ISSN: 2350-0328
International Journal of AdvancedResearch in Science, Engineering and Technology
Vol. 11, Issue 12, December 2024

Differential Heat, Gibbs Energy, and the Mechanism of Carbonyl Sulfide Adsorption on Zeolite KA (MSS-558)

Marufjon Asfandiyorov, Mirzokhid Kokhkharov, Khayot Bakhronov

Assistant of the Tashkent University of Information Technologies named after Muhammad al-Khwarizmi, Uzbekistan, Tashkent
Doctor of Chemical Sciences, Associate Professor, Namangan Engineering Technological Institute, Namangan, Uzbekistan
Associate professor, Tashkent University of Information Technologies named after Muhammad al-Khwarizmi, Tashkent, Uzbekistan.

ABSTRACT: This article presents experimentally obtained values of the differential heat of carbonyl sulfide adsorption at 303 K on the LTA-type zeolite KA (MSS-558). The differential heat values were measured using a Tian-Calvet type DAC-1-1A microcalorimeter connected to a high-vacuum system. A regular correlation was established between the amount of carbonyl sulfide adsorbed on zeolite KA (MSS-558) and the corresponding differential heat values. Furthermore, the adsorption mechanism up to the region where the differential heat decreases to the condensation heat of carbonyl sulfide, as well as the law of volume filling of the zeolite by carbonyl sulfide molecules, was identified. Under experimental conditions, the adsorption capacity of zeolite KA (MSS-558) for carbonyl sulfide was shown to be 0.3 mmol/g per gram of zeolite. In the initial stage, under the influence of carbonyl sulfide molecules, K^+ cations in the structure of zeolite KA (MSS-558) migrate from the internal matrix to the surface, forming ion-molecular complexes with the carbonyl sulfide 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, and the adsorption enthalpy decreases to 27 kJ/mol.

KEYWORDS: zeolite, adsorption, energy, Gibbs energy, enthalpy, temperature, microcalorimeter, carbonyl sulfide.

I.INTRODUCTION

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.

To date, in the development of technologies for the production of microporous adsorbents for adsorption processes, it is necessary to justify the following scientific solutions: the selection of suitable local sorption raw materials for the synthesis of synthetic zeolites of types A, X, Y, ZSM, and others; the determination of the crystalline structure and the formation of ion-molecular complexes through the sorption of polar, non-polar, and quadrupole molecules on the obtained microporous adsorbents [1–4]; the study of the quantity, distribution, and migration of cations at active centers within micropores [5–10]; and the need to establish the complete molecular mechanism of adsorption processes on adsorbents [11–16].

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 [17–19].

Worldwide, research is being conducted on the adsorption processes of polar, non-polar, quadrupole, and aromatic molecules, with a focus on determining the mechanisms and thermodynamic functions. Priority areas include the synthesis of microporous adsorbents; improvement of their composition; synthesis of synthetic zeolites and determination of their adsorption properties; and enhancement of their selective sorption capabilities through cation exchange in zeolites of types A, X, Y, and ZSM [5–16].

In zeolites, all atoms accessible to the adsorbing molecules can serve as adsorption centers. Thus, adsorption centers can include extraframework 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.

There is limited data on the mechanism and thermodynamic functions of the adsorption processes involving sulfur-containing molecules, such as hydrogen sulfide and carbonyl sulfide.

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 [20–23]. 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.

II. SIGNIFICANCE OF THE SYSTEM

Zeolites are currently widely used for drying and purifying various natural gases, separating gases, and cleaning toxic gases produced during combustion that cause significant environmental harm when released into the atmosphere. They are also considered among the most important catalysts for processing hydrocarbon raw materials. In gas separation and as catalysts, KA zeolites belong to a highly efficient group of zeolites. In this study, the methodology is explained in Section III, the experimental results are presented in Section IV, and future research and conclusions are discussed in Section V.

III. METHODOLOGY

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 be used confidently 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 adsorption mechanism. The principle of operation of the adsorption-calorimetric installation is described in detail in the works of the authors [5, 7-8, 12-14, 16].

IV. EXPERIMENTAL RESULTS

In this article, the differential heat of adsorption of carbonyl sulfide on synthetic zeolite KA (MSS-558) was determined using an adsorption-calorimetric experimental method. The Gibbs energy was calculated based on the work done during the change in gas volume at constant temperature, and the adsorption mechanism was described. The adsorption mechanism was thoroughly analyzed based on the differential heat of carbonyl sulfide adsorption on KA (MSS-558) zeolite at 303 K. The unit cell composition of the studied zeolite is represented by the formula $K_{4.63}Al_{10.62}H_{72}Na_6O_{91.32}Si_{25.38}$. Based on its chemical composition, the amount of potassium cations in 1 gram of zeolite is 1 mmol/g.

Table 1 presents the values of differential heat and Gibbs energy as functions of the adsorption amount.

Table 1.

№	*a*, mmol/g	Q, kJ/mol	ΔG, kJ/mol
1.	0.008	107.2	23.8
2.	0.029	90.8	19.1
3.	0.037	73.5	17.4
4.	0.045	55.8	16.2
5.	0.055	42.9	15.0
6.	0.066	33.7	13.8
7.	0.073	35.0	12.5
8.	0.085	35.9	11.3
9.	0.104	26.9	10.2
10.	0.157	24.7	9.0
11.	0.300	22.3	7.8

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.

Figure 1 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 [6–24]. 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.

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.

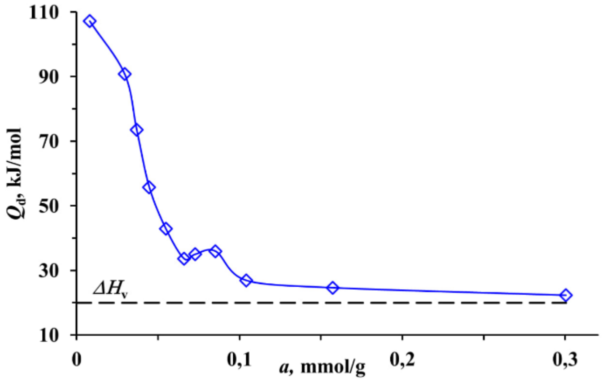

Figure 1. Differential Heat (Q_d) of Carbonyl Sulfide Molecule Adsorption on Zeolite KA (MSS-558). The dashed line represents the condensation heat of carbonyl sulfide molecules at 303 K.

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 2 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.

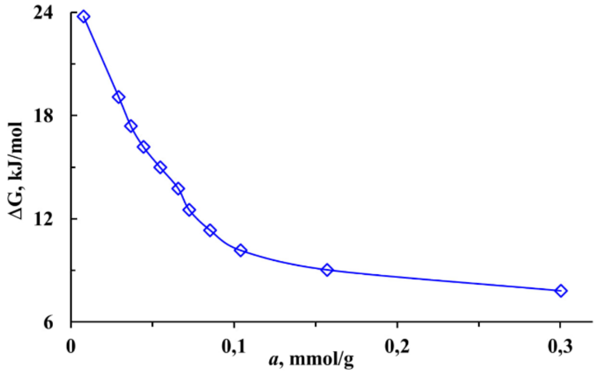

Figure 2. Variation of Gibbs Energy during the Adsorption of Carbonyl Sulfide Molecules on Zeolite KA (MSS-558) at 303 K.

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.

V. CONCLUSION AND FUTURE WORK

In the adsorption-calorimetric study, the differential heat and Gibbs energy of carbonyl sulfide molecule adsorption on the nanostructured zeolite KA (MSS-558) were investigated. The results demonstrated that carbonyl sulfide molecules are adsorbed on the surface of the zeolite and that the adsorption process corresponds to physical adsorption. It was found that the differential heat of adsorption and Gibbs energy vary depending on the amount of potassium cations in the zeolite structure. Under the influence of carbonyl sulfide molecules, the migration of potassium cations to the surface of the zeolite was observed.

REFERENCES

1. Kapil Narwal, R. Kempers, P. G. O’Brien. Adsorbent-Adsorbate Pairs for Solar Thermal Energy Storage in Residential Heating Applications: A Comparative Study //Proceedings of The Canadian Society for Mechanical Engineering International Congress 2018 May 27-30, 2018, Toronto, On, Canada
2. Fracaroli A. M. et al. Metal–organic frameworks with precisely designed interior for carbon dioxide capture in the presence of water. Journal of the American Chemical Society 136, P.8863-8866 (2014).
3. Henninger S., Schmidt F. & Henning H.-M. Water adsorption characteristics of novel materials for heat transformation applications. Applied thermal engineering 30, P.1692–1702 (2010).
4. Narayanan S., Yang S., Kim H. & Wang E. N. Optimization of adsorption processes for climate control and thermal energy storage. International Journal of Heat and Mass Transfer 77, P.288–300 (2014).
5. Rakhmatkariyeva F.G., Abdurakhmonov E.B., Yakubov Y.Y. “Volumetric Analysis of Benzene Vapor Adsorption on LiLSX Zeolite in a High Vacuum Adsorption Device”. International Journal of Advanced Science and Technology; 2020, 8(29): pp. 3442-3448.
6. Abdurakhmonov E.B., Rakhmatkarieva F.G., Ergashev O.K., Ochilov G.M. “Energetic Characteristics Of The Process Of Adsorption Of Benzene In Zeolites NaX And NaY”. International Journal of Future Generation Communication and Networking; 2020, 4(13): pp. 246–252.
7. Ergashev O., Bakhronov Kh., Akhmedova N., Abdullayeva Sh., Khalilov S.and Kholikov K. “Calorimetric study of methanol adsorption in LiZSM-5 and CsZSM-5 zeolites”. E3S Web of Conferences 401, 02023 (2023), https://doi.org/10.1051/e3sconf/202340102023
8. Bakhronov Kh., Ergashev O., Sultonov A., Kholmedov H., Ganievand A., Asfandiyorov M. “Basic thermodynamic characteristics and isotherm of ammonia adsorption in NaZSM-5 and LiZSM-5 zeolites”. E3S Web of Conferences 401, 02025 (2023), https://doi.org/10.1051/e3sconf/202340102025
9. Kokharov M.X., Axmedov U.K., Rakhmatkarieva F.G., Abdurakhmonov E.B. “Investigation of water sorption to Ca$_5$Na$_3$A zeolite at adsorption of micro calorimetric device”. International Journal of Advanced Research in Science, Engineering and Technology; 2020, 5(7): pp.13939-13944.
10. Abdurakhmonov E.B., Rakhmatkarieva F.G., Ergashev O.K. “Determination of ammonia’s adsorption properties in NaLSX zeolite by calorimetric method”. International Journal of Materials and Chemistry; 2020, 10(2): c.17-22.
11. Abdurakhmonov E.B. “Thermodynamics of benzene adsorption in NaLSX zeolite”. International Journal of Advanced Research in Science”. Engineering and Technology; 2020, 7(10): pp. 15314-15320
12. Abdulkhaev T., Nuridinov O., Bakhronov Kh. “Differential heats of orta-xylene in zeolite AgZSM-5”. E-Global Congress Hosted online from Dubai, U.A.E., E-Conference; 2023: pp.120-122. https://eglobalcongress.com/index.php/egc/article/view/54/49
13. Abdulkhaev T., Kuldasheva Sh., Bakhronov Kh., Ganiev A. “Enthalpy and the mechanism of water adsorptionin zeolite AgZSM-5”. International Conference on Developments in Education Hosted from Saint Petersburg. -Russia; 2023: pp.81-84, https://www.econferencezone.org/index.php/ecz/article/view/2024/1877
14. Esonkulova N., Ahkmadov M., Bakhronov Kh. “Isotherm adsorption of toluene and zeolite Cu^{2+}ZSM-5”. International Conference on Developments in Education Hosted from Delhi. -India; 2023: pp.49-52, https://econferencezone.org/index.php/ecz/article/view/2137
15. Boddenberg B., Rakhmatkariev G.U., Viets J., Bakhronov Kh.N. “Statistical thermodynamics of ammonia-alkali cation complexes in zeolite ZSM-5”. Proceeding 12th International Zeolite Conference, 1998, USA, pp.481-488.
16. Esonkulova N., Kh.Bakhronov, Absalyamova I., Ahkmadov M. “Entropy and thermokinetics of toluene adsorption on Cu^{2+}ZSM-5 zeolite”. International Conference on Developments in Education Hosted from Bursa. -Turkey; 2023: pp.40-44, https://econferencezone.org/index.php/ecz/article/view/2137
17. Broussard L., Schoemaker D.P.The Structures of Synthetic Molekular Sieves //J.Amer Chem. Soc.,1960. - v.82. pp.1041
18. Howell P.A. A refinement of the cation positions in synthetic zeolite type A //Acta Crystallogr.,1960.- v.13. pp.737-741
19. Breck D.W., Cryctalline molecular sieves //J. Chem Educ.,1964. - v.41. - p.678.
20. Koxxarov M., Asfandiyorov M., Axmadov M. Isotherm of ammonia adsorption on CaA (M-34) zeolite //Models and methods for increasing the efficiency of innovative Research: a collection scientific works of the International scientific conference 11 SEPTEMBER 2024 - Berlin: Part . pp.56-60.
21. Koxxarov M., Sobirzhonova S., Asfandiyorov M. Isotherm of ammonia adsorption in zeolite CaA (M-22) //E- Global Congress Hosted online from Dubai, U.A.E., E-Conference, 30th December 2023, ISSN (E): 2836-3612, pp.67-72.
22. Kokhkharov M., Rakhmatkarieva F., Mamadaliev U., Kholmedov Kh., Bakhronov Kh., Ganiev A. Hydrogen sulfide adsorption isotherms in zeolite CaA (M-34) //Universum: химия и биология: электрон научн журн., 2024 год, 11(125). -С.15-20.
23. Kokhkharov M., Enthalpy and entropy change of methanethiol adsorption in zeolite CaA (M-22) //Mental Enlightenment Scientific-Methodological Journal, 2024, vol.5, issue 10, pp.171-178.
24. Tukhtayev F.S., Negmatov S.S., Negmatova K.S., Shonazarova N.U., Djalilova I.S., Sadinova O.O. Study of the kinetic properties of the developed composite polymer sorbents in various solutions// Austrian Journal of Technical and Natural Sciences № 11–12 2021, November – December, pp. 227-231
25. Tukhtayev F.S., Negmatov S.S., Karimova D.A., Malikova A.R., Kamalova D.I.. Research of Kinetic Sorption of Cu2+ Ions in CuSO4 Solution by Composite Polymeric Sorbents Under Various Conditions// JARDCS. Journal advanced research in dynamical and control systems. June 27. 2020. Volume 12. Special Issue 06. pp. 505-511. SCOPUS.

26. Tukhtayev F.S., Negmatova K.S., Karimova D.A. Research of Kinetic Sorption of Pb^{2+} Ions in $Pb(NO_3)_2$ Solution by Composite Polymeric Sorbents Under Various Conditions.// IJARSET. International journal advanced research in science, engineering and technology. India. June. 2020. Volume 7. Issue 6. pp. 14036-14043.

27. Tukhtayev F.S., Negmatov S.S., Shonazarova N.U. Study of the degree of sorption of sorbents in $Pb(NO_3)_2$ solution. EURASIAN JOURNAL OF ACADEMIC RESEARCH. Received: 28th June 2022. Accepted: 01st July 2022. Online: 30th July 2022. pp. 319-323.