

Basic thermodynamic characteristics and isotherm of ammonia adsorption in NaZSM-5 and LiZSM-5 zeolites

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Abstract. This paper presents the results of isotherm and basic (ΔH , ΔF , and ΔS) thermodynamic characteristics of ammonia adsorption in Na zeolites_{2,87} ZSM-5 and Li_{3,37} ZSM-5; also the adsorption isotherm is described by the bulk micro-pore filling theory (BFM) equations. The correlation between adsorption-energy characteristics is found, and the molecular mechanism of ammonia adsorption in Na_{2,87}ZSM-5 and Li_{3,37}ZSM-5 zeolites in the whole filling region is revealed. The ammonia adsorbed in NaZSM-5 and LiZSM-5 zeolites is located in the first coordination sphere with Na⁺ and Li⁺ cations, forming octa- and hexa-ammonia complexes. From the adsorption thermokinetics, it was determined that Li⁺ cations are located in the screened positions of the ZSM-5 zeolite crystal lattice. The adsorption of ammonia molecule results in Li⁺ cations migration from the zeolite lattice into junctions formed by the intersection of straight and zigzag channels and the formation of ion/molecular complexes of various multiplicity in them. It was determined that the average molar entropy of ammonia adsorption on NaZSM-5 and LiZSM-5 zeolites indicates that the mobility of ammonia molecules in the zeolite is below the liquid phase and close to the mobility of the solid phase, indicating a strong limitation of mobility of ammonia adsorbed on the cations.

1 Introduction

Volatile Organic Compounds (VOCs) visibly pollute the atmosphere and harm human health. These compounds destroy the ozone layer (1 molecule of chlorine compound destroys 100000 ozone molecules). The products of human industrial activity are aromatic hydrocarbons, chloroalkenes, alcohols, aromatic hydrocarbons, and carbon dioxide, which is a strategic gas in many industrial processes. Large quantities of carbon dioxide are emitted into the atmosphere and cause global environmental problems. It is a product of combustion and greenhouse gas; capturing it for reuse is a major problem facing our society today. One

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way to recover carbon dioxide is by using the adsorption process. Recently, the sorption method is increasingly being used to reduce and control emissions as the most efficient and economical. The potential material for selective adsorption and carbon dioxide separation is adsorbents.

Worldwide adsorbents derived from natural raw materials and synthetically produced adsorbents are widely used in various industrial, construction, agricultural and other fields [1-9]. Nanoporous molecular sieves - zeolites are widely used adsorbents with selective action and a wide range of applications. The chemical composition of molecular sieves, widely used in chemistry and oil and gas processing technology, as well as for solving several chemicals, and environmental problems, is one of the main indicators of their quality. The cationic composition of zeolites determines their ion-exchange properties, resistance to aggressive substances and high temperatures, ability to modify, and several other technological characteristics. The development of zeolite synthesis technology is connected with the necessity of controlling the content of ion-exchange elements (Na, Li, K, Cs, H, Cu, etc.) in them.

Due to their unique properties, zeolites have found many applications in various industries, and their annual turnover in the world market amounts to several million tons. Zeolites are most widely used in gas and petrochemicals, ion exchange (water purification and softening), adsorption and separation of vapors and gases, and removing impurities (particularly harmful and environmentally hazardous) from gases and solutions. In addition, zeolites are increasingly used in ecology, agriculture, animal husbandry, paper industry, and construction [10].

Anticipated new applications of zeolites described in the literature include molecular electronics, quantum dots/chains, zeolite electrodes, batteries, non-linear optical materials, and chemical sensors. Recently, there have been research reports on using zeolites as low dielectric constant materials for microprocessors [11-12].

In [13], various types of natural and synthetic zeolites and the possibilities of their application as molecular sieves in heterogeneous catalysis are described. Controlled synthesis makes it possible to purposefully produce zeolites for highly selective adsorption in solving environmental problems, in organic chemical synthesis, and for separating gas mixtures. Structures of various types of zeolites, including ZSM-5, -11, -20, -48, VPI-5, $AlPO_4-5$, SAPO-5, used lately, are given. It is pointed out that zeolites have a great future in electrical engineering, membrane technology, and as indicators (sensors).

One of the highly effective catalysts for various petrochemical and refinery processes is ZSM-5 type zeolites. Part of the reason for their wide popularity is the unique ability of these zeolites to catalyze the process of obtaining high-octane gasoline with high octane number [OV>95] from non-oil raw materials, such as methanol, as well as to directly convert methanol or ethanol into a mixture of hydrocarbons [9, 14-18]. Therefore, the all-around study of physicochemical and especially energetic characteristics of zeolites like ZSM-5 is of great theoretical and practical importance. The study of adsorption properties of adsorbents gives useful information on structural characteristics and possibilities of practical application.

Knowing the nature of the active centers and estimating their concentration is a prerequisite for classifying adsorbents. Therefore, a comprehensive study of the physicochemical and energetic characteristics of ZSM-5 type zeolites is of great theoretical and practical importance. In this connection, the accumulation and systematization of the most important thermodynamic characteristics of adsorption systems, one of the components of which is a zeolite, is of great importance. Thus, in particular, in the refining industry, in catalytic processes of isomerization, deparaffinization, cracking, and aromatization, mainly in the liquid phase, they have proved to be the most effective. Therefore, a comprehensive study of the adsorption properties of ZSM-5 type zeolites provides useful information about

structural characteristics and possibilities of practical application. Adsorption on these zeolites strongly depends on the cations present in the structure. Because of the large space between the adsorption centers, the zeolite is ideally suited for model studies of adsorption behavior.

In conclusion, it should be mentioned that ZSM-5 type zeolites can be widely used in ecology, pharmaceuticals, etc., as highly efficient adsorbents for drying and purification of preliminary products from undesirable impurities. Moreover, the enhanced thermal, acidic, and hydrothermal stability of SHF zeolites gives them unique adsorption and catalytic properties, which are of great practical and theoretical importance. Apparently, high stability is also due to the application of pentasil-type zeolites in oil refining, the petrochemical industry, and other catalytic processes (especially in obtaining hydrocarbons from methanol).

The various physicochemical properties of ZSM-5 have been investigated using various characterization techniques, including X-ray diffraction, BET (Brunauer-Emmett-Teller) surface area, Fourier transforms infrared, and scanning electron microscopy [19-20].

The authors [21] measured pore sizes by positron annihilation spectroscopy and analyzed the porous structure of pure silica-type MFI zeolite and zeolite films obtained by centrifugation process with low dielectric constant values. Micropore sizes in the silica zeolite and the films, 0.55 ± 0.03 nm, determined by the positron annihilation method, agree with the data of crystallographic measurements. Experiments carried out by positron annihilation spectroscopy revealed that mesopores in zeolite films are open and interconnected; their size is 2.3-2.6 nm.

The structure of zeolites is characterized by the presence of intracrystalline pores and cavities of molecular size, which allowed the authors [22] to consider zeolites, in addition to their obvious use as form-selective catalysts, as noncatalytic microreactors in which reactions between several isolated molecules of a certain size and shape can take place. Examples of three such reactions are considered and analyzed: photochemical haloidation, ketone photoreaction, and Diels- Alder reaction.

Among the techniques that have been used successfully in the second half of the last century, IR and NMR are the most popular. However, no single method can fully describe acid centers' nature, amount, strength, localization, and lifetime value. The ICS, for example, characterizes hydroxyl groups and surface compounds formed by the interaction of bases such as pyridine and ammonia with BCC and LCC. The strength of the adsorbate-adsorbent interaction and, therefore, the "acidity strength" can be estimated by conducting a temperature-programmed desorption of the adsorbate. A more direct and accurate method for determining the strength of acidity and its distribution along the spectrum of acid centers is the calorimetric measurement of the heat obtained during the adsorption of bases. It follows that the most interesting and accurate information is obtained by a complex study of the same system by different methods.

In a study of ammonia adsorption in HZSM-5 zeolite, it was found that two types of acid centers are present in zeolites: Bronsteadian and Lewisian. The Bronsteadian or protonic acidity is due to structural OH-groups in zeolites, capable of giving off a proton. The Lewis or aprotic acid centers are capable of attaching an electron pair. The role of such centers is played by triple-coordinated aluminum atoms (Al^{3+}) and silicon atoms (Si^{3+}), carrying a positive charge and cations compensating the negative charge of alumina tetrahedrons. The authors investigated the properties of complexes formed in HZSM-5 and CuZSM-5 zeolites upon adsorption of ammonia and nitromethane [23-24].

Carbon dioxide and para-xylene adsorption on ZSM-5 zeolites at 303 K was studied using calorimetric methods [25-26]. It was shown that the measured adsorption isotherms were well described by the Dubinin-Radushkevich equation. This indicates that the adsorption of CO_2 and p-xylene proceeds not on the zeolite surface but inside, following

the mechanism of volume filling of micropores. The micropore volume and the characteristic adsorption energy were determined.

There are a large number of data on the adsorption of organic substances in pentasil-type zeolites, which were obtained by various physical and chemical methods of investigation. However, data obtained by the adsorption-calorimetric method are scarce, which puts on the agenda the task of further detailed study of adsorption properties of ZSM-5-type zeolites concerning ammonia molecules as well as obtaining basic thermodynamic characteristics of these systems. Moreover, the adsorption-calorimetric method applied in this study reveals the mechanism of adsorption processes taking place on adsorbents and catalysts. Using adsorption measurements, one can obtain data on various factors (e.g., channel size, pore volume, localization of cations, etc.) related to the structure of a particular zeolite. The study of the adsorption of various substances in zeolites of type ZSM-5 is of particular interest. Adsorption on these zeolites strongly depends on cations present in the structure. Because of the large space between the adsorption centers, the zeolite is ideally suited for model studies of adsorption behavior.

However, some questions on the specific structure of zeolites, especially those relating to the problem of dispersion of active centers, the mechanism of adsorption of polar and nonpolar molecules, and the nature and involvement of defects in adsorption, are still unclear. The solution to these questions is decisive for the successful application of adsorbents and the directional regulation of their properties. Also, it makes it possible to study and establish general regularities of adsorption and catalysis.

Differential heat of adsorption together with other differential adsorption energetic characteristics (enthalpy, free energy, and entropy) most fully characterize the physical, chemical, crystallochemical, and geometrical nature of the adsorbent surface and allows the study of adsorption phenomena on a molecular structural level.

This paper studies isotherms, differential heat, entropy, and kinetics of ammonia adsorption in NaZSM-5 and LiZSM-5 zeolites at 303 K. The unit cell composition of NaZSM-5 is $\text{Na}_{2,87}[(\text{SiO}_2)_{93,13}(\text{AlO}_2)_{2,87}]$, LiZSM-5 - $\text{Li}_{3,37}[(\text{SiO}_2)_{96,63}(\text{AlO}_2)_{3,37}]$.

2 Testing methods

For measurements of isotherms and differential adsorption heats, a system consisting of a universal high-vacuum adsorption unit and a Tian-Calvet-type, DAK-1-1A thermally conductive differential microcalorimeter connected to it was used, which has high accuracy and stability. The instrument's calorimeter sensitivity is extremely high, and its reliability is high (it can measure about 0.2 μW thermal power). It can be used confidently to measure the heat of processes of almost unlimited duration. The calorimeter makes it possible to obtain the thermokinetics of the process of adsorption systems under study, which is very important for elucidating the adsorption mechanism.

Despite its outer insulating shells, it is not adiabatic, as the heat released in it is introduced from the calorimeter chamber as is released and dissipated into the large metal block. Although the temperature of the calorimeter chamber changes only slightly, the instrument cannot be called strictly isothermal; it detects small temperature changes, which are unavoidable and form the basis of measurements.

Most of the heat (about 99%) released into the calorimeter chamber is dissipated into the calorimeter block immediately after release. Only about 1% of the heat released remains in the calorimeter chamber, raising its temperature slightly. The measurement is mainly concerned with the heat flux that passes through the surface of the calorimeter chamber and the calorimeter block.

The adsorption-calorimetric method used in this work provides highly accurate molar thermodynamic characteristics and reveals detailed mechanisms of adsorption processes

occurring on adsorbents and catalysts. Adsorption measurements and adsorbate dosing were carried out using a universal high-vacuum adsorption unit. The unit allows adsorbate dosing by both gas-volume and volume-liquid methods. We used a BARATRON B 627 membrane pressure gauge to measure the equilibrium pressures.

3 Results and discussion

To characterize the adsorption properties of the zeolite, the differential heat and isotherms of ammonia adsorption were measured, and the entropy and free energy of ammonia adsorption were calculated.

The solvation of alkali metal cations by ammonia in solutions and the gas phase has been the subject of many experimental and theoretical studies [23, 27-32]. The solvation of cations located on the surface and in the volume of microporous materials, such as zeolites, is a process of a more complex nature since here the interaction of cations and adsorbate molecules with the anionic solid matrix must be taken into account, which may hinder or even prevent the complex formation in the cation/molecule system.

The pentasil zeolites NaZSM-5 and LiZSM-5 have absolutely identical aluminosilicate frameworks and almost identical amounts of exchangeable Na and Li cations (0.5 and 0.577 mmol/g). One would expect that their adsorption properties towards the same substance (NH₃) should also be basically the same. However, a study of the differential heats of adsorption of ammonia vapor at 303 K on these zeolites showed signs of similarity and substantial difference in their adsorption properties.

The heat of adsorption of polar molecules on the NaZSM-5 zeolite is characterized by a stepwise drop of adsorption heat, indicating the stoichiometric interaction of these molecules with Na⁺ cations compensating the negative charge of the lattice. Thus, for the adsorption of water and alcohols, we have steps corresponding to the formation of Na(H₂O)⁺₄, Na(CH₃OH)⁺₄, and Na(C₂H₅OH)⁺₄ complexes [25-26, 32-33]. In the case of ammonia on the NaZSM-5 zeolite, we unexpectedly found the formation of Na(NH₃)⁺₈ complexes. A tangle is formed, in the center of which there is a Na⁺ cation and 24 hydrogen atoms on the outer shell. This ball is located in the crossing of straight and zigzag channels of NaZSM-5 zeolite. Very few ammonia molecules can be adsorbed on the silica gel. The heat of adsorption decreases linearly from 70 kJ/mole to 30 kJ/mole with 0.5 N/M adsorption [23].

The adsorption isotherm of ammonia on NaZSM-5 zeolite in semi-logarithmic coordinates is shown in Figure 1. Equilibrium pressures at low fillings reach $P/P = 10_s^{-9}$, indicating strong ammonia adsorption. The adsorption isotherm is brought to ~8 N/M (molecule/cation) at relative pressures $P/P_s = 5.4 \cdot 10^{-2}$ (or to 473 torrs). Figure 1 shows that a step is formed in the adsorption region (when the equilibrium pressure reaches 2. 10^{-3} torr), i.e., the adsorption of two ammonia molecules onto the cation. Then a more rapid rise in pressure is observed, accompanied by forming S-dimensional complexes around the Na⁺ cations.

The isotherm of ammonia adsorption on the NaZSM-5 zeolite is described by the three-term VMOT equation for small fills of two to eight molecules/cation [34].

$$a=2.042\exp[-(A/41.55)^2]+1.4\exp[-(A/18.77)^4]+1.5\exp[-(A/7.35)^2] \quad (1)$$

Figure 1 shows that the data calculated from this equation agree well with the experimental data.

Figure 2 shows the differential heat of ammonia adsorption on NaZSM-5 zeolite. The

initial heat of adsorption is 110 kJ/mole. The heat of adsorption is also in perfect agreement with the isotherm (Figure 2). Two ammonia molecules adsorb with a heat of ~ 80 kJ/mole, varying little with filling. The adsorption of further ammonia molecules is accompanied by a sharp decrease in heat.

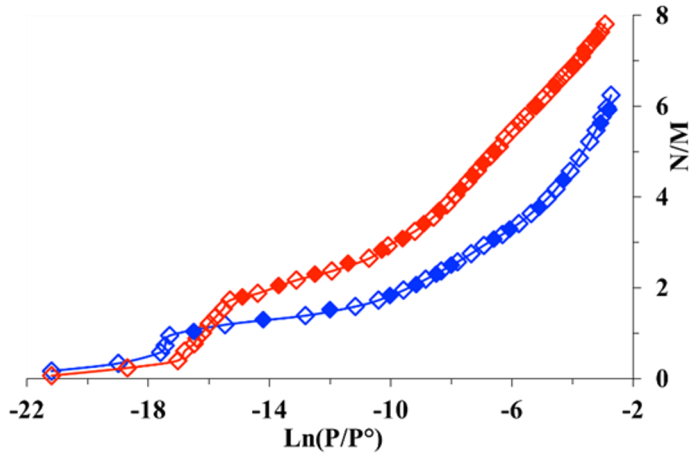


Fig. 1. Ammonia adsorption isotherms on NaZSM-5 and LiZSM-5 zeolites. \diamond, \square experimental points. \square, \square -points calculated using VMOT.

Before the adsorption of $6\text{NH}_3/\text{Na}_3^+$, the curve forms an extended plateau at 47 kJ/mole. A total of 8 ammonia molecules per cation are adsorbed, after which the heat decreases to the condensation heat of ammonia (20 kJ/mole). Extremes in the heat curve are observed around the adsorption of 6-8 molecules.

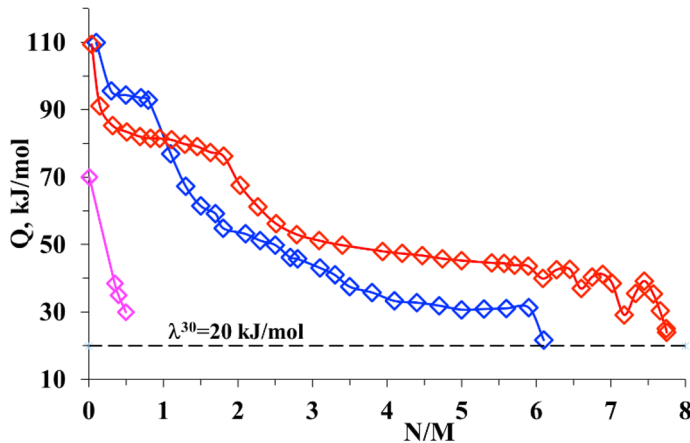


Fig. 2. Differential heat of adsorption of ammonia on zeolites: \diamond -NaZSM-5, \diamond -LiZSM-5 and \diamond -silicalite. Horizontal dashed line is heat of condensation.

The entropy diagram (Figure 3) clearly shows that the entire entropy curve is below the entropy of liquid ammonia (the entropy of liquid ammonia is taken as zero), indicating a strong limitation of the mobility of the ammonia adsorbed on the cation. The entropy also confirms the strong interaction of ammonia on the NaZSM-5 zeolite with the Na^+ cation in the ratio $2\text{NH}_3:\text{Na}^+ = 2:1$.

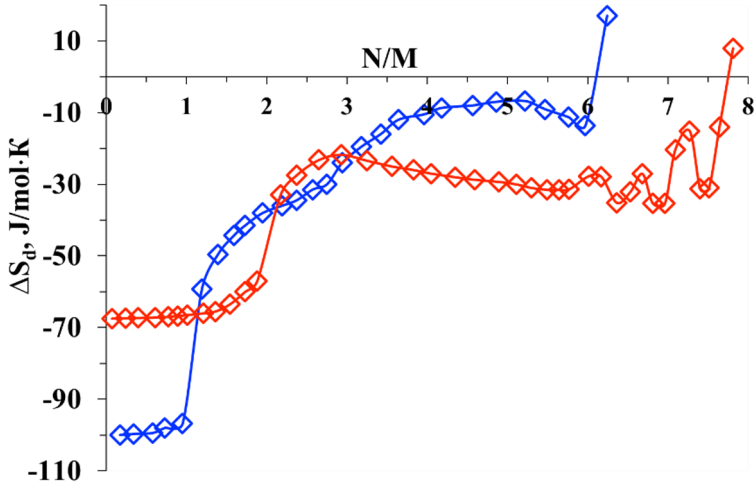


Fig. 3. Entropy of ammonia adsorption on zeolites \diamond -NaZSM-5 и \diamond -LiZSM-5.

Figure 2 shows that before the adsorption of 2 N/M, the entropy (ΔS_d) does not change from a minimum value (-67 J/K·mole). Then with filling, the adsorption entropy of ammonia increases to -23 J/K·mole at 3 N/M adsorption. Until adsorption of 6 N/M ΔS_d decreases to -32 J/K·mol. The entropy curve then shows extremes as in the heat, and at adsorption of about 8 N/M, the entropy rises to the entropy level of liquid ammonia. The thermokinetics of ammonia adsorption on NaZSM-5 zeolite indicates that the first 3 ammonia molecules adsorb at a low rate (Figure 4). This retardation is particularly noticeable in adsorbing the first two ammonia molecules.

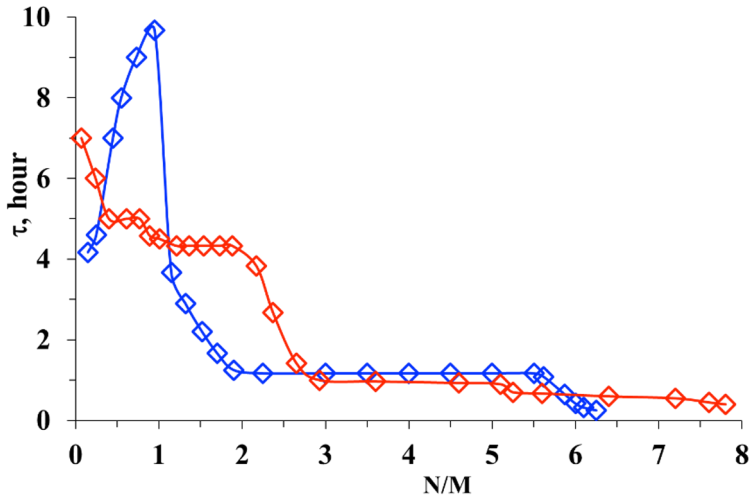


Fig. 4. Adsorption equilibrium time as function of ammonia adsorption on zeolites \diamond -NaZSM-5 and \diamond -LiZSM-5.

Before filling with 1 N/M, the adsorption equilibrium process occurs on average in 5 hours, and with adsorption of 2 N/M in ~4 hours. The process then accelerates sharply, and at 3 N/M, adsorption stabilizes, and until adsorption of 5 N/M, the equilibrium is established in 1 hour. Then, by forming a step, it is established in 30 min at an adsorption

rate of 5 N/M to 8 N/M.

The isotherm of ammonia adsorption on LiZSM-5 in semi-logarithmic coordinates is shown in Figure 1. The equilibrium pressures at low fillings also reach $P/P = 10^{-9}$ as in NaZSM-5 zeolite, indicating strong ammonia adsorption. The adsorption isotherm is brought to 6.25 N/M at relative pressures of $P/P_s = 6.522 \cdot 10^{-2}$ (or up to 571 torrs).

The isotherm of ammonia adsorption on LiZSM-5 zeolite is similar to the isotherm of adsorption on NaZSM-5 zeolite (Figure 2), but with the difference that, firstly, the length of the step is half as long. This indicates that the high-energy complex is formed with only one ammonia molecule. Secondly, figure 2 shows that up to the ratio $\text{NH}_3:\text{Li}^+ - 1:1$, the isotherm curve is located above the abscissa axis, indicating that ammonia molecules interact more strongly with Li cations⁺ than with Na⁺ cations. Starting with 2 N/M, the pressure rises sharply, and the adsorption isotherm curve on the LiZSM-5 zeolite is below the adsorption isotherm curve on the NaZSM-5 zeolite.

The isotherm of ammonia adsorption on the LiZSM-5 zeolite is described by the three-term TOSM equation for small fills of one to six molecules per cation [34]:

$$a = 1.103 \exp[-(A/49.06)^3] + 1.122 \exp[-(A/20.17)^4] + 1.85 \exp[-(A/9.40)^3] \quad (2)$$

Figure 2 shows that the calculated data agree with the experimental data.

The heat of ammonia adsorption on LiZSM-5 zeolite is also following the isotherm. A high-energy complex is formed with only one NH_3 molecule (~93 kJ/mole). With filling, the heat of adsorption changes from 93 kJ/mole to 54 kJ/mole with 2 N/M adsorption.

Further, with increasing adsorption, there is a successive formation of Li⁺ cation complexes with three and four ammonia molecules with a linear decrease in the heat to 34 kJ/mole. The adsorption of the fifth and sixth ammonia molecule proceeds with a constant heat of 31 kJ/mole, which drops sharply to a condensation heat of 20 kJ/mole on completion.

The Li complexes⁺ with six water molecules are located at the intersections of the straight and zigzag channels. This is due to the small size of the Li cation compared to Na⁺, i.e., the larger Na⁺ can hold more ammonia molecules on the surface.

The entropy of the ammonia adsorbed on the Li cation⁺, as in the case of NaZSM-5, is located below the entropy of the liquid ammonia (Figure 3), indicating the retarded state of the ammonia molecules in the zeolite. Figure 3 shows that before 1 N/M adsorption, the entropy (ΔS_d) does not change from a minimum value (-100 J/K·mole). Starting at 2 N/M, the adsorption entropy of ammonia rises sharply to -37 J/K·mole at 2 N/M adsorption. Then ΔS_d gradually increases to the entropy of liquid ammonia at 6.25 N/M adsorption.

However, the thermokinetics are dramatically different (Figure 4). It passes a maximum (~10 hours) just at the filling corresponding to the adsorption of ammonia on Li⁺ at a ratio of 1:1. This character of the curve is caused by the diffusion of Li⁺ in the inter-channel space. Then with filling, the establishment of the adsorption equilibrium accelerates sharply and stabilizes at 2 N/M adsorption, and further, the equilibrium is established in ~1 hour.

Thus, the ammonia adsorbed in the NaZSM-5 and LiZSM-5 zeolites settles in the first coordination sphere with Na⁺ and Li⁺ cations, forming octa- and hexa-ammonia complexes.

4 Conclusions

Adsorption-calorimetric studies of ammonia adsorption on NaZSM-5 and LiZSM-5 zeolites have been performed. Complete thermodynamic characteristics of ammonia adsorption on these zeolites have been obtained. The step character of isotherm, heat, entropy, and kinetics of ammonia adsorption has been revealed. A correlation between the adsorption energetic characteristics and the molecular mechanism of ammonia adsorption on NaZSM-5 and LiZSM-5 zeolites throughout the filling range is found. The ammonia adsorbed in NaZSM-5 and LiZSM-5 zeolites is located in the first coordination sphere with Na^+ and Li^+ cations, forming octa- and hexa- ammonia complexes. The adsorption isotherms are described by the equations of the volumetric micropore filling theory (VCLT). The heat of adsorption correlated with the number of sodium and lithium cations in the zeolite structures. It was shown that the adsorption properties of ZSM-5 zeolites depend on the type of cation and the structure of fragments of ZSM-5 zeolite structure. It was stated that Li^+ cations are located in screened positions of the ZSM-5 zeolite crystal lattice. Ammonia adsorption leads to the migration of Li^+ cations from the zeolite lattice into junctions formed by the intersection of straight and zigzag channels and to the formation of ion/molecular complexes of various multiplicity in them.

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