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ISOTHERM OF AMMONIA ADSORPTION IN ZEOLITE CaA (M-22)

Koxxarov M.[1],
Sobirzhonova S.[1],
Asfandiyorov M.[2]
[1]Namangan Institute of Engineering and Technology Namangan, Uzbekistan
Email: mirzo199008@mail.ru

[2]Tashkent University of Information Technologies named after Muhammad al-Khwarizmi

Abstract

The article presents experimentally obtained values of the adsorption isotherm of ammonia molecules in synthetic zeolite CaA (M-22) at a temperature of 303 K. Isotherm values were measured using an improved microcalorimeter connected to a universal high vacuum apparatus. The differential values of the free energy were calculated from the equilibrium values of the pressure. In CaA (M-22) zeolite, a regular relationship between the amount of adsorption and energy properties of ammonia molecules, as well as the sorption mechanism from the initial area of adsorption to the area of condensation heat of ammonia and the regularity of ammonia molecules filling the volume of zeolite were determined. Under experimental conditions, the adsorption capacity of this zeolite for ammonia was found to be 10.5 mmol/g in 1 g of zeolite. It was determined that 40% of the total adsorption is sorbed up to the equilibrium pressure of 1 torr, 50% up to 6 torr pressure, 60% up to 24 torr pressure, 65% up to 50 torr pressure and 100% at 467 torr pressure.

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

The adsorption isotherm was measured with high accuracy (enthalpy 0.2 µJ, small values of pressure with an accuracy of 10^{-5} torr) and stability using a system consisting of a Tiana-Calve type DAK-1-1A differential automated microcalorimeter connected to a universal high-vacuum device. The adsorption-calorimetric method used in the research allows obtaining molar thermodynamic characteristics, as well as revealing the detailed mechanisms of adsorbent-adsorbate and adsorbate-adsorbate sorption processes. Adsorption measurements and dosage of adsorbate were performed using a high-vacuum adsorption device.

The device allows dosing of adsorbate by gas-volume and volume-liquid methods. B627 diaphragm baratron was used to measure the equilibrium pressure up to $10^{-5} \div 0{,}8$ torr, U manometer was used to measure the pressures at $R>0.8$ torr. The adsorption-calorimetric method allows to study nano-, micro-, mesostructured adsorbents and their surface-active surfaces, to reveal in detail the main thermodynamic properties and mechanisms of adsorption processes in which adsorbents occur.

In order to obtain environmentally friendly gas from natural gases, the demand for drying them from water vapor, cleaning them from gases such as hydrogen sulfide, and preventing environmental problems caused by the release of greenhouse gases, including carbon (IV) oxide into the atmosphere, is increasing year by year. For this purpose, synthetically produced zeolites are widely used to avoid the above-mentioned problems. It is important to achieve scientific and practical innovations based on the results of the research conducted on the synthesis of zeolites with high adsorption and catalytic properties, increasing the level of their selectivity.

Aluminosilicate zeolites with a porous crystal framework structure. The frameworks of zeolites are composed of interconnected tetrahedral [SiO_4] and [AlO_4], the ends of which are connected by oxygen atoms. The unique arrangement of aluminum atoms in the structure is one of the properties of aluminosilicates. Al and Si atoms are arranged in the tetrahedral coordination position in all aluminosilicates with respect to oxygen and are isomorphically substituted for silicon in the general silicon-oxygen framework. The negative charge of the tetrahedron is neutralized by various alkaline or alkaline earth positive cations located in the zeolite voids. The composition of all synthetic zeolites can be described by the following chemical formula:

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

where n-metal cation valency, x-SiO_2/Al_2O_3 molar ratio, y-number of moles of water.

CaA (M-22), CaA (M-34), Ca_5Na_3A (MISS 624) and Ca_4Na_4A (Horst 50/50) zeolites are considered to be the main active centers of Ca^{2+} and Na^+ cations in A-type zeolites. Also, since the amount of cations is in different proportions, adsorbate plays an important role in the amount of sorption of molecules. By determining the main thermodynamic characteristics of the adsorption of test molecules such as carbon dioxide, benzene, water and ammonia, the amount, nature and strength of energetically active centers in the same type of crystallographic positions are determined [1-10].

Step change of adsorption enthalpy of water and carbon IV oxide molecules in zeolites of type A (M-22, M-34, MISS-624, Horst 50/50) with alkaline earth and alkaline earth metal cations is the result of stoichiometric interaction with Ca^{2+} and Na^+ cations. For example, water molecules in CaA_1, CaA_2 and $CaNaA_1$ zeolites contain $22H_2O$/e.c., $28H_2O$/e.c. and $30H_2O$/e.c. respectively, $7CO_2$/e.c., $6CO_2$/e.c., $8CO_2$/e.c. and $9CO_2$/e.c. respectively, in CaA_1, CaA_2, $CaNaA_1$ and $CaNaA_2$ zeolites of carbon IV oxide molecules. A stepwise change in the formation of ion-molecular complexes has been determined [1-3, 10].

This article presents the results of adsorption isotherm, as well as the mechanism of adsorption, obtained by the method of adsorption-calorimetric experiment on synthetic zeolite of ammonia CaA (M-22). In the adsorption study, the adsorption of ammonia on CaA (M-22) zeolite at 303 K was studied and the adsorption isotherm was fully analyzed. The unit cell composition of this zeolite is $Ca_{2,975}Na_{1,194}(SiO_2)_{12}(AlO_2)_{12})$. Based on its chemical composition, the amount of calcium cations in 1 g of zeolite is 1.89 mmol/g and the amount of sodium cations is 0.76 mmol/g.

The isotherm of ammonia adsorption on CaA (M-22) zeolite in logarithmic coordinates is presented in Fig. 1. At small saturations of the adsorption volume, the equilibrium relative pressure at the adsorption amount of 0.05 mmol/g is equal to $P/P_s=8{,}11\cdot10^{-7}$ (R=0.00674 torr). In this case, P_s =8750 torr represents the saturation pressure of ammonia at a temperature of 303 K. Due to the high relative pressure of ammonia, the experiment was carried out up to 467 torr. The adsorption isotherm was brought to the adsorption amount of 10.35 mmol/g at a relative pressure of P/P_s=0.0534 (or R=467 torr).

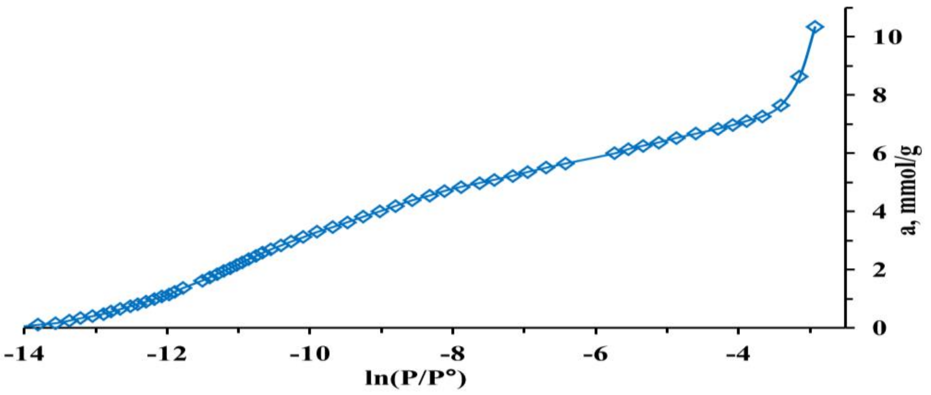

Figure 1. Adsorption isotherm of ammonia at 303 K on CaA (M-22) zeolite.

The adsorption isotherm shows that cations in the zeolite matrix are in a strong ion-molecular complex bond with ammonia molecules in the initial region. The isotherm initially moves almost linearly towards the abscissa axis at the adsorption amount of ~0.76 mmol/g up to $P/P_s=4\cdot10^{-6}$ (R=0.04 torr).

Based on the chemical composition of zeolite, the amount of sodium cations is equal to 0.76 mmol/g, that is, at the adsorption amount of ~0.8 mmol/g, ammonia molecules form a $1NH_3:Na^+$ monomer ion-molecular complex with sodium cations in zeolite. The isotherm changes linearly with a partial tilt to $P/P_s=1\cdot10^{-5}$ (R=0.088 torr) ~1.52 mmol/g adsorption of $2NH_3:Na^+$ dimer, 2.3 mmol/g adsorption amount and $P/P_s=1.76\cdot10^{-4}$ (R=0.154 torr) at a relative pressure of $3NH_3:Na^+$ trimer, 3 mmol/g adsorption amount and $P/P_s=3.5\cdot10^{-4}$ (R=0.34 torr) at a relative pressure of $4NH_3:Na^+$ tetramer ion-molecular complex is formed. The subsequent adsorption isotherm graph of ammonia molecules changes regardless of the amount of sodium cations in the zeolite, which means that the adsorption process in the first coordination sphere with sodium cations of ammonia molecules is completed. This is also confirmed by the relative increase in the equilibrium pressure after the formation of the $4NH_3:Na^+$ tetramer ion-molecular complex.

The regular change of the isotherm in accordance with the zeolite active centers corresponds to the amount of calcium cations, the second active center in its content, ~1,9 mmol/g, that is, ammonia molecules begin to adsorb on Ca^{2+} cations. Value of relative pressure $P/P_s=6\cdot10^{-4}$ (R=6 torr) and 5 mmmol/g adsorption of $1NH_3:Ca^{2+}$ monomer, amount of adsorption 6.8 mmol/g and relative pressure $P/P_s=0.0137$ (R=120 torr) $2NH_3:Ca^{2+}$ dimer forms ion-molecular complexes.

At the adsorption enthalpy obtained in the experiment, after the adsorption amount of ~7 mmol/g, the enthalpy decreases to the heat of condensation of ammonia. But the change in differential enthalpy and entropy (above the entropy of liquid ammonia) changes in accordance with the amount of calcium cations in the zeolite and increases sharply, that is, ammonia molecules in the second coordination sphere of calcium cations adsorbate-adsorbate (ammonia-ammonia) with an adsorption amount of 8.7 mmol/g and $P/P_s=0,05$ (R=380 torr) at a relative pressure of $Ca^{2+}:2NH_3:NH_3$ complex, the next 1.64 mmol/g ammonia molecules are also 10.52 mmol/g adsorption in the second coordination sphere and

P/P_s=0,054 (R=467 torr) at a relative pressure of the sorption process ends by forming a $Ca^{2+}:2NH_3:2NH_3$ complex.

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