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ADSORPTION PROPERTIES AND THERMAL EQUILIBRIUM METHYL MERCAPTAN ON LiX ZEOLITE

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Abstract: The article deals with the processes of methylmercaptan adsorption on zeolite LiX, as well as the results of differential heat of adsorption, isotherm, entropy and thermal equilibrium time, based on those obtained in high-vacuum adsorption device. With the help of exact formulae, the number of methylmercaptan molecules adsorbed into zeolite LiX, under vacuum conditions is proved. The causes of global environmental problems, their consequences and approaches to solve these problems are also discussed.

Keywords: zeolite LiX, methylmercaptan, microcalorimeter, differential heat, adsorption isotherm.

Annotatsiya: Maqolada metilmerkaptanning LiX zeolitida adsorbsiyasi jarayonlari, shuningdek, yuqori vakuumli adsorbsion qurilmada olinganlar asosida adsorbsiyaning differensial issiqligi, izoterm, entropiya va issiqlik muvozanat vaqti natijalari ko‘rib chiqiladi. Aniq formulalar yordamida vakuum sharoitida LiX zeolitiga adsorbsiyalangan metilmerkaptan molekulalari soni isbotlangan. Global ekologik muammolarning kelib chiqish sabablari, ularning oqibatlari va ushbu muammolarni hal qilish yo'llari ham ko'rib chiqiladi [1].

Kalit so‘zlar: zeolit LiX, metilmerkaptan, mikrokalorimetr, differensial issiqlik, adsorbsiya izotermasi.

Аннотация: В статье рассмотрены процессы адсорбции метилмеркаптана на цеолите LiX, а также результаты расчета дифференциальной теплоты адсорбции, изотермы, энтропии и времени теплового равновесия, полученные в высоковакуумной адсорбционной установке. С помощью точных формул доказано количество молекул метилмеркаптана, адсорбированных на цеолите LiX в условиях вакуума. Также рассмотрены причины глобальных экологических проблем, их последствия и пути решения этих проблем [1].

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Ключевые слова: цеолит LiX, метилмеркаптан, микрокалориметр, дифференциальная теплота, изотерма адсорбции.

Introduction

Methyl mercaptan (CH_3SH), a volatile sulfur-containing compound, is widely encountered in various industrial processes, including natural gas refining, petrochemical manufacturing, and pulp production. Due to its toxicity, strong odor, and corrosive nature, the efficient removal of methyl mercaptan from gas streams is critical for both environmental protection and industrial safety. Among the various technologies employed for this purpose, adsorption using porous solid materials offers a cost-effective and energy-efficient solution.

Zeolites, particularly LiX-type zeolites (a lithium-exchanged form of faujasite-type X zeolite), have garnered attention due to their high thermal stability, well-defined pore structure, and strong interaction with polar and weakly polar molecules such as CH_3SH. The presence of Li^+ cations enhances the electrostatic interactions between the adsorbent and the adsorbate, thus improving adsorption capacity and selectivity. Understanding the adsorption behavior and thermal equilibrium characteristics of methyl mercaptan on LiX zeolite is essential for optimizing its application in gas purification systems.

This study aims to investigate the adsorption properties of methyl mercaptan on LiX zeolite under controlled conditions and to evaluate the thermal equilibrium behavior associated with the adsorption process. Special attention is given to the influence of temperature, pressure, and surface properties on the adsorption capacity and energetics. The findings contribute to the development of more efficient adsorbent materials for sulfur compound removal and provide fundamental insights into the interaction mechanisms between zeolites and organosulfur compounds.

LITERATURE ANALYSIS. Efficiency of mercaptans removal from gas depends on their properties: methylmercaptan (CH_3SH) is extracted from gas by 35-45 %, ethylmercaptan (C_2H_5SH) - 10-15 %, propylmercaptan (C_3H_7SH) - 0,1 %.

Industrial use of ferromanganese nodules as adsorbent for purification of gases from hydrogen sulfide and mercaptans is more expedient to apply for small volumes of gas (up to 2000 m^3/day) with low (up to 0,5 % wt.) concentration of hydrogen sulfide. In this case replacement of adsorbent will have to be made not more often than 1-2 times a year.

Expenses on reagents make 80-100 dollars/t of hydrogen sulfide. Available data show that in the process of gas purification up to 50-80 % of methylmercaptan and 30-60 % of carbon sulfide from initial content can be removed.

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Adsorbate molecules (CH_4S) will be adsorbed in the adsorbent supercavity if the size of the inlet window of type X zeolite is 13 Å and the size of methylmercaptan molecule taken as adsorbate is about 4.7 Å [1].

METHODS AND MATERIALS. In zeolite LiX, the ln index of the adsorption isotherm of methylmercaptan molecules at initial saturation is equal to 9.71, which indicates their penetration into the depth of the zeolite matrix in this process. The growth of the adsorption isotherm graph goes with a slight change to ln=-9, this is explained by strong adsorption on the supercavities of the zeolite. The adsorption value up to this value is 0.34 mmol/g. Most of the cations are located in the SII position and the rest in the SI and SIII positions.

Due to the small size of the entrance window in the SI and SIII cavities, methylmercaptan molecules cannot penetrate directly. Therefore, migration of cations from the small space to the large space is observed. Initially, methylmercaptan forms molecular monocomplexes with cations due to weak bonds. At initial saturations, the isotherm values are small because methylmercaptan molecules bound by weak chemical bonds with lithium cations are firmly located in the zeolite cavities [2].

RESULTS AND DISCUSSION. A slow increase in the isotherm plot is observed until the adsorption value reaches 1.8 mmol/g. This is attributed to the localization of methylmercaptan molecules. It was further observed that the plot of adsorption isotherm increases vertically. The saturated vapor pressure of methylmercaptan is 1515 mmHg. The adsorption isotherm of methylmercaptan on LiX zeolite was studied at a pressure up to 1 atm, i.e. 760 mmHg. In the study, a vertical growth of the isotherm graph in the range from 2 mmol/g to 4.5 mmol/g was observed. And this indicates saturation of methylmercaptan molecules [3]. It is found that 4-4.5 methylmercaptan molecules are in highly excited state.

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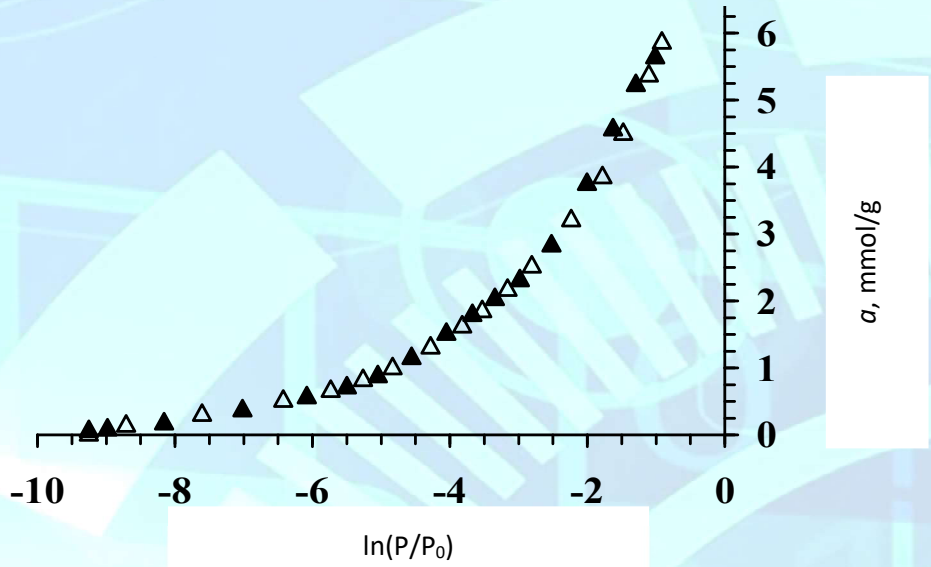


Figure 1. The adsorption isotherm of methylmerkaptan in zeolite LiX at a temperature of 303 K. Δ-experimental value; -the value of the points calculated on the basis of the equations of MVFT

A good correlation between the heats of adsorption and the isotherm is observed. The isotherm (Figure-1) also, like the heats of adsorption, has three segments. When adsorbed on Li^+ cations, it rises sharply at the SIII' position, then slopes to the adsorption axis and rises to 0.34 mmol/g (SI'). After the inflection, the isotherm with a slight slope to the adsorption axis grows linearly to saturation (SII).

The adsorption isotherm of methylmercaptan on LiX zeolite is satisfactorily described by the three-dimensional micropore volume-filling theory (MVFT) equation

a =1.22exp[-(A/15.98)3]+1.33exp[-(A/11.27)5]+3.57exp[-(A/4.05)3],

Where: a-adsorption in micropores in mmol/g, A=RTln (Po/P) is adsorption energy in kJ/mol. In microporous synthetic zeolite LiX, methylmercaptan molecules at adsorption of initial saturations have an isotherm In=-9.25. This indicates the penetration of the zeolite into the supercavities. Hence, the value of adsorption is 0.145 mmHg with atmospheric pressure equal to 0.0002. The adsorption isotherm plot of methylmercaptan molecules goes with a slight increase until the adsorption isotherm reaches In = -4.93, and this is because there is a strong adsorption in the super cavities of the zeolite. The amount of adsorption up to this value is 1.24 mmol/g [3-4].

Most of the Li^+ cations will be in SII spaces and the rest in SI and SIII spaces. Methylmercaptan molecules cannot penetrate directly due to the small size of the entrance window in the SI and SIII cavities.

Therefore, at adsorption values up to 1.24 mmol/g, the isotherm growth is slow. The migration of metal cations and protons from the small space to the large

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space is observed as a result of saturation of Li+ cations with methylmercaptan molecules in the SII space. Initially, methylmercaptan with cations forms molecular monocomplexes (Li(CH3SH)) due to weak bonds.

In the range from 2.8 mmol/g to 5.5 mmol/g, an increase in the isotherm plot in the vertical position was observed. This indicates the saturation of methylmercaptan molecules. In particular, 5-5.8 methylmercaptan molecules were found to be in a highly excited state.

where: a-adsorption in micropores in mmol/g, A=RTln(Po/P) adsorption energy in kJ/mol.

Figure -2 shows a plot of the differential heat change (Qd,kJ/mol) based on the value (a,mol/g) of adsorption of methylmercaptan molecules in zeolite LiX. Condensation of the heat of adsorption of methyl mercaptan (ΔH v) is indicated by dashed lines. At initial saturations, the amount of adsorption of methylmercaptan molecules is 0.02 mmol/g and the differential heat is 55.63 kJ/mol.

The higher heat of adsorption results in the consumption of more time for the distribution of methylmercaptan molecules to metal cations and equilibrium formation due to the large amount of unsorbed cations in the supercavities of zeolite and the low amount of methyl mercaptan molecules. And so this phenomenon can be explained by the high energy content in the sorbate affecting the walls of aluminum and silicon oxides forming the zeolite structure [5].

When adsorption reaches 0.25 mmol/g, the differential heat is 49.38 kJ/mol. For the sorption of 0.5 mmol/g of methylmercaptan molecules, 5.8 kJ/mol of energy is consumed. With this energy consumption, the differential heat decreases from 49.38 kJ/mol to 43.25 kJ/mol. This process runs from 0.77 mmol to 4.37 mmol/g and will be ~2.0 times higher than the value of thermal condensation of adsorbate. The differential heat of adsorption of methylmercaptan molecules after 5 mmol/g drops sharply and equates to the heat of condensation.

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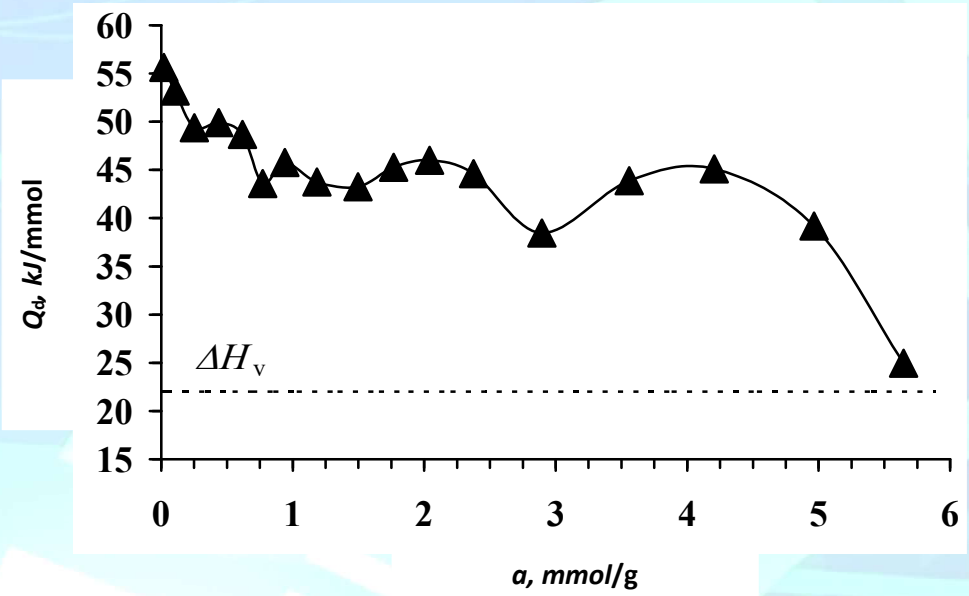


Figure 2. Differential heat of adsorption of methylmerkaptan on zeolite LiX at a temperature of 303 K. The horizontal dashed lines represent thermal condensation of methylmerkaptan molecules at a temperature of 303 K.

A slight decrease in the heat of adsorption is observed when the adsorption reaches 0.77 mmol/g. In this case, the differential heat will be 43.25 kJ/mol. When subsequent molecules of methylmercaptan are adsorbed, a slight increase in differential heat is observed. This is accompanied by temperature jumps due to the fact that methylmercaptan sorbed in the zeolite is sorbed to one cation in the SII cavity and adsorbed in the next adsorption center.

In the next step, that is, the heat of the methylmercaptan molecule after 1.5 mmol/g will be 38.46 kJ/mol, and the amount of adsorption will be 2.90 mmol/g. The arrangement of three CH_4S/Li^+ complexes and one CH_4S/H^+ complex is tetrahedron-shaped, and such clusters fill almost all the free spaces of the supercavities. At the last stage, the heat slightly increases and sharply decreases depending on the heat of condensation of methylmercaptan at 303 K.

The adsorption process of 2.75 mmol/g methylmercaptan molecules proceeds between 2.90 mmol/g and 5.65 mmol/g. This indicates that the process terminates at a pressure of 1 atmosphere. In this process, the cations at positions SI and SIII move into the supercavity. As these positions are located near the supercavity and the heat of adsorption increases slightly due to the migration of cations. The cations are mainly located near the entrance window. Due to this, the differential heat will not be too high [6].

A total of 5.65 mmol/g of methylmercaptan molecule is adsorbed in one supercavity of LiX zeolite.

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Conclusion: The isotherm of methylmercaptan to synthetic zeolite NaX was characterized using the micropore volume theory equation with three states. The adsorbed molecules adsorbed more densely and redistribution of 0.53 mmol/g methylmercaptan molecules occurred. The redistribution of methylmercaptan molecules into NaX zeolite mainly starts after adsorption of 4.97 mmol/g. In the zeolite matrix, the methylmercaptan molecules are sedentary and therefore the average integral differential entropy is -47.11 J/mol*K. At the initial stages of saturation, adsorption of methylmercaptan molecules adsorbed on the zeolite takes a little longer than the thermal equilibrium time, i.e., lasts for 5 hours. As the saturation of methylmercaptan molecules increases, the adsorption thermokinetics decreases to a few tens of minutes.

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