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Methilmercaptane Adsorption by Molecular Sieve NaX in Wide Range of Equilibrium Pressures and Temperatures

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ABSTRACT: The isotherms of CH_3SH adsorption in NaX zeolite at 273, 298, 333 and 373 K. have been measured. Isosteric heats and entropies of CH_3SH adsorption in NaX were calculated. The mechanism of CH_3SH adsorption in NaX zeolite was established. The isotherms of adsorption were quantitatively reproduced by one- and two-term VMOT equations from zero filling to saturation.

KEYWORDS: NaX molecular sieve, water, ion-molecular complexes, isotherms, differential heats and entropies of adsorption**.**

I. INTRODUCTION

Nowadays hydrogen sulfide, organic sulfur compounds and methyl mercaptan, may be present in natural gas, gas condensate and petroleum products. To purify organosulfur compounds, it is advisable to use zeolites.

It is advisable to use NaX zeolites for purifying natural gas from trace amounts of methyl mercaptan. The use of zeolites containing the same amount of Ca^{2+} and Na^{+} cations is impractical due to its ability to catalyze the decomposition of methyl mercaptan into methane and elemental sulfur, clogging the pores of the adsorbent and disabling it. The widespread use of molecular sieves to clean oil products from various impurities is due to their unusual properties: the ability of zeolites to reversibly adsorb methyl mercaptan or various substances in a gaseous state, zeolite cations can be easily exchanged for any other positive ion.

By the way, we set a goal to measure the adsorption isotherms of (a) methyl mercaptan in the NaX zeolite in the temperature range from 273 to 373 and based on the isotherms measured at different temperatures, calculate the isosteric heats (Q_d) and entropy (ΔS_d) of adsorption and identify the mechanism adsorption. The information obtained can be used to select an effective adsorbent for the purification of natural gas and oil products from sulfur-containing compounds.

II, METHODS OF RESEARCH

The chemical composition of fully dehydrated $(Na_{86}(AlO_2)_{86}(SiO_2)_{106}$ was determined by elemental analysis. To this end, a method was developed for the decomposition of samples of synthetic zeolites with simultaneous determination of moisture and organic impurities and atomic absorption determination (Perkin - Elmer 3030B) of exchange Na cations [1]. This approach excludes the influence of structure-forming elements (Al, Si) and fluctuations in sample moisture on the analysis results.

The studies were carried out on a universal high-vacuum volumetric installation, which allows dosage of the adsorbate by both gas-volumetric and volumetric-liquid methods, with an accuracy of 0.1% [2, 3]. The adsorption unit is a vacuum glass apparatus with a capillary micro burette and mercury gates. The installation consists of an ampoule with an adsorbent, a measuring part, a storage system, a liquid and gas preparation, and a pumping system (zeolite and fore vacuum pumps). Using a B-630 catheter with an accuracy of 0.01 mm, the level of mercury was measured in a U-shaped manometer with an inner diameter of 12 mm. Low pressures were determined by a McLeod pressure gauge.

Before the inlet of methyl mercaptan, the sample was heated and subjected to high vacuum pumping at 350º C for 10 hours.

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III. RESULTS AND ITS DISCUSSION

Zeolite-type zeolites have a cubic face-centered diamond-type lattice [2]. In large cavities of the zeolite NaX (faujasite), cations are located in the SIII 'positions (at the 12-membered oxygen rings) and SII (in the center of the six-membered oxygen rings), and in the small cavities at the SI' position. Cations in these positions are slightly extended from six-membered rings towards the center of small cavities [4]. The cations in the SI position are located in the centers of the hexagonal prisms.

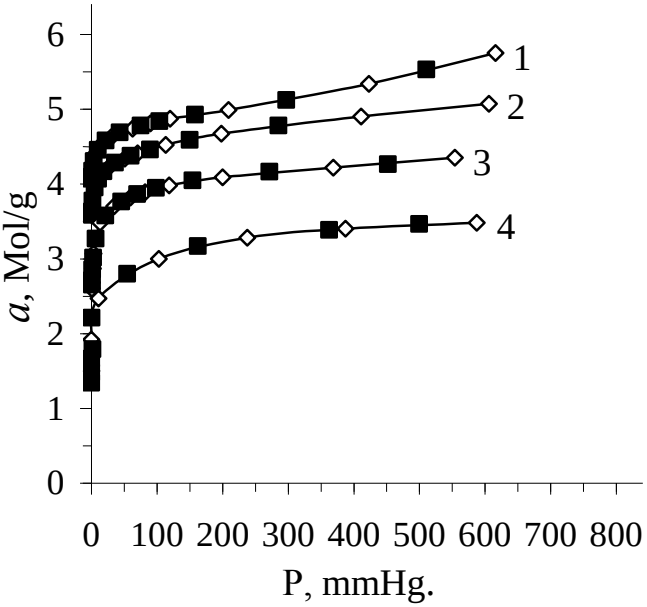

Fig. 1. Dependence of adsorption (a) of CH_3SH in NaX zeolite on pressure (P): 1 - 273 K; 2 - 298 K; 3 - 333 K; 4 - 373 K. Black dots are calculated using the TOZM equation.

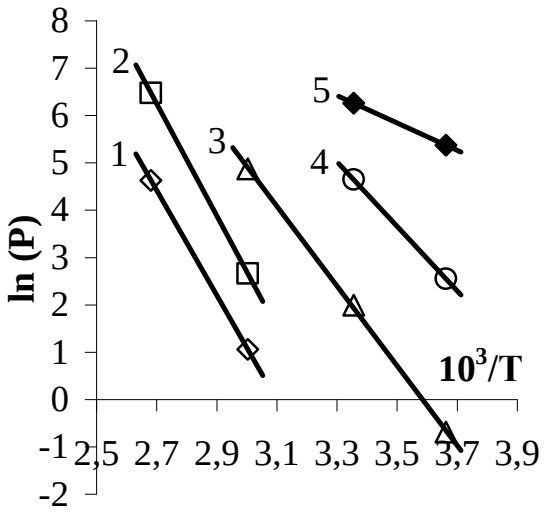

Fig. 2. Dependence of the logarithm of pressure (ln P) CH_3SH in NaX zeolite on the inverse temperature (10^3/T), corresponding to various amounts of adsorbed substance (mmol / g): 1 - 3.0; 2 - 3.5; 3 to 4.0; 4-4.5; 5 - 5.0.

Figure 1 shows the adsorption isotherms of CH_3SH in NaX at various temperatures (273, 298, 333, and 373 K). The adsorption capacity of NaX for CH_3SH is higher than in type A zeolite. The CH_3SH adsorption isotherms in zeolites are satisfactorily described by the one- and two-membered TOZM equations [5, 6]. Below are the equations of adsorption isotherms measured at temperatures of 273, 298, 333 and 373 K:

273 К $a = 4{,}699\exp[-(A/40{,}09)^2] + 0{,}676\exp[-(A/3{,}62)^2]$;
278 К $a = 4{,}605\exp[-(A/35{,}91)^2] + 0{,}457\exp[-(A/5{,}27)^2]$;
333 К $a = 4{,}338\exp[-(A/33{,}3)^2] + 0{,}2\exp[-(A/6{,}66)^4]$;
373 К $a = 3{,}65\exp[-(A/25{,}0)^3]$.

On the basis of adsorption isotherms, isotheres were calculated — lines of temperature dependence of equilibrium pressures at constant adsorption values. The isotheres in the lgP - T^{-1} coordinates are linear, their inclination to the temperature axis changes with increasing filling of the adsorbent surface (Fig. 2). The isosteric heats of adsorption were calculated from the slope of the isotheres (Fig. 3). The molar entropy of adsorption was calculated from the data of heats and the dependence of the maximum adsorption work on the amount of adsorbed methyl mercaptan (Fig. 4).

The unit cell of zeolite NaX contains 86 Na^+ cations. In terms of 1/8 ea. - 10.7 Na^+. Cations are distributed as follows: 4 in SII and SI 'in the large and small cavities, the remaining 2.7 in the large cavity in position SIII '[4].

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The curve of isosteric heats of adsorption of CH_3SH in NaX has a wavy appearance. The first wave extends to 4 mmol / g with an energy varying from 91.58 to 98.52 kJ / mol and falling to 69.39 kJ / mol. The second decreases from 69.39 to 24.1 kJ / mol in the range from 4 to 5 mmol / g. 4 mmol / g correspond to 6.7 CH_3SH ea.

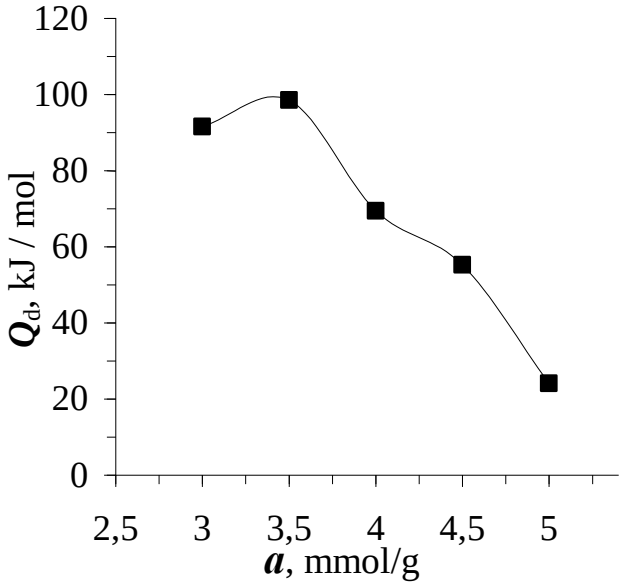

Fig. 3. Dependence of differential isosteric heats (Q_d) of adsorption of CH_3SH in NaX zeolite on adsorption (a).

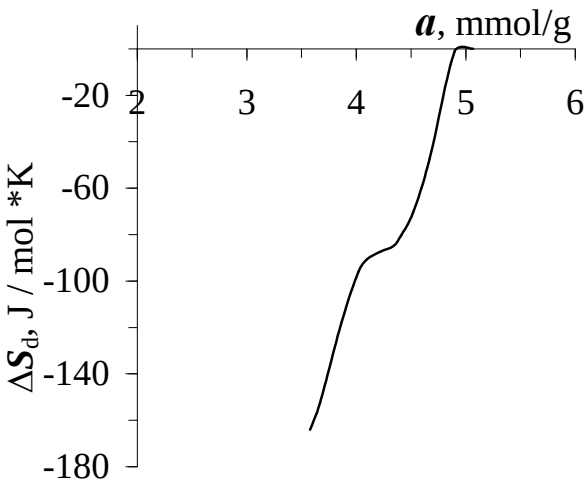

Fig. 4: Differential entropy (ΔS_d) adsorption CH_3SH in zeolite NaX from adsorption (a). The entropy of liquid CH_3SH is taken to be zero.

This is as much as the cations in the SIII 'and SII positions (2.7 + 4 = 6.7) located in the super cavity. It follows that at the first stage methyl mercaptan is adsorbed on cations in the SIII 'and SII positions in a 1: 1 ratio. At the second stage (from 4 to 5 mmol / g), 1 mmol / g of methyl mercaptan or 1.68 CH_3SH / e. Further adsorption, apparently, proceeds on SIII 'cations, as on the most accessible cations in an open position. Due to the limited zeolite volume, not all SIII 'cations (2.7) form a binary complex with methyl mercaptan, but only a part of them (1.7). Thus, NaX zeolite contains 8.4 methyl mercaptan molecules per 1/8 ea, of which 4.4 are adsorbed on SIII 'cations, with 1.7 cations forming binary complexes, and 1 monomeric complexes. The remaining 4 molecules of methyl mercaptan are adsorbed on SII cations.

The molar differential entropy of CH_3SH adsorption in NaX (Fig. 4) was calculated from the data of heats and free adsorption energy. Adsorption entropy is delayed from the entropy of liquid methyl mercaptan. In general, entropy is located in the negative region, reaching low values of -160 J / mol * K, which indicates that the state of methyl mercaptan in the zeolite matrix is strongly inhibited. Entropy is growing rapidly with filling, but does not cross the zero line - the entropy of liquid methyl mercaptan.

Adsorption and thermodynamic studies of the adsorption of methyl mercaptan vapors in NaX zeolite at temperatures of 273, 298, 333 and 373 K were carried out.

Mole differential values of enthalpy, free energy and adsorption entropy were calculated, which served as the basis for the molecular-structural and thermodynamic correlations of the adsorption properties of NaX.

It has been established that the adsorption centers in the NaX zeolite are Na^+ cations at positions SIII 'and SII, with which methyl mercaptan molecules form 6.7 monomeric CH_3SH/Na^+ complexes per super cavity. The remaining unfilled zeolite volume is filled with another 1.7 methyl mercaptan molecules, which, apparently, attach to sodium cations at position SIII 'to form binary complexes $(CH_3SH)_2/Na^+$ located at the 12-membered oxygen rings of each super cavity.

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IV. CONCLUSION

Thereby, each super cavity contains 8.4 complexes of methyl mercaptan with the Na^+ cation. The mobility of methyl mercaptan molecules in the zeolite matrix is greatly inhibited.

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