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

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Abstract. This paper presents isotherms and basic (∆H, ∆F, ∆S) thermodynamic characteristics of methanol adsorption in LiZSM-5 and CsZSM-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 (VMO). The correlation between the adsorption-energy characteristics is found, and the molecular mechanism of methanol adsorption in LiZSM-5 and CsZSM-5 zeolites throughout the filling region is revealed. Methanol adsorbed in LiZSM-5 and CsZSM-5 zeolites is located in the first coordination sphere with cations Li+ and Cs+, 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.
A more direct and accurate method for determining the strength of acidity and its interaction consists of reversible two-step adsorption on approximately energetically equal and non-interacting adsorption centers. The standard entropy changes are also calculated by statistical mechanics.

Recently, anticipated new applications of zeolites described in the literature have appeared in journals of heterogeneous systems. Hundreds of publications devoted to various aspects of adsorption on these substances (particularly harmful and environmentally hazardous) from gases and solutions. In addition, zeolites are increasingly being used in ecology, agriculture (especially cardboard), and construction [10].

The study of adsorption phenomena on a molecular structural level. Chemical, crystallochemical characteristics of adsorption processes occurring on adsorbents and investigation. The adsorption isotherms are available, which have been obtained by various physicochemical methods, differential heat of adsorption together with other differential adsorption enthalpy, free energy, and entropy most fully characterize the physical, chemical, and geometrical nature of the adsorbent surface. Differential heat of adsorption is obtained by a complex study of the same system by different calorimetric methods applied in this work reveals the accuracy of the adsorption processes, mainly in the liquid phase. Conversion of methanol into hydrocarbons in acid catalysis is most effective in catalytic medium zeolite catalysts [24]. Zeolites derived from natural raw materials and synthetically produced are used as a filler in the production of high-value chemicals [11].

B. Bonelli et al. used adsorption microcalorimetry and vibrational spectroscopy to study the interaction of zeolites with water molecules and Na cations. The standard entropy changes are also measured by CO adsorption and softening), adsorption and separation of vapors and gases for microprocessors in the petrochemical and refining industry. Particularly in the refining industry, they have proved to be salable chemicals [11]. Zeolites are increasingly being used in ecology, agriculture, and construction [10].

Differential heat of adsorption together with other differential adsorption isotherms provide interesting data on the adsorption of substances on zeolites. Several works on structure-property relationships and the classification of zeolites type catalysts are highly effective catalysts for various processes in the petrochemical and refining industry that is now considered an important and feasible non-petrochemical way of producing valuable chemicals [11].

From the point of view of adsorption, cracking, deparaffination, distillation, thermal, and chemical purification of petrochemical and refining industry, zeolites are increasingly being used in ecology, agriculture, and construction [10]. Worldwide zeolites are used as a filler in the production of high-value chemicals [11]. Zeolites derived from natural raw materials and synthetically produced are used as a filler in the production of high-value chemicals [11].

Articles in the literature describe the wide application of zeolites in gas and petrochemistry, ion exchange (water treatment, soil improvement, purification gases, and purification of waste water) and softening), adsorption and separation of vapors and gases for microprocessors in the petrochemical and refining industry.
2 Testing methods

The testing methods used in this work are based on the adsorption of methanol on LiZSM-5 zeolite. The adsorption equilibrium is reached at a temperature of 303 K and a pressure of 723 K for 10 hours. The adsorption capacity is measured using a universal high-precision calorimeter consisting of a universal high-vacuum differential microcalorimeter and a Tian Calvet calorimeter. The calorimeter makes it possible to obtain the differential heat curve of adsorption forms a high degree of accuracy and stability.

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Fig. 1. Differential heat of methanol adsorption on zeolites: △-LiZSM-5, □-CsZSM-5, ○-NaZSM-5, ▶-silicalite. The horizontal dashed line is heat of condensation. This result also confirms our established phenomenon of 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/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 $\sim 0.18$ cm$^3$/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]:

$$a=1.1\exp[-A/30,17^2]+1.586\exp[-A/13,36^2]+1.122\exp[-A/7,16^2]$$

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 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 adsorption.
Fig. 2. Adsorption equilibrium time as function of methanol adsorption value on zeolites: △ - LiZSM-5, □ - CsZSM-5, ○ - NaZSM-5, → - 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 Li\(^{+}\) cation, so initially \(\Delta S\) decreases from \(-6 \text{ J/K mole}\) to \(-30 \text{ J/K mole}\) at 6 N/M adsorption and rises again to \(-2.5 \text{ J/K mole}\) at 7.6 N/M adsorption.

Fig. 3. Adsorption isotherms of methanol on zeolites: △ - LiZSM-5, □ - CsZSM-5, ○ - NaZSM-5, → - silicalite. △, □, ○, → - experimental points, ▲, ■ - points calculated with VMOT.
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 Li\(^+\) cations and Na\(^+\) cations. In the case of the Cs\(^+\) cation, only 3 methanol molecules interact with the Cs\(^+\) cation. This difference can be easily explained if we consider the size of the 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 (Figure 1) is the same value (~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\(\cdot\)mol and rises to the entropy of liquid methanol. This entire section of the entropy curve corresponds to methanol adsorption without appreciable participation of Cs\(^+\) cations, then eats in channels and intersections not containing 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\(\cdot\)mol to \(-9\) J/K\(\cdot\)mol at 4 N/M adsorption. Further \(\Delta S_a\) passes through a minimum of \(-25\) J/K\(\cdot\)mol and rises to the entropy of liquid methanol. The mean molecular 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 E3S Web of Conferences 401, 02023 (2023) CONMECHYDRO - 2023 https://doi.org/10.1051/e3sconf/202340102023)
solid phase, indicating a strong inhibition of mobility of methanol adsorbed on methanol ammonia adsorption on LiZSM structures. It was shown that the adsorption properties of ZSM zeolites depend on the adsorption mechanism, adsorption energy, and the structure of fragments of ZSM5 zeolite structure. It was found that the amount of adsorbed molecules. It was determined that the adsorption isotherm of methanol on CsZSM5 and CsZSM5 zeolites in the whole filling region has been revealed. Methanol adsorption of methanol on silica [31 even at small fillings of 5% and 5% greater than 1N/M. When comparing the adsorption isotherm of methanol on CsZSM5 and CsZSM5 zeolites, it was found that the equilibrium is brought at about 0.147 P/Ps (or to P=96.6 torr) and 0.87 P/Ps (or to P=135 torr) on CsZSM5 zeolite. The formation of complexes proceeds much faster (1 hour on average). In general, the equilibrium is established in more than 4 hours (Figure 2). The formation of complexes rises steeply and the isotherm curving towards the axis of the charge density a=1.928 exp[-(A/2.0)^2]+1.031 exp[-(A/8.4)^2]+0.48 exp[-(A/5.63)^2] 4 Conclusions

4 Conclusions
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