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Abstract

Full Text

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COMPOSITION OF UNIT CELLS AND LIMITING ADSORPTION VOLUMES OF DEHYDRATED CRYSTALS OF SYNTHETIC ZEOLITES

In recent years, synthetic zeolites of types A and X have been finding ever-increasing practical application as highly effective adsorbents, especially for the separation of gas mixtures and the deep purification and drying of gases. Zeolites are obtained by hydrothermal synthesis in the form of crystals with dimensions on the order of a micron. In technology, zeolites of types A and X are usually used in the form of granules, tablets, or beads consisting of the crystalline powder of the zeolites proper and binder additives (10-15%). With a rational method of granulation, an additive of binder that is practically inert in the adsorption sense causes, in proportion to its content, a decrease in the adsorption properties of the granules in comparison with the original crystalline zeolite. Therefore, the principal scientific interest lies in the consideration of the structural and adsorption properties of dehydrated zeolite crystals.

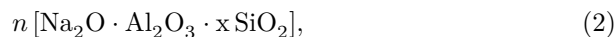
Synthetic zeolites of types A and X in the fully hydrated state are continuous crystalline substances possessing a rigid aluminosilicate framework. As a result of dehydration, carried out under evacuation at a temperature of 350°, voids or cavities of sizes strictly definite for each type of zeolite are formed in the zeolite crystals. These voids constitute the primary porous structure of dehydrated zeolite crystals. The parameters of the primary porous structure (the shape and size of the pores and of the narrower entrances into them, or “windows”) are well known from X-ray structural investigations. Therefore, for dehydrated zeolites the total volumes of the primary pores, or limiting adsorption volumes, can be calculated on the basis of data on their chemical composition and crystal structure.

The chemical composition of dehydrated synthetic zeolites A or X in oxide form can be expressed as:

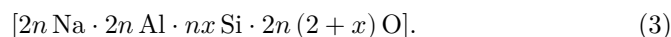


where x denotes the molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$. Both types of zeolite have cubic unit cells of crystals, the parameters of which a_0 (the cube edge) are known

from X-ray structural data. Then the composition of the unit cell in oxide form will be expressed as:



where the number n brings into agreement the content of the atoms (ions) Na, Al, Si, and O in the aluminosilicate framework of the unit cell with the X-ray structural data. The composition of the unit cell of a zeolite crystal according to (2) can be expressed in atomic form as:



According to X-ray structural data, the unit cell of a crystal of synthetic zeolite A contains one cuboctahedral (sodalite)

structural unit consisting of 24 ions (Al + Si) and 36 O ions, as well as 3 four-membered oxygen bridges, in which the total content of oxygen ions is 12. In all, the aluminosilicate framework of the unit cell of zeolite A contains 24 ions (Al + Si) and 48 oxygen ions⁽¹⁻³⁾.

According to analogous X-ray structural data, the unit cell of a crystal of synthetic zeolite X contains 8 cubooctahedral units, which include $24 \cdot 8 = 192$ ions (Al + Si) and $36 \cdot 8 = 288$ O ions. In addition, 96 O ions are contained in 16 six-membered oxygen bridges belonging to one unit cell^(3,4). In all, the unit cell of zeolite X contains 192 ions (Al + Si) and 384 O ions. Fourier analysis does not make it possible to determine the positions of all ion-exchange cations and, consequently, their total amounts in the unit cells of zeolites A and X.

On the basis of the chemical composition of the unit cell of zeolite in form (3) and the numbers of ions (Al + Si) and O contained in it, obtained from X-ray structural measurements, one can obtain a relation between x and n for each type of zeolite. Let us consider the derivation of this relation for the example of zeolite X. According to the formula for the composition of the unit cell (3), the number of ions (Al + Si) is expressed as $2n + nx = 192$, or

$$n(2+x) = 192. \quad (4)$$

In an analogous way we obtain the same relation (4), taking into account the number of oxygen ions in the unit cell. We arrive at the same conclusion from the condition of electroneutrality of the unit cell, containing positive ions Na^+ , Al^{3+} , and Si^{4+} and negative ions O^{2-} :

$$2n \cdot 1 + 2n \cdot 3 + nx \cdot 4 = 384 \cdot 2, \quad (5)$$

from which formula (4) follows.

According to (4), for zeolite NaX it follows that:

$$n = \frac{192}{2 + x}. \quad (6)$$

The analogous formula for zeolite NaA has the form:

$$n = \frac{24}{2 + x}. \quad (7)$$

Table 1 contains, as examples, characteristics of the composition and parameters of the unit cells of crystals of zeolites of types A and X from the Linde firm according to data of various investigators. The formulas given in the table—

Table 1

Zeolite	Lit. source	x	n	$a_0, \text{Å}$	Formula of type (3) for the unit cell
NaA	(¹)	2.00	6	12.32	12 Na · 12 Al · 12 Si · 48 (O)
NaA	(³)	2.00	6	12.30 ± 0.01	12 Na · 12 Al · 12 Si · 48 (O)
NaA	(²)	1.87	6.205	12.273 ± 0.003	12.40 Na · 12.40 Al · 11.60 Si · 48 (O)
NaX	(³)	2.8	40	24.91 ± 0.02	80 Na · 80 Al · 112 Si · 384 (O)
NaX	(⁴)	2.67	41.11	24.94	82.22 Na · 82.22 Al · 109.78 Si · 384 (O)

formulas of the zeolites satisfy the X-ray structural data for the total content of ions (Al + Si) and O ions in the unit cells of the crystals. Obviously, the values of n have the character of statistical averages.

According to the data of the table, the main difference in the chemical composition of the aluminosilicate frameworks of zeolites A and X consists: 1) in the different relative content of Al and Si ions entering into the aluminosilicate and silico-

oxygen tetrahedra, from which the cubooctahedral structural units are built, and 2) in the different mutual linkage of the cubooctahedral units—by means of four-membered oxygen bridges in zeolite A and, correspondingly, six-membered oxygen bridges in zeolite X. Thus, the cubooctahedral unit of zeolite A contains 12Al^{3+} , 12Si^{4+} , and 36O^{2-} , while the cubooctahedral unit of zeolite X contains 10Al^{3+} , 14Si^{4+} , and 36O^{2-} . Of the 12O^{2-} per cubooctahedral unit in zeolites A and X, these belong to oxygen bridges. The excess negative charges of the cubooctahedral units and of the corresponding oxygen bridges are compensated by Na^+ , which determines their number in the zeolite.

The variable values of x , and in particular those somewhat smaller than 2 for NaA, may be explained: 1) according to Barrer, for NaA ($x=2$), by occlusion of NaAlO_2 molecules in the cavities of the zeolite, and 2) from our point of view, by a kind of isomorphous replacement of part of the silico-oxygen tetrahedra in the cubooctahedral structural units by alumino-oxygen tetrahedra. Concrete examples of cubooctahedral units with different relative contents of Al and Si ions are the cubooctahedra of zeolites NaA and NaX. We allow for the possibility of small deviations from Löwenstein's rule for NaA ($x < 2$), which should manifest themselves in a lowered stability of the aluminosilicate framework of the zeolite.

Such isomorphous substitution has no substantial effect on the parameters a_0 of the elementary crystal unit cells. Thus, the parameter a_0 of NaX, calculated per one cubooctahedral unit ($24.92 : 2 = 12.46 \text{ \AA}$), differs very little from the values of a_0 for NaA given in the table.

In some cases, especially for zeolite samples obtained under laboratory conditions, the ratio of the numbers of Na and Al atoms, according to chemical analysis data, is somewhat below unity, usually by not more than 10%. It is not excluded that this is the result of ion exchange of a small fraction of Na^+ for H^+ , due to the presence of appreciable amounts of carbonic acid in the ordinary distilled water used for washing zeolite crystals. According to preliminary observations, this effect is manifested to a greater extent upon prolonged washing of the zeolite.

The form and dimensions of the cavities of the unit cell of dehydrated crystals of synthetic zeolites of type A, known from X-ray structural data, make it possible to calculate easily the total volumes of the cavities of the unit cell and the limiting adsorption volumes per unit mass of dehydrated crystals, accessible to adsorbed molecules of different sizes. This problem is more difficult to solve for zeolites of type X, owing to the arrangement of the centers of the cubooctahedral units at the nodes of the crystal lattice characteristic of diamond, i.e., to the nonsymmetric arrangement of the cavities in the unit cell. In the present work

an attempt is made to solve this problem by calculating the apparent volume of the cubooctahedral unit from X-ray structural data for the unit cell of zeolite A and taking into account the volumes of four-membered and six-membered oxygen bridges in the aluminosilicate frameworks of the unit cells of zeolites A and X.

In accordance with the model of the aluminosilicate framework of zeolite NaA⁽²⁾, the unit cell of the crystal contains one cubooctahedral structural unit and 3 corresponding four-membered oxygen bridges. On the other hand, per one unit cell there is one large cavity of practically spherical form with a diameter of 11.4 Å^(1,2) and a volume of 776 Å³, and one small cavity inside the cubooctahedron with a diameter of 6.6 Å^(1,2) and a volume of 150 Å³. If a_0 is the unit-cell parameter of NaA, then the apparent volume of the cubooctahedral structural unit V_{ko} in the aluminosilicate framework of the zeolite is expressed as:

$$V_{ko} = a_0^3 - (776 + 3V_{4m}), \quad (8)$$

where V_{4m} is the volume of a four-membered oxygen bridge.

It is easy to construct a model of a four-membered oxygen bridge connecting, through oxygen ions, the (Al, Si) ions located at the vertices of the four-membered windows of adjacent cubooctahedral units. Taking, according to⁽³⁾, the bond length (Al, Si)–O as 1.67 Å and, consequently, the side length of the four-membered window as 3.34 Å, and placing the oxygen ions of the bridge at the centers of the straight lines connecting the (Al, Si) ions of adjacent cubooctahedra, we obtain, for an oxygen-ion radius of 1.4 Å, a radius of the circumscribed circle for the normal section through the middle of the four-membered oxygen bridge of 3.7 Å. If such an oxygen bridge is represented as a cylinder with radius 3.7 Å and height equal to the diameter of the oxygen ion, 2.8 Å, its volume will be 116 Å³. According to⁽⁸⁾, at $a_0 = 12.273 \pm 0.003$ Å⁽²⁾, i.e., for a unit-cell volume of 1848 Å³, the apparent volume of the cubooctahedral unit will be 724 Å³.

The unit cell of zeolite NaX with $a_0 = 24.94$ Å⁽⁴⁾ and a volume of 15513 Å³ contains 8 cubooctahedral units and 16 six-membered oxygen bridges connecting them. If V_{6m} is the volume of one six-membered bridge, then the total volume of the 8 large cavities (“super-cages”) V_6 contained in the unit cell is expressed as:

$$V_6 = 15513 - 8 \cdot 724 - 16V_{6m}. \quad (9)$$

In the same way as for the four-membered oxygen bridge, according to the constructed model of a six-membered bridge with the same parameters (the (Al, Si)–O bond lengths and the oxygen-ion radius), the radius of the circumscribed circle for the normal section through the middle of the bridge will be 4.8 Å. If such an oxygen bridge is represented as a cylinder with radius 4.8 Å and height

equal to the diameter of the oxygen ion, 2.8 Å, then its volume V_{6m} will be 202 Å³. Substituting this value into formula (9), we obtain $V_6 = 6490$ Å³. Only the volume of these cavities is accessible to most molecules of adsorbed substances, such as nitrogen, hydrocarbons, etc.

For water molecules, in addition to the large cavities, the internal or small cavities of the cubooctahedra, with volumes of 150 Å³ for each cubooctahedron, are accessible through the “windows” in the cubooctahedra. The total volume of the small cavities in the unit cell of zeolite NaX is: $V_m = 150 \cdot 8 = 1200$ Å³. The total volume of the cavities of the unit cell of zeolite NaX accessible to water molecules is:

$$V = V_6 + V_m = 6490 + 1200 = 7690 \text{ Å}^3. \quad (10)$$

According to Barrer, one unit cell of fully hydrated zeolite NaX contains 256 water molecules (⁴). This number of water molecules corresponds to the volume of a liquid of normal density, or to a limiting adsorption volume of 7670 Å³, practically coinciding with the calculated volume V .

In conclusion, the author considers it a pleasant duty to express gratitude to N. A. Shishakov for discussing the results obtained.

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