *J. Phys. Chem.* **100** (1996) 12489
70. R. Barrer, J. Suterland, *Proc. R. Soc. A-Math. Phys.* **237** (1956) 439
71. W.J. Mortier, *Compilation of Extra-Framework Sites in Zeolites*, Butterworth Scientific Limited, Guildford, 1982
72. P. Jacobs, H. Beyer, J. Valyon, *Zeolites* **1** (1981) 161
73. K. De Meyer, S. Chempath, J. Denayer, J. Martens, R. Snurr, G. Baron, J. *Phys. Chem., B* **107** (2003) 10760
74. P. Titus, *J. Phys. Chem., C* **115** (2011) 3346
75. K. M. A. De Meyer, M. Kurt, S. Chempath, J. Denayer, J. Martens, A. Johan, R. Snurr, G. Baron, *J. Phys. Chem., B* **107** (2003) 10760
76. R. Barrer, R. Gibbons, *Trans. Faraday Soc.* **59** (1963) 2875
77. NIST Chemistry WebBook, http://www.webbook.nist.gov/chemistry/
78. H. Zou, M. Li, J. Shen, A. Auroux, *J. Therm. Anal. Calorim.* **72** (2003) 209.