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ISOTHERM OF AMMONIA ADSORPTION ON ZEOLITE CaA (MSS-622)

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Abstract: This article presents the experimentally obtained values of the adsorption isotherm of ammonia molecules on zeolitite CaA (MSS-622) at a temperature of 303 K. The isotherm was measured using a DAC-1-1A microcalorimeter connected to a universal high-vacuum device. The relationship between the amount of ammonia adsorption and its energetic characteristics on CaA (MSS-622) zeolite was established. Additionally, the sorption mechanism from the initial adsorption stage to the experimental range and the filling behavior of ammonia molecules in the zeolite's volume were determined. Under experimental conditions, the adsorption capacity of this zeolite for ammonia was found to be 10.2 mmol/g per gram of zeolite. It was determined that 43% of the total adsorption occurs at an equilibrium pressure of 0.33 torr, 53% at 1.4 torr, 71% at 25 torr, 80% at 200 torr, 98% at 476 torr, and 100% at 614 torr. The adsorption isotherm was reinterpreted using the three-term equation of the volumetric filling theory of micropores (VMOT), and the theoretically calculated values were shown to fully match the experimental data. It was proven that ammonia molecules initially form tetrameric ion-molecular complexes $4NH_3{:}Na^+$ with sodium cations and subsequently trimeric complexes $3NH_3{:}Ca^{2+}$ with calcium cations in the first coordination sphere of the zeolite.

Keywords: adsorption, enthalpy, free energy, isotherm, pressure, relative pressure, microcalorimeter, ammonia.

Introduction. To prevent environmental pollution, it is essential to purify natural gases by removing moisture, sulfur, and nitrogen compounds, as well as to mitigate ecological issues caused by the release of carbon dioxide (CO_2) into the atmosphere. One of the most effective solutions to these problems is the use of synthetic zeolites, which possess exceptional sorption and catalytic properties not found in nature. Scientific research focused on synthesizing new generations of highly adsorptive and catalytically active zeolites, as well as enhancing their selectivity, enables their practical application in industrial processes.

The family of synthetic zeolites with high sorption and catalytic properties includes aluminosilicate zeolites such as MFI, MOR, FAU, and LTA. The sorption and catalytic characteristics of these zeolites can be modified by replacing aluminum and silicon atoms in their structure with chemically similar elements from groups III, IV, and V of the periodic table, such as gallium, germanium, and phosphorus [1]. One of the unique features of zeolites is the presence of water molecules in their crystalline structure, which can evaporate upon heating up to 450°C without disrupting the crystal lattice. Additionally, the mobility of alkali and alkaline earth metal cations, as well as water molecules, enables ion exchange, further enhancing their versatility [2-4].

The sorption and catalytic properties of MFI, MOR, FAU, and LTA zeolites vary due to differences in their crystal lattice structure and composition [5-17]. In LTA-type zeolites, particularly CaA (M-22), CaA (M-34), Ca_5Na_3A (MSS-624), and Ca_4Na_4A (Horst-50/50), Ca^{2+} and Na^{+} cations serve as the primary active centers. The adsorption capacity of these zeolites depends significantly on the ratio of these cations, influencing the amount of adsorbed molecules. By studying the sorption of probe molecules such as water, ammonia, benzene (as an aromatic hydrocarbon), and carbon dioxide (as a binary acid oxide), it is possible to determine the number, nature, and strength of energetically active adsorption centers in specific crystallographic positions. For instance, the number of adsorbed water molecules per unit cell in CaA (M-22), CaA (M-34), and Ca_4Na_4A (Horst-50/50) zeolites has been found to be $22H_2O$/u.c., $28H_2O$/u.c., and $30H_2O$/u.c., respectively. Similarly, the formation of ion-molecular complexes with carbon dioxide molecules follows a stepwise adsorption pattern, with CaA (M-22), CaA (M-34), Ca_5Na_3A (MSS-624), and Ca_4Na_4A (Horst-50/50) adsorbing $7CO_2$/u.c., $6CO_2$/u.c., $8CO_2$/u.c., and $9CO_2$/u.c., respectively [18-27].

This study presents the adsorption isotherm of ammonia on synthetic CaA (MSS-622) zeolite, obtained through an adsorption-calorimetric experimental method. The logarithmic and relative pressure values of the adsorption isotherm, as well as the adsorption mechanism, are discussed in detail.

Methods and Materials. The adsorption-calorimetric method used in this study allows for obtaining the fundamental thermodynamic characteristics (ΔH, ΔG, ΔS) and provides a detailed understanding of the sorption mechanisms in zeolites. The experiments were conducted using a high-vacuum adsorption-calorimetric apparatus, which was adapted for measuring the amount of adsorbate using gas-volume and volumetric-liquid methods. A modified Tian-Calvet type DAC-1-1A microcalorimeter, known for its high precision and stability, was used as the microcalorimetric component.

The adsorption behavior of ammonia on CaA (MSS-622) zeolite at a temperature of 303 K was investigated, and the adsorption isotherm and mechanism were thoroughly analyzed. The elemental unit cell composition of this zeolite is expressed as $Ca_5Na_3[(AlO_2)_{12}(SiO_2)_{12}]$). Based on its chemical composition, as well as the crystal lattice structure and the presence of active adsorption positions S_I, S_{II}, and S_{III} in the zeolite, the amount of calcium cations in 1 g of zeolite is 1.9 mmol/g (total calcium content across all positions is 2.95 mmol/g), while the amount of sodium cations is 1.1 mmol/g (total sodium content across all positions is 1.77 mmol/g).

Results. The adsorption isotherm of ammonia on Ca_5Na_3A (MSS-624) zeolite in logarithmic coordinates is shown in Figure 1.

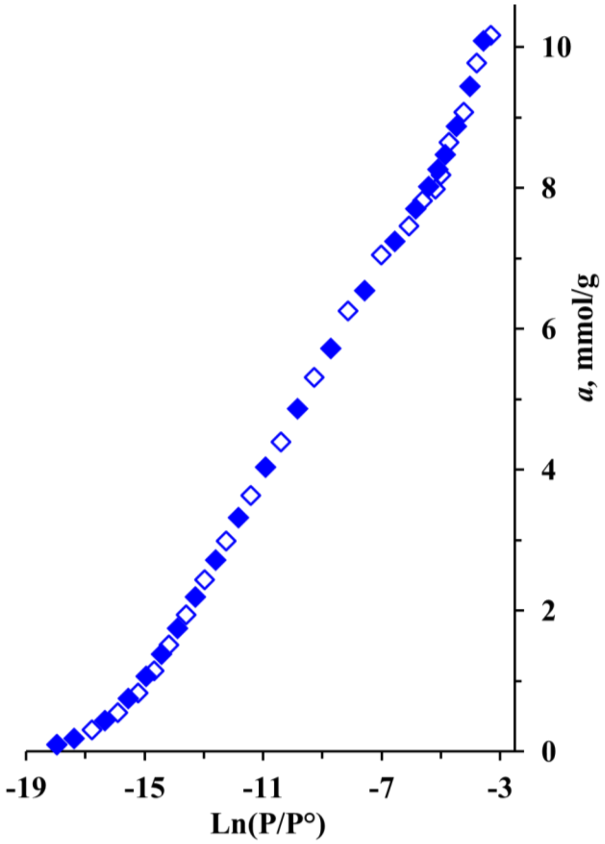

Figure 1. Adsorption isotherm of ammonia on CaA (MSS-624) zeolite at 303 K. ◇– experimental data, ♦–values from the general equation of the micropore volume filling theory (VMOT)

At small adsorption saturation levels, an adsorption amount of 0.1 mmol/g corresponds to an equilibrium relative pressure logarithm of LnP/P_s=-15.5 ($P/P_s=8.11\cdot10^{-7}$ or P=0.00674 torr). Here, P_s=8750 torr represents the saturation pressure of ammonia at 303 K. Due to the relatively high ammonia pressure, the experiment was carried out up to 614 torr, and the adsorption isotherm reached an adsorption amount of 10.2 mmol/g at a relative pressure of P/P_s=0.07 (or P=614 torr). The initial region of the adsorption isotherm indicates that the cations within the zeolite matrix form strong ion-molecular complex bonds with ammonia molecules. Initially, the isotherm approaches the abscissa axis up to $P/P_s=2.5\cdot10^{-7}$ (P=0.0022 torr) at an adsorption amount of approximately 1.14

mmol/g. Based on the chemical composition of the zeolite, the sodium cation content is 1.1 mmol/g, meaning that at an adsorption amount of ~1.14 mmol/g, ammonia molecules form a $1NH_3:Na^+$ monomer ion-molecular complex with the sodium cations in the zeolite. The isotherm then follows a linear progression up to $LnP/P_s=-7.96$ ($P/P_s=0.000038$ or P=0.33 torr), sequentially forming $2NH_3:Na^+$ dimer, $3NH_3:Na^+$ trimer, and $4NH_3:Na^+$ tetramer ion-molecular complexes at an adsorption amount of approximately 4.4 mmol/g.

During the subsequent adsorption of ammonia molecules, the isotherm changes independently of the sodium cation content in the zeolite. This indicates that the adsorption process of ammonia molecules within the first coordination sphere of sodium cations has been completed. The gradual increase in equilibrium pressure following the formation of the 4NH3:Na+ tetramer ion-molecular complex also confirms this phenomenon.

The linear and systematic change in the isotherm at the active centers of the zeolite corresponds to the second active center of its structure, which is the calcium cations (~1.9 mmol/g). This means that ammonia molecules begin to adsorb at the Ca^{2+} cation sites of the zeolite. At a relative pressure of $LnP/P_s=-5.7$ ($P/P_s=0.000755$ or P=6.6 torr) and an adsorption amount of 6.3 mmol/g, ammonia molecules form the $1NH_3:Ca^{2+}$ monomer complex with the calcium cations in the zeolite. At $LnP/P_s=-2.55$ ($P/P_s=0.023$ or P=201 torr) and an adsorption amount of 8.2 mmol/g, the $2NH_3:Ca^{2+}$ dimer complex is formed. At an adsorption amount of 10.1 mmol/g, the $3NH_3:Ca^{2+}$ trimer complex is formed, marking the completion of ammonia adsorption on calcium cations and the linear transformation of the isotherm. The sorption process within the experimental range is completed at an adsorption amount of 10.2 mmol/g.

From the adsorption isotherm, it is evident that ammonia molecules form a $4NH_3:Na^+$ tetramer complex with sodium cations and a $3NH_3:Ca^{2+}$ trimer complex with calcium cations in the Ca_5Na_3A (MSS-624) zeolite, ultimately leading to the formation of the $7NH_3:Ca_5Na_3A$ (MSS-624) complex as the final adsorbate/adsorbent structure.

The adsorption isotherm of ammonia on the CaA (MSS-624) zeolite is fully characterized by the three-term equation of the micropore volume filling theory (VMOT) [28].

$$a=5.12\exp[-(A/34.4)^5]+3.77\exp[-(A/20.57)^3]+3.94\exp[-(A/9.07)^3] \quad (1)$$

Here, a – represents the adsorption value (mmol/g), while $A=RTlnP_s/P$ denotes the free energy, which expresses the work performed (kJ/mol) to transfer the gas into the equilibrium gas phase. From Figure 1, it can be observed that the values calculated based on the micropore volume filling theory (VMOT) completely correspond to the experimentally obtained adsorption amount of 10.2 mmol/g. The first term of the equation represents the adsorption of ammonia molecules at the sodium cation active sites of the zeolite, the second term corresponds to the calcium cation sites, and the third term, obtained from the extrapolation of the isotherm in the VMOT equation, expresses the adsorption amount at relative pressures up to the saturation pressure of ammonia.

Since the adsorption process follows an exponential equation, the second term of Equation 1 has almost no effect up to the relative pressure of P/P_s=0.0000377 (P=0.33 torr) at low saturation pressure, while the third term has almost no effect up to the relative pressure of P/Ps=0.03 (P=260 torr) at low saturation pressure. Figure 2 presents the experimentally obtained values of the adsorption isotherm of ammonia molecules on CaA (MSS-624) zeolite as a function of relative pressure in P/Ps coordinates, along with the isotherm recalculated based on the general equation of the micropore volume filling theory (VMOT). The isotherm corresponds to Type I classification according to Brunauer, indicating that the studied zeolite consists solely of micropores, where ammonia molecules are adsorbed within the micropores of the zeolite. The isotherm in P/P_s coordinates confirms the sorption mechanism derived from the isotherm presented in logarithmic coordinates (Figure 2).

At the initial stage, the equilibrium relative pressure $P/P_s=3{,}8\cdot10^{-5}$ (P=0.33 torr) increases rather slowly up to an adsorption amount of 4.4 mmol/g. This is due to the relatively strong interaction between the adsorbate and the zeolite. On the other hand, the adsorption amount of 4.4 mmol/g is four times greater than the amount of sodium cations in the zeolite (1.1 mmol/g). Thus, as explained in the logarithmic coordinate graph of the isotherm, ammonia molecules form a tetramer $4NH_3{:}Na^+$ ion-molecular complex with sodium cations in the zeolite, and the sorption process is completed at the sodium cations in the first coordination sphere of the zeolite. This complex corresponds to an equilibrium pressure of P=0.33 torr and 43% of the total adsorption.

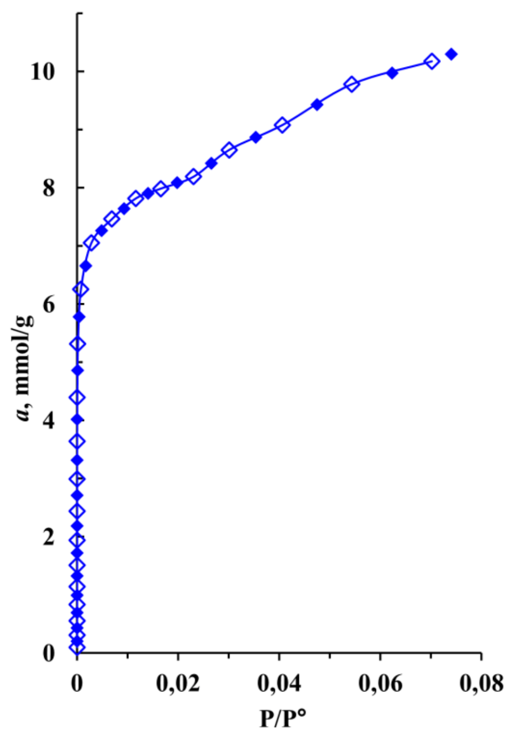

Figure 2. Adsorption isotherm of ammonia molecules on CaA (MSS-624) zeolite at 303 K in P/P_s coordinates. ◊–experimental data, ♦–values from the general equation of the micropore volume filling theory (VMOT)

With the increase in adsorption volume saturation, the next ammonia molecules are adsorbed on calcium cations. In forming the monomer $1NH_3:Ca^{2+}$ ion-molecular mechanism, the equilibrium relative pressure starts to increase significantly. When the monomer $1NH_3:Ca^{2+}$ mechanism is fully formed, the adsorption reaches 6.3 mmol/g, and the relative pressure increases up to $P/P_s=7.55\times10^{-3}$ (P=6.6 torr). The adsorption amount corresponding to this complex accounts for 62% of the total adsorption. The formation of the dimer $2NH_3:Ca^{2+}$ ion-molecular complex mechanism occurs with a sharp increase in equilibrium relative pressure at $P/P_s=0.023$ (P=201 torr), and at 8.2 mmol/g adsorption, the 2:1 ratio adsorbate/zeolite complex is fully formed.

The adsorption amount associated with this complex corresponds to 80% of the total adsorption. The small bend in the isotherm at 8.2 mmol/g adsorption also confirms the complete formation of the dimer ion-molecular complex of ammonia molecules with calcium cations in the zeolite, as well as the change in the amount of calcium cations, which are the second active center of the zeolite (1.9 mmol/g), in multiples.

The next ammonia molecules increase in adsorption at an equilibrium relative pressure from P/Ps=0.023 (P=201 torr) to $P/P_s=0.07$ (P=615 torr), forming the trimer $3NH_3:Ca^{2+}$ ion-molecular complex at 10.1 mmol/g adsorption. In general, the sorption process in this zeolite ends with the formation of the $7NH_3:Ca_5Na_3A$ (MSS-624) ion-molecular mechanism with metal cations in the zeolite.

In the Ca_5Na_3A (MSS-624) nanostructured zeolite, the coefficients in the equation of the mathematical apparatus of the isotherm were calculated based on the experimentally obtained adsorption isotherm values of ammonia molecules and the general formula of the Volume Micro Pore Theory (VMOT). It was determined that the adsorption isotherm varies proportionally and systematically with the amount of Na^+ and Ca^{2+} cations in the zeolite (Figure 2). It was proven based on the VMOT equation that in the SI and SII positions of the zeolite, sodium cations in the first coordination sphere form a tetramer $4NH_3:Na^+$, and calcium cations in the first coordination sphere form a trimer $3NH_3:Ca^{2+}$ ion-molecular complex.

Conclusion. The adsorption isotherm of ammonia molecules on the nanostructured zeolite Ca_5Na_3A (MSS-624) was studied, and the free energy values were calculated. It was determined that in the SI and SII positions of the zeolite, sodium cations form a tetrameric ion-molecular complex ($4NH_3:Na^+$) in the first coordination sphere, while calcium cations form a trimeric ion-molecular complex ($3NH_3:Ca^{2+}$) in the first coordination sphere. The adsorption amount coefficients obtained based on the volumetric micropore filling theory (VMOT) were found to be in full agreement with the experimentally observed adsorption mechanism. At a pressure of 0.33 torr, 43% of the total adsorption was observed, corresponding to the formation of a $4NH_3:Na^+$ tetrameric complex with sodium cations. At 6.6 torr, 61% of the adsorption was recorded, corresponding to the formation of a $1NH_3:Ca^{2+}$ monomeric complex. At 201 torr, 80% of the total adsorption took place, forming a $2NH_3:Ca^{2+}$ dimeric complex, while at 614 torr, the ammonia molecules formed a $3NH_3:Ca^{2+}$ trimeric ion-molecular complex.

References

1. Corma A., D.Kumar. Micro- and Meso-Porous Materials as Catalysts. In "New Trends in Material Chemistry"; 1997, vol. 498: pp.403-408.

2. J.V. Smith, "Zeolite Structure." Chemistry of Zeolites and Catalysis on Zeolites, Moscow, "Mir," 1980, pp. 11-14.

3. Ohman L., Ganemi B., Bjornbom E., Rahkamaa K., Keiski R., Paul J. "Catalyst preparation through ionexchange of zeolite Cu-, Ni-, Pd-, CuNi- and CuPdZSM-5". Mater. Chem. Phys. Vol. 73. 2002. P. 263- 267.

4. Liyan Q., Murashov V., White M.A. "Zeolite 4A: heat capacity and thermodynamic properties". Solid State Sciences; 2000, №2: pp.841-846.

5. Baerlocher C., McCusker L.B., Olson D.H. "Atlas of Zeolite Framework Types", 6th edn., Elsevier, Amsterdam, 2007: p.399.

6. 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

7. 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

8. 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

9. 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

10. 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

11. 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

12. 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, p.481-488.

13. Ergashev O.K., Kokharov M.Kh., Abdurakhmanov E.B. "Energy of carbon dioxide adsorption in CaA zeolite". Universum: chemistry and biology: scientific journal; 2019, 7(61). P. 23-26. https://7universum.com/ru/nature/archive/item/7548

14. Rakhmatkariyeva F.G., Koxxarov M.X., Bakhronov Kh.N. Isotherm Of Ammonia Adsorption In Zeolite CaA (M-22) //Scientific and Technical Journal Namangan Institute of Engineering and Technology Volume 8, Issue 4, 2023 y. pp.103-109.

15. Rakhmatkarieva F., Kokhkharov M., Bakhronov Kh., Differential heat and mechanism of ammonia adsorption on zeolite CaA (M-22) //International Journal of Advanced Research in Science, Engineering and Technology Vol. 10, Issue 11, 2023, pp.21258-21261.

16. Reymov A., Raxmatkarieva F., Koxxarov M., Bakhronov Kh., Isotherm of ammonia adsorption in zeolite CaA (M-34) //Science and Education in Karakalpakstan, 2024, №3/2, ISSN 2181-9203, pp.257-262.

17. Kokhkharov M., Rakhmatkarieva F., Bakhronov Kh., Rakhmatullaeva M, Absalyamova I., Karimov Y. Differential entropy and thermokinetics of ammonia molecule adsorption on CaA zeolite (M-22) //E3S Web of Conferences 563, 01024, ICESTE 2024.

18. Kokhkharov M., Rakhmatkarieva F., Bakhronov Kh., Akhmedova N., Rakhmatullaeva M., Karimov Y. Adsorption isotherm, differential heat, and sorption mechanism of ammonia on CaA zeolite //E3S Web of Conferences 587, 01017 Green Energy 2024.

19. Khokharov M.Kh., Akhmedov U.K., Rakhmatkarieva F.G., Abdurakhmonov E.B., "Energy of Carbon (IV) Oxide Adsorption on Ca4Na4A Zeolite." *Namangan Engineering-Technological Institute Scientific-Technical Journal*, 2020, 1(5): pp. 142-148.

20. Kokharov M.X., Axmedov U.K., Rakhmatkarieva F.G., Abdurakhmonov E.B. "Investigation of water sorption to Ca_5Na_3A zeolite at adsorption of micro calorimetric device". International Journal of Advanced Research in Science, Engineering and Technology; 2020, 5(7): pp.13939-13944.

21. Abdurakhmonov E.B., Rakhmatkarieva F.G., Yakubov Y.Y., Abdulhaev T.D., Khudaybergenov M.S., "Differential Heats of Adsorption of Benzene Vapors in LiLSX Zeolite." *Universum: Chemistry and Biology*, 2020, 6(72): pp. 60-63.

22. Abdurakhmonov E.B., Ergashev O.K., "Thermokinetics of Ammonia Adsorption in NaLSX Zeolite." *Universum: Chemistry and Biology*, 2020, 8(74): pp. 5-8.

23. Abdurakhmonov E.B., "Entropy of Benzene Adsorption in NaLSX Zeolite." *Universum: Chemistry and Biology*, 2020, 8(74): pp. 12-15.

24. 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.

25. 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

26. 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.

27. 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.

27. Abdurakhmonov E.B., "Mechanisms of Adsorption of Polar, Nonpolar, and Quadrupolar Molecules in Synthetic Zeolites of the FAU and 5A Types." Abstract of the Doctor of Chemical Sciences (DSc) Dissertation, Tashkent, 2020, 63 pages.

28. Rakhmatkariev G.U., Isirikyan A.A., "Complete Description of the Adsorption Isotherm Using the Equations of the Theory of Volume Filling of Micropores." *Izv. AN SSSR, Ser. Khim.*, 1988, No. 11, pp. 2644-2645.

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