ISSN 2181-8622

Manufacturing technology problems

Scientific and Technical Journal Namangan Institute of Engineering and Technology

INDEX COPERNICUS INTERNATIONAL

Volume 9
Issue 4
2024

Google Scholar Crossref doi SLIB.UZ Scientific library of Uzbekistan

UDC: **541.183:536.658**

WATER VAPOR ADSORPTION ISOTHERM IN ZEOLITES REGENERATED BY MICROWAVE THERMOXIDATION METHOD

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Abstract: The research work carried out experimental work on the regeneration of synthetic zeolites of type A. Synthetic zeolites used in industry for drying and cleaning natural gas were regenerated by thermal and thermooxidation methods. The structure, adsorption capacity and chemical composition of the regenerated zeolites were studied. Work was carried out to improve the process by accelerating the regeneration by the thermooxidation method using microwaves.

Keywords: regeneration, synthetic zeolite, CaA, NaA, NaX, thermal oxidation, microwavesб adsorption calorimeter.

Introduction. Molecular sieves (zeolites) of the CaA, NaA and especially NaX brands are widely used as adsorbents for drying and purifying high-sulfur natural and petroleum gases. Their adsorption capacity largely depends on the content of H_2O, CO_2 and higher hydrocarbons in gases, operating conditions and the degree of purification and ranges from 2 to 18%. The presence of heavy hydrocarbon vapors in the gas has a significant effect on the capacity of zeolites for sulfur compounds.

Materials and methods. In the research work, we used the thermal and thermooxidation method to process zeolite samples obtained from gas industry waste, NaA and CaA zeolites, which had lost their adsorption properties, at a temperature of up to 723 K for 2-3 hours. The released gaseous substances were extracted using a vacuum pump. Changes in the adsorption capacities of the samples over time were determined by the microcalorimetric method and compared with the above data.

In the second method, the effect of microwaves on heated zeolite samples was studied. When the ampoule containing the zeolite sample reached a temperature of 323-373 K, radiation was applied using a 915 MHz magnetron. The observed physicochemical changes will serve as the basis for theoretical and practical studies of the mechanisms of the effect of microwaves on adsorbates.

Results. Adsorption methods are based on the selective absorption (adsorption) of sulfur compounds by solid sorbents. As a rule, adsorption is carried out at a temperature of 293–323 K and elevated pressure, and regeneration (desorption) of the adsorbent saturated with sulfur compounds is carried out at low pressure and a temperature of 373-623 K. For regeneration, any of the inert gases, low-sulfur natural or petroleum gas, water vapor, etc. are passed through the adsorbent layer [1–3].

Molecular sieves (zeolites) of the CaA, NaA and especially NaX brands are widely used as adsorbents for drying and purifying high-sulfur natural and petroleum gases. Their adsorption capacity largely depends on the content of H_2O, CO_2 and higher hydrocarbons in gases, operating conditions and the degree of purification and ranges from 2 to 18%. The presence of heavy hydrocarbon vapors in the gas has a significant effect on the capacity of zeolites for sulfur compounds. According to the degree of sorption on zeolites, the compounds that make up natural gas can be arranged in the following order: H_2O>RSH>H_2S>COS>CO_2.

The main problem with adsorption purification of gas on zeolites from hydrogen sulfide in the presence of CO_2 is that during the adsorption of CO_2 and H_2S, carbon oxide disulfide (COS) is formed according to the reaction: $CO_2 + H_2S = COS + H_2O$.

Although the equilibrium constant of this reaction is small and amounts to $6.6 \cdot 10^{-6}$ at 298 K, however, the almost complete removal of H_2O vapors in the frontal layer of the zeolite shifts the equilibrium to the right, and this leads to the formation of significant concentrations of COS. Zeolite regeneration is carried out with nitrogen, low-sulfur natural or petroleum gas, and the content of sulfur substances in the regeneration gases (regenerates) increases by 5-10 times compared to the original. In addition to coals and zeolites, aluminum oxide, bauxite, aluminosilicates, etc. are also used in the purification process. The advantage of adsorption methods is the possibility of carrying out the process at low temperatures, as well as fine purification of gases not only from hydrogen sulfide, mercaptans, organic sulfides, but also from such substances that are difficult to remove by other methods as thiophene and its derivatives. This method also has a number of significant disadvantages. Almost all gases contain a certain amount of H_2O, CO_2, higher hydrocarbon vapors, which are well adsorbed by coals and zeolites, which reduces the sulfur capacity of adsorbents. The periodic cleaning process requires the installation of several parallel operating columns: some absorb sulfur substances (adsorption stage), and others regenerate adsorbents. [11–13].

In the thermal oxidation process, a mixture of filtered and dried air and nitrogen in a ratio of 1:4 was used. As a result of using this method for CaA, the regeneration process, which lasts a relatively long time, was shortened and the active desorption temperature was reached quickly. The time spent on the process was on average 1.5-2 hours, and the total mass change was 8.5%. At the same time, the separation of relatively light fractions up to 573 K was 7.2%. The process reached 723 K in 2 hours, and active thermal oxidation lasted 1.5 hours.

The adsorption isotherm, differential heat, entropy and thermokinetics of water vapor on regenerated NaX and CaA zeolites were studied. [4–10].

In carrying out the process of determining the full thermodynamic properties of the adsorption of H_2O vapor and CO_2 gases on regenerated zeolites, a system consisting of a universal high-vacuum adsorption device and a Tian-Calve, DAK-1-1 type differential microcalorimeter connected to it was used to measure the differential heats and isotherms of adsorption by the adsorption calorimetric method.

Figure 1 shows the water adsorption isotherm (ln) for water adsorption on CaA zeolite at a temperature of 303 K at a relative pressure of ~10^{-6} p/p^0 (p^0 is the saturated water vapor pressure, where p^0 (303K) = 31.8 mm.Hg.). The adsorption amount is expressed in mmol/g. The adsorption isotherm was studied in three parts. In the first part, the adsorption isotherm of water molecules on CaA zeolite initially starts at -16.3 and the adsorption amount is ~0.5 mmol/g. This indicates that one water molecule is adsorbed at every two e.g. The isotherm rises steeply until it reaches -10.76 and the adsorption reaches 4.79 mmol/g. In the second stage, the isotherm partially bends towards the adsorption axis again from -10.40 to -8.30, where the adsorption amount is 6.58 mmol/g. Until the adsorption reaches 6.23 mmol/g., the isotherm rises steeply from -8.30 to -5.7. In the third stage, with the adsorption of the next two water molecules, the isotherm sharply bends towards the ordinate axis, and the isotherm increases from -5.7 to -2.8, resulting in 11.37 mmol/g. With the partial bend of the isotherm, two water molecules are adsorbed, and the equilibrium isotherm index is -1.5. Then, approaching the saturation pressure of water vapor, i.e. up to 29 mm.cm., 4.19 mmol/g of water molecules are adsorbed, resulting in a total of 16.7 Mmol/g in each cell. The process ends with the formation of.

Water adsorption on CaA zeolite was expressed by the TMVF (the theory of micropore volumetric fulling) equation;

$$a = 6{,}9\exp[A/32{,}09)^6]+3{,}62\exp[A/17.97)^8]+5.8\exp[A/2.87)^1] \quad (1)$$

$$a=6{,}19\exp[-A/28{,}25)^3]+3{,}38\exp[-A/10{,}4)^6]+4{,}68\exp[-A/4{,}88)^1] \quad (2)$$

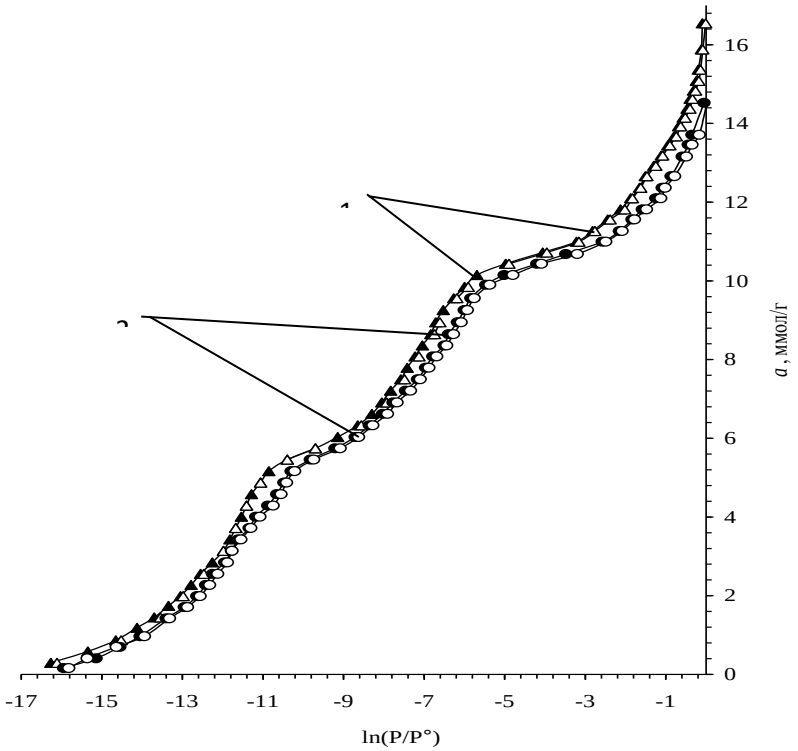

Fig. 1. Water adsorption isotherm on CaA zeolite at 303K. (1)- CaA zeolite; (2)- regenerated CaA zeolite

Here, a is the number of water molecules adsorbed in the micropores, i.e. mmol/g, A = RTln (P°/P – 1 mmol/g. The work done to transfer the vapor from the surface (pressure P°) to the equilibrium gas phase (pressure P).

Figure 2 shows the differential heat of adsorption (Qd) of water on CaA zeolite at 303 K. The long lines are the heat of condensation of water at 303 K (ΔHv = 43.5 kJ/mol). Due to the small size of water molecules, they directly enter the zeolite voids and, as a result of their interaction with the oxygen atoms that bind silicon and aluminum during entry, the heat of adsorption is high. It is observed that water molecules are in a mobile state until they are distributed in the cations in the zeolite micropores.

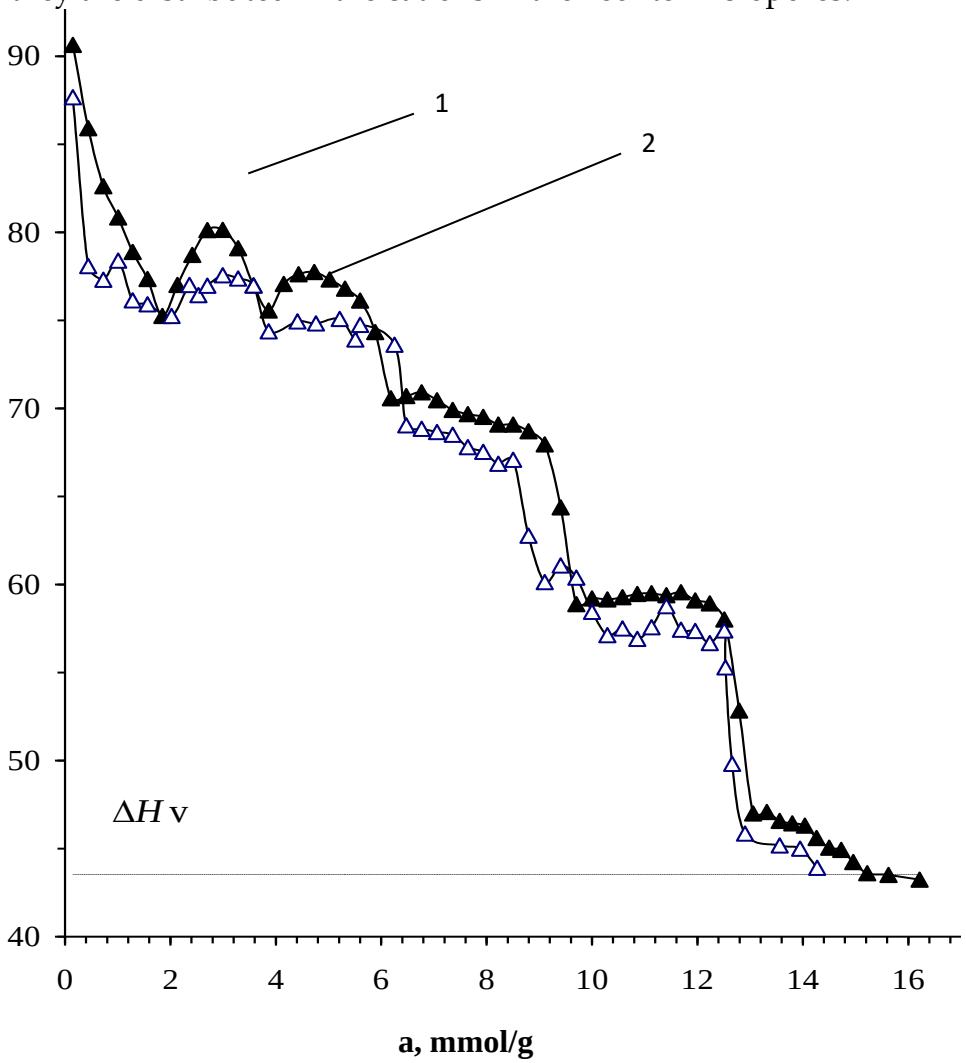

Fig. 2. Differential heat of water adsorption on CaA zeolite at 303K. Horizontal dashed line - heat of condensation (1)- CaA zeolite; (2)-regenerated CaA zeolite

The differential heat of adsorption of water on CaA zeolite (starting at 0.14 mmol/g) starts at ~91 kJ/mol and reaches ~0.59 mmol/g, reaching Qd=84 kJ/mol, 1.79 mmol/g. (Qd=~75kJ/mol). The heat of adsorption of the next two molecules (2.99x1.67=5 H2O/e.y.) increases from 75 kJ/mol to 80 kJ/mol, and when 2.14 mmol/g. is formed, the differential heat decreases again to 75 kJ/mol. Up to 6 mmol/g. adsorption, that is, when the next

2.39x1.67=4 water molecules are adsorbed, the heat first increases partially, then decreases to 70 kJ/mol. When 9.58x1.67=16 water molecules are adsorbed, the heat decreases to 59 kJ/mol, forming a step.

Discussion. Until it reaches 12.57 mmol/g. the differential heat of adsorption proceeds almost unchanged. When 13.17 mmol/g is formed, the heat increases again to 47 kJ/mol, and the heat of condensation is equal to the heat of adsorption of the next 2.99x1.67=5 water molecules, i.e., a total of 25 Mmol/g is formed on the active centers of the zeolite. Until the complete adsorption reaches 16.2 mmol/g, the heat is formed by the adsorbate-adsorbate interaction during the adsorption of water molecules.

In the lattice of type A zeolites, not all metal cations are located in the same position. The SI vacancy is located in the center of the six-membered oxygen ring, i.e., the Ca^{2+}I cations are located in the center of this six-membered oxygen ring and almost fill the entire volume. The SII center, where the Ca^{2+} II cations are located in the plane of the eight-membered oxygen rings, slightly displaced from the center. The SIII center, where the Ca^{2+} III cations are located opposite the four-membered rings and within the α-spaces, with one Ca^{2+} cation located approximately 1.7 Å from the plane of the ring. The stepwise appearance of the heat of adsorption is considered to be the stoichiometric interaction of the water molecule with the coordination unsaturated Ca^{2+} cations. A total of 16.2 mmol/g of water molecules are adsorbed on the CaA zeolite, and 14.4 mmol/g of water molecules on the regenerated CaA zeolite.

The graph expressed in the TMVF equation also corresponds to the isotherm obtained as a result of the experiment. It is also clearly seen that the isotherm changes linearly during the adsorption of the first H_2O molecule, and also increases linearly during the adsorption of the next 4.19*1.67=7 water molecules, and it coincides at each stage.

Conclusion. In the lattice of type A zeolites, not all metal cations are located in the same position. The SI vacancy is located in the center of the six-membered oxygen ring, i.e., the Ca^{2+}I cations are located in the center of this six-membered oxygen ring and almost fill the entire volume. The SII center, where the Ca^{2+} II cations are located in the plane of the eight-membered oxygen rings, slightly displaced from the center. The SIII center, where the Ca^{2+} III cations are located opposite the four-membered rings and within the α-spaces, with one Ca^{2+} cation located approximately 1.7 Å from the plane of the ring. The stepwise appearance of the heat of adsorption is considered to be the stoichiometric interaction of the water molecule with the coordination unsaturated Ca^{2+} cations. A total of 16.2 mmol/g of water molecules are adsorbed on the CaA zeolite, and 14.4 mmol/g of water molecules on the regenerated CaA zeolite.

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