Basic energy characteristics and isotherm of methanol adsorption on Cu$^{2+}$ZSM-5 zeolite

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Abstract. This paper presents isotherm results and basic ($\Delta H$, $\Delta F$, and $\Delta S$) thermodynamic characteristics of methanol adsorption in Cu$^{2+}$ZSM-5 zeolite. The trinomial equation of adsorption isotherm by the bulk micropore filling theory (VMOT) is also described. A correlation between adsorption-energy characteristics was found and molecular mechanisms of methanol adsorption in Cu$^{2+}$ZSM-5 zeolite were revealed in the whole filling region. It was determined that Cu$^{2+}$ cations are located in shielded positions of the crystal lattice of zeolite ZSM-5. Adsorption of methanol molecule leads to the migration of Cu$^{2+}$ cations from the zeolite lattice to the crossings formed by the intersection of straight and zigzag channels and to the formation of ion/molecular complexes of different multiplicity in them. It was found that small polar methanol molecules form high-energy hepta complexes with Cu$^{2+}$ cation and are located in the first coordination sphere in Cu$^{2+}$ZSM-5 zeolite. It was determined that the average molar entropy ($\Delta S$) of methanol adsorption indicates that in the zeolite the mobility of methanol molecules is lower than the liquid phase and close to the mobility of the solid phase.

1 Introduction

The study of adsorption properties of adsorbents provides useful information on structural characteristics and possibilities of practical applications. In the world, adsorbents derived from natural raw materials and synthetically derived adsorbents are widely used in various fields of industry, construction, agriculture and other areas [1-9]. Adsorbents of selective action and wide range of application are nano-porous molecular sieves - zeolites. The most common area of their application is the oil and gas industry. ZSM-5 type catalysts are highly effective catalysts for various processes in petrochemical and oil refining industry. Part of the reason for the wide popularity was the unique ability of these zeolites to catalyse the process of obtaining high-octane gasoline with high octane number [OH>95] from non-petroleum feedstock, such as from methanol, as well as directly convert methanol or ethanol.
into a mixture of hydrocarbons [1, 10]. Therefore, all side study of physicochemical and especially energetic characteristics of zeolites of ZSM-5 type is of great theoretical and practical importance.
towards hydrocarbon molecules as well as polar molecules and obtaining the main thermodynamic characteristics of these systems. In addition, the adsorption calorimetric method applied in this work allows to reveal the mechanism of adsorption processes occurring on adsorbents and catalysts. Adsorption measurements can be used to obtain data on various factors (e.g. channel sizes, pore volume, cation localisation, etc.) related to the structure of a particular zeolite. Of particular interest is the study of adsorption of various substances in zeolites of the ZSM-5 type. Adsorption on these zeolites strongly depends on the cations present in the structure. Because of the large space between adsorption centres, the zeolite is ideal for model studies of adsorption behaviour.

In this paper, the isotherms, differential heats, entropy and kinetics of methanol adsorption in CuZSM-5 zeolite at 303 K have been studied. Unit cell composition of Cu\(^{2+}\)ZSM-5\(^{-}\)Cu\(^{1.7}\)\([\text{SiO}_2\text{]}^{96.13}\text{[AlO}_2\]^{3.87}\]

2 Testing methods

2.1 Adsorption measurements

The adsorption calorimetric method used in this work makes it possible to obtain highly accurate molar thermodynamic characteristics and to reveal 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 volumetric-liquid methods. Methanol was dosed from a pre-calibrated microcapillary with a cross-section of 0.095 mm\(^2\), the liquid level in which was measured using a cathetometer B-630 with an accuracy of 0.01 mm. To prevent vapour condensation on the walls of the capillary, its temperature was maintained by an electric heater slightly higher than the temperature of the liquid in the capillary. To measure equilibrium pressures, we used a BARATRON B 627 membrane manometer. A modified DAC-1-1A thermally conductive microcalorimeter with high accuracy and stability was used as a calorimeter. Despite its external insulating shells, it is non-adiabatic because the heat released in it is introduced from the calorimeter chamber as it is released and dissipated in a large metal block. Although the temperature of the calorimetric chamber changes only slightly, the apparatus cannot be called strictly isothermal; it exhibits small changes in temperature, which are inevitable and form the basis of measurement. Most of the heat (about 99%) released in the calorimeter chamber is dissipated in its block immediately after release. Only about 1% of the released heat remains in the calorimeter chamber, increasing its temperature very slightly. The measurement is mainly concerned with the heat flux that passes through the surface of the calorimeter chamber and the calorimeter block.

3 Results and discussion

To characterise the adsorption properties of zeolite, the differential heats and isotherms of methanol adsorption were measured and the entropy and free energy of methanol adsorption were calculated. 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 complexation in the cation/molecule system. Pentasil zeolites Cu\(^{2+}\)ZSM-5 and NaZSM-5 possess absolutely identical alumina-silica frameworks and differ almost twofold in the amounts of exchangeable Cu\(^{2+}\) and Na cations (0.3 and 0.5 mmol/g). One might have expected, since the charge of copper cations is twice...
that of sodium cations, that their adsorption properties towards the same substance (CH\textsubscript{3}OH) should also be essentially the same. Indeed, in fact, when investigating the differential heats of adsorption of methanol vapour at 303 K on these zeolites, signs of both similarity and substantial similarity of their adsorption properties were found \[26-29\].

Differentia\_l heats of adsorption of methanol vapour on zeolite Cu\textsuperscript{2+}ZSM-5 are presented in Fig. 1. The curve of differential heats of adsorption of methanol on zeolite Cu\textsuperscript{2+}ZSM-5 can be divided into 2 sections corresponding to the region of high heats of adsorption. These are adsorption of an average of 7 alcohol molecules per cation, when the heat varies from 115 kJ/mol to 52 kJ/mol; and a region of relatively low (48 kJ/mol) adsorption of another 6 alcohol molecules. The initial heat of adsorption (excluding adsorption on the impurity centre) is 115 kJ/mol. At higher fillings they pass the maximum and at adsorption of 0.3 mmol/g they fall again to the level of 110 kJ/mol, i.e. the curve of differential heats of adsorption forms a high-energy step at the level of 110 kJ/mol. The high-energy adsorption of methanol with Cu\textsuperscript{2+} cation proceeds in a 1:1 ratio. This result also confirms our established phenomenon of diffusion of Cu\textsuperscript{2+} cation from the side channels of the zeolite, as in the case of Li\textsuperscript{+} cation \[24-25\]. At a ratio of 1:1 all cations are located in the interstices, where the formation of S-dimensional complexes methanol/ Cu\textsuperscript{2+}.

Then with increasing adsorption there is a consecutive formation of complexes of Cu\textsuperscript{2+} cation with two, three, four, five, six and seven alcohol molecules with decreasing heat from 110 kJ/mol to 52 kJ/mol. The minimum on the curve corresponds exactly to the hepta complex Cu\textsuperscript{2+} with seven methanol molecules. This complex due to its size can fit only in the interstices of the straight and zigzag channels of the zeolite. Adsorption of the next six molecules of methanol goes with a wave-like change of heat, then again decreases to the heat of condensation and goes already in the “silicate” part of the zeolite, i.e. in the part where there are no Cu\textsuperscript{2+} cations. The total adsorption of methanol on zeolite Cu\textsuperscript{2+}ZSM-5 is 13 molecules (\~4 mmol/g) of methanol per cation.

In general, the heat of adsorption of methanol (Fig.1) on zeolite Cu\textsuperscript{2+}ZSM-5 is significantly higher than on NaZSM-5, LiZSM-5, CsZSM-5 and silicalite \[26-29\]. The increased heat of adsorption of methanol on zeolite Cu\textsuperscript{2+}ZSM-5 is characterised by high surface charge density of divalent copper cations.

**Fig.1.** Differential heats of methanol adsorption on Cu\textsuperscript{2+}ZSM-5 zeolite. The horizontal dashed line is the heat of condensation.
the zeolite to be the same as that of a normal liquid at the temperature of the experiment and calculate the volume occupied by a methanol molecule at saturation, it turns out that methanol occupies $\sim 0.17 \text{ cm}^3/\text{g}$ of the sorption volume of the Cu$^{2+}$ZSM-5 zeolite, which is $\sim 91\%$.

The isotherm in semi-logarithmic coordinates is shown in Figure 2 and it confirms the energetic data. The equilibrium pressures at low fillings reach $P/P_0 = 1.67 \times 10^{-6}$, indicating strong sorption of methanol on zeolite Cu$^{2+}$ZSM-5, but in general it is located below the curve $s$ of isotherms on zeolite NaZSM-5 and above the curves on silicalite [26-28].

Fig. 2. Adsorption isotherm of methanol on Cu$^{2+}$ZSM-5 zeolite. $\bullet$ points calculated using VMOT.

The adsorption isotherm of methanol is fully described by the trinomial VMOT equation [29-31]:

\[
a = 2.322 \exp\left(-\frac{A}{11.86}\right) + 0.538 \exp\left(-\frac{A}{19.43}\right) + 1.313 \exp\left(-\frac{A}{8.15}\right)
\]

Fig. 2 shows that the calculated data are in good agreement with the experimental data.

Fig. 3. Entropy of methanol adsorption on zeolites Cu$^{2+}$ZSM-5.

The molar differential entropy ($\Delta S_d$) of methanol adsorption on zeolite Cu$^{2+}$ZSM-5 is

$\Delta S_{int.} = -65 \text{ J/mol-K}$

$\Delta S_{d} = -120 \text{ J/mol-K}$
delayed from the entropy of liquid methanol, and is all below zero (Fig. 3). It confirms the strong 1:1 interaction of methanol with Cu\(^{2+}\) cation.

\[ \Delta S_d \text{initially decreases from } -210 \text{ J/K} \cdot \text{mol} \text{ to } -260 \text{ J/K} \cdot \text{mol} \text{ forming CH}_3\text{OH/Cu}^{2+} \text{ monocomplex at 0.3 N/M adsorption. Further } S_d \text{ gradually increases to } -20 \text{ J/mol at adsorption of 2.1 mmol/g.} \]

Further adsorption takes place in the "silicate" part of the zeolite. Methanol molecules interact much more strongly in the "silicate" part than on Na cation and silicate. The average molar (\(-65\) kJ/mol) entropy of adsorption indicates that the mobility of alcohol in zeolite Cu\(^{2+}\) ZSM-5 is lower than the mobility of methanol in the liquid phase and close to its mobility in the solid phase.

4 Conclusions

Full thermodynamic characteristics of methanol adsorption on zeolite Cu\(^{2+}\) ZSM-5 have been obtained. The step character of heat and entropy of methanol adsorption was revealed. The correlation between adsorption energy characteristics was found and the molecular mechanism of methanol adsorption in zeolite Cu\(^{2+}\) ZSM-5 in the whole filling region was revealed. It was found that Cu\(^{2+}\) cations are located in shielded positions of the crystal lattice of zeolite ZSM-5. Methanol adsorption leads to the migration of Cu\(^{2+}\) cations from the zeolite lattice into the intersections formed by the intersection of straight and zigzag channels and the formation of ion/molecular complexes of different multiplicity in them. Polar methanol molecules form high-energy heptocomplexes with Cu\(^{2+}\) cation and are located in the first coordination sphere in Cu\(^{2+}\) ZSM-5 zeolite. The average molar entropy of methanol adsorption indicates that in the zeolite the mobility of methanol molecules is lower than the liquid phase and close to the mobility of the solid phase.

References

30. М. М. Дубинин, Г. У. Рахматкарьев, и А. А. Исирикян, Попытки описать микропористые структуры на основе теории равновесной адсорбции в микропорах (Сборник трудов поисследований процессов адсорбции и адсорбентов, под редакцией М. М. Дубинина, Ташкент, 1979)