ISSN 2181-8622

Manufacturing technology problems

Scientific and Technical Journal Namangan Institute of Engineering and Technology

INDEX COPERNICUS INTERNATIONAL

Volume 10
Issue 1
2025

Google Scholar Crossref doi SLIB.UZ Scientific library of Uzbekistan

DIFFERENTIAL HEAT OF AMMONIA ADSORPTION AND ADSORPTION MECHANISM IN Ca_4Na_4A ZEOLITE

ERGASHEV OYBEK

Professor, Namangan Institute of Engineering and Technology, Namangan, Uzbekistan
Phone.: (0895) 303-3565, E-mail.: okergashev711@gmail.com

BAKHRONOV HAYOT

Associate Professor, Tashkent University of Information Technologies
named after Muhammad al-Khwarizmi, Tashkent, Uzbekistan
Phone.: (0897) 710-3758, E-mail.: baxronov@mail.ru
**Corresponding author*

SOBIRJONOVA SURAYYO

PhD student, Namangan Institute of Engineering and Technology, Namangan, Uzbekistan
Phone.: (0891) 182-7242, E-mail.: sobirjonovasurayyo59@gmail.com

KOKHAROV MIRZOKHID

Associate Professor, Namangan Institute of Engineering and Technology, Namangan, Uzbekistan
Phone.: (0893) 572-0208, E-mail.: mirzo199008@mail.ru

MAMADALIYEV UTKURBEK

Independent Researcher, Namangan Institute of Engineering and Technology, Namangan, Uzbekistan
Phone.: (0893) 446-3333, E-mail.: mamadaliyev1989@mail.ru

Abstract: This article presents the experimentally obtained values of differential enthalpy of ammonia adsorption at 303 K in Ca_4Na_4A (Horst-50/50) zeolite of the LTA type. The enthalpy values were measured using a modified Tian-Calvet-type DAC-1-1A microcalorimeter connected to a universal high-vacuum device. The regular relationship between the amount of ammonia adsorption and differential enthalpy in Ca_4Na_4A (Horst-50/50) zeolite, as well as the adsorption mechanism from the initial region to the condensation heat of ammonia, and the filling of the zeolite volume by ammonia molecules, was determined. Under experimental conditions, the adsorption capacity of Ca_4Na_4A (Horst-50/50) zeolite for ammonia was found to be 8.8 mmol/g. The differential heat values were found to vary according to the number of Na^+ and Ca^{2+} cations in the zeolite structure, with ammonia molecules forming pentameric $5NH_3{:}Na^+$ ion-molecular complexes with sodium cations and dimeric $3NH_3{:}Ca^{2+}$ ion-molecular complexes with calcium cations in the first coordination sphere of the zeolite.

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

Introduction. Worldwide, the process of obtaining purified gas from natural gas without adequately removing additional chemical components, as well as the release of harmful gases into the atmosphere from the combustion of secondary gases in industrial and manufacturing processes, is leading to increasing environmental issues each year. The combustion of naturally occurring gases with various compositions results in the release of sulfur compounds and nitrogenous compounds that are hazardous to human health and plant life. Additionally, the emission of large amounts of carbon (IV) oxide into the atmosphere negatively affects human health. Consequently, the global demand for solutions to prevent environmental problems is increasing year by year. Millions of tons of synthetic zeolites are produced to address these issues, specifically for the purification and drying of gases from various unwanted components. In particular,

synthetic zeolites play an indispensable role in the oil and gas industry due to their exceptional adsorption and catalytic properties. This, in turn, necessitates the synthesis of a new generation of zeolites with high adsorption and catalytic efficiency and the practical application of research aimed at enhancing their selectivity characteristics.

At present, zeolites are widely used as adsorbents and catalysts in natural gas drying, petroleum, and petrochemical processing industries. To enhance and scientifically substantiate the catalytic activity of zeolites, it is essential to continuously conduct fundamental research on the theoretical principles of sorption processes using modern scientific research methods. The widespread industrial application of zeolites and their use as catalysts have become the focus of interest and research for many scientists [1].

X-ray structural analysis has revealed that aluminosilicate zeolites of types A, X, and Y are composed of cubic-octahedral structural units. Each cubic-octahedral unit consists of 24 structural element tetrahedra formed by AlO_4 ва SiO_4 groups, in which oxygen ions are shared among tetrahedra. Each cubic-octahedral unit is connected by 36 oxygen ions and contains 240 ions (Al + Si), forming a stable structure. Each cubic-octahedral unit consists of six four-membered and eight six-membered rings [2].

The AlO_4 and SiO_4 oxides in the zeolite framework have a negative charge of “minus one.” Consequently, the tetrahedral zeolite framework requires the presence of an equivalent amount of cations to balance this charge. This requirement is related to the need to compensate for the excess electron charge in the Al_2O_4 tetrahedral groups. The aluminum atom (Al) has three independent s- and p-electrons, and through interactions with four surrounding oxygen atoms, it forms equal-value electron pairs, gaining one additional electron in the process [3].

The structural difference between A and X zeolites lies in the spatial arrangement of cubic-octahedral structural units within their framework [2, 4, 5]. In type A zeolites, the cubic-octahedral units form a simple cubic lattice, where each unit is connected to six neighboring units through four-membered oxygen-bridged rings. The voids between the eight cubic-octahedral units form large cavities [3]. The amount of negative charge in the crystal lattice of a zeolite depends on the Si/Al ratio, and different amounts of cations are introduced to fully or partially compensate for this charge. These cations may be alkali metals or alkaline earth metals, and depending on the type of cation, the adsorption and catalytic properties of zeolites vary. Before being used in various industrial sectors, the adsorption properties of zeolites must be thoroughly studied.

In LTA-type zeolites, Ca^{2+} and Na^{+} cations serve as the main active sites. The amount of adsorbate molecules adsorbed depends on the quantity and ratio of these cations. By determining the fundamental thermodynamic characteristics of adsorption for polar molecules such as water and ammonia, the number, nature, and strength of energetically active centers in crystallographic positions of the same type can be identified [6-15]. Scientific studies have investigated the adsorption of various physicochemical substances on LTA-type zeolites using methods such as NMR, SEM, X-ray structural analysis, IR spectroscopy, and gas chromatography [1, 3-4]. However, these methods are not

sufficient for studying the adsorption energetics of different molecules on adsorbents and for determining the mechanism of the sorption process. The use of a high-vacuum adsorption calorimetric device for studying adsorption energetics is expected to yield more precise results.

This article presents the enthalpy and isotherm results of ammonia adsorption on synthetic Ca_4Na_4A (Horst-50/50) zeolite obtained through adsorption calorimetric experiments, as well as the adsorption mechanism.

Research methods and materials. For measurements of isotherms and differential adsorption heats, a system consisting of a universal high-vacuum adsorption unit and a Tian-Calvet-type, DAK-1-1A thermally conductive differential microcalorimeter connected to it was used, which has high accuracy and stability. The instrument's calorimeter sensitivity is extremely high, and its reliability is high. It can be used confidently to measure the heat of processes of almost unlimited duration. The calorimeter makes it possible to obtain the thermokinetics of the process of adsorption systems under study, which is very important for elucidating the adsorption mechanism. Most of the heat (about 99%) released into the calorimeter chamber is dissipated into the calorimeter block immediately after release. Only about 1% of the heat released remains in the calorimeter chamber, raising its temperature slightly. The measurement is mainly concerned with the heat flux that passes through the surface of the calorimeter chamber and the calorimeter block. The adsorption-calorimetric method used in this work provides highly accurate molar thermodynamic characteristics and reveals detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. Adsorption measurements and adsorbate dosing were carried out using a universal high-vacuum adsorption unit. The unit allows adsorbate dosing by both gas-volume and volume-liquid methods. We used a BARATRON B 627 membrane pressure gauge to measure the equilibrium pressures.

The adsorption of ammonia on Ca_4Na_4A (Horst-50/50) zeolite at 303 K was investigated, and the adsorption isotherm was fully analyzed. The unit cell composition of this zeolite is expressed as $Ca_4Na_4[(AlO_2)_{12}(SiO_2)_{12}]$). Based on its chemical composition, the amount of calcium and sodium cations in 1 gram of zeolite is 2.38 mmol/g. However, the active adsorption sites in the zeolite are located at S_I, S_{II}, and S_{III} positions, with ammonia molecules being adsorbed only at the S_I and S_{II} positions. Therefore, not all calcium and sodium cations present in the zeolite participate in the adsorption process.

Results. The dependence of the differential heat of adsorption of ammonia on the adsorption amount in Ca_4Na_4A (Horst-50/50) zeolite is presented in Figure 1. Researchers have shown that the stepwise variation of enthalpy for various physicochemically different molecules adsorbed on synthetic zeolites such as MFI, MOR, FAU, and LTA correlates with the number of cations in their structure [6-22]. For example, in the case of ammonia adsorption on CaA (M-22) zeolite, the formation of the first step in differential enthalpy at an adsorption amount of 0.76 mmol/g corresponds to the number of sodium cations in the zeolite structure and indicates the formation of an adsorbate/adsorbent monomeric $1NH_3{:}Na^+$ ion-molecular complex. As the zeolite becomes saturated, enthalpy

changes stepwise at 1.5 mmol/g adsorption to form a dimeric $2NH_3:Na^+$ complex, at 2.3 mmol/g adsorption to form a trimeric $3NH_3:Na^+$ complex, and at 3.0 mmol/g adsorption to form a tetrameric $4NH_3:Na^+$ ion-molecular complex with a wave-like enthalpy change. Additionally, the partial increase in enthalpy (by 2.7 kJ/mol) during the formation of trimeric $3NH_3:Na^+$ and tetrameric $4NH_3:Na^+$ complexes was attributed to additional energy release due to weak Van der Waals interactions between ammonia molecules. The stepwise change in differential enthalpy up to an adsorption amount of 3.0 mmol/g corresponds to the number of sodium cations (0.76 mmol/g), confirming that ammonia is initially adsorbed only on sodium cations. Subsequent changes in differential enthalpy at adsorption amounts of 1.9 mmol/g indicate ammonia sorption on calcium cations, with the formation of monomeric $1NH_3:Ca^{2+}$ and dimeric $2\ NH_3:Ca^{2+}$ ion-molecular complexes at adsorption amounts of 4.9 mmol/g and 6.4 mmol/g, respectively. Notably, two ammonia molecules adsorbed on calcium cations interact with additional ammonia molecules via Van der Waals forces, leading to the formation of an adsorbent/adsorbate/adsorbate complex $Ca^{2+}:2NH_3:2NH_3$ and, in general, an adsorbate/zeolite complex $8NH_3$:CaA (M-22).

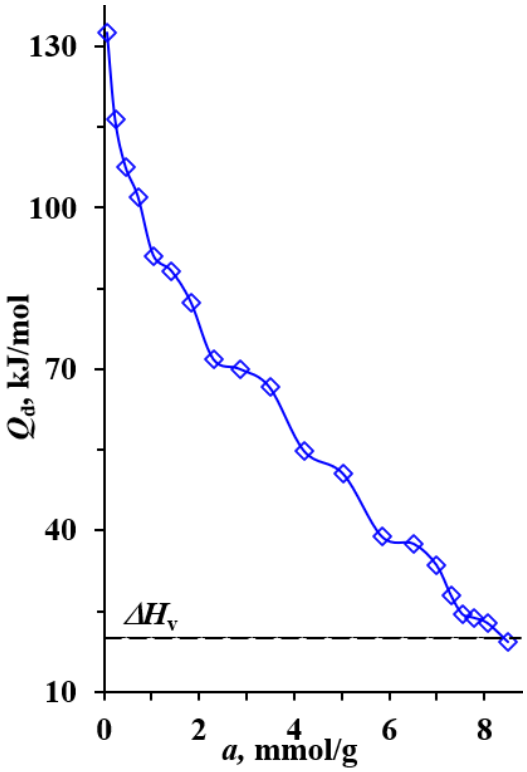

Figure 1. Differential heat of adsorption (Q_d) of ammonia on Ca_4Na_4A (Horst-50/50) zeolite at 303 K. The dashed line represents the condensation heat of ammonia at 303 K

However, the sorption mechanism observed in the present study for Ca_4Na_4A (Horst-50/50) zeolite differs significantly from previously reported mechanisms. At the initial stage, a differential heat (enthalpy) of ~133 kJ/mol was recorded at an adsorption

amount of 0.07 mmol/g. This high value is explained by the additional interaction of ammonia molecules with OH-hydroxyl groups in the crystal structure (Figure 1).

As the amount of adsorption increases, the differential enthalpy value decreases. At approximately ~1,1÷1,2 mmol/g adsorption, the first stage occurs at 92 kJ/mol. With the saturation of the sorption volume, the second stage appears at 2.2 mmol/g adsorption, where the enthalpy decreases to approximately ~80 kJ/mol. The third stage forms at ~3.2÷3.8 mmol/g adsorption with an enthalpy of 70 kJ/mol, followed by the fourth stage at ~4.6 mmol/g, the fifth at 5.5 mmol/g, and the sixth, seventh, and eighth stages at adsorption amounts of 6.8 mmol/g, 7.7 mmol/g, and 8.8 mmol/g, respectively.

Based on the chemical composition of the Ca_4Na_4A (Horst-50/50) zeolite studied in this research, the amount of calcium and sodium cations in 1 g of zeolite is equal, at 2.38 mmol/g each. The active sites of the zeolite consist of S_I, S_{II}, and S_{III} positions, but adsorbate molecules can only be adsorbed at the active sites in SI and SII positions. This indicates that not all calcium and sodium cations in the zeolite structure participate fully in the adsorption process. This raises an important question: To what extent do ammonia molecules form ion-molecular mechanisms with calcium and sodium cations in different ratios? Do ammonia molecules adsorb first onto calcium cations or sodium cations?

From Figure 1, the stepwise change in the amount of ammonia molecule adsorption as a function of differential enthalpy is approximately ~1.1 mmol/g. This indicates that 1.1 mmol/g of calcium and sodium cations in the zeolite structure act as the primary active sites in the sorption process. The linear variation in the isotherm of ammonia adsorption in Ca_4Na_4A (Horst-50/50) up to 5.5 mmol/g suggests that in LTA-type zeolites, polar molecules such as water and ammonia are initially adsorbed onto sodium cations due to their small size and high surface charge density. Consequently, within the adsorption range of 1.1–5.5 mmol/g, ammonia molecules sequentially form ion-molecular complexes with sodium cations, ranging from $1NH_3{:}Na^+$ monomer to $5NH_3{:}Na^+$ pentamer.

At higher adsorption levels, the differential enthalpy of ammonia adsorption approximates the adsorption enthalpy observed in CaA (M-22) and CaA (M-34) zeolites, indicating that the next ammonia molecules are adsorbed onto calcium cations. As the sorption volume becomes saturated, at 6.8 mmol/g, the differential enthalpy decreases to 38 kJ/mol, forming a monomeric complex $1NH_3{:}Ca^{2+}$ at stage 6. At 7.8 mmol/g, the differential enthalpy decreases to 25 kJ/mol, forming a dimeric complex $2NH_3{:}Ca^{2+}$. At 8.8 mmol/g, ammonia molecules form a trimeric complex $3NH_3{:}Ca^{2+}$, marking the completion of the sorption process on calcium cations in this zeolite. In general, in Ca_4Na_4A (Horst-50/50) zeolite, ammonia molecules form $8NH_3$:CaA (Horst-50/50) ion-molecular complexes in the adsorbate/zeolite system.

Conclusion. The differential enthalpy of ammonia adsorption in the nanostructured Ca_4Na_4A (Horst-50/50) zeolite was studied using the adsorption-calorimetric method. Within the experimental pressure range (up to 567 torr), the sorption process mechanism and the filling pattern of the zeolite volume by ammonia molecules were determined. At low saturation levels, ammonia molecules were found to

form pentameric $5NH_3:Na^+$ and trimeric $3NH_3:Ca^{2+}$ ion-molecular complexes with sodium and calcium cations in the S_I and S_{II} positions of the zeolite's first coordination sphere. No ammonia adsorption was observed in the second coordination sphere of the zeolite. Overall, it was confirmed that ammonia molecules in Ca_4Na_4A (Horst-50/50) zeolite form ion-molecular complexes of the type $8NH_3$:CaA (Horst-50/50) in the adsorbate/zeolite system.

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CONTENTS

CHEMICAL SCIENCES

TECHNICAL SCIENCES: MECHANICS AND MECHANICAL ENGINEERING