

# Calorimetric study of methanol adsorption in LiZSM-5 and CsZSM-5 zeolites

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**Abstract.** This paper presents isotherms and basic ( $\Delta H$ ,  $\Delta F$ , and  $\Delta S$ ) thermodynamic characteristics of methanol adsorption in Li<sub>3,37</sub>ZSM-5 and Cs<sub>3,17</sub>ZSM-5 zeolites obtained by the calorimetric method. For measurements of isotherms and differential heat of adsorption, a system consisting of a universal high-vacuum adsorption unit and an attached differential modified Tian-Calvet type microcalorimeter, DAC-1-1A, which directly quantifies and qualifies the nature and forces of adsorption interaction, was used. The adsorption isotherm is described by the equations of the volumetric micropore filling theory (VMOT). The correlation between the adsorption-energy characteristics is found, and the molecular mechanism of methanol adsorption in Li<sub>3,37</sub>ZSM-5 and Cs<sub>3,17</sub>ZSM-5 zeolites throughout the filling region is revealed. Methanol adsorbed in Li<sub>3,37</sub>ZSM-5 and Cs<sub>3,17</sub>ZSM-5 zeolites is located in the first coordination sphere with cations Li<sup>+</sup> and Cs<sup>+</sup>, forming tetra- and trimeric complexes. It is found that the charge density significantly affects the adsorption mechanism, the adsorption energy, and the number of adsorbed molecules. It was determined that the average molar entropy of ammonia adsorption on LiZSM-5 and CsZSM-5 zeolites indicates that the mobility of methanol molecules in the zeolite is below the liquid phase and close to the mobility of the solid phase, indicating a strong inhibition of mobility of methanol adsorbed on cations. This work shows how calorimetric data can complement crystal structure results and detect subtle adsorbent/adsorbate interactions at the molecular level.

## 1 Introduction

One of the main tasks of colloid chemistry is to study the amount, strength, and nature of the active centers of dispersed substances, which makes it possible to solve many theoretical questions about adsorption and catalysis.

The adsorption phenomenon of gases and vapors underlies many chemical and biological processes, and for a long-time, researchers have been interested in it for purely practical purposes. The study of adsorption energy of gases and vapors is of paramount importance not only for understanding interesting phenomena and practically valuable processes occurring on various synthetic zeolites but also for accumulation, systematization, and standardization of the most important thermodynamic characteristics

of heterogeneous systems, one of whose components is zeolite.

Most zeolites are used for technical and waste water treatment, soil improvement, hydroponics, as a filler in food grade paper and cardboard, and drying and purifying gases, as an adsorbent, ion exchanger, catalyst, etc.

Worldwide, zeolites derived from natural raw materials and synthetically produced are widely used in various industrial, construction, agricultural and other applications [1-9]. Zeolites are most widely used in gas and petrochemistry, 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 being used in ecology, agriculture, animal husbandry, paper industry, and construction [10].

ZSM-5-type catalysts are highly effective catalysts for various processes in the petrochemical and refining industry. Particularly in the refining industry, they have proved most effective in catalytic isomerization, deparaffinization, cracking, and aromatization processes, mainly in the liquid phase. Conversion of methanol into hydrocarbons in acid medium zeolite catalysts is now considered an important and feasible non-petroleum way of producing valuable chemicals [11-22].

Part of the reason for their wide popularity is the unique ability of these zeolites to catalyze the production of high-octane gasoline from non-oil feedstocks, such as methanol. It was exactly this feature of ZSM-5 zeolites that attracted the attention of many researchers. Hundreds of publications devoted to various aspects of adsorption on these zeolites have appeared in journals and works on structure studies.

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 [23-24].

B. Bonelli et al. used adsorption microcalorimetry and vibrational spectroscopy to study the interaction at room temperature of CO<sub>2</sub> with Na-ZSM-5 zeolite [25]. They confirmed that these interactions consist of reversible two-step adsorption on approximately energetically equal and non-interacting adsorption centers, constituting an ideal thermodynamic ensemble. From adsorption isotherms obtained by volumetric and calorimetric methods, we calculated the standard changes in enthalpy and Gibbs free energy for 1:1 and 1:2 adsorption adducts formed by CO<sub>2</sub> molecules and Na<sup>+</sup> cations. The standard entropy changes are also determined in this work. All vibrational modes were measured, and the entropy of the adsorption phase was calculated by statistical mechanics.

A more direct and accurate method for determining the strength of acidity and its distribution along the spectrum of acid centers is provided by the calorimetric measurement of the heat obtained by the adsorption of bases [26-27]. It follows that the most interesting and accurate information is obtained by a complex study of the same system by different methods.

A large number of data on the adsorption of organic substances in pentasil-type zeolites are available, which have been obtained by various physico-chemical methods of investigation. The adsorption-calorimetric method applied in this work reveals the mechanism of adsorption processes occurring on adsorbents and catalysts.

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.

## 2 Testing methods

To solve the problem, the adsorption-calorimetric method of investigation was applied, giving a direct quantitative and qualitative characterization of the nature and forces of adsorption interaction. For measurements of isotherms and differential heat of adsorption, a system consisting of a universal high-vacuum adsorption unit and a Tian-Calvet-type, DAC-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  $\mu\text{W}$  thermal power). The calorimeter makes it possible to obtain the thermokinetics of the process of the adsorption systems under study, which is very important for elucidating the adsorption mechanism.

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 very slightly. The measurement is mainly concerned with the heat flux that passes through the calorimeter chamber's surface and the block.

The adsorption-calorimetric method used in this work provides highly accurate mole 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.

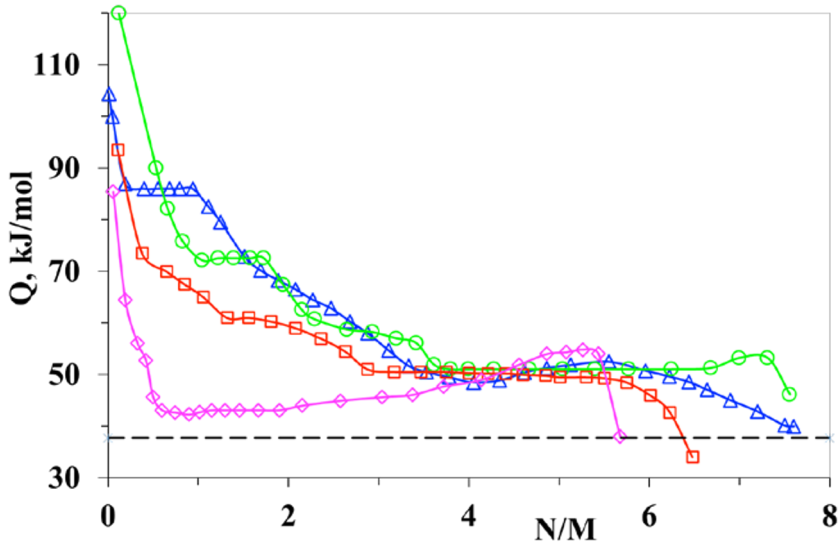
In this work, isotherms, differential heat, entropy, and kinetics of ammonia methanol adsorption in LiZSM-5 and CsZSM-5 (Si/Al=27.5) zeolites at 303 K are studied. The unit cell composition of LiZSM-5 is  $\text{Li}_{3,37}[(\text{SiO}_2)_{96,63}(\text{AlO}_2)_{3,37}]$ , CsZSM-5 is  $\text{Cs}_{3,17}[(\text{SiO}_2)_{95,23}(\text{AlO}_2)_{3,17}]$ ; hence the  $\text{Li}^+$  and  $\text{Cs}^+$  cations content are on average  $\sim 3.37/\text{e.c.}$  and  $\sim 3.17/\text{e.c.}$ , respectively. Before starting the experiment, the adsorbent was evacuated at 723 K for 10 hours to a high vacuum ( $10^{-5}$  torr).

## 3 Results and discussion

One of the remarkable features of ZSM-5 type zeolites is their ability to synthesize high octane gasoline from lower alcohols [28]. We investigated the differential heat of methanol adsorption on LiZSM-5 and CsZSM-5 zeolites.

Figure 1 shows the differential heat of methanol adsorption in LiZSM-5 zeolite. The differential heat curve of adsorption forms a high-energy step at 86 kJ/mol. The high-energy adsorption of methanol with  $\text{Li}^+$  cation proceeds at a ratio of 1:1. Further, with increasing adsorption, there is the successive formation of  $\text{Li}^+$  cation complexes with two, three, and four alcohol molecules with a decrease in heat from 86 kJ/mole to 48.5 kJ/mol. The minimum on the curve corresponds exactly to the tetrahedral  $\text{Li}^+$  complex with four methanol molecules. Due to its size, this complex can only fit in the intersections of the straight and zigzag channels of the zeolite. The adsorption of the next four methanol molecules first proceeds with an increase in heat to 52.5 kJ/mole at adsorption of 5.55 N/M, then decreases again to the condensation heat and proceeds already in the "silicate" part of the zeolite, that is, in the part where no  $\text{Li}^+$  cations. The total adsorption of methanol on LiZSM-5 zeolite is 8 methanol molecules per cation.

The time for the adsorption equilibrium, just as in the case of water adsorption, passes through a maximum (6 hours.) at methanol to  $\text{Li}^+$  ratio of 1:1 (Fig. 1).



**Fig. 1.** Differential heat of methanol adsorption on zeolites:  $\Delta$ -LiZSM-5,  $\square$ -CsZSM-5,  $\circ$ -NaZSM-5,  $\diamond$  -silicalite. The horizontal dashed line is heat of condensation.

This result also confirms our established phenomenon of  $\text{Li}^+$  cation diffusion from the side channels of zeolite. At a ratio of 1:1, all cations are located in the intersections, where S-measured methanol/ $\text{Li}^+$  complexes are formed.

The adsorption equilibrium process accelerates sharply up to 1.6 h at high fillings. (2 N/M), then slows down again, and the equilibrium is established in 2.6 hours at an adsorption rate of 3 N/M. The adsorption rate at 3.4 N/M then stabilizes, and the equilibrium is established in an average of 1 hour.

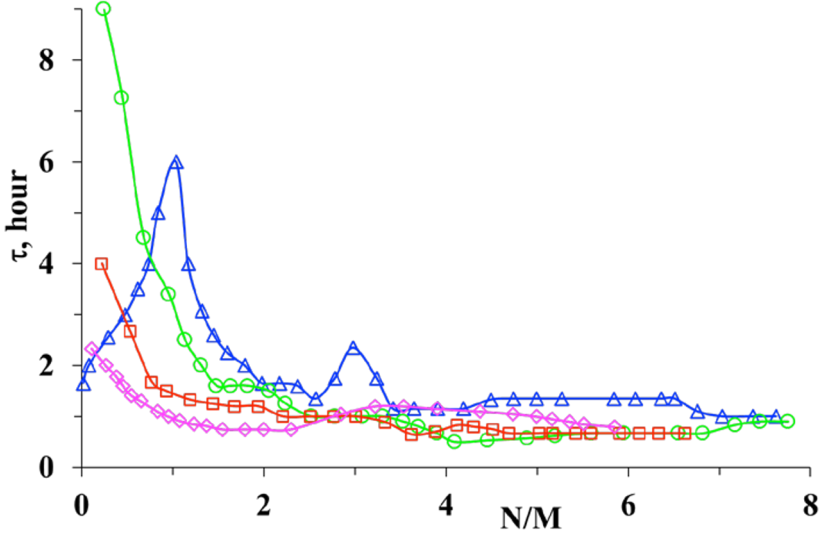
The adsorption isotherm of methanol on LiZSM-5 zeolite is brought to 7.62 N/M at relative pressures  $P/P_s=0.826$  (or up to  $P=124$  torr). If the density of methanol in zeolite is assumed to be the same as that of normal liquid at a temperature of experiment and the volume occupied by methanol molecule at saturation is calculated, then it turns out that methanol occupies  $\sim 0.18 \text{ cm}^3/\text{g}$  sorption volume of zeolite LiZSM-5, which is  $\sim 93\%$ .

An isotherm of methanol adsorption on LiZSM-5 zeolite in semi-logarithmic coordinates is shown in Figure 2, and it confirms the energy data. The equilibrium pressures at low fillings reach  $P/P_s=10^{-7}$ , which indicates strong sorption of methanol. The adsorption isotherm of methanol is almost completely described by the three-term VMOT equation from small fills up to 6.5 molecules/cation [29]:

$$a=1, 1 \exp[-A/30, 17]^5] + 1, 586 \exp[-A/13, 36]^2] + 1, 122 \exp[-A/7, 16]^3] \quad (1)$$

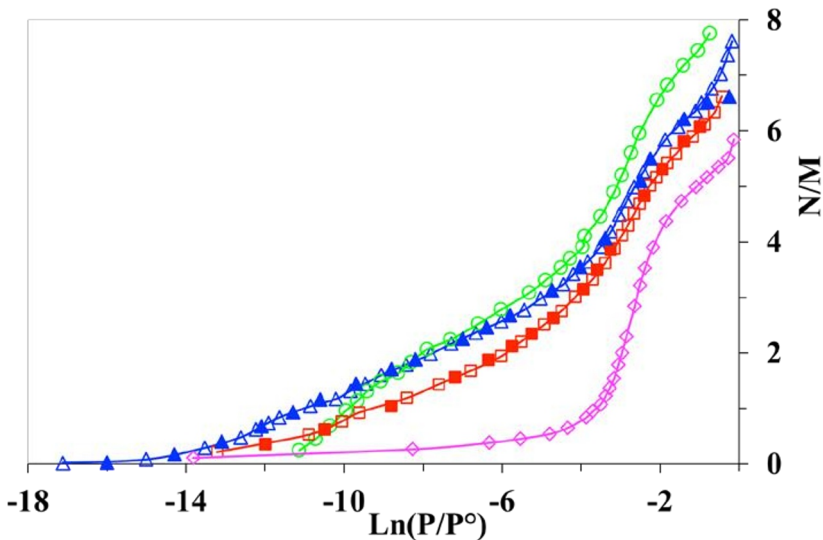
Fig.2 shows that the calculated data agree with the experimental data.

The molar differential entropy ( $\Delta S_d$ ) of methanol adsorption on LiZSM-5 zeolite is plotted against the entropy of liquid methanol and is all below zero (Figure 4). It confirms the strong interaction of methanol with the cation  $\text{Li}^+$  in a 1:1 ratio.  $\Delta S_d$  first increases from a minimum value (-70 J/K·mole) to -49 J/K·mole at 0.3 N/M adsorption, then decreases again to -69 J/K·mole at 1 N/M adsorption. Then  $\Delta S_d$  changes gradually to -6 J/mole at 4 N/M adsorptions.



**Fig. 2.** Adsorption equilibrium time as function of methanol adsorption value on zeolites:  $\Delta$ -LiZSM-5,  $\square$ -CsZSM-5,  $\circ$ -NaZSM-5,  $\diamond$ -silicalite.

Further adsorption takes place in the "silicate" part of the zeolite. Methanol molecules interact more strongly in the "silicate" part than in the 4 N/M adsorption on the  $\text{Li}^+$  cation, so initially  $\Delta S_a$  decreases from -6 J/K·mole to -30 J/K·mole at 6 N/M adsorption and rises again to -2.5 J/K·mole at 7.6 N/M adsorption.



**Fig. 3.** Adsorption isotherms of methanol on zeolites:  $\Delta$ -LiZSM-5,  $\square$ -CsZSM-5,  $\circ$ -NaZSM-5,  $\diamond$ -silicalite.  $\Delta$ ,  $\square$ ,  $\circ$ ,  $\diamond$ - experimental points.  $\blacktriangle$ ,  $\blacksquare$ -points calculated with VMOT.

The mean mole entropy of adsorption indicates that the mobility of alcohol in the LiZSM-5 zeolite is lower than that of methanol in the liquid phase and close to its mobility in the solid phase.

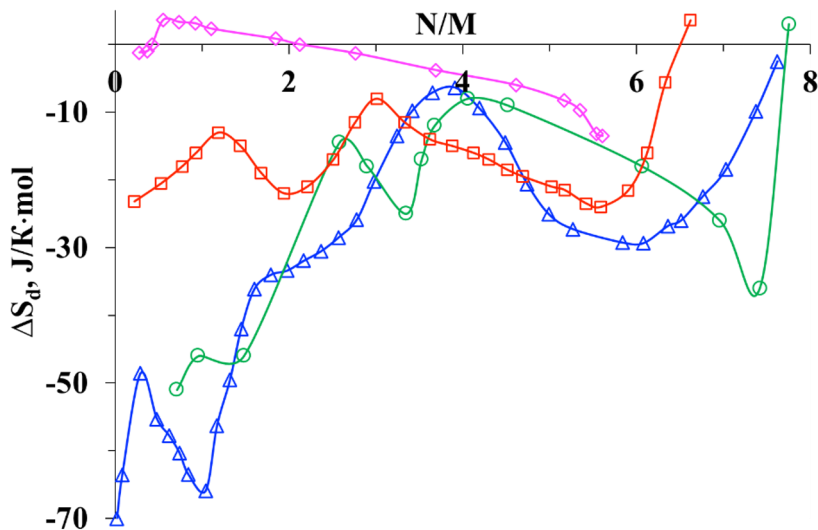


Fig. 4. Methanol adsorption entropy on zeolites:  $\Delta$ -LiZSM-5,  $\square$ -CsZSM-5,  $\circ$ -NaZSM-5,  $\diamond$ -silicalite.

The differential heat curve for methanol adsorption on CsZSM-5 zeolite can be divided into 2 areas corresponding to a region of high adsorption heats (Figure 1). These are the adsorption of an average of 3 alcohol molecules per cation when the heat varies from 78 kJ/mole to 50 kJ/mole, and the region of relatively low (50 kJ/mole) - another 3 alcohol molecules.

Methanol adsorbed in ZSM-5 zeolites forms tetra complexes with  $\text{Li}^+$  cations and  $\text{Na}^+$  [30]. In the case of the  $\text{Cs}^+$  cation, only 3 methanol molecules interact with the  $\text{Cs}^+$  cation. This difference can be easily explained if we consider the size of the  $\text{Cs}^+$  cation, which is much larger than the listed cations. After saturation of all cations with methanol molecules, adsorption already occurs in the cation-free part of ZSM-5 zeolite. The heat of adsorption in this part Q (Figure 1) is the same value ( $\sim 50$  kJ/mole) for three zeolites LiZSM-5, NaZSM-5, and CsZSM-5 [30]. However, four methanol molecules are adsorbed in the silicate part in the LiZSM-5 and NaZSM-5 zeolites, and three methanol molecules are adsorbed in the CsZSM-5 zeolite.

Methanol adsorption entropy on CsZSM-5 zeolite agrees with the results of Q (Figure 4). The appearance of each of the extremes indicates the completion of one of the adsorption types. The first maximum corresponds to completing the monomer complex  $\text{CH}_3\text{OH}/\text{Cs}^+$ .

The minimum corresponds to  $2\text{CH}_3\text{OH}/\text{Cs}^+$ , and the next maximum corresponds to  $3\text{CH}_3\text{OH}/\text{Cs}^+$ . Thus, the formation of a three-dimensional molecule/cation complex is complete. Then the entropy, as in the LiZSM-5 zeolite, goes through a deep minimum of  $-25$  J/K·mol and rises to the entropy of liquid methanol. This entire section of the entropy curve corresponds to methanol adsorption without appreciable participation of  $\text{Cs}^+$  cations, then eats in channels and intersections not containing  $\text{Cs}^+$  cations. The mean molecular entropy of adsorption indicates that the mobility of alcohol in the CsZSM-5 zeolite is lower than that of methanol in the liquid phase. However, the entropy of methanol adsorption (Figure 4) on NaZSM-5 zeolite [30] increases from a minimum value of  $-50$  J/K·mole to  $-9$  J/K·mole at 4 N/M adsorptions. Further  $\Delta S_a$  passes through a minimum of  $-25$  J/K·mole and rises to the entropy of liquid methanol. The mean mole entropy of adsorption indicates that the mobility of methanol in the silicate (Figure 4) is closer to that of methanol in the liquid phase [31, 32]. When comparing the entropy diagrams of methanol, it can be seen (Figure

4) that the methanol state in LiZSM-5, CsZSM-5, and NaZSM-5 zeolites is more localized than in silicate.

The adsorption isotherm of methanol on zeolite CsZSM-5 is brought to 6.62 N/M at relative pressures  $P/P_s = 0.644$  (or to  $P=96.6$  torr). If the density of methanol in zeolite is assumed to be the same as that of normal liquid at a temperature of experiment and the volume occupied by methanol molecule at saturation is calculated, then it turns out that methanol occupies  $\sim 0.147$  cm<sup>3</sup>/g sorption volume of zeolite CsZSM-5, which is  $\Delta 85\%$ . The adsorption isotherm of methanol on NaZSM-5 zeolite and silicate is brought to 8.6 N/M at relative pressures  $P/P_s=0.9$  (or to  $P=135$  torr) and 5.85 N/M at relative pressures  $P/P_s=0.87$  (or to  $P=131$  torr), then eats it is 93% and 20% of sorption volume [30-32].

The Isotherm of methanol adsorption on zeolite CsZSM-5 in semi-logarithmic coordinates is presented in Figure 3, and it is S-shaped. In the area of methanol adsorption on cations, it is concave, then rises steeply upwards along the axis of adsorption, and in the final stage, curving rises towards the axis of ordinates. Adsorption of methanol on CsZSM-5 is inferior to zeolites LiZSM-5 and NaZSM-5 both in strength and in several adsorbed molecules but considerably exceeds silicate.

The adsorption isotherm of methanol on CsZSM-5 is completely described by the three-term VMOT equation [29]:

$$a = 1.928 \exp[-(A/20.0)^2] + 1.031 \exp[-(A/8.4)^3] + 0.48 \exp[-(A/5.63)^2] \quad (2)$$

Fig.3 shows that the calculated data agree with the experimental data.

When comparing the curves of isotherms (figure 3), it can be seen that in the case of adsorption of methanol on silica [31-32], even at small fillings, the equilibrium pressure rises steeply and the isotherm is located lower than the isotherms of methanol adsorption on zeolites LiZSM-5, CsZSM-5 and NaZSM-5 [30].

The process of formation of the  $1\text{CH}_3\text{OH}/\text{Cs}^+$  complex is slow. The equilibrium is established in more than 4 hours (Figure 2). The formation of complexes greater than 1N/M proceeds much faster (1 hour on average). In general, the time of adsorption equilibrium establishment depending on methanol adsorption value on CsZSM-5 zeolite is faster than on LiZSM-5 zeolite.

## 4 Conclusions

Calorimetric studies of methanol adsorption on LiZSM-5 and CsZSM-5 zeolites have been carried out. Complete thermodynamic characteristics of methanol adsorption on these zeolites have been obtained. The correlation between the adsorption-energetic characteristics has been found, and the molecular mechanism of methanol adsorption on LiZSM-5 and CsZSM-5 zeolites in the whole filling region has been revealed. Methanol adsorbed in LiZSM-5 and CsZSM-5 zeolites is arranged in the first coordination sphere with  $\text{Li}^+$  and  $\text{Cs}^+$  cations, forming tetra- and trimeric complexes. The adsorption isotherms are described by the equations of the volumetric micropore filling theory (VMOT). The heat of adsorption correlates with the number of lithium and cesium 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 found that the charge density significantly affects the adsorption mechanism, adsorption energy, and the amount of adsorbed molecules. It was determined that the average molar entropy of ammonia adsorption on LiZSM-5 and CsZSM-5 zeolites indicates that the mobility of methanol molecules in the zeolite is below the liquid phase and close to the mobility of the solid phase, indicating a strong inhibition of mobility of methanol adsorbed on cations.

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