DIFFERENTIAL ENTROPY OF ADSORPTION In Ca5Na3 SEOLITE

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Abstract

For the first time the main energy characteristics of ammonia adsorption in zeolite Ca5Na3A (MSS-624) were determined by adsorption-microcalorimetric method, differential values of free energy and entropy of adsorption were calculated, as well as the correlation between adsorption-energy characteristics and crystallochemical structure of adsorbent was found and the detailed molecular mechanism of formation of ion-molecular clusters of ammonia with cations in zeolite in the whole region of filling of nano-structured pore space of adsorbent was revealed. The stepwise character of the entropy of ammonia adsorption is revealed. The extended low entropy region correlates with the number of sodium and calcium cations in the zeolite structure. The average molar integral entropy of ammonia adsorption on zeolite Ca5Na3A (MSS-624) was found to be -61 J/mol□ K and indicates that in the zeolite the mobility of ammonia molecules is lower than the liquid phase and close to the mobility of the solid phase, leading to a strong inhibition of the mobility of adsorption on ammonia cations.

Keywords: zeolite, adsorption, entropy, isotherm, temperature, microcalorimeter, ammonia.

The application of type A zeolites is extremely wide. They are used as dehumidifiers, for purification of gases from harmful impurities, for separation of substances.

The aluminosilicate skeleton of type A zeolites consists of cubo-octahedral structural units. Each cubo-octahedron is built of 24 elementary structural units - AlO4 and SiO4 tetrahedrons, and the adjacent tetrahedrons have common oxygen ions. Each cubo-octahedron contains 24 ions (Al+Si) bound by 36 oxygen ions. Each cubo-octahedron has six four- membered and eight six-membered windows [1-4]

The tetrahedral Al in the zeolite framework makes the presence of cations in amounts strictly equivalent to the Al content obligatory. This circumstance is connected with the necessity to compensate the excess electron charge in tetrahedral Al4/2 groups, in which Al, having only three valence s, p-electrons of its own, forms equivalent pairwise electronic bonds with each of the four-surrounding oxygen at the expense of attracting one additional electron. In this connection, unlike electroneutral SiO_2 frameworks, (Al, Si) O_2 frameworks will carry excessive negative charges, the number of which will correspond to the number of (Al, O)-tetrahedrons in them. For example, in zeolites containing alkaline and alkaline-earth cations, the amount of Me_2O+MeO is such that the ratio (Me_2O+MeO): Al_2O_3=1 [5].

The difference in the structure of aluminosilicate skeletons of zeolites A and X lies in the different spatial arrangement of cubo-octahedral structural units [6-9]. In type A zeolite, the cubo-octahedrons form a simple cubic lattice [5]. Each cubo-octahedron is connected to neighbouring six four-membered oxygen bridges. The spaces between the eight cubo-octahedrons are large cavities.

The studies carried out in the world are mainly aimed at studying the structure of zeolites and the arrangement of cations in them. There are few data on the study of the mechanism and thermodynamic functions of the adsorption process of ammonia molecules.

There are a large number of data on adsorption in LTA-type zeolites, which have been obtained by various physicochemical methods of investigation. However, the data obtained by adsorption-calorimetric method are few, which puts on the agenda the task of further detailed study of adsorption properties of zeolites of Ca_5Na_3A (MSS-624) type and obtaining the main thermodynamic characteristics of these systems.

In determining the differential heat of adsorption, two methods are the main ones: calorimetric and isosteric.

The adsorption-calorimetric method used in this work makes it possible to obtain highly accurate molar thermodynamic characteristics, as well as to reveal detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. A modified DAK- 1-1A thermally conductive microcalorimeter with high accuracy and stability was used as a calorimeter. We used a BARATRON B627 membrane manometer to measure equilibrium pressures.

In this work, the isotherm and entropy of ammonia adsorption in zeolite Ca_5Na_3A (MSS-624) at 303 K have been studied. The unit cell composition of this zeolite is represented by $Ca_5Na_3[(AlO_2)_{12}(SiO_2)_{12}]$) and consists of SI, SII and SIII positions. According to the chemical composition, the amount of calcium cations per 1 g of zeolite is 2.95 mmol/g, and the amount of sodium cations is 1.77 mmol/g.

At adsorption of H_2O by NaA zeolite, three distinctly pronounced regions of high (100 kJ/mol) adsorption heats, a transition region and a region of relatively low (60 kJ/mol) adsorption heats are observed on the isotherm. It is assumed that the first two regions reflect the interaction of

H2O molecules with cations in SII and SIII positions, and the third region corresponds to the adsorption of H2O on cations in SI positions [10]. In the case of adsorption of NH3 in zeolite NaA, as in the case of H2O, the first molecules of NH3 interact with Na+ cations in positions SII and SIII, and when there is one molecule of NH3 for each cation, the interaction with Na+ cations in positions SI begins [11].

Studies of adsorption processes of polar, nonpolar, quadrupole and aromatic molecules are carried out in the world to determine the mechanism and thermodynamic functions, including the following priority directions: synthesis of microporous adsorbents; improvement of their composition; synthesis of synthetic zeolites and determination of their adsorption properties; enhancement of selectivity of their absorption properties due to the exchange of cations in the composition of zeolites of A, X, Y and LSX types [12-15].

Dependence of molar differential entropy of ammonia adsorption (□ S) on zeolite Ca5Na3A (MSS-624) on filling is presented in Fig.1 (entropy of liquid ammonia is taken as zero). The entropy of ammonia adsorption in zeolite Ca5Na3A (MSS-624) differs from the entropy of water and carbon dioxide adsorption in zeolites CaA (M-22), NaA and Ca4Na4A [14-15], which indicates the different nature and mechanism of ammonia, water and carbon dioxide adsorption in these zeolites. In general, it is located below the entropy of liquid ammonia, indicating that the mobility of ammonia molecules in the zeolite is limited.

The curve has a stepped appearance, which can be divided into 8 fragments. The first 4 fragments of 1.77 mmol/g, 1 fragment of 2.89 mmol/g and 1 fragment of 2 mmol/g of which the curve passes above the entropy level of liquid ammonia

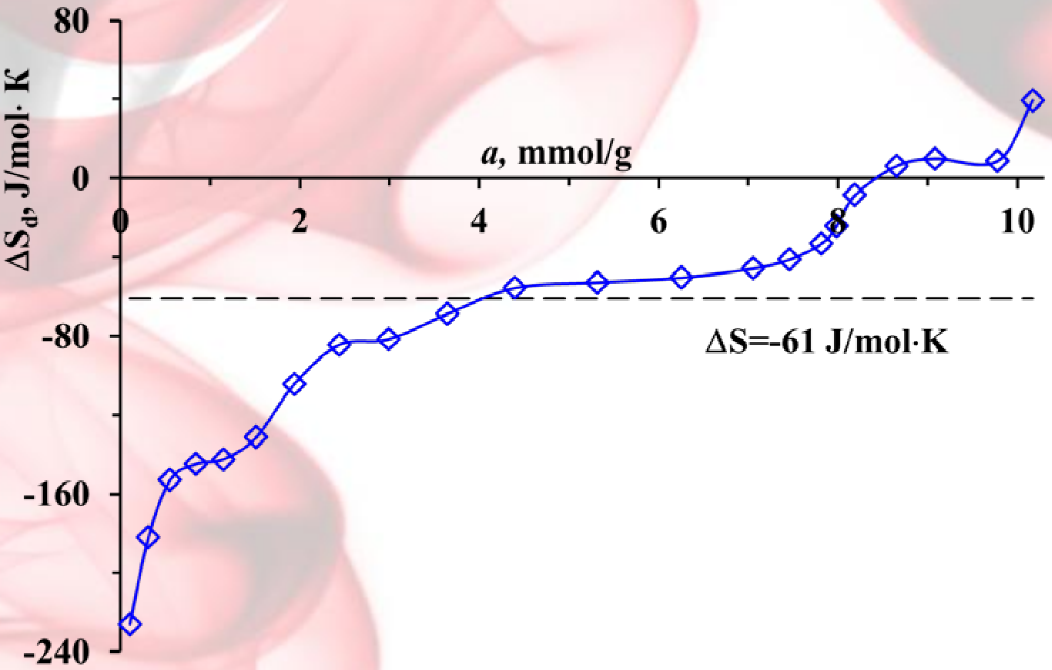

Figure 1. Differential entropy of ammonia adsorption in Ca5Na3A zeolite (MSS-624). The horizontal dashed line is the mean molar integral entropy.

The entropy of ammonia adsorption in Ca5Na3A zeolite (MSS-624) starts from -226 J/mol.K at 1.77 mmol/g and increases to -120 J/mol□K. According to the chemical composition of zeolite, the adsorption value of 1.77 mmol/g corresponds to the amount of sodium cations, that is, ammonia molecules adsorb on sodium cations in zeolite and form 1NH3:Na+ ion-molecular complex in the first coordination sphere. Then, at an adsorption value of □3.5 mmol/g, the entropy gradually increases to -75 J/mol□K and a 2NH3:Na+ dimeric complex is formed. When another complex is formed with each sodium cation, the ammonia molecules first increase to -53 J/mol□K at an adsorption of 5.3 mmol/g forming a 3NH3:Na trimeric complex+ . The entropy first increases and then decreases due to the release of additional heat under the action of mutual Wan-der-Waals forces of ammonia molecules during the formation of the complete tetrameric complex and limitation of the mobility of ammonia molecules as a result of this force [15]. This situation is also manifested in the formation of tetrameric complex 4NH3:Na+, i.e. entropy increases to -46 J/mol□K at adsorption of 7 mmol/g forming 4NH3:Na+ ion-molecular complex.

The entropy change as a function of adsorption value during the subsequent sorption of ammonia molecules does not correspond to the value of 1.77 mmol/g sodium in zeolite. It means that the process of sorption by ion-molecular mechanism of ammonia and sodium in the first coordination sphere is completed. But it can be seen from the graph that the entropy change as a function of adsorption value corresponds to □3 mmol/g (Fig. 1). This value is equal to 2.95 mmol/g of calcium cations in the zeolite. Consequently, subsequent ammonia molecules adsorb on calcium cations. When the adsorbate/cationic monomer 1NH3:Ca2+ is formed in the first coordination sphere of ammonia molecules with calcium cations, the entropy increases to -8 J/mol K at 8 mmol/g adsorption. At □10 mmol/g, the entropy increases to 10 J/mol K, i.e., above the entropy value of liquid ammonia. Adsorption on calcium cations is completed by a monomeric 1NH3:Ca2+ ion-molecular mechanism. The molar average integral entropy of adsorption is -61 J/mol K, indicating the retarded state of ammonia molecules in the zeolite

The adsorption entropy of adsorption of ammonia molecules in nanostructured zeolite Ca5Na3A (MSS-624) was obtained as a result of adsorption-calorimetric study. A stepwise change in the differential entropy of adsorption as a function of the amount of sodium and calcium cations in the zeolite was found. Ammonia molecules initially form tetrameric ion-molecular complexes 4NH3:Na+ in the first coordination sphere with sodium cations and monomeric ion-molecular complexes 1NH3:Ca2+ with calcium cations. The average molar integral entropy of adsorption is -61 J/mol□K, which indicates the loss of mobility of adsorbed ammonia molecules in the pores of zeolite Ca5Na3A (MSS-624.

REFERENCES

1. J.Sun, C.Bonneau, A.Cantin, A.Corma, M.J.Diaz-Cabañas, M.Moliner, D.Zhang, M.Li and X.Zou Nature, 458, 1154-1157 (2009)
2. A.B.Pinar, L.Gomez-Hortiguela, J.Perez-Pariente Cooperative Structure Directing Role of the Cage-Forming Tetramethylammonium Cation and the Bulkier Benzylmethylpyrrolidinium in the Synthesis of Zeolite Ferrierite //Chemistry of Materials 2007 19 (23), 5617-5626
3. A.S.Kovo. Development of Zeolite X and Y from Ahoko Nigerian Kaolin //Chemical Engineering: First Year Ph.D Report Manchester The University of Manchester. 2008. - P. 119-125.
4. Q.Miao. Z.Zhou, J.Yang, J.Lu, S.Yan, J.Wang. Synthesis of NaA zeolite from kaolin source //Chem. Eng. China 2009. - No 3(1). - P. 8-11.
5. M.L.Pavlova, O.S.Travkinab, R.A.Basimovaa, I.N.Pavlovab, B.I.Kutepovb. Binder-Free Syntheses of High-Performance Zeolites A and X from Kaolin //Petroleum Chemistry 2009. - Vol. 49. - No. 1. - P. 36-41.
6. X.Li et al. Zeolite Y adsorbents with high vapor uptake capacity and robust cycling stability for potential applications in advanced adsorption heat pumps. Microporous and Mesoporous Materials 201, P.151-159 (2015).
7. J.Rouquerol, F.Rouquerol, P.Llewellyn, G.Maurin, K.S.Sing Adsorption by powders and porous solids: principles, methodology and applications. (Academic press, 2013).
8. M.B. Desta, J. Thermodyn. Batch sorption experiments: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto Teff straw (Eragrostis tef) agricultural waste,. P.375830 (2013) 6, http://dx.doi.org/10.1155/2013/375830.
9. H.Blank, M.Bulow, G.Finger. NaA- Zeolith adsorbiert n-geptan. Z.Chem.,-1974, V. 14, -№.2., -P.76-77.
10. Т.Р.Бруева, А.Л. Клячко-Гурвич Теплота и кинетика адсорбции аммиака на цеолитах //Шестая всесоюзн. конф. по калориметрии. Тбилиси, Мецниереба, -1973, -С.186.
11. V.Smil. Energy Transitions: Global and National Perspectives; 2017.
12. A.Álvarez, A.Bansode, A.Urakawa, A.V.Bavykina, T. A.Wezendonk, M.Makkee, J.Gascon, F.Kapteijn. Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed Carbon Dioxide Hydrogenation Processes. Chem. Rev. 2017, 117 (14), P.9804-9838.
13. Ф.Г.Рахматкариева, Г.У.Рахматкариев Ион-молекулярные комплексы в наноструктурированных цеолитах NaA и NaA(NaBO2) //Узбекский химический журнал, 2016, №4. - С.3-9.

14. M.H.Kokharov, U.K.Axmedov, F.G.Rakhmatkarieva, E.B.Abdurakhmonov Investigation of water sorption to Ca5Na3A zeolite at adsorption of micro calorimetric device //International Journal of Advanced Research in Science, Engineering and Technology Vol. 7, Issue 5, May 2020 y. P. 13939- 13944.
15. F.Rakhmatkarieva, M.Kokhkharov, Kh.Bakhronov Adsorption of Ammonia on CaA (M-22) Zeolite Differential Heat and Mechanism //International Journal of AdvancedResearch in Science, Engineering and Technology Vol. 10, Issue 11, November 2023, -PP. 21258-21261