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Isotherm and main thermodynamic characteristics of adsorption of carbonyl sulfide molecules on zeolite KA (MSS-558)

Oybek Ergashev[1], Khayot Bakhronov[2*], Marufjon Asfandiyorov[3], Mirzokhid Kokhkharov[4], Abror Ganiev[5], Nodira Akhmedova[6], Shaxnoza Tulyaganova[7], Kamoliddin Nazirov[8], Nazirahon Esonkulova[9]
[1,4]Namangan State Technical University, Namangan, Uzbekistan; okergashev711@gmail.com (O.E) mirzo199008@mail.ru (M.K)
[2,3,5,6,7,8]Tashkent University of Information Technologies named after Muhammad al-Khwarizmi, Tashkent, Uzbekistan; baxronov@mail.ru (K.B.) masfandiyorov@tuit.uz (M.A) ganiyev58@mail.ru (A.G) nodiraxon2402@gmail.com (N.A) tulyaganovashahnoza87@gmail.com (S.T) nazirov@tuit.uz (K.N)
[9]Kokand state University, Kokand, Uzbekistan; naziraxon.esonqulova@mail.ru (N.E)

Abstract: This paper presents experimental results of isotherm and basic thermodynamic characteristics of COS molecules on zeolite KA. Differential values of adsorption free energy and entropy were calculated, and a correlation was found between adsorption-energetic characteristics and the crystallochemical structure of the adsorbent. A regular correlation was established between the amount of COS adsorbed on zeolite KA and the corresponding differential heat values. In the initial stage, under the influence of COS molecules, K+ cations in the structure of zeolite KA migrate from the internal matrix to the surface, forming ion-molecular complexes with the COS molecules. It was shown that at an adsorption amount of 0.1 mmol/g, the K+ cations completely migrate to the surface of the zeolite. Based on the BET equation, it was shown that the monolayer adsorption capacity of COS molecules on KA zeolite is 0.01 mmol/g. The average value of the molar integral entropy of COS adsorption on KA zeolite was -13 J/mol·K, which indicates that the mobility of COS molecules in the zeolite is lower than in the liquid phase and is close to that in the solid phase, leading to a strong inhibition of adsorption mobility on the COS cations.

Keywords: *Adsorption, Carbonyl sulfide, Enthalpy, Relative pressure, Isotherm, Gibbs energy, Microcalorimeter, Zeolite.*

1. Introduction

There are many types of zeolites in the world, which can mainly be divided into two categories: natural zeolites and synthetic zeolites. After systematic research was carried out on natural zeolites, scientists at research centers began focusing on synthesizing defect-free zeolites artificially [1].

By the mid-20th century, the industrial synthesis of zeolites had been established, and for the first time, the synthesis of small-pore zeolites under high temperature and high pressure marked a new era in zeolite synthesis. In the 1950s, zeolites of types A, X, and Y were synthesized at low temperature and low pressure for commercial use. Zeolite A was the first synthetic zeolite to be widely used for separating oxygen from argon. The development of low-temperature hydrothermal synthesis technology created favorable conditions for large-scale industrial production of zeolites [2-7].

At present, there are more than 100 types of artificially synthesized zeolites, among which the A, X, Y, M, and ZSM types are the most widespread and are used in various sectors of industry [8]. In recent years, synthetic zeolites containing elements other than silicon and aluminum have been developed and are being used in the field of catalysis. Many important industrial catalytic reactions cannot be separated

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* Correspondence: baxronov@mail.ru

from molecular sieve catalysts—for example, catalytic cracking, hydrocracking, isomerization, reforming, disproportionation, and transalkylation reactions. Molecular sieves are also increasingly used in the production of environmentally friendly fine chemicals. They have become one of the most important families of catalysts. The 3A molecular sieve has the smallest pore size and can only adsorb water molecules, having very low adsorption capacity for atmospheric H_2 and O_2 (<0.5%), which makes it suitable for drying air in insulating glass interlayers.

In the global production of environmentally friendly fuel materials from natural gas and oil, the harmful compounds contained in these raw materials negatively affect technological processes and the quality of the final products. In natural gas drying processes and in the production of fuels that meet Euro standards, the removal of nitrogen- and sulfur-containing compounds is essential. This purification is carried out using zeolites of types A, X, Y, ZSM, and others. Therefore, the synthesis of microporous adsorbents with high sorption capacity and the achievement of new scientific and practical results are of great importance.

The most common representatives of the zeolite group include natrolite, chabazite, heulandite, stilbite, mordenite, clinoptilolite, and others. The crystalline structure of both natural and synthetic zeolites is formed by tetrahedral SiO_2 and AlO_2 groups, which are connected by shared vertices into a three-dimensional framework. This framework is penetrated by cavities and channels (windows) ranging from 2 to 15 Å in size. The open framework-cavity structure of zeolites, $[AlSi]O_4^-$, carries a negative charge, which is compensated by counter-ions (such as metal cations, ammonium, alkylammonium, and others introduced via ion-exchange mechanisms), as well as water molecules that are easily removed by dehydration.

Zeolites possess unique properties. They are microporous crystalline substances. Their crystallinity ensures mechanical and chemical stability, as well as uniform and controllable pore, channel, and cavity sizes. These properties enable the use of zeolites as molecular sieves, adsorbents, and detergents. The wide variability in the chemical composition of zeolites allows for the purposeful modification of their physicochemical properties. The size of zeolite cavities does not exceed 2 nm. The physicochemical and chemical properties of substances can change significantly under confinement conditions—when molecules are enclosed in pores comparable in size to the molecules themselves. The structural framework of zeolites, with its specific arrangement of defects and chemically active centers, can serve as a matrix for conducting targeted chemical reactions. Zeolites are increasingly being used as catalysts. Zeolite-based petroleum cracking is one of the most important industrial applications of zeolites. The nanoscale size of the cavities, the potential for orderly arrangement of active centers, and the selective and directional effects on molecular chemical groups make zeolites not only tools of nanotechnology, but also its objects of study [9-11].

For adsorption processes, the synthesis of nanoporous molecular sieve zeolites is not only important due to their high sorption properties, but also for their ability to adsorb molecules of various sizes. To obtain zeolites with these characteristics, it is essential to select suitable raw materials, determine the thermodynamic properties of the synthesized adsorbents, investigate the formation and localization of ion-molecular complexes within the zeolite matrix, study the thermokinetics of adsorption and ion exchange in the zeolite structure, understand the migration patterns of cations, and ultimately identify the complete molecular mechanism of zeolite adsorption.

Globally, there is a growing demand each year to purify natural gases for the production of environmentally friendly gas. This includes drying them from water vapor, removing sulfur-containing compounds, and preventing the release of carbon dioxide—a greenhouse gas—into the atmosphere. Zeolites are widely used to address these issues. The synthesis of highly adsorptive zeolites and the study of their adsorption properties play a crucial role in achieving both scientific and practical advancements.

Aluminosilicate synthetic zeolites play an important role in gas purification and petrochemical processes, particularly in solving the aforementioned issues. One of their unique features is the possibility of substituting the aluminum and silicon atoms in the aluminosilicate zeolite structure with other trivalent or pentavalent elements—such as gallium, germanium, and phosphorus—which are chemically similar. This allows for modification of their sorption and catalytic properties [12]. Furthermore, water molecules present in the internal crystal structure can evaporate at a temperature of 450°C without damaging the crystal lattice. The mobility of alkali and alkaline earth cations, along with water molecules within the zeolite structure, enables ion exchange capabilities [13-15].

Zeolites, with their porous crystal framework structure, are considered aluminosilicate adsorbents. Their frameworks are composed of interconnected tetrahedral [SiO_4] and [AlO_4] units, linked at their corners by oxygen atoms. The specific positioning of aluminum atoms within the structure is a characteristic feature of aluminosilicates. In all aluminosilicates, Al and Si atoms occupy tetrahedral coordination around oxygen atoms, with Al substituting isomorphically for Si in the silicate framework. The negative charge of the tetrahedra is balanced by various alkali or alkaline earth metal cations located within the zeolite cavities. The composition of all synthetic zeolites can be represented by the following general chemical formula:

$$Me_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O,$$

Here, n is the valency of the metal cation, x is the molar ratio of SiO_2/Al_2O_3, and y is the number of moles of water.

One of the most widely used synthetic adsorbents is KA zeolite. Its effective pore diameter is 3 Å, which allows it to selectively adsorb only those molecules in a liquid whose dynamic diameter is less than 3 Å. Molecular sieve 3A is an excellent desiccant primarily used for water adsorption. KA zeolites are used for dehydration, drying, moisture removal, paraffin removal, drying and purification of cracked petroleum gases, dehydration of C_2 and C_3 fractions, drying and purification of ethylene, propylene, butylene, butadiene, pentane, alcohol dehydration, and purification of methane, ethane, and propane feedstocks. They are also used for purifying liquid carbon dioxide, drying dissolved acetylene, and drying and purifying water, air, gases, and polar liquids (such as methanol, ethanol), as well as for natural gas drying and purification, among others.

In zeolites, all atoms accessible to the adsorbing molecules can serve as adsorption centers. Thus, adsorption centers can include extra framework atoms such as bulky cations and hydroxyl groups, as well as framework oxygen atoms that form the walls of the cavities. The accessibility of the framework aluminum atom depends on its coordination state: under normal tetrahedral coordination with oxygen atoms, the aluminum is effectively shielded by oxygen; however, under tri-coordination in areas of anionic vacancies, the aluminum atom may act as an adsorption center.

It is well known that LTA zeolites exist in several forms, including NaA (molecular sieve type 4 Å), CaA (molecular sieve type 5 Å), and KA (molecular sieve type 3 Å). The thermodynamic properties and adsorption mechanisms of polar, non-polar, and quadrupole molecules on NaA and CaA zeolites have been thoroughly studied [16-19]. Although the adsorption characteristics of various molecules with different sizes and physicochemical properties, including sulfur-containing compounds, on KA zeolite have been investigated using X-ray and spectroscopic methods, there is still a lack of scientific research focused on the fundamental thermodynamic characteristics of these systems [20-23].

2. Testing Methods

For measurements of isotherms and differential adsorption heats 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 μW thermal power). It can be used with confidence to measure the heat of processes of almost unlimited duration. The calorimeter makes it possible to obtain the thermokinetics of the process of adsorption systems under study, which is very important for elucidating the mechanism of adsorption.

Despite its outer insulating shells, it is not adiabatic, as the heat released in it is introduced from the calorimeter chamber as it is released and dissipated into the large metal block. Although the temperature of the calorimeter chamber changes only slightly, the instrument cannot be called strictly isothermal; it detects small temperature changes, which are unavoidable and form the basis of measurements.

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 surface of the calorimeter chamber and the calorimeter block.

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

The adsorption-calorimetric method used in this work provides highly accurate molar thermodynamic characteristics and reveals detailed mechanisms of ad-sorption 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. The principle of operation of the adsorption-calorimetric device used in this work is presented in the works of the authors [19, 24-27].

3. Results and Discussion

The unit cell composition of this zeolite is represented as $K_{4.63}Al_{10.62}H_{72}Na_{6}O_{91.32}Si_{25.38}$. Based on its chemical formula, the amount of potassium cations in 1 gram of the zeolite is equivalent to 1 mmol/g. KA (MSS-558) zeolite was synthesized via the hydrothermal method in a special autoclave using chemically pure oxides [28].

Table 1 provides the experimentally obtained values of the adsorption amount, equilibrium pressure, and differential heat of adsorption of carbonyl sulfide on KA (MSS-558) zeolite, as well as the theoretically calculated Gibbs free energy and entropy changes [29]. Due to the high saturation pressure of carbonyl sulfide at the experimental temperature (303 K) — 11245 torr — the adsorption parameters were measured up to a relative pressure of $P/P_s = 0.045$.

The Gibbs free energy was calculated as the work done during the change in gas volume at constant temperature, i.e., from the free energy, using the following equation:

$$\Delta G=-A=-RT\ln(P/P_s)=RT\ln(P_s/P) \qquad (1)$$

where R is the universal gas constant, T is the experimental temperature, and P_s=11245 torr.

Table 1.
The dependence of the main thermodynamic characteristics on the adsorption amount.

No	*a*, mmol/g	P, torr	P/P_s	Q, kJ/mol	ΔG, kJ/mol	ΔS, kJ/mol·K
1.	0.008	0.9	0.0001	107	24	-209
2.	0.029	5.8	0.0005	91	19	-171
3.	0.037	11.3	0.0010	73	17	-119
4.	0.045	18.2	0.0016	56	16	-65
5.	0.055	29.3	0.0026	43	15	-26
6.	0.066	47.5	0.0042	34	14	0
7.	0.073	78.3	0.0070	35	13	-8
8.	0.085	124.3	0.0111	36	11	-15
9.	0.104	198.8	0.0177	27	10	11
10	0.157	312.1	0.0278	25	9	14
11	0.300	506.2	0.0450	22	8	18

The adsorption entropy was calculated using the following Gibbs-Helmholtz formula:

$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_a - \lambda) + RT \ln P_S / P}{T} \quad (1)$$

where, λ is the condensation heat, and ΔH and ΔG are the changes in enthalpy and free energy when transitioning from the standard state to the adsorbed state.

The adsorption isotherm of carbonyl sulfide on KA (MSS-558) zeolite is shown in Figure 1. At low saturation levels, the equilibrium relative pressure is $P/P_s=8\cdot10^{-5}$ (P=0.9 torr), indicating relatively weak adsorption of carbonyl sulfide molecules on the zeolite. The adsorption isotherm reaches an adsorption capacity of 0.3 mmol/g at a relative pressure of $P/P_s=0.045$ (P=506 torr). The effective pore diameter of the KA zeolite is 3 Å, which is approximately equal to the size of the carbonyl sulfide molecule (~3 Å). The adsorption isotherm corresponds to Type II according to the Brunauer classification. Therefore, based on the above values and the Brunauer isotherm distribution, it can be concluded that carbonyl sulfide molecules are adsorbed on the external surface of the zeolite.

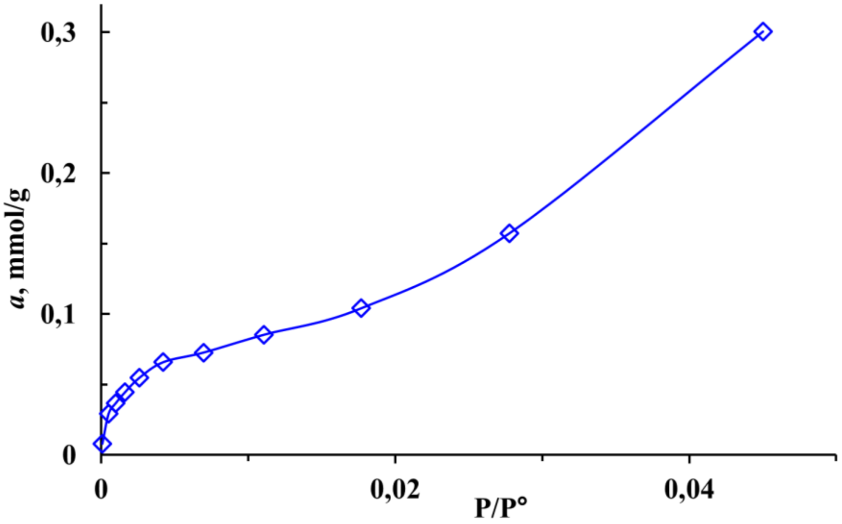

Figure 1.
Adsorption isotherm of carbonyl sulfide molecules on KA (MSS-558) zeolite.

Up to an adsorption amount of 0.066 mmol/g, the relative pressure ($P/P_s=0.004$, P=48 torr) increases slowly. This indicates that the adsorption of carbonyl sulfide molecules on the surface of KA (MSS-558) zeolite occurs with relatively strong intermolecular interactions. The isotherm shows a linear increase up to an adsorption amount of 0.1 mmol/g and a relative pressure of $P/P_s=0.0177$ (P=200 torr). Starting from $P/P_s=0.0177$, the equilibrium relative pressure increases sharply, and the adsorption process completes at a relative pressure of $P/P_s=0.045$ (P=506 torr) and an adsorption amount of 0.3 mmol/g.

The overall view of the adsorption isotherm of carbonyl sulfide molecules on KA (MSS-558) zeolite in BET coordinates is presented in Figure 2. The nearly linear change in the isotherm up to an adsorption amount of 0.1 mmol/g corresponds to a linear trend in the relative pressure region.

Based on the chemical composition of KA (MSS-558) zeolite ($K_{4.63}Al_{10.62}H_{72}Na_6O_{91.32}Si_{25.38}$), the amount of potassium cations in 1 gram of zeolite is 1 mmol/g. The linear variation of the isotherm in both relative pressure and BET coordinates is proportional to the potassium content of the zeolite. This is associated with the migration of potassium cations to the zeolite surface and the formation of ion–molecular complexes with carbonyl sulfide molecules.

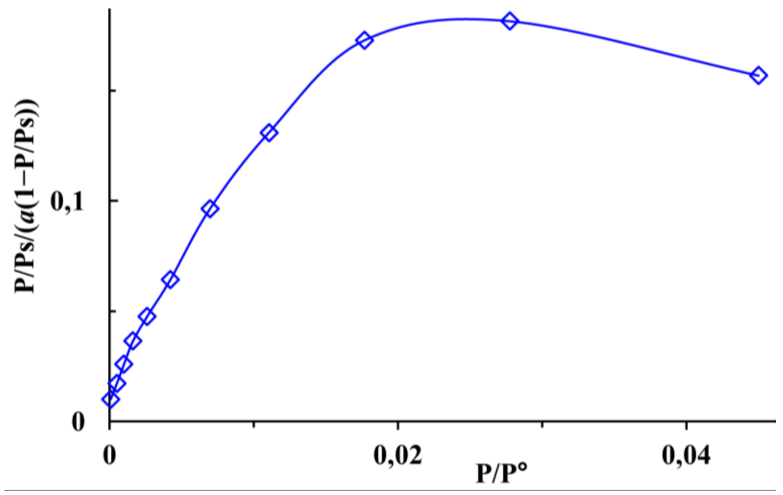

Figure 2.
BET plot of the adsorption isotherm of carbonyl sulfide molecules on KA (MSS-558) zeolite.

Figure 3 presents the linear region of the adsorption isotherm of carbonyl sulfide on KA (MSS-558) zeolite, calculated using the BET equation, from the initial relative pressure value P/P_s=0.00008 to P/P_s=0.0016.

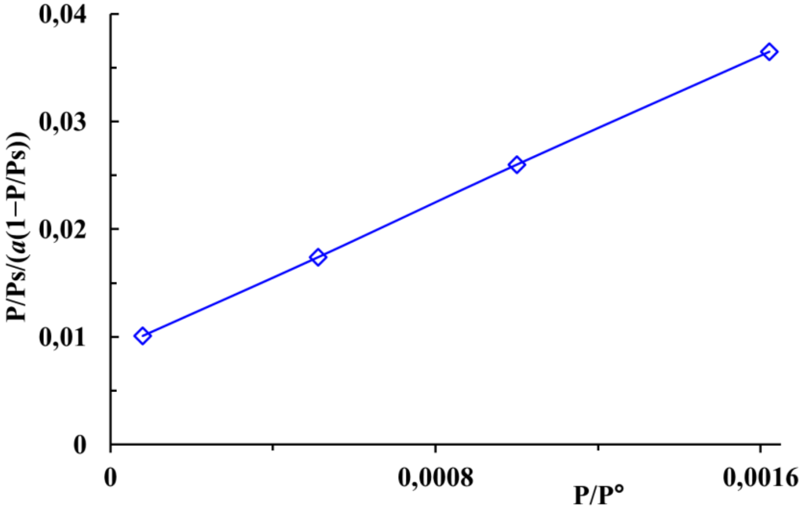

Figure 3.
BET plot of the adsorption isotherm of carbonyl sulfide molecules on KA (MSS-558) zeolite.

From Figure 3, it was determined that the monolayer adsorption amount of carbonyl sulfide molecules is a_m=0.01 mmol/g.

The adsorption isotherm of carbonyl sulfide on KA (MSS-558) zeolite at low pressure values demonstrates that the interaction between the adsorbent and adsorbate is sufficiently strong. This indicates the formation of donor–acceptor bonds between the carbonyl sulfide molecules and the potassium cations in the zeolite.

To determine the sorption-catalytic properties of various types of synthetic zeolites obtained by different methods, as well as their hydrophilic, hydrophobic, and organophilic characteristics, various organic groups can be introduced into the zeolite framework. The synthesis of new-generation zeolites with rare organometallic framework structures, without using organic structure-directing agents (SDAs), allows the production of LTA, MOF, FAU, Y, and β-type zeolites [30-32]. This also includes MFI-type zeolites (such as silicalite, Ti-silicalite-1 (TS-1), Fe-silicalite-1), MEL (ZSM-11 zeolite, which differs from ZSM-5 by having only straight channels), and TON (ZSM-22 zeolite with a one-dimensional channel system), as well as new-generation zeolites of the ZMM family such as MRE, ZSM-8, MTW, ZSM-20, MTT, ZSM-34, ZSM-35, ZSM-38, ZSM-39, ZSM-40, and MFS. The development of such technologies enables their application across various industries, including gas purification and drying, as well as the prevention of organic compounds from being released into the atmosphere [33-43].

Carbonyl sulfide (COS) is considered one of the most dangerous substances for the human body. It is formed as a result of the reaction between carbon monoxide (CO) and sulfur at a temperature of 3500°C. If the air contains 1000 molecules of carbonyl sulfide per one million, it can cause serious illnesses; at concentrations of 1400 molecules per million, it can be lethal. Therefore, since carbonyl sulfide is produced through reactions between carbon- and sulfur-containing compounds, it is advisable to remove it from partially combusted (waste) gases. One of the most effective methods for this is purification using zeolites. For this purpose, it is essential to study the adsorption behavior of carbonyl sulfide on zeolites with different cation compositions.

The adsorption isotherm of carbonyl sulfide on KA (MSS-558) zeolite in logarithmic coordinates is presented in Figure 4. The logarithmic function graph of the isotherm provides a clearer understanding of the adsorption mechanism of carbonyl sulfide molecules on KA zeolite. At low saturation levels of the adsorption volume, the isotherm at an adsorption amount of 0.008 mmol/g corresponds to $\mathrm{Ln}(P/P_s)=-9{,}4$. Here, $P_s=11245$ torr, which represents the saturation pressure of carbonyl sulfide at a temperature of 303 K. Due to the high relative pressure of carbonyl sulfide, the isotherm was measured up to 506 torr.

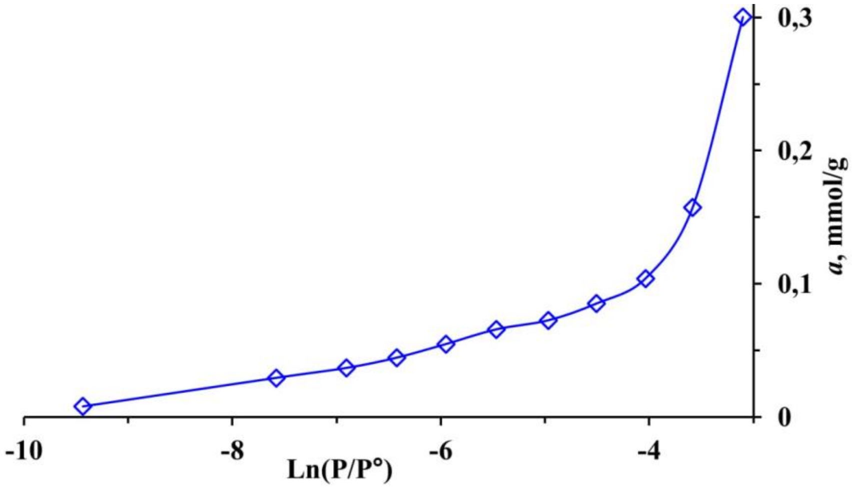

Figure 4.
Logarithmic coordinate isotherm of COS adsorption at 303 K on KA (MSS-558) zeolite.

In the initial region of the adsorption isotherm, the interaction between cations in the zeolite matrix and carbonyl sulfide molecules indicates the formation of strong ion-molecular complexes. The isotherm progresses almost linearly toward the abscissa axis up to an adsorption amount of approximately ~0.1 mmol/g and $\mathrm{Ln}(P/P_s)=-4$. The adsorption amount of 0.1 mmol/g is proportional to the amount of potassium cations in the zeolite composition. This reflects the process of carbonyl sulfide molecules being adsorbed onto the potassium cations located on the surface of the zeolite.

Zeolites are aluminosilicates with a porous crystalline framework structure. Their framework consists of interconnected tetrahedral units of [SiO_4] and [AlO_4], linked at the corners by oxygen atoms. A distinctive feature of aluminosilicates is the specific arrangement of aluminum atoms. In all aluminosilicates, Al and Si atoms occupy tetrahedral coordination, and aluminum substitutes for silicon isomorphically in the silicate framework. The negative charge of the tetrahedral structure is neutralized by various alkali or alkaline earth metal cations located in the pores. These cations are capable of migration [18-23, 44-54].

In this zeolite as well, potassium cations migrate to the surface under the influence of adsorbed carbonyl sulfide molecules. According to the BET adsorption theory, the adsorbate molecules form multilayer carbonyl sulfide layers.

Figure 5 shows the differential heat of adsorption of carbonyl sulfide molecules on KA (MSS-558) zeolite. It is known that for synthetic zeolites (MFI, MOR, FAU, LTA), the differential heat of adsorption of adsorbate molecules of different physicochemical nature typically changes in a stepwise manner [42-59]. However, since the size of the carbonyl sulfide molecule (2.7 Å) is close to the size of the channels in KA zeolite (3 Å), the sorption process occurs not within the inner matrix of the zeolite but mainly on its surface [20-23].

In the initial stage of the sorption process, at an adsorption amount of 0.008 mmol/g, the differential heat (enthalpy) is approximately ~107 kJ/mol. This indicates that under the influence of carbonyl sulfide molecules, potassium cations migrate from the inner matrix of the zeolite to its surface, and each carbonyl sulfide molecule initially forms ion-molecular complexes with several potassium cations. As the adsorption amount increases, the potassium cations redistribute, and the differential heat decreases sharply as the potassium cations complete their migration to the surface of the zeolite. At an adsorption amount of 0.03 mmol/g, the differential enthalpy decreases to 91 kJ/mol, forming a plateau.

As the sorption surface becomes saturated, the differential heat sharply decreases from 34 kJ/mol at an adsorption level of 0.066 mmol/g. At 0.085 mmol/g adsorption, the heat value slightly increases by 2 kJ/mol to 36 kJ/mol, forming a second plateau. This 2 kJ/mol increase in differential heat is attributed to Van der Waals interactions between carbonyl sulfide molecules. At an adsorption of 0.1 mmol/g, the differential heat decreases to 27 kJ/mol. This value is ten times lower than the amount of potassium cations in the zeolite, indicating that under the influence of these cations, the carbonyl sulfide molecules form up to 10 adsorption layers on the surface of the zeolite.

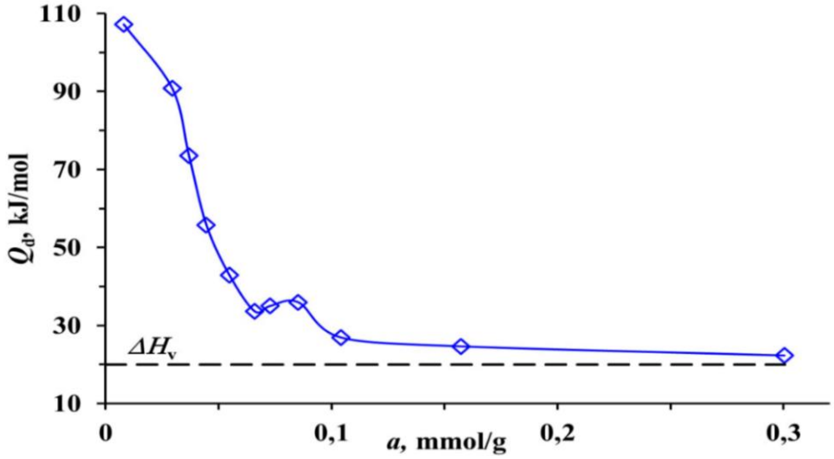

Figure 5.
Differential Heat (Q_d) of Carbonyl Sulfide Molecule Adsorption on Zeolite KA (MSS-558). The dashed line represents the condensation heat of carbonyl sulfide molecules at 303 K.

With the continued adsorption of carbonyl sulfide molecules, the differential heat linearly approaches the condensation heat of carbonyl sulfide (20 kJ/mol). This suggests that subsequent adsorption occurs primarily via adsorbate–adsorbate interactions. At an experimental pressure of 506 torr and an adsorption capacity of 0.3 mmol/g, the differential heat decreases to 22 kJ/mol, marking the end of the sorption process.

Figure 6 shows the relationship between the change in Gibbs energy and the amount of carbonyl sulfide adsorbed on zeolite KA (MSS-558). The Gibbs energy values indicate that the sorption process corresponds to physical adsorption, and its trend closely mirrors the changes in differential heat. At 0.008 mmol/g adsorption, the change in Gibbs energy is approximately ~24 kJ/mol. As the sorption surface becomes saturated with carbonyl sulfide molecules, Gibbs energy sharply decreases and reaches 10 kJ/mol at 0.1 mmol/g adsorption, exhibiting a stepwise pattern. This stepwise change corresponds to the similar stepwise behavior observed in the differential heat profile.

Based on the chemical composition of the zeolite $K_{4.63}Al_{10.62}H_{72}Na_6O_{91.32}Si_{25.38}$, the amount of potassium cations in the structure is equal to 1 mmol/g. The initially high Gibbs energy and its sharp decrease as the sorption surface becomes saturated confirm the migration of potassium cations, as well as the formation of ion-molecular complexes between the initial carbonyl sulfide molecules and several potassium cations.

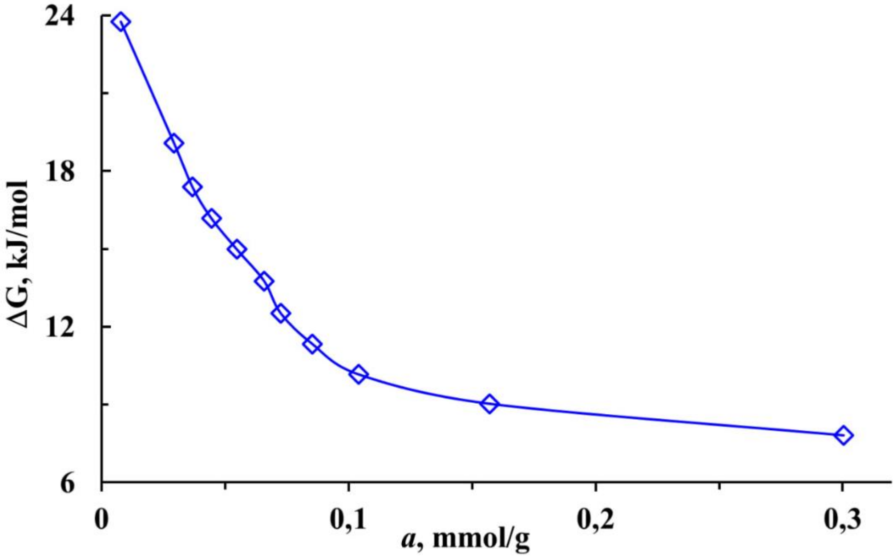

Figure 6.
Variation of Gibbs Energy during the Adsorption of Carbonyl Sulfide Molecules on Zeolite KA (MSS-558) at 303 K.

The subsequent redistribution of potassium cations during the adsorption of additional carbonyl sulfide molecules is also indicated. The amount of adsorption corresponding to a decrease in Gibbs energy to 10 kJ/mol is ten times lower than the total amount of potassium cations in the zeolite, suggesting that, like the differential heat, carbonyl sulfide molecules form up to 10-layer structures on the surface of the zeolite. In the region between 0.1 mmol/g and the experimental maximum of 0.3 mmol/g adsorption, the change in Gibbs energy is 2 kJ/mol, which is also equal to the 2 kJ/mol variation in differential heat. This indicates that the subsequent carbonyl sulfide molecules are adsorbed via weak Van der Waals forces through adsorbate–adsorbate interactions.

The change in the molar differential entropy *(ΔS_a)* of carbonyl sulfide molecules adsorption on KA (MSS-558) nanostructured zeolite as a function of adsorption saturation is shown in Figure 7 (with the entropy of liquid carbonyl sulfide taken as zero).

The molar differential entropy of carbonyl sulfide adsorption on KA (MSS-558) zeolite can be divided into 3 regions. The first region lies below the entropy of liquid carbonyl sulfide, the second region corresponds to the average entropy value, and the third region lies above the entropy of liquid carbonyl sulfide.

Although carbonyl sulfide molecules are slightly smaller in size compared to the micropore size of the KA zeolite, they are adsorbed on the surface part of the zeolite. The sorption processes on the surface belong to the type of physical adsorption.

In the initial region, the entropy change is equal to -210 J/mol·K. This value indicates that the mobility of the initially adsorbed carbonyl sulfide molecules on the zeolite surface is significantly restricted, meaning that the adsorbate/adsorbent interaction is strong. This raises the question of whether the sorption process is chemical adsorption or physical adsorption. It is known that primarily physical sorption occurs on the surface of zeolites. The limited mobility of carbonyl sulfide molecules in the initial region of adsorption is related to the migration of potassium cations in the composition of KA zeolite to the surface part of the zeolite and the formation of $COS:K^+$ complexes. Several potassium cations interact with each initially adsorbed carbonyl sulfide molecule. However, during the subsequent adsorption of carbonyl sulfide molecules, the potassium cations are redistributed.

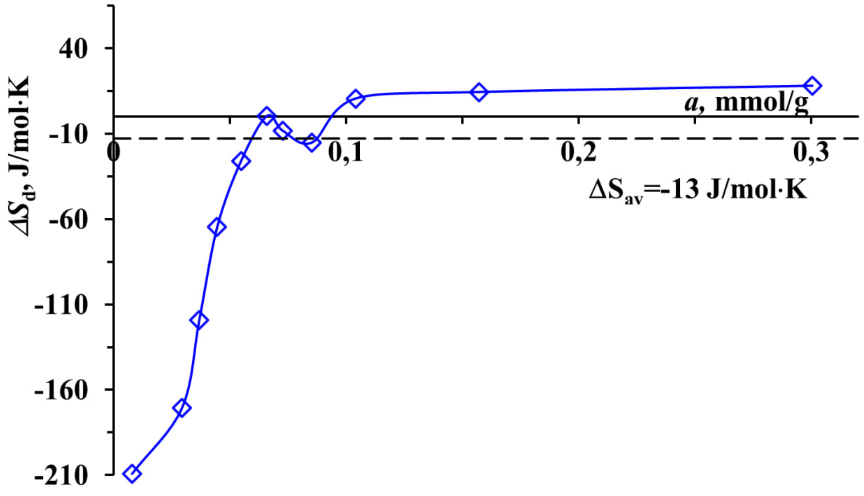

Figure 7.
Differential entropy of carbonyl sulfide adsorption on KA (MSS-558) zeolite. The horizontal dashed line – average molar integral entropy.

As the sorption surface becomes saturated, the entropy begins to increase sharply and reaches zero at an adsorption amount of 0.066 mmol/g. At 0.09 mmol/g adsorption, the entropy decreases to -13 J/mol·K. This decrease is due to the Van der Waals interactions between carbonyl sulfide molecules, which partially restricts the mobility of the adsorbate molecules. At an adsorption amount of 0.1 mmol/g, the entropy increases to 10.6 J/mol·K and remains almost unchanged until the sorption process is complete. Based on the chemical composition of the zeolite, the amount of potassium cations is 1 mmol/g. Thus, only 10% of the total potassium cations participate in the sorption process. On the other hand, multilayer adsorption of adsorbate molecules occurs on the surface of the zeolite, so the adsorption amount at constant entropy is proportional to the amount of potassium cations in the composition of the zeolite.

The average value of the molar differential entropy of carbonyl sulfide adsorption on KA (MSS-558) zeolite is -13 J/mol·K, which is lower than the entropy of liquid carbonyl sulfide molecules at the experimental temperature. This indicates the restricted mobility of carbonyl sulfide molecules.

The time of establishing adsorption equilibrium depending on the adsorption value, i.e. the thermokinetics of carbonyl sulfide adsorption (τ) on the surface of zeolite KA (MSS-558) from the filling is shown in Figure 8. The change in the thermokinetics of adsorption of carbonyl sulfide molecules confirms the change in enthalpy, entropy and isotherm depending on adsorption. The thermokinetics of carbonyl sulfide adsorption on zeolite KA (MSS-558) differs from the thermokinetics of adsorption of substance molecules in LTA type zeolites [38-44] which indicates, as well as in the isotherm, enthalpy and entropy, a different nature and mechanism of carbonyl sulfide adsorption in these zeolites.

The thermokinetics of carbonyl sulfide adsorption on zeolite KA (MSS-558) begins at ~6 hours and increases to 13 hours at 0.03 mmol/g. As shown above, according to the chemical composition of the zeolite, the adsorption value of 0.03 mmol/g correlates with the amount of potassium cations in the zeolite, that is, carbonyl sulfide molecules are adsorbed on potassium cations in the zeolite and form an ion-molecular complex COS:K^+ in the first coordination sphere. Then, at an adsorption value of □0.06 mmol/g, the thermokinetics decreases to 6 hours. With the formation of the next complex with each potassium cation of the carbonyl sulfide molecule, the thermokinetics increases to 9 hours at an adsorption of 0.1 mmol/g. At an adsorption value of 0.1 mmol/g, the increase in thermokinetics, both in enthalpy, Gibbs energy and entropy change, proves that the migration of potassium cations to the zeolite surface is complete. The decrease in thermokinetics, at an adsorption of more than 0.1 mmol/g, is due to the release of additional heat under the action of mutual Van der Waals forces of carbonyl sulfide molecules during the formation of a multidimensional layer as a result of this force [45].

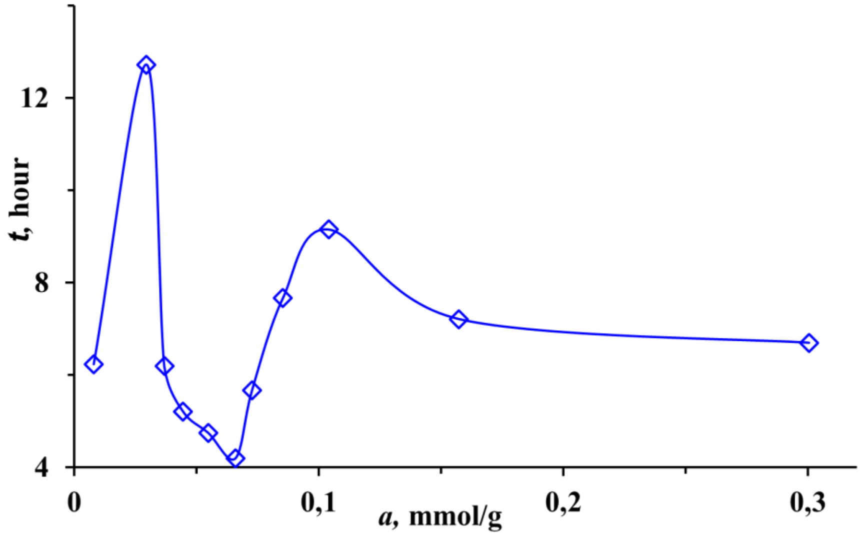

Figure 8.
Time to establish adsorption equilibrium depending on the adsorption value of carbonyl sulfide on zeolite KA (MSS-558).

The time of establishing the adsorption equilibrium depending on the adsorption value during subsequent sorption of carbonyl sulfide molecules, as entropy, does not correspond to the value of 0.1 mmol/g of potassium in the zeolite. This means that the process of sorption on the zeolite surface by the ion-molecular mechanism of carbonyl sulfide and potassium in the first coordination sphere has ended. The time of establishing the adsorption equilibrium depending on the adsorption value during subsequent sorption of carbonyl sulfide molecules does not change until the total adsorption of 0.3

mmol/g, i.e. subsequent carbonyl sulfide molecules interact as adsorbate/adsorbate with the initial carbonyl sulfide molecules adsorbed on potassium cations.

4. Conclusion

As a result of the adsorption-calorimetric study, the isotherm, enthalpy, entropy and time of establishing adsorption equilibrium were obtained depending on the adsorption value of carbonyl sulfide molecules in the nanostructured zeolite KA (MSS-558). Based on the obtained results, it was proven that carbonyl sulfide molecules are sorbed on the zeolite surface and the adsorption process corresponds to physical adsorption. It was found that potassium cations migrate to the zeolite surface under the influence of carbonyl sulfide molecules. A stepwise change in the differential isotherm, enthalpy, entropy, Gibbs energy and thermokinetics of adsorption was established depending on the number of potassium cations in the zeolite, i.e. the enthalpy, entropy and thermokinetics of adsorption correlate with the number of potassium cations in the zeolite structures. It is shown that the adsorption properties of KA (MSS-558) zeolites depend on the type of cations, as well as on the structure of the fragments of the KA (MSS-558) zeolite structure. Ammonia molecules initially form ion-molecular complexes COS:K^+ in the first coordination sphere with potassium cations. It is proven that ammonia molecules interact as an adsorbate/adsorbate with the initial carbonyl sulfide molecules adsorbed on potassium calcium cations and form a K^+:COS:COS ion-molecular complex. It is determined that the average molar integral entropy of ammonia adsorption on KA (MSS-558) zeolite. is -13 J/mol·K, indicating that in the zeolite the mobility of carbonyl sulfide molecules is lower than the liquid phase and close to the mobility of the solid phase, which indicates a strong inhibition of the mobility of carbonyl sulfide adsorbed on cations.

Transparency:

The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.

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