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EFFECT OF ZEOLITES MODIFICATION ON THEIR ADSORPTION PROPERTIES

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Atmospheric air pollution is determined by the functioning of both technogenic and natural sources of pollution. The main anthropogenic sources of pollution are: transport, industrial enterprises, energy facilities and agriculture. In order to select a rational and effective method of atmospheric emissions purification from harmful components, systematic study was carried out to identify the potential of natural zeolites of Georgia. In particular, four samples of zeolite-containing rocks were investigated: analcime, clinoptilolite, phillipsite, mordenite and their modified forms. By means of the chromatographic method of researching the adsorption properties of natural zeolites, the best adsorption capability of mordenite and its modified hydrogen form obtained by two methods towards nitrogen oxides has been revealed. The perspective and profitability of using the hydrogen form of mordenite treated with ammonium in the processes of purification of nitrous gases from exhaust gases is shown, as well as the possibility of using the recovered products (aqueous solutions of ammonium salts) obtained from its regeneration as a nitrogen fertilizer in agriculture. The experimental adsorption purification of the sample (H-mordenite) was carried out in the process of research. The sample was taken from the outlet pipe of the contact apparatus in the ammonia oxidation shop of the nitric acid production enterprise of LLC "Rustavi Azoti". It has been found that the modified mordenites can be proposed as an environmentally friendly, highly efficient sorbent in the processes of air purification from toxic impurities. Of the two forms of H-mordenite investigated, the adsorption data obtained for NH_4^+-ion-modified mordenite is approximately 20 % better than the acid-modified form. It should be noted that the use of granulated zeolites (mordenite) in adsorbers with dense packing is very effective. It is also important from the economic point of view that it is possible to reuse spent high-silica sorbents after their regeneration by oxidation method, since such zeolites are resistant to oxidants, such as hydroxyl radicals, ozone, etc., and it is possible to regenerate them without removing them from adsorber.

***Keywords**: natural zeolites, clinoptilolite, mordenite, adsorption, off-gases*

INTRODUCTION

Despite the introduction of clean technologies in the industrial, energy and transport sectors, air pollution remains a serious problem in the world. About 200 countries of the world are making joint efforts to limit the causes of climate change processes and their negative impacts within the framework of the United Nations Framework Convention on Climate Change (UNFCCC) [1–3].

Despite the many efforts made to solve air pollution problems, overcoming these challenges is still difficult, since the effectiveness of the measures taken depends largely on the economic development of countries, their organizational and legal-institutional capacity, and the level of public awareness.

Despite the existence of numerous means of decontamination of harmful components of gases dispersed in the atmosphere, the choice of rational and effective methods of purification is very relevant. Among such methods, adsorption methods are of particular importance [4, 5].

Adsorption methods are based on the selective absorption of certain components from gas mixtures using an adsorbent. Adsorption can provide an advantage over expensive and energy intensive alternative methods such as distillation, absorption or other methods, especially at low and medium efficiency [6].

The use of natural zeolites in adsorption processes for gas purification is less studied. Zeolites, because of their inherent ability to adsorb polar compounds, have long been considered as excellent candidate materials for separation and purification of gases. Moreover, certain zeolites are known to occur abundantly in nature. These attributes notwithstanding, the use of natural zeolites has been small in comparison to that of synthetic zeolites and other adsorbents in commercial gas separations utilizing adsorption [7].

Synthetic zeolites have played an important role in the development of adsorption process technologies for many separation processes. Although, the adsorption characteristics of natural zeolites make it possible to use them as adsorbents for various vapors, liquids and solids. The economic feasibility of adsorption processes is largely due to the versatility of zeolites [8].

Natural and modified forms of Georgian clinoptilolite [9–12] have been used to absorb of nitrogen oxides from industrial gases. In early works [11], the adsorption properties of acid-treated forms of Trans Carpathian and Georgian clinoptilolites were investigated. It is shown that the hydrogen form of clinoptilolite from the Dzegvi locality (Georgia) is more active. Probably, it is caused by the change of chemical nature of adsorption centers and porous structure of minerals.

The adsorption properties of clinoptilolite Dzegvi (Georgia) for N_2O and NO was studied, and it is shown that adsorption of N_2O is described by the equation of micropore filling theory, and adsorption of NO is described by the Langmuir equation, *i.e.*, it accumulates on the surface of the adsorbent [12]. Dzegvi clinoptilolite is also used to purify exhaust gases in power plants. It allows to purify nitrogen oxides up to the maximum permissible value [13].

Adsorption of nitrogen oxides from gases of nuclear fuel reprocessing was studied on natural H-mordenite from Itago (Japan), where it is assumed that the reduction of nitrogen oxides occurs in the adsorption zone [14]. In the processes of high-purity purification of gas mixtures from nitrogen oxides american scientists use natural and synthetic zeolites, the surface or pores of which contain carbon particles [15].

There are many natural zeolites, of which a small number, including clinoptilolite, shabasite, mordenite, erionite, ferrierite, and phyllipsite, offer the greatest promise for gas separation. Patents and other literature were reviewed to identify separation and purification processes for which these zeolites have potential. The abundance of natural zeolites and low cost of raw material rarely compensate for disadvantages such as variable composition, low purity, and often poorer separation performance compared to the more preferred synthetic zeolites. The results show that these natural zeolites are particularly well suited for the removal of gas impurities [16].

In order to select a rational and effective method of atmospheric emissions purification from harmful components, systematic study was carried out in previous works to reveal the potential of natural zeolites of Georgia, in particular, four samples of zeolite-containing rocks were investigated: analcime, clinoptilolite, phillipsite, mordenite and their modified forms [17–23].

The article studies the possibility of using the hydrogen form of mordenite in air purification processes containing a mixture of nitrogen oxides.

MATERIALS AND METHODS

To study the adsorption and separation properties of natural zeolites in relation to some aggressive gases polluting the atmosphere (CO, NO, CO_2, N_2O), the method of gas-adsorption chromatography was used [24–28].

The separation of the prepared model mixture (air, CO, NO, CO_2, N_2O) was tested at different temperatures of the chromatographic column and different flow rates of the air carrier. Based on the results obtained and the corresponding calculations, the optimal conditions of analysis and sorbent with the best sorption properties – natural mordenite – were selected.

The nature of the cation and the degree of substitution in zeolites have a significant effect on the interaction of the adsorbent with the sorbate and on the retention time. When modifying zeolites, because of the unusual structure and nature of exchangeable cations, it is possible to obtain cation-substituted forms of a cardinally different nature.

Chemical modification opens up wide possibilities for regulating the molecular sieve and catalytic properties of mordenite [23, 25–28]. The maximum adsorption volume of mordenite ranges from 0.076–0.09 cm^3/g. The difference in molecular sieve properties is due to the different arrangement of sodium cations, which in narrow pores of mordenite are located in large twelve-membered channels (0.59–0.47 nm) and thus narrow their effective diameter. And in wide pores they are localized in the depths of niches composed of double eight-membered rings (0.39–0.47 nm), and do not prevent the penetration of large molecules into large channels.

Natural mordenite of Bolnisi-Ratevani deposit with zeolite-phase content of ~ 50–60 %

[29, 30] was used in this work, the ratio of Si/Al is within 4.5–5.5.

With this in mind the hydrogen form of mordenite obtained by two different methods was studied [5, 31]:

1. Acid treatment with HCl;
2. Treatment of zeolites with ammonium salts followed by thermolysis, which makes it possible to obtain H-forms [5].

The work developed a chromatographic method of quantitative analysis to control the concentration of corrosive gases.

RESULTS AND DISCUSSION

The static method was used in the work to prepare a model mixture of three different concentrations:

1. air – 25 %, NO–25 %, NO_2–25 %, N_2O–25 %
2. air – 50 %, NO–16.5 %, NO_2–16.5 %, N_2O–16 %
3. air – 75 %, NO–8.5 %, NO_2–8.5 %, N_2O–8.5 %.

The oxides required for the analysis were obtained under laboratory conditions.

The experiment was performed on a gas chromatograph at room temperature with a katharometer detector. Under the selected optimal conditions, the best partitioning was obtained for all three concentrations of the model mixture.

The solid adsorbent purification processes are based on the laws of adsorption dynamics.

To study the adsorption properties of H-mordenite obtained by both methods, a laboratory flow-type dynamic device was specially designed [32].

The plant that was used to study adsorption under dynamic conditions consists of three parts: 1) a glass adsorption column, 2) a cylindrical electric furnace, 3) Glass mixer (stirrer) for preparation of gas mixtures of different concentrations. The investigated mixture was passed through the prepared zeolite samples placed in a glass adsorption column. The experiment was carried out at 25 and 50 °C.

Basic information about the functioning of the zeolite layer was obtained by isoplanes. The tests were carried out until the zeolite layer was completely saturated. From the obtained graphical data (isoplanes), the corresponding adsorption indicators [33] were calculated at different granularities and temperatures of zeolite (Fig. 1).

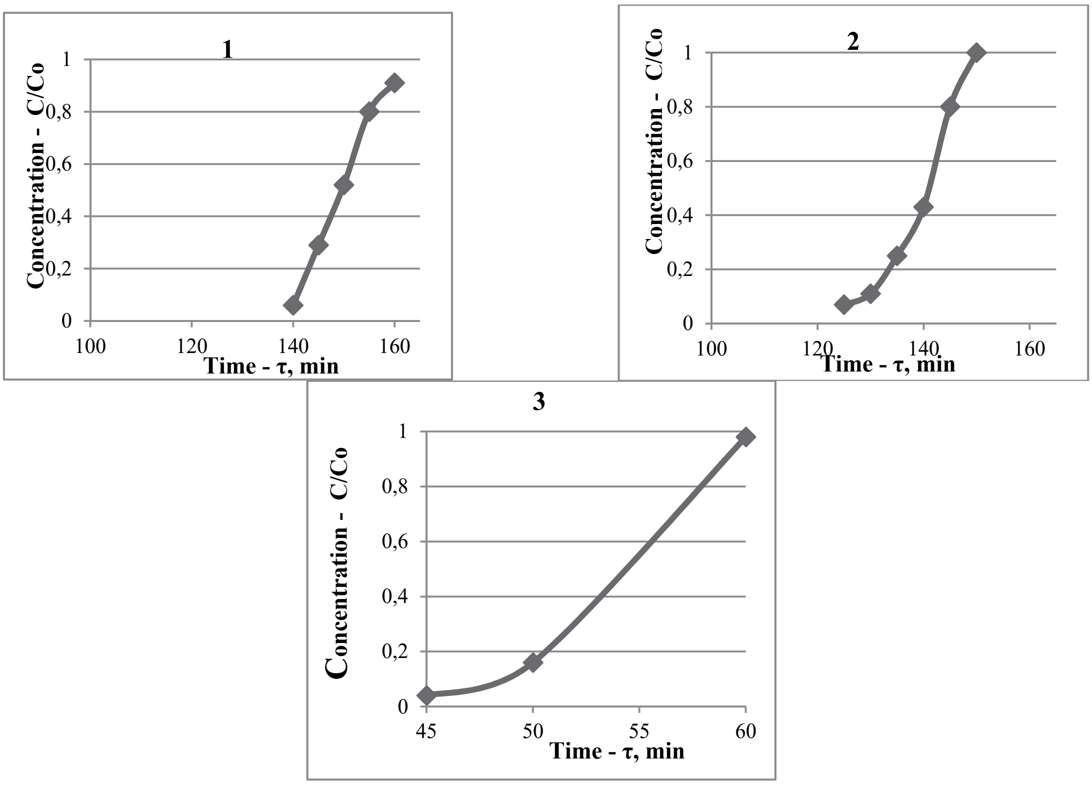

Fig. 1. N_2O adsorption output curves (isoplanes) on H-mordenite: *1* – Adsorption column temperature 25 °C, zeolite granularity 0.25–0.315 mm; *2* – Adsorption column temperature 25 °C, zeolite granularity 0.5–1.0 mm; *3* – Adsorption column temperature 50 °C, zeolite granularity 0.25–0.315 mm

The dynamic adsorption capability of the adsorbent layer (a_d) characterizes the amount of substance absorbed before the moment of "breakthrough" (τ_b.) and attributed to the mass of loading of the entire adsorber. From the "moment of breakthrough", extracted substance appears in the outgoing stream and its concentration begins to increase progressively. Between the time of protective action of the sorbent layer and the length of the adsorber (L) there is a dependence determined by the formula of N.A. Shilov [34]:

$$\tau_b = KL - \tau_o \ ,$$

where K – coefficient of the protective action, showing the time taken by the 1 cm high adsorbent layer retains the absorbed substance in a stationary mode; τ_o – time loss of protective action associated with the initial period of formation of the adsorbate distribution curve; L – height of loading of the adsorbent layer (in this case 24 cm);

The equilibrium adsorption activity of the sorbent layer depends on the nature of the adsorbate and adsorbent (a_{eq}) and was calculated by the formula [34]:

$$a_{eq.} = W\tau_b C_o + W\Delta\tau C_o \frac{\varphi}{V} \ ,$$

where W is the volume rate of the flow (cm^3/min); τ_b – time of protective actions of the sorbent layer; C_o – initial concentration of sorbate (% wt.); $\Delta\tau$ – difference in sorbent layer performance time to complete saturation (τ_{eq}), *i.e.*, the time of occurrence of the maximum (equilibrium) concentration and breakthrough concentration (τ_b) through the sorbent layer (min); φ – coefficient of the symmetry of the output curves or the distribution curves, *i.e.*, the degree of underutilization of the adsorption capacity; V – mass of the loaded adsorbent.

The size of the working layer L_o, determined from the output curves reflecting pollutant concentration rise behind the adsorbent layer with time, is an important characteristic of the dynamics of the adsorption process. The value of L_o, the length of the mass-transfer zone, was determined on the basis of the obtained isoplanes according to the Michaels-Trable equation [34, 35]. Efficiency of the sorbent layer adsorptive capacity (η) is determined by the ratio of the dynamic adsorptive capacity of the layer to the equilibrium adsorptive capacity of the sorbent layer (Table 1).

From the results obtained it has been found that reducing the grain size of the adsorbent to a certain limit improves the dynamic characteristics, while increasing the temperature negatively affects the purification process. Therefore, the process of air purification from nitrogen oxides (NO, NO_2, N_2O) is better performed at the temperature of 25 °C on H-mordenite treated with NH_4^+, which grain size is 0.25–0.315 mm (Table 1, 2).

As can be seen from the data, the H-forms obtained from the NH_4-form and the acid treatment of Na zeolite differ from each other. In both cases H^+ ions are involved in cation exchange process. Probably, when hydrogenous forms are obtained from ammonium forms, there is a gradual increase in the number of protons as a result of thermolysis of ammonium cations. During acid treatment of zeolite a large number of protons is initially present in the solution, far exceeding the amount of sodium even at low acid concentrations (0.01 N). This results in the simultaneous substitution of Na^+ for H^+ and the effect of a proton on the Al/O bond, which is accompanied by bond breaking and the formation of hydroxogroups and L-centers.

In the development of adsorption methods for purification of industrial emissions from harmful impurities, the processes associated with the restoration of adsorbent activity (regeneration) are relevant. The need to extend adsorbent lifetime and reduce operating costs for cleaning requires the search for effective regeneration methods. The use of this or that method is determined by the specificity of adsorption-desorption processes [36].

During adsorption process, "etching" of the adsorbent by undesirable impurities (nitrogen oxides) takes place. Several regeneration methods (thermovacuum, thermogas, displacement regeneration) were tested for purification of adsorbent (saturated from impurities). It was recognized expedient to use a combined method of thermal and displacement regeneration.

Displacement regeneration is carried out by displacing the adsorbed substances with another component. This method is effectively used in adsorption processes on zeolites [35].

Ammonium hydroxide (NH_4OH) was used as the extracting component in this work. The mordenite layer was treated at room temperature with a weak aqueous solution of NH_4OH with a defined pH. The saturated mordenite was treated until the initial pH of NH_4OH equaled the pH of the final regeneration product. After that, the adsorption column was washed with water.

The remaining water (after regeneration) in the porous structure of mordenite was removed (dehydration) by heating. The study of zeolites behavior during dehydration is relevant, since their sorption, catalytic and molecular sieve properties are revealed exactly in the dehydrated state [37].

Table 1. Effect of sorbent grain size on adsorption characteristics of H-mordenite with respect to N_2O ($t_{c.}$ – 25 °C)

Adsorption dynamics index	**0.25–0.315 mm**		**0.5–1.0 mm**	
	H-mordenite treated with NH_4^+	**H-mordenite treated with acid**	**H-mordenite treated with NH_4^+**	**H-mordenite treated with acid**
L_0 – Length of Mass transfer Zone, cm	3.45	4.31	3.96	4.95
a_d – Dynamic activity of the sorbent with respect to gas, g/100 g	25.80	20.64	23.70	18.96
a_e – Equilibrium activity of the sorbent with respect to the gas, g/100 g	27.50	22.00	26.40	21.12
η – Degree of use of sorbent activity, %	93.82	75.05	89.77	71.82

Table 2. Effect of temperature on the adsorption characteristics of H-mordenite with respect to N_2O

Adsorption dynamics index	**Temperature of the adsorption column at 25 °C**		**Temperature of the adsorption column at 50 °C**	
	H-mordenite treated with NH_4^+	**H-mordenite treated with acid**	**H-mordenite treated with NH_4^+**	**H-mordenite treated with acid**
L_0 – Length of Mass transfer Zone, cm	3.45	4.31	3.85	4.81
a_d – Dynamic activity of the sorbent with respect to gas, g/100 g	25.80	20.64	9.12	7.29
a_e – Equilibrium activity of the sorbent with respect to the gas, g/100 g	27.50	22.00	10.20	8.16
η – Degree of use of sorbent activity, %	93.82	75.05	89.40	71.52

During the study, dehydration of mordenite was carried out in the temperature range of 80–400 °C. The adsorption column was firstly warming up to 100 °C for 1 hour, and then for 3 hours – in three modes to temperatures of 200, 300 and 400 °C in the flow of inert gas (dry nitrogen) – desorbent.

By the example of N_2O the influence of regeneration temperature on the value of adsorption of mordenite hydrogen form and on the time of protective action of the sorbent layer was studied. The corresponding adsorption output curves were plotted (isoplanes, Fig. 2).

The obtained results show that the optimum temperature of mordenite regeneration, corresponding to the maximum value of dynamic activity and degree of activity of the sorbent layer, is 350–400 °C. After several cycles of sample operation (adsorption-desorption), the above parameters slightly decrease and remain constant.

The developed method of mordenite regeneration is important because the aqueous solution of ammonium salts obtained after passing through the adsorption column can be used in agriculture as a nitrogen fertilizer, and the regenerated mordenite can be used in the processes of air purification from harmful components.

According to a simplified scheme, experimental adsorption purification of a sample taken from the outlet pipe of the contact apparatus in the ammonia oxidation shop of the nitric acid production enterprise of LLC “Rustavi Azoti” was carried out.

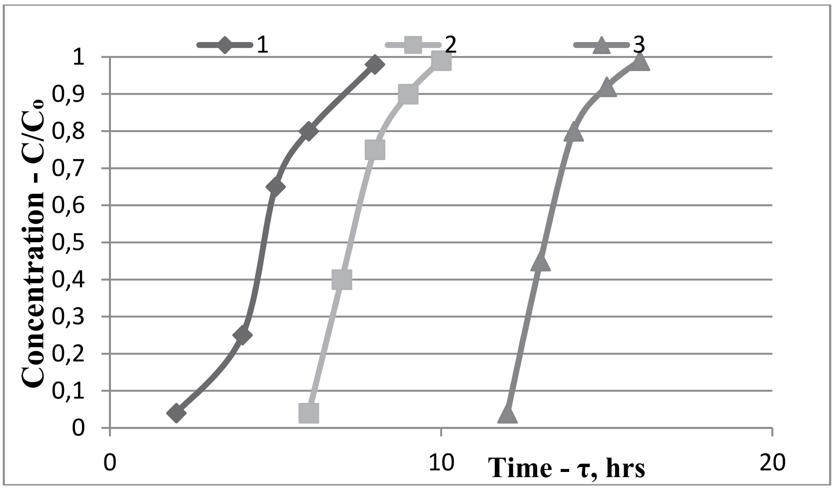

Fig. 2. N_2O adsorption output curves (isoplanes) on H-mordenite: *1* – 200, *2* – 300 and *3* – 400 °C

In the adsorption column (24 cm×1 cm) of laboratory equipment, the analytical sample was moved at a speed of 100 ml/min. About 18 L of gaseous mixture passed through the column in 3 hours. After the specified time, a control sample was taken from the adsorption column for chromatographic analysis.

The percentage composition of oxides in the samples was calculated from the data of chromatograms by the planimetric method. For the sample taken at the beginning of the analysis, their content is respectively equal:

Air – 19.57 %; NO – 31.55 %; NO_2 – 22.14 %; N_2O – 26.75 %,

and on the sample taken at the outlet of the column –

Air – 53.39 %; NO – 21.96 %; NO_2 –13.05 %; N_2O – 11.61 %.

It should be noted that the speed of the purified gas-air mixture is quite high (100 ml/min), and the length of the adsorption column (24 cm) is very small, so the concentration of nitrogen oxides at the output of the column decreased by 2 times. When optimal conditions are selected, complete absorption of nitrogen oxides is achieved, which confirms the feasibility of using the hydrogen form of natural mordenite in the processes of purification of air from nitrogen oxides.

CONCLUSION

It has been found that the modified mordenites can be proposed as an environmentally friendly, highly efficient sorbent in the processes of air purification from toxic impurities. Of the two forms of H-mordenite investigated, the adsorption data obtained for NH_4^+-ion-modified mordenite is approximately 20 % better than the acid-modified form.

It should be noted that the use of granulated zeolites (mordenite) in adsorbers with dense packing is very effective. It is also important from the economic point of view that it is possible to reuse spent high-silica sorbents after their regeneration by oxidation method, since such zeolites are resistant to oxidants, such as hydroxyl radicals, ozone, *etc.*, and it is possible to regenerate them without removing them from adsorber.

Вплив модифікації цеолітів на їхні адсорбційні властивості

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Забруднення атмосферного повітря визначається функціонуванням як техногенних, так і природних джерел забруднення. Основними антропогенними джерелами забруднення є: транспорт, промислові підприємства, об'єкти енергетики та сільського господарства. З метою вибору раціонального та ефективного методу очищення атмосферних викидів від шкідливих компонентів, було проведено систематичне дослідження з виявлення потенціалу природних цеолітів Грузії. Зокрема, досліджено чотири зразки цеолітовмісних порід: анальцим, клиноптилоліт, філіпсит, морденіт та їхні модифіковані форми. За допомогою хроматографічного методу дослідження адсорбційних властивостей природних цеолітів виявлено найкращу адсорбційну здатність до оксидів азоту морденіту та його модифікованої водневої форми, отриманої двома методами. Показано перспективність і рентабельність використання водневої форми морденіту, обробленого амонієм, у процесах очищення нітрозних газів від вихлопних газів, а також можливість використання отриманих від його регенерації регенерованих продуктів (водних розчинів солей амонію) як азотне добриво в сільському господарстві. У процесі досліджень проведено експериментальне адсорбційне очищення зразка (Н-морденіт). Пробу відбирали з випускного патрубка контактного апарата цеху окиснення амоніаку підприємства з виробництва азотної кислоти ТОВ «Руставі Азоти». Встановлено, що модифіковані морденіти можуть бути запропоновані як екологічно чистий, високоефективний сорбент у процесах очищення повітря від токсичних домішок. З двох досліджених форм Н-морденіту дані про адсорбцію, отримані для морденіту, модифікованого іонами NH_4^+, приблизно на 20 % кращі, ніж для форми, модифікованої кислотою. Слід зазначити, що використання гранульованих цеолітів (морденіту) в адсорберах з щільною упаковкою є дуже ефективним. Також з економічної точки зору можливе повторне використання відпрацьованих висококремнеземних сорбентів після їх регенерації методом окиснення, оскільки такі цеоліти стійкі до окиснювачів, таких як гідроксильні радикали, озон тощо, і їх можливо, регенерувати без вилучення з адсорбера.

***Ключові слова**: природні цеоліти, клиноптилоліт, морденіт, адсорбція, вихідні гази*

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