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NEW SUBSTANCES, MATERIALS, AND COATINGS

Thermal Activation of Type X Zeolites in the Presence of Carbon Dioxide

E. N. Ivanova[a], A. A. Averin[b], M. B. Alekhina[a],
N. P. Sokolova[b], and T. V. Kon'kova[a]

[a] Mendeleev Russian State Chemical Engineering University, Moscow, Russia
[b] Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 199071 Russia
e-mail: katjuchka1@mail.ru

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Abstract—It is found that the highest value of the separation factor of the nitrogen–oxygen mixture is observed for zeolite activated in the presence of 2 vol % CO_2 in nitrogen. It is shown on the basis of IR studies that the formation of bicarbonate structures is most characteristic for this sample.

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INTRODUCTION

Adsorption technology allows efficiently extracting from atmospheric air such gases as nitrogen and oxygen. The operation of the corresponding setups is based on the principle of short-cycle heatless adsorption (SCA) [1, 2].

High and stable adsorption capacity of zeolites by nitrogen and the high separation factor of the nitrogen–oxygen mixture are of primary importance for setups for adsorption air separation yielding oxygen that is carried out with application of zeolites. Extensive material on nitrogen and oxygen adsorption by zeolites of different types has been accumulated in the literature. Many authors suggest that type X zeolites are the best adsorbents for nitrogen for producing oxygen using the short-cycle adsorption technique [2–5]. As follows from these publications, enhancement of adsorption capacity of type X zeolites with respect to nitrogen is achieved by providing a Si/Al ratio close to unity in zeolites (here, LSX type zeolites), increasing the amount of cations in zeolites, and varying the cation composition, as well as via thorough preconditioning (activation) of zeolites before loading them into adsorbers [2].

Unfortunately, there are practically no data in the literature on the conditions of zeolite preactivation before their usage. In the course of optimization of the zeolite activation process conducted using the methods of experiment planning [6–8], our aim was to determine the pretreatment conditions of adsorbents providing the highest separation factors during the adsorption separation of air. Temperature (x_1), heating rate (x_2), composition (x_3), and specific volume of the purged gas (x_4) were considered as factors affecting the activation process. Residual water content in zeolites after activation (y_1), their equilibrium capacities with respect to nitrogen (y_2) and oxygen (y_3), and separation factor of the nitrogen–oxygen mixture ($y_4 = y_2/y_3$) were selected as the criteria. The optimum conditions for the activation process were sought using industrial X type zeolites. The parametric sensitivity of the chosen criteria to variation of the four factors was studied, and the combination of the values of factors determining the optimum activation conditions in the studied range was determined. Our studies [7, 8] indicated the positive effect of the presence of a small amount of carbon dioxide in the purged gas (nitrogen) in the course of NaX zeolite activation at 300–400°C on the following nitrogen adsorption by activated zeolite at the room temperature and the value of the separation factor of the nitrogen–oxygen mixture. Factor analysis showed that the significant factors in the studied range were only x_3 (CO_2 amount in nitrogen) and x_2 (adsorbent heating rate), while the factor x_3 that influenced the optimization criterion considerably.

There are indications in the literature [9–13] that carbon dioxide is chemosorbed on zeolites approximately under the same conditions that correspond to activation. According to the IR spectroscopy data in the literature, molecules of chemosorbed carbon dioxide can be in the form of carbonate/bicarbonate ions near sodium cations located in the S_I sites (in the windows leading to small cavities of zeolite X [14]). However, the spectrum of such structures in the case of CO_2 adsorption on zeolites differs from the spectrum of such structures in the case of CO_2 chemosorption by

Table 1. Results of mass spectrometric analysis of NaX zeolite

Item no.	Element	At %	Item no.	Element	At %
1	Li	–	12	Cl	0.0382
2	B	0.0080	13	K	0.2939
3	C	0.0836	14	Ca	0.3224
4	O	60.0351	15	Ti	0.0440
5	F	0.0049	16	Cr	0.0035
6	Na	6.8625	17	Mn	0.0058
7	Mg	1.5619	18	Fe	0.2165
8	Al	11.1806	19	Co	0.0001
9	Si	19.2800	20	Ni	0.0030
10	P	0.0135	21	Cu	0.0035
11	S	0.0286	22	Other (V, Zn, Ba, Sr, Y, Zr, Rb)	0.0103

oxides. Many authors of publications have concluded on this basis that formation of such structures occurs as a result of appearance of a bond between the carbon atom in CO_2 and surface oxygen atom of the zeolite framework. It is thought that the reaction occurs in close vicinity to the exchange cation, due to which the forming carbonate ion is stabilized by the positive charge of the cation. Preadsorption of a small amount of water on the zeolite favors CO_2 adsorption and formation of surface carbonate structures. The authors of [9] assumed that the S_{III} sites served as centers of formation of carbonate structures during adsorption on zeolites LiX, NaX, and KX.

Jacobs et al. [10, 11] described carbonate compounds formed as a result of CO_2 adsorption on NaX zeolite at 25°C. These compounds corresponded to a carbon dioxide molecule in the bent configuration polarized by a weakly screened cation and interacting with oxygen on the zeolite crystalline lattice. In the opinion of Jacobs, the sodium cation capable of forming carbonate compounds was the Na^+ ion located at the S_{III} site in the large cavity of zeolite X, near the four–membered window. It was assumed in [12] that only oxygen atoms of the negatively charged $[AlO_4]^-$ tetrahedron of the zeolite crystalline lattice participated in formation of the chemical bond.

The aim of this work was to study the effect of carbon dioxide in the purged gas during activation of zeolite NaX on the state of its surface and character of nitrogen and oxygen adsorption. Zeolite surface was studied using the Fourier transform infrared spectroscopy technique.

EXPERIMENTAL

Experiments were conducted using industrial zeolite NaX granulated with a binder. The granules had a spherical shape; the granule size was 1.6–2.5 mm. Before the studies, zeolites were milled and the fraction with the size of 1–2 mm was sifted out. Zeolite bulk density determined after zeolite dehydration at 350°C in the flow of nitrogen was 0.63 g/cm^3.

Elemental analysis of zeolites was carried out at the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, using an EMAL-2 laser mass spectrometer. The level of quantification of the method is 10^{-4} to 10^{-5} at %.

Before activation, zeolite samples were saturated by water until equilibrium was reached. Zeolites were activated in the flow of nitrogen in a quartz dynamic column equipped by electrical winding and heat insulation. The column was connected to a thermostat controller and a timer for maintaining the given heating rate and the time of zeolite conditioning at the given temperature. The purged gas (nitrogen) was supplied from a pressure vessel to the column; its consumption was 0.3 L/min. The conditions of NaX zeolite activation were as follows: the temperature was 400°C, the heating rate was 3.5°/min, the specific volume of purged nitrogen was 0.59×10^{-3} L N_2/L of zeolite, carbon dioxide content in nitrogen x_3 was 0–5 vol %.

After activation, hot zeolite granules were placed into a glass capillary and sealed, after which these samples were subjected to spectroscopic studies.

IR spectra were registered using a System 200 Fourier IR spectrometer (Perkin Elmer) equipped by the diffuse reflection add-on in the frequency range of 400–4000 cm^{-1}. The sample was loaded into a cup with a diameter of 11 mm [15].

For comparison, IR spectra of nonactivated zeolite samples were also obtained: those of the initial zeolite, of the sample after saturation by water vapors until the equilibrium state was reached in a dessicator, of the sample after storage in a closed weighing cup, and of a sample after conditioning in air in a weighing cup with no lid.

The residual water content in zeolite was determined as the difference between the mass of the crucible with a zeolite sample after activation and after calcination at 900°C divided by the sample weight after calcination. The equilibrium values of nitrogen and oxygen adsorption on zeolite samples were determined using the volumetric technique based on the experimental kinetic curves of gas adsorption. All measurements were carried out at 25°C and at atmospheric pressure. Oxygen and nitrogen from pressure vessels were used as adsorbates. The calibration gas was helium.

Oxygen, nitrogen, helium, and carbon dioxide were produced at the Russian Research Centre Kurchatov Institute and had the following grades: oxygen of especially pure grade, 99.999 vol % O_2; nitrogen of technical grade, 99.9 vol % N_2; helium of A grade, 99.995 vol % helium; carbon dioxide of technical grade, 99.8 vol % CO_2.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of elemental analysis of zeolite NaX are presented in Table 1. As seen in Table 1, mostly sodium (6.86 at. %) and magnesium (1.56 at. %) cations are present in the sample, but there are also small amounts of calcium, potassium, and iron ions that could be introduced into the sample together with the binder.

The results of experiments regarding the effect of CO_2 content in nitrogen in the course of activation of zeolite NaX on the residual amount of water in zeolite and its nitrogen and oxygen adsorption properties are presented in Table 2.

As follows from Table 2, the highest value of the separation factor of the nitrogen—oxygen mixture is reached on the sample activated at the CO_2 content in the purged gas being 2 vol %. This sample is characterized by the highest value of residual water content and also the highest values of equilibrium capacities with respect to nitrogen and oxygen among all the activated zeolite samples.

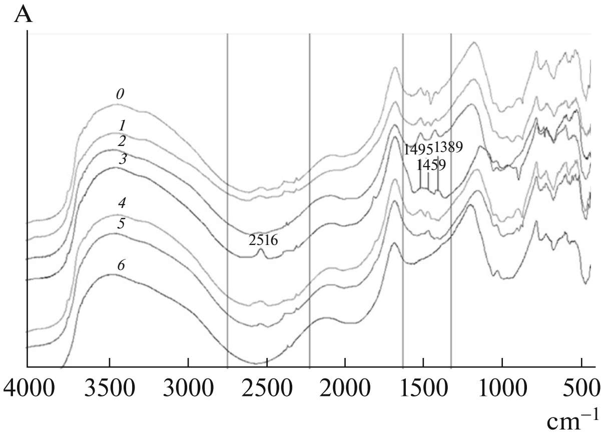
Figure shows IR spectra of samples of NaX zeolite after activation for the content of carbon dioxide in nitrogen of 0–5 vol % (curves *0–5*). It also shows for comparison the spectrum of the initial, nonactivated zeolite sample (curve *6*).

As seen in the figure, the general appearance of the spectrum for the sample activated by addition of 2 vol % CO_2 differs from the other curves by the presence of an absorption band (AB) at 2516 cm^{-1} and by the doublet maximum shape in the range of 1550–1300 cm^{-1}.

It is known [16] that ABs in IR spectra of gaseous CO_2 are present at 2350 and 667 cm^{-1}. Table 3 contains the data on attribution of absorption bands in IR spectra of zeolite NaX on the basis of vibrations of carbon dioxide and water molecules physically adsorbed on zeolite, OH groups on the zeolite surface, and chemosorbed carbon dioxide.

As is seen in Table 3, spectra of activated samples contain both physically adsorbed H_2O molecules and hydroxyl groups.

As seen in figure and Table 3, the spectra of all the initial and activated samples contain low-intensity ABs at 2352–2373 cm^{-1} that correspond to the nondissociated molecular surface compound, i.e., physically sorbed CO_2. These bands appear in the range of 2350–2370 cm^{-1} and represent antisymmetric vibration of physically adsorbed CO_2 molecules (ν_{as}).



IR spectra of NaX zeolite after activation: (*0–5*) carbon dioxide content in the purged gas being 0, 1, 2, 3, 4, 5 vol %, respectively; (*6*) spectrum of the initial sample that was not subjected to activation.

Paper [9] studies IR spectra of CO_2 adsorbed by zeolites LiX, NaX, KX. These spectra manifest appearance of AB of the antisymmetric linear vibration of physically adsorbed CO_2 molecules at 2368 cm^{-1} for LiX, at 2355 cm^{-1} for NaX, and at 2348 cm^{-1} for KX. The dependence of the frequency of this AB on the cation type points to interactions between the adsorbed CO_2 molecule and zeolite cation and to preservation of the linear structure of molecules in the adsorbed state.

Adsorption bands at 667 cm^{-1} characteristic for deformation vibrations (δ) of gaseous CO_2 are observed only in the spectra of the initial samples.

The authors of [9, 14, 17] observed three main ABs for water molecules on zeolites. They included narrow AB of vibrations of individual OH groups in the range of 3690–3700 cm^{-1}, a wide band characteristic for OH groups with hydrogen bonds between them in the range of 3250–3400 cm^{-1}, and H–O–H vibrations at 1645–1660 cm^{-1}. ABs at 3740, 3650, and 1640–1645 cm^{-1} characteristic for hydroxyl groups and physically adsorbed water molecules were observed in the spectra of the studied samples. Broad ABs in the range of 3540 cm^{-1} characteristic for low—frequency OH

Table 2. Effect of CO_2 content in nitrogen in the course of NaX zeolite activation on the residual amount of water in zeolite and its nitrogen and oxygen adsorption properties

x_3, vol %	y_1, g/100 g	y_2, cm^3/g	y_3, cm^3/g	y_4
0	2.87	8.33	3.89	2.14
1.0	2.14	7.58	3.77	2.01
2.0	3.21	15.94	4.62	3.45
3.0	2.28	7.00	4.17	1.68
4.0	2.42	6.88	4.10	1.68
5.0	2.62	6.22	4.39	1.42

Table 3. Attribution of absorption bands in IR spectra of activated NaX zeolite samples and samples after storage under diverse conditions

Treatment conditions	Absorption bands in IR spectra, cm^{-1}									
	physically adsorbed CO_2		hydroxyl groups [14]			physically adsorbed H_2O molecules	carbonates, CO_3^{2-}	bicarbonates, HCO_3^-		
	antisymmetric vibration of physically adsorbed CO_2 molecule, ν_{as}, 2349	deformation vibration of CO_2 molecule, δ, 667	surface OH groups, ~3740	high-frequency OH groups, ~3650	low-frequency OH groups, ~3540	deformation vibrations of H_2O molecules, 1645	ν_3 1400–1460	3300–2500	1670–1250	1000
Initial	2359, 2346	670	no	3653	no	1643	no	no	1658	1012
Initial after saturation by water vapors in a dessicator	2353, 2350	667	3745	3654	3539	1645	no	no	1660	1007
Initial after conditioning in air	2364, 2346	680	no	3653	3533	1646	1446	2520	1663	1012
Initial, storage in a closed weighing bottle	2363, 2352	669	3740, 3745	3654	3536	1641	1452	2520	1665	1010
Activated sample, % CO_2 0	2365	no	3740	3653	3542	1657	1452	2520	1657, 1451, 1390	1015
1	2373	no	3739	no	3527	1661	1452	2520	1661, 1495, 1449	1015
2	2367	no	3740	3654	3452	1659	no	3304, 2516	1659, 1495, 1459, 1389	1015
3	2352	no	3739	3654	3542	1645	1458	3301, 2530	1662, 1498, 1413	1015
4	2366, 2364	no	no	3654	3542	1658	1453	3300, 3245, 3240, 2523	1658, 1497, 1447, 1404	1020
5	2370	no	3740	3654	3544	1650	1458, 1403	3301, 3244, 2521	1660, 1567, 1497, 1458, 1405	1017

groups were observed in all the studied samples. ABs of individual OH groups at 3690 cm^{-1} were absent in all the studied samples. A broad band characteristic for vibrations of OH groups with a hydrogen bond between them in the range of 3250–3400 cm^{-1} was present in all samples (see figure).

In addition, the IR spectra contained several ABs in the range of 1200–1700 cm^{-1}. According to the definition provided in [8–10], they correspond to chemosorbed CO_2.

Monograph by I.I. Plyusnina [18] describes the technique of determination of mineral carbonates on the basis of their IR spectra. The main frequencies of vibration spectra of carbonates active in the infrared spectrum are ν_1 in the range of 1000–1100 cm^{-1} corresponding to the CO_3^{2-} ion in the form of a pyramid, ν_2 in the range of 830–900 cm^{-1} corresponding to the CO_3^{2-} ion in the form a triangle and pyramid, and ν_3 in the range of 1400–1460 cm^{-1}, and ν_4 in the range of 670–730 cm^{-1}. Practically all the studied spectra of zeolite NaX contained absorption bands corresponding to ν_1, ν_2, ν_4. This is apparently related to the fact that they coincide with the vibration frequencies in IR spectra of zeolite NaX [14]: 1060 and 971 cm^{-1} are antisymmetric valence vibrations of zeolite; 746, 690, and 668 cm^{-1} are symmetric valence vibrations of zeolite.

Weak ABs in the range of 1452 cm^{-1} are characteristic for carbonate compounds formed on zeolites X as a result of interaction with carbon dioxide molecules. These compounds correspond to CO_2 molecules adsorbed either in the linear configuration on cations, or in the nonlinear configuration in the form of carbonate or bicarbonate ions.

Such ABs are described in [9–11]. They were obtained by adsorption of CO_2 on NaCa faujasites at 350–400°C. Similar bands were registered for type *X* and *Y* zeolites with Mg^{2+} cations [19]. The authors attributed the intensive doublet at 1665 and 1325 cm^{-1} preserved in the spectrum up to 500°C to a carbonate compound similar to the compound on the MgO surface.

The products of reaction between CO_2 and hydroxyl groups on the zeolite surface are bicarbonates characterized by absorption bands at 3605, 1640, 1480, and 1235 cm^{-1} [17]. Monograph [18] attributes to bicarbonates complex-structure bonds in the ranges of 3300–2500, 1670–1250, 1000, 835, and 720 cm^{-1}. In the opinion of the authors of [18], the radical transformation of the spectrum is due to rearrangement of the anion complex from CO_3^{2-} to HCO_3^{-}.

Figure shows the range of IR spectra of the studied samples of zeolite NaX at 2520 cm^{-1}. These bands are typical for bicarbonate ions [18]. As seen from the figure, the highest-intensity AB is observed at 2516 cm^{-1} for the sample activated by adding 2 vol % of CO_2 to nitrogen.

Figure corresponds to the wavenumber range of 1670–1250 cm^{-1}. This range obviously includes both carbonate and bicarbonate ions. As follows from the figure, formation of doublet and further triplet ABs in zeolite spectra is observed at an increase in carbon dioxide content in nitrogen.

Low–intensity ABs characteristic for bicarbonates are present in the spectra of all the samples in the range of 1007–1020 cm^{-1}.

Apparently, the optimum conditions for formation of bicarbonate ions in zeolite are implemented in the course of its activation as a result of addition of 2 vol % CO_2 into nitrogen. Judging by the data of Table these are ABs at 2516 cm^{-1} and in the range of 1450–1380 cm^{-1}.

The presence of a considerable amount of carbonized cations in large cavities apparently prevents migration of a part of ion-exchange cations into small cavities and hexagonal prisms and thus provides high cationic activity in large cavities and high sample activity with respect to nitrogen.

To date, what the source of the third oxygen atom in CO_3^{2-} groups is has been the subject of debate. It is clear that the water oxygen in hydrated zeolite forms can be involved in formation of the CO_3^{2-} ion. Two possibilities have been considered in the literature for dehydrated zeolites: these are either framework oxygen atoms or oxo compounds. It is stated in [20] that it is oxo compounds that serve as a source of oxygen for carbonate formation. Various calculation methods and computer simulation are used in the works of A.V. Larin et al. [20, 21] to describe interaction between CO_2 molecules and zeolites of different types. The authors of [21] suggest that the bicarbonate structure is most realistic in the case of chemosorbed CO_2 in zeolite NaX.

CONCLUSIONS

Zeolite NaX samples have been activated under optimum conditions using different CO_2 amounts in nitrogen, their IR spectra have been measured, and their adsorption properties with respect to air macrocomponents have been determined.

It is found on the basis of the results of the conducted studies that zeolite NaX activated in the presence of 2 vol % CO_2 in nitrogen possesses the highest capacity with respect to nitrogen and oxygen and the highest residual water content. IR spectrometry studies have shown that it is this sample that manifests the absorption band with the highest intensity at 2516 cm^{-1} in the range characteristic for the bicarbonate structure.

Apparently, bicarbonate structures located in the large zeolite cavity near cations block the windows leading to small cavities and hexagonal prisms and prevent migration of cations (under high-temperature conditions) to migrate from large cavities to small cavities and prisms. Presumably, when the carbon dioxide content in nitrogen in the course of activation is above 2 vol %, formation of carbonates prevails or density of bicarbonates in cavities becomes too high. This is indicated by intense AB doublets and triplets in IR spectra in the range of 1500–1380 cm^{-1}. This results in a decrease in nitrogen adsorption.

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