E- Global Congress
Hosted online from Dubai, U. A. E., E - Conference.
Date: 28th February 2025
Website: https://eglobalcongress.com/index.php/egc
ISSN (E): 2836-3612

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

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Abstract

This article presents the experimentally obtained values of the adsorption isotherm of ammonia molecules on synthetic zeolite CaA (MSS-622) at a temperature of 303 K. The isotherm values were measured using a microcalorimeter connected to a universal high-vacuum device. The differential values of free energy were calculated based on equilibrium pressure values. A regular relationship between the adsorption amount and the energetic properties of ammonia molecules on CaA (MSS-622) zeolite was identified. Additionally, the sorption mechanism and the law of ammonia molecules filling the zeolite volume were determined, ranging from the initial adsorption region to the condensation heat region of ammonia. 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 established that 44% of total adsorption occurs at an equilibrium pressure of 0.33 mmHg, 53% at 1.4 mmHg, 71% at 25 mmHg, 80% at 200 mmHg, 98% at 476 mmHg, and 100% at 614 mmHg. The adsorption isotherm was reinterpreted using the volumetric micropore filling theory (VMOT) with a three-term equation, and it was demonstrated that the theoretically calculated values fully correspond to the experimental data.

Keywords: adsorption, pressure, relative pressure, isotherm, microcalorimeter, ammonia, VMOT.

Zeolites are characterized by the names MFI, MOR, FAU, and LTA, which reflect their crystal lattice structure and composition, without deviating from their highest symmetry [1]. These zeolites exhibit distinct catalytic properties and thermodynamic characteristics in the adsorption of various types of molecules, including polar, nonpolar, and quadrupolar molecules [2-7].

The CaA (M-22), CaA (M-34), Ca_5Na_3A (MSS-624) and Ca_4Na_4A (Horst-50/50) zeolites contain Ca^{2+} and Na^+ cations as their primary active sites. The quantity and ratio of these cations play a crucial role in determining the adsorption capacity of sorbate molecules. By analyzing the main thermodynamic characteristics of test molecules such as water, ammonia, benzene, and carbon dioxide, it is possible to determine the number, nature, and strength of energetically active sites located in the same type of crystallographic positions [8-15]. For example, it has been established that water molecules form stepwise adsorption complexes of $22H_2O$/elementary cell, $28H_2O$/elementary cell, and $30H_2O$/elementary cell in CaA_1, CaA_2 and $CaNaA_1$ zeolites, respectively. Similarly, carbon dioxide molecules form ion-molecular complexes with stepwise variations of $7CO_2$/elementary cell, $6CO_2$/elementary cell, $8CO_2$/elementary cell, and $9CO_2$/elementary cell in CaA_2, CaA_2, $CaNaA_2$, and $CaNaA_2$ zeolites, respectively [9-12, 15].

This article presents the enthalpy and isotherm results of ammonia adsorption on synthetic Ca_5Na_3A (MSS-624) zeolite, obtained using an adsorption-calorimetric experimental method, along with the adsorption mechanism.

The adsorption-calorimetric method used in this study enables the acquisition of highly accurate fundamental thermodynamic characteristics and provides a detailed understanding of the sorption mechanisms occurring in the zeolite. The apparatus is designed to measure the amount of adsorbate using both gas-volume and volumetric-liquid methods. A modified Tian-Calvet type DAC-1-1A microcalorimeter, known for its high precision and stability, was used in the study.

The adsorption of ammonia on Ca_5Na_3A (MSS-624) zeolite at 303 K was investigated, and the adsorption isotherm was thoroughly analyzed. The elementary cell composition of this zeolite is represented as $Ca_5Na_3[(AlO_2)_{12}(SiO_2)_{12}]$). Based on its chemical composition, the amount of calcium cations in 1 g of zeolite is 2.95 mmol/g, while the amount of sodium cations is 1.77 mmol/g.

The logarithmic coordinate adsorption isotherm of ammonia on Ca_5Na_3A (MSS-624) zeolite is presented in Figure 1. At low adsorption volumes, with an adsorption amount of 0.1 mmol/g, the equilibrium relative pressure logarithm is LnP/P_s=-15.5 ($P/P_s=8.11\cdot10^{-7}$, P=0.00674 torr). Here, P_s=8750 torr represents the saturation pressure of ammonia at 303 K. Due to the high relative pressure of ammonia, the experiment was conducted up to 614 torr. The adsorption isotherm reached an adsorption quantity of 10.2 mmol/g at a relative pressure of P/P_s=0.07 (or P=614 torr).

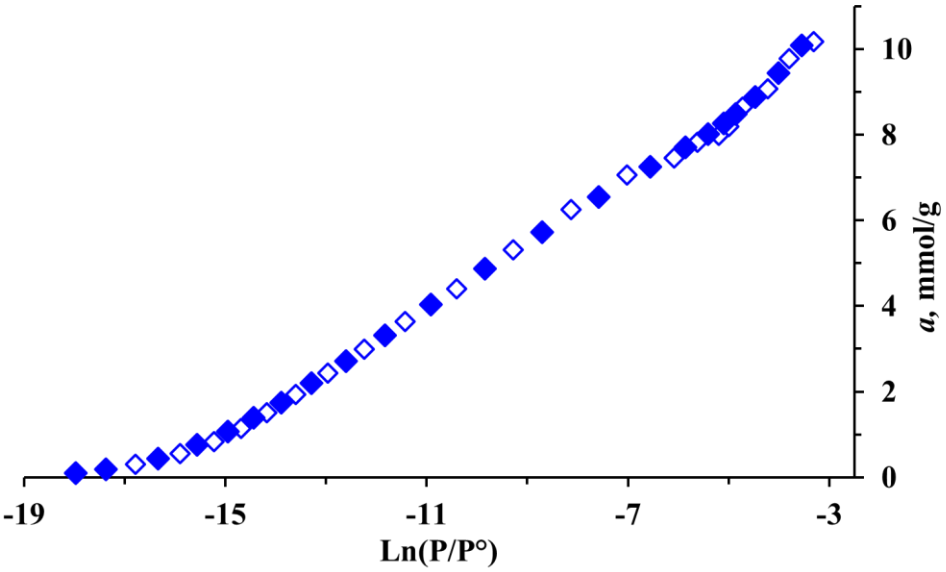

Figure 1. Adsorption isotherm of ammonia on CaA (MSS-624) zeolite at 303 K. ◊–experimental data, ♦–values from the general equation of the micropore volume filling theory (VMOT).

At the initial stage of the adsorption isotherm, the cations in the zeolite matrix form strong ion-molecular complexes with ammonia molecules. The isotherm first extends toward the abscissa at $P/P_s=2.5\cdot10^{-7}$ (P=0.0022 torr) with an adsorption quantity of approximately 1.8 mmol/g. According to the chemical composition of the zeolite, the amount of sodium cations is 1.77

mmol/g. This means that at ~1.8 mmol/g adsorption, ammonia molecules form $1NH_3:Na^+$ monomer ion-molecular complexes with sodium cations in the zeolite structure. The isotherm then varies linearly up to $LnP/P_s=-7$ ($P/P_s=0.0009$ or $P=7.8$ torr), sequentially forming $2NH_3:Na^+$ dimers, $3NH_3:Na^+$ trimers, and $4NH_3:Na^+$ tetramer ion-molecular complexes. Beyond this point, ammonia adsorption no longer depends on the number of sodium cations in the zeolite, indicating that adsorption in the first coordination sphere of sodium cations is complete. The formation of the $4NH_3:Na^+$ tetramer ion-molecular complex is further confirmed by a relative increase in equilibrium pressure.

The systematic variation of the isotherm in correspondence with the active centers of the zeolite suggests the presence of a second active site—calcium cations—with a quantity of ~2.95 mmol/g. This means ammonia molecules begin to adsorb onto Ca^{2+} cations. At a relative pressure of $P/P_s=0.07$ ($P=614$ torr) and an adsorption of 10.2 mmol/g, a $1NH_3:Ca^{2+}$ monomer ion-molecular complex is formed, marking the end of the adsorption process within the experimental range. From the adsorption isotherm, it is determined that ammonia molecules form a tetramer $4NH_3:Na^{2+}$ complex with sodium cations and a monomer $1NH_3:Ca^{2+}$ complex with calcium cations, resulting in an overall $6NH_3:Ca_5Na_3A$ (MSS-624) ion-molecular complex.

The ammonia adsorption isotherm on CaA (MSS-624) zeolite is fully characterized by the three-term VMOT equation [15]:

$$a=5{,}12\exp[-(A/34{,}4)^5] + 3{,}77\exp[-(A/20{,}57)^3] + 3{,}94\exp[-(A/9{,}07)^3] \quad (1)$$

Here, a is the adsorption value (mmol/g), and **$A=RTln(P_s/P)$** represents the free energy, which expresses the work (kJ/mol) performed when transferring gas to the equilibrium gas phase. From **Figure 1**, it is observed that the values calculated using VMOT fully correspond to the experimentally obtained adsorption amount up to **10 mmol/g**. The first term of the equation represents the adsorption of ammonia molecules at the sodium cation active centers of the zeolite, the second term corresponds to adsorption at both sodium and calcium cationic centers, and the third term describes adsorption exclusively at calcium cationic centers.

Since the adsorption process follows an exponential equation, the third term of Equation 1 has almost no effect at low saturation pressure **P/P_s=0.03** (P=260 torr), indicating that the process is weak and represents adsorption caused by Van der Waals interactions.

CONCLUSION

The adsorption isotherm of ammonia molecules on nanostructured zeolite Ca_5Na_3A (MSS-624) was studied, and free energy values were calculated. It was determined that sodium cations in **S_I** and **S_{II}** positions form **tetrameric** $4NH_3:Na^+$ **ion-molecular complexes**, while calcium cations form **monomeric** $4NH_3:Na^+$ **ion-molecular complexes**. In general, ammonia molecules form $6NH_3:Ca_5Na_3A$ (MSS-624) **ion-molecular complexes**.

At low saturation values of the sorption volume, the saturation coefficient was experimentally determined to be 0.44 at an equilibrium pressure of 0.33 mmHg, 0.53 at 1.4 mmHg, 0.71 at 25 mmHg, and 0.8 at 200 mmHg. The adsorption isotherm was redefined using the **three-term equation of the volumetric micropore saturation theory (VMOT)**, and the theoretically calculated values fully matched the experimental results.

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