

Cation Positions in Cerium X Zeolites

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The cation positions and the resulting changes, which were caused by the replacement of sodium ions by cerium ions, in the zeolite framework of cerium exchanged 13X-type molecular sieves, $0.3 \text{ Na}_2\text{O} \cdot 13.0 \text{ Ce}_2\text{O}_3 \cdot 44.0 \text{ Al}_2\text{O}_3 \cdot 104.0 \text{ SiO}_2 \cdot n \text{ H}_2\text{O}$, have been determined by structural studies using X-ray powder data. In the exchanged sieve ($a_0 = 25.10 \pm 0.02 \text{ \AA}$), in which nearly all of the remaining 2% of sodium oxide has been removed by $(\text{NH}_4)_2\text{SO}_4$ exchange, cerium ions were found to partially occupy site S4 in the large cavity and site S2 in the sodalite cage. When this material was calcined at 540°C in a nitrogen atmosphere ($a_0 = 24.94 \pm 0.02 \text{ \AA}$), the cerium cations were found to migrate to sites S1, S2, and S5 with the majority of the cations being in S2. Site S1 is in the hexagonal prism and is the least accessible site.

Upon dehydration of the material at 540°C in air ($a_0 = 24.86 \pm 0.02 \text{ \AA}$), however, the cations moved to sites S1 and S2 only, with the majority of them being in S2 sites. The three cations (on the average) per sodalite cage which occupied S2 sites displayed a strong repulsion for each other. This repulsion resulted in a significant distortion of the sodalite cage. The greater cationic repulsion observed when calcination was done in air versus a much lesser repulsion when calcination was done in a nitrogen atmosphere is due to the oxidation of at least 50% of the Ce^{3+} cations to the $4+$ oxidation state.

For the hydrated sample the occupancy factor of S4 sites is 0.66. The population parameter of S2 is 0.69 and 0.74 for the nitrogen calcined zeolite and for the air calcined zeolite with the corresponding closest Ce-O distances for this site being 2.56 and 2.66 \AA , respectively.

INTRODUCTION

Synthetic zeolites X and Y, which have the same framework structure as the natural mineral faujasite (1-5), possess favorable catalytic properties that make them useful in the petroleum industry (6). These synthetic zeolites which are usually prepared in the sodium form are exchanged with polyvalent cations or hydrogen to render sieves with superior catalytic activity (7, 8). One group of polyvalent cations which have been found to give a material of high stability and activity are the rare earth metals.

In order to gain a better understanding of the properties of these materials, it is necessary to know the positions of the cations in the zeolites. Both X and Y zeo-

lites are cubic and belong to the space group $Fd\bar{3}m$. The faujasite framework is made of $\text{Si}(\text{Al})\text{-O}_4$ tetrahedrons which are linked together by the sharing of oxygen atoms so that there are always two oxygen atoms for each $\text{Si}(\text{Al})$ atom. These tetrahedrons are joined to form a truncated cubo-octahedral unit which is termed the "sodalite cage or unit" and which consists of eight hexagonal rings containing six oxygen atoms each [six-membered rings (6MR)] and six square rings with four oxygen atoms [four-membered rings (4MR)]. The basic formula for the sodalite unit is $\text{Si}(\text{Al})_{24}\text{O}_{36}$. Each sodalite cage is joined to four others in a tetrahedral arrangement. These cages are joined via six oxygens that connect two 6-membered rings

TABLE 1
ATOMIC COORDINATES^a FOR CERIUM X SIEVES^b

Atom	Occupancy parameter	X	Y	Z	T
Cerium X hydrate					
T(Si,Al)	1.0	-0.0560(15)	0.1218(10)	0.0353(21)	0.40
O(1)	1.0	0.0000	0.1136(23)	-0.1136(23)	2.00
O(2)	1.0	-0.0056(34)	-0.0056(34)	0.1414(24)	2.00
O(3)	1.0	0.1662(20)	0.1662(20)	-0.0213(35)	1.97(2.9)
O(4)	1.0	0.1830(22)	0.1830(22)	0.3149(31)	1.00
O _w (1)(S1)	0.71(12)	0.0000	0.0000	0.0000	5.14(6.9)
Ce(2)(S2)	0.28(2)	0.0581(11)	0.0581(11)	0.0581(11)	4.13(2.1)
O _w (3)(S3)	1.00	0.1748(29)	0.1748(29)	0.1748(29)	1.50
Ce(4)(S4)	0.66(2)	0.2393(5)	0.2393(5)	0.2393(5)	1.55(0.7)
Cerium X calcined in nitrogen					
T(Si,Al)	1.0	0.0567(7)	0.1219(7)	0.0314(10)	0.06(0.6)
O(1)	1.0	0.0000	0.1070(12)	-0.1070(12)	3.14(1.5)
O(2)	1.0	-0.0035(14)	-0.0035(14)	0.1296(13)	0.59(1.1)
O(3)	1.0	0.1767(13)	0.1767(13)	-0.0369(15)	1.11(1.2)
O(4)	1.0	0.1696(12)	0.1696(12)	0.3154(21)	0.36(1.6)
Ce1(S1)	0.26(1)	0.0000	0.0000	0.0000	2.82(2.3)
Ce2(S2)	0.71(1)	0.0650(3)	0.0650(3)	0.0650(3)	2.08(0.4)
O _w (2)(U)	0.18(14)	0.1250	0.1250	0.1250	3.50
Ce(5)(S5)	0.16(1)	0.5000	0.5000	0.5000	2.50
Cerium X calcined in air					
T(Si,Al)	1.0	-0.0598(15)	0.1264(8)	0.0350(9)	0.37(0.8)
O(1)	1.0	0.0000	0.1160(19)	-0.1160(19)	0.31(2.2)
O(2)	1.0	-0.0256(20)	-0.0256(20)	0.1280(18)	3.17(2.6)
O(3)	1.0	0.1680(14)	0.1680(14)	-0.0439(24)	2.38(1.9)
O(4)	1.0	0.1812(16)	0.1812(16)	0.3036(25)	0.89(1.9)
Ce(1)(S1)	0.20(2)	0.0000	0.0000	0.0000	1.50
Ce(2)(S2)	0.74(1)	0.0565(4)	0.0565(4)	0.0565(4)	3.40(0.6)
O _w (2)(U)	0.78(18)	0.1250	0.1250	0.1250	2.29(9.1)

^a Origin at $\bar{3}M$.

^b Estimated standard deviations (σ) are in parentheses.

or hexagonal faces to form a hexagonal prism (D6MR). The bridging oxygens are generally labeled O(1) (see Table 1). The 12 oxygen atoms comprising the two 6MR of the hexagonal prism are conventionally termed O(2) and O(3). This tetrahedral arrangement of sodalite cages results in large cavities having rings of 12 oxygen atoms [12-membered rings-(12MR)]. Entrances into these cavities from within the sodalite unit are through the second set of tetrahedrally arranged 6MR which are composed of oxygens labeled O(2) and O(4).

In general, there are six sites (9, 10) available to nonframework ions (see Fig.

1). These sites all have coordinates xxx and are: (1) S1 which is in the center of the hexagonal prism; (2) S2 which is within the sodalite cage approximately 1 Å from the 6MR that comprises the hexagonal prism; (3) U which is in the center of the sodalite cage; (4) S3 which is within the sodalite cage approximately 1 Å from the center of the 6MR which opens into the large cavity; (5) S4 in the large pore about 1 Å from the center of the 6MR of S3; and (6) S5 which is in the center of the 12-membered ring.

Olson *et al.* (10) have reported the structures of cerium exchanged natural faujasite and lanthanum X. Cerium ions

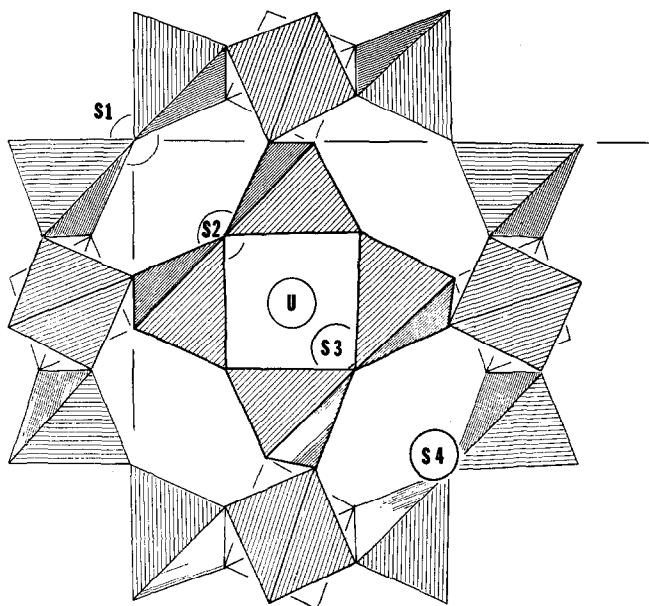


FIG. 1. Projection of the sodalite cage for faujasite showing the available nonframework sites. Site 5 is in the center of the 12MR and is not shown here.

were found to occupy S5 sites and to be randomly located in the supercages in hydrated cerium exchanged natural faujasite. Upon calcination all the cerium ions migrated to S2 sites in the sodalite cage. In hydrated lanthanum X, lanthanum ions occupy sites S2 and S4 with water being in S3. Calcination results in the movement of all the lanthanum ions to S2. Smith *et al.* (9) have reported the cation positions for calcined LaY at room temperature and 725°C. Lanthanum occupies S2 sites at room temperature and at 725°C some of the cations migrate to sites S1 and S4. Bennett and Smith (11-14) have published a series of articles on lanthanum exchanged natural faujasite and hydrated LaX. They found lanthanum ions to occupy sites S2 and S5; and S2, S4, and S5; respectively. They studied calcined samples of both materials at several temperatures and found in all cases that lanthanum ion occupied S1, S2, and S4 sites. We have studied the cation distribution in CeX sieves because we were interested in discerning whether this distribution would be any different or the structure altered in any manner due to the ease of oxidation of Ce^{3+} to Ce^{4+} .

METHODS

Since single crystals of synthetic faujasite are quite difficult to obtain, it was necessary to use the less accurate powder techniques in which non-unique reflections must be utilized. In order to understand the structural changes which occur during each step of the preparation of the material, CeX sieves were studied (1) in the hydrated form, (2) in the activated form after calcination in a nitrogen atmosphere, (3) in the activated form after calcination in air. The samples were prepared from a commercial NaX sieve which is manufactured by the Davison Division of the W. R. Grace & Co. The starting NaX sieve was thoroughly washed with deionized water to remove excess caustic and other water-soluble impurities. The unit cell composition of the NaX sieve as determined by chemical analysis was $42.2 Na_2O \cdot 44.0 Al_2O_3 \cdot 103.9 SiO_2 \cdot nH_2O$. The cerium chloride used for the exchanges was obtained from the American Potash & Chemical Co. (purity of 99%). To prepare the hydrated CeX sieve, the NaX starting material was exchanged by contact with an excess of

cerium(III) chloride solution. The exchange was carried out at the boiling temperature of the solution in a nitrogen atmosphere. Hydrogen was bubbled through the cerium chloride solution prior to the exchange. The cerium exchange of the molecular sieve was repeated under the same circumstances with a fresh cerium chloride solution. The resulting cake was washed and then calcined at 540°C for 2 hr in a flow of dry nitrogen. The sieve obtained still contained 1.2% Na₂O. The remaining sodium ions were ammonium exchanged by contacting the sieve with an excess of ammonium sulfate solution at boiling temperature under nitrogen. The resulting white material was finally washed and dried at 100°C. This material is the sample which is termed CeX hydrate.

The nitrogen calcined CeX sieve, Ce³⁺X, was made by heating the CeX hydrate material at 540°C for 2 hr in a flow of dry nitrogen. A gray-white powder resulted. The air calcined CeX sieve (Ce⁴⁺, Ce³⁺)X, was obtained by calcining CeX hydrate at 540°C for 2 hr in a muffle furnace in contact with the atmosphere. A yellowish material resulted. The samples were analyzed by X-ray spectroscopy for the alumina, silica, and rare earth content and by flame photometry for the sodium content. The results showed that the unit cell formula was 0.3 Na₂O·13.0 Ce₂O₃·44.0 Al₂O₃·104.0 SiO₂·nH₂O. Since the univalent cation equivalent of the cerium ions does not equal the number of aluminum ions, it was assumed that the excess negative charges are compensated by hydrogen ions resulting from the ammonium sulfate exchange. Chemical analysis also indicated that in the air calcined sample at least 50% of the cerium ions had been oxidized to the tetravalent state.

The unit cell values were 25.10 ± 0.02, 24.94 ± 0.02, and 24.86 ± 0.02 Å for the hydrated, N₂ calcined, and air calcined samples, respectively. The X-ray diffraction intensity data on the hydrated sample were collected on a Norelco powder diffractometer equipped with a Geiger counter as a detector. On the other two samples a Hamner solid state detection system

equipped with a scintillation counter and pulse height analyzer was employed. X-Ray scans were taken using Cu K α radiation, 0.006-in. receiving slit, and a scanning speed of 1/8°/minute. The two theta region between 5 to 65° was scanned at three different attenuations, 1000/2, 500/4, and 200 counts/8 sec, in order to record the strongest and the weakest reflections. A total of 96 observations, some of which were combinations of several reflections, could be recorded in this range. The X-ray peaks were planimeted at least three times each to obtain the average area. Whenever a particular observation was recorded at more than one attenuation, the average value of the two or three observation was used as the intensity of that peak. All the samples used were equilibrated with the atmosphere before data collection was commenced.

Three-Dimensional Fourier Analyses and Least-Squares Refinement

The three-dimensional Fourier program used was written by Dr. F. R. Ahmed (15) of the National Research Council of Canada. Only those observations which were due to single reflections or to the coincidence of two reflections were used in computing the initial electron density maps. A series of computer programs written by Mr. R. Coelho of our research center and one of us (FDH) for the IBM 360 Model 30 were used to reduce the observed intensities to observed structure factors. The structure factors were assigned the algebraic signs calculated on the basis of the framework alone.

The least-squares refinement program employed was written by Dr. Walter C. Hamilton (16) of Brookhaven National Laboratory and is a general program to refine powder pattern data for any structure for which the appropriate subroutine defining the observations in terms of the structural parameters has been written. Such subroutines were written by one of us (FDH) for the three structures under study. This program was run on the Univac 1108 computer at the University of Maryland through the cooperation of Dr. James

Stewart. Since in these structures there were 34 or more parameters, the framework parameters only and the extra-framework parameters alone were varied alternatively in successive least-squares cycles in order to keep the over-determination ratio as large as possible. Site occupancy factors and temperature factors were never varied in the same cycle because they are closely correlated.

Refinement was performed on the weighted intensities where the weighting scheme used was that of Cruickshank (17)

$$w = 1/(a + b F_o + c F_o^2),$$

with all the coefficients adjusted to give the best weighting scheme for each set of data. The quantity minimized was $\Sigma w(I_{\text{obs}} - I_{\text{calc}})^2$. In these equations w is the weight, I_{obs} and I_{calc} are observed and calculated intensities, and F_o is the observed structure factor, which in this case was replaced by the observed intensity. The tetrahedral scattering factors employed were the weighted average of $f_{\text{Si}^{2+}}$, interpolated from f_{Si} and $f_{\text{Si}^{3+}}$, and $f_{\text{Al}^{3+}}$, (18) with the weights assigned according to the silicon to aluminum ratio of 1.182 as determined by X-ray spectroscopy. For oxygen and cerium, f_{O} and f_{Ce} form factors were used (18).

RESULTS

A. Cerium X Hydrate

The framework parameters and cation positions reported by Olson *et al.* (10) for lanthanum X hydrate were used as starting values. The Fourier map calculated on the basis of the signs resulting from the framework alone showed extra peaks besides those assigned to the metal cations. These peaks were attributed to water molecules. Refinement was terminated at an $R(I)$ value of 0.151, where $R(I) = [\Sigma w(I_{\text{obs}} - I_{\text{calc}})^2 / \Sigma w(I_{\text{obs}}^2)]^{1/2}$. The final atomic coordinates, thermal parameters and occupancies are given in Table 1. The occupancy of the water molecule in S3 was fixed at 1.00, since any refinement of it led to a

higher value. A value of the occupancy factor greater than 1.00 would indicate that this site may be occupied by a mixture of water molecules and cerium ions. The observed and calculated intensities and structure factors are given in Table 2. A projection of the sodalite cage for this structure is given in Fig. 2.

Cerium ions were found to occupy sites S2 and S4 with occupancy parameters of 0.28 and 0.66. Unlike the lanthanum X (10) case no cerium ions were found to occupy S5 sites. Site S1 was found to be partially occupied by water and as men-

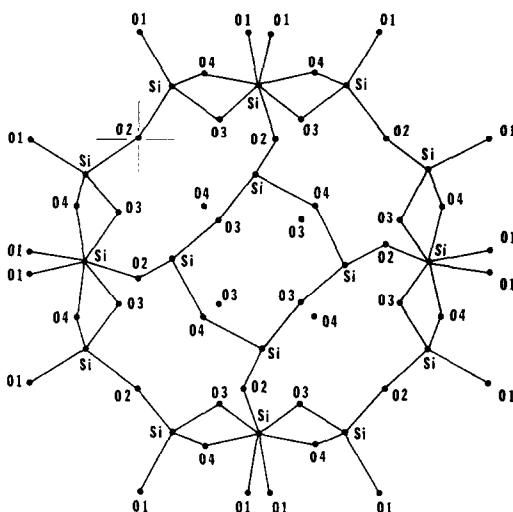


FIG. 2. View of the sodalite cage for CeX hydrate, in projection down the cell edge. Some of the O(1) and O(2) atoms have been omitted for clarity.

tioned above, S3 seems to be occupied by a mixture of water molecules and cerium ions (about two cerium ions/unit cell). Cerium in site S2 is coordinated to the three O(3)s of the sodalite 6MR belonging to the hexagonal prism and to the water oxygen occupying S1 with distances of 2.19 and 2.53 Å respectively. This cerium ion is also coordinated by three water oxygens from S3 as second nearest neighbors at a distance of 2.99 Å. This coordination is similar to that found in calcined LaX and hydrated LaX (10), where in the former the La^{3+} in S2 is surrounded by three lattice oxygens and three water oxygens all

at $2.5 \pm 0.1 \text{ \AA}$. The cerium ions in S4 have three O(2)s as nearest neighbors at a distance of 2.52 \AA and three O(4)s and one O_w(3) as next nearest neighbors at distances of 2.75 and 2.80 \AA , respectively. All the framework oxygens are from the 6MR opening into the supercage.

The average silicon or aluminum to oxygen distance of $1.73 \pm 0.07 \text{ \AA}$ is somewhat long compared to other values which have been reported (3–5, 10) and compared to the value of 1.676 reported by Jones (19) for feldspars of the same silicon to aluminum ratio. However, this value is still within 1σ of the value reported by Jones.

B. Cerium X Calcined in a Nitrogen Atmosphere, $Ce^{3+}X$

The framework parameters reported by Olson *et al.* (10) for calcined lanthanum X were used to calculate the signs of the observed structure factors from which the Fourier map was computed. Three crystallographically different cerium peaks and one water peak were detected. Initially two of the three cerium peaks (S1 and S5) were thought to be water, but least-squares refinement of the complete structure strongly indicated that these peaks must be due to cerium ions. Refinement was terminated at an $R(I)$ value of 0.105. The final coordinates, thermal parameters and occupancy factors are given in Table 1. A projection of the sodalite unit for this structure is given in Fig. 3.

Cerium ions were found to occupy S1, S2, and S5 sites with population parameters of 0.26, 0.71, and 0.16. Site U was found to be occupied by roughly one water molecule per unit cell. However, as shown in Table 1, the large standard deviation of the population parameter for this site makes its occupancy uncertain. The cerium ions in S2 sites are coordinated to three O(3)s at distances of $2.56(4) \text{ \AA}$. Cerium in site S1 coordinated to all six of the O(3)s of the D6MR at a distance of $2.74(3) \text{ \AA}$ each. The Ce(2)–Ce(2) distance is $4.23(1) \text{ \AA}$.

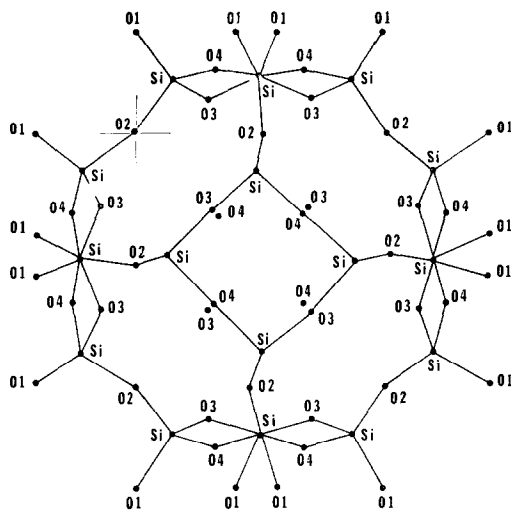


FIG. 3. View of the sodalite cage for CeX calcined in nitrogen, in projection down the cell edge. Some of the O(1) and O(2) atoms have been omitted for clarity.

The framework coordinates changed only slightly from the values reported for LaX (10). The average of the tetrahedral (Si, Al)–O bond lengths is 1.63 \AA with (Si, Al)–O(1) distance of 1.53 \AA being rather short to the standard value of 1.676 \AA .

C. Cerium X Calcined in Air, $(Ce^{4+}, Ce^{3+})X$

From an electron density map calculated in the same manner as the one for the nitrogen calcined sample, two cerium peaks and one nonframework oxygen peak were detected. The cerium peaks occurred at sites S1 and S2 and the oxygen peak at site U. Refinement of this model using the framework parameters and the extra-framework coordinates selected from the Fourier map would not proceed below an R value of 0.34 when the refinement was attempted by the same procedure as that used on the first two samples. This procedure consisted of refining the extra-framework parameters only until the R value dropped below 0.23 and then in alternating cycles refining the framework parameters and the extra-framework parameters. Since initial refinement of the extra-framework

TABLE 2 (Continued)

13 3 1	1849	3014	5	6	554	130	25	12	*	76	344	8	-18
11 7 3			614	784			159	-77	*			124	283
9 7 7			44	56			444	-215	*			59	-136
12 6 0			0	0			0	0	*	76	90	0	0
10 8 4			185	236			27	13	*			132	143
12 6 2	* 97	230	150	-230	397	129	305	-174	*	76	0	134	-2
13 3 3	* 97	404	214	436	954	512	362	265	*	897	719	529	474
9 9 5	*		7	14			569	417	*			387	347
8 8 8	419	306	781	668	* 157	53	461	-280	*	76	47	336	-264
13 5 1	2077	2675	572	-650	3729	2887	266	234	*	1766	1077	31	24
11 7 5			416	-473			622	-547	*			227	-177
14 0 0			0	0			0	0	*			0	0
12 6 4			115	-131			693	-610	*			629	-491
14 2 0	2401	2316	117	-398	2944	2838	222	-218	*	2019	1634	162	-143
10 10 0			1366	-1342			1650	-1619	*			1249	-1123
10 8 6			254	-249			238	-234	*			350	-315
13 5 3	746	1473	34	-48	2373	2662	591	-626	*	1120	1195	322	-332
11 9 1			165	-232			364	-385	*			100	103
14 2 2			410	-576			394	417	*			186	193
10 10 2			407	-572			365	386	*			578	597
12 8 0	396	846	460	673	* 78	30	206	128	*	76	310	204	412
11 9 3	1298	1078	519	-673	1003	1235	352	-390	*	76	189	9	14
9 9 7			15	14			436	-484	*			205	-324
14 4 0			0	0			0	0	*	76	71	0	0
12 8 2			291	265			242	-249	*			146	141
14 4 2	* 97	510	143	-328	* 78	370	134	-291	*	76	613	50	-143
12 6 6	*		93	-212	*		86	-186	*			155	440
10 10 4	*		161	-161	*		34	-74	*			120	341
13 7 1	* 97	1420	101	388	* 554	409	39	-33	*	76	627	99	264
13 5 5	*		184	-704			511	-439	*			88	-254
11 7 7	*		31	118			237	-204	*			130	-373
12 8 4	* 97	39	169	107	* 78	6	153	-41	*	76	44	151	-115
15 1 1	714	515	184	-156	659	226	618	362	*	76	253	212	387
13 7 3			407	345			84	-49	*			15	27
13 10 2			14	-12			14	-12	*			21	38
14 4 4			208	-177	* 78	508	218	-555	*	76	62	184	-166
10 8 8			133	113	*		4	11	*			111	100
14 6 0	* 97	0	244	15	* 78	432	221	518	*	76	420	218	513
15 3 1	* 97	327	174	-319	* 78	92	40	43	*	76	15	155	68
14 6 2	775	539	3	-2			116	176	*	76	63	152	139
10 10 6			697	-581	*		140	-152	*			45	-41
15 3 3	1197	1080	100	95	3156	3598	777	-829	*	2884	2622	610	-331
13 7 5			392	372			399	425	*			371	582
11 11 1			663	630			964	1029	*			892	851
9 9 9			247	-235			650	694	*			684	653
12 10 0	* 97	270	0	0			0	0	*			0	0
12 8 6	*		178	297			205	219	*			214	-204
14 6 4	* 97	78	86	77	* 78	120	140	173	*	331	413	292	326
12 10 2	*		158	142	*		84	-103	*			165	-184
15 5 1	1246	1340	4	4	694	1101	203	256	*	372	1239	214	391
13 9 1			550	-570			172	-217	*			163	-297
11 11 3			426	442			300	-378	*			271	-494
11 9 7			166	172			349	439	*			138	251
16 0 0	* 941	819	1614	1506	632	1092	1332	1750	*	331	822	966	1524
15 5 3	* 97	40	173	111	600	603	24	-24	*	76	1057	92	344
13 9 3	*		65	42			317	-318	*			137	-510
16 2 0	* 97	13	0	0			0	0	*	552	714	0	0
14 3 0	*		0	0			0	0	*			0	0
12 10 4	*		185	-66			336	-337	*			445	-507
16 2 2	* 97	489	121	-270	1336	1870	574	-679	*	662	1175	389	-518
14 8 2	*		153	-342			199	-235	*			328	-437
10 10 8	*		94	210			781	889	*			345	460
13 7 7	* 1071	1512	117	-139	1256	1338	68	-70	*	952	1837	612	-851
11 11 5			806	-958			870	-898	*			573	-796
14 6 6			343	-407			409	422	*			67	93
16 4 0	3894	3806	573	543	968	1407	438	528	*	76	275	228	435
12 8 8			857	811			735	886	*			74	142
15 7 1			582	-600	811	921	326	-347	*	662	1957	285	-490
15 8 5			880	-597			192	-25	*			209	-359
13 9 5			628	-647			348	-370	*			349	-600
16 4 2	* 97	114	179	194			256	-273	*			160	275
14 8 4	*		71	-76			4	5	*			72	-123
12 10 6	* 97	923	194	-597	* 235	495	304	-440	*	76	851	173	-579
15 7 3	1564	403	642	326	* 78	439	29	68	*	152	1	246	-14
11 9 9			632	321	*		246	58	*			6	0
16 4 4	1807	2071	103	110	* 706	445	27	22	*	938	271	50	27
12 12 0			1223	1310			1069	849	*			1235	663
17 1 1			719	-770	758	1805	627	-968	*	552	653	573	-624
13 11 1			222	238			151	-734	*			24	26
11 11 7			283	303			107	165	*			190	-207
16 4 0	* 97	0	0	0			0	0	*			0	0
12 12 2	*		241	17			415	-440	*			300	-326
16 4 2	* 1622	1700	114	-117	921	1539	204	-243	*	952	2184	197	-299
14 16 0			467	-478			344	-444	*			134	-203
14 4 6			741	-759			534	-690	*			594	-901
17 3 1	* 97	592	108	266	* 78	84	113	-116	*	76	195	35	56
15 5 5	*		166	-410	*		71	73	*			55	-88
13 3 3	*		37	90	*		107	-110	*			96	154
13 9 7	*		11	-27	*		63	-65	*			137	-220
14 10 2	* 97	149	173	-214	* 78	55	125	-105	*	76	42	2	2
10 10 10	*		256	-317	*		326	272	*			442	-329
12 12 4	* 97	215	288	425	* 78	0	261	10	*	76	285	257	499

NOTE - AN ASTERISK (*) DENOTES AN UNSERVED REFLECTION

S1 and S2 sites are 0.20 and 0.74, respectively. On the average 6 out of the available 8 U sites/unit cell are occupied by non-framework oxygen. The cerium ions in S2 sites are coordinated to three O(3)s at distances of 2.66(6) Å and the oxygen species in site U at a distance of 2.954(9) Å (see

Table 4). The distance of closest approach for these cerium ions is 4.82(2) Å. Cerium in site S1 has as its nearest neighbors the six O(3)s of the D6MR at distance of 3.09(4) Å each.

As stated earlier, the framework atoms underwent significant shifts with O(2)

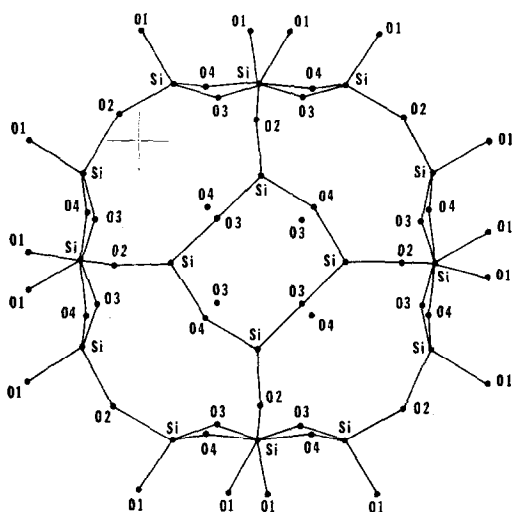


FIG. 4. View of the sodalite cage for CeX calcined in air, in projection down the cell edge. Some of the O(1) and O(2) atoms have been omitted for clarity.

moving as much as 0.5 Å in the x and y directions. The average (Si,Al)-O distances is 1.67 Å with (Si,Al)-O(2) being 1.73(6) Å and (Si,Al)-O(4) being 1.61(4) Å. Since these differences in distances are within 2σ of the average value and the standard (Si,Al)-O distance sighted earlier, no physical significance can be attributed to them.

DISCUSSION

The average of the (Si,Al)-O distances for the three structures are 1.73, 1.63, and 1.67 Å for hydrated CeX, Ce³⁺X and (Ce⁴⁺, Ce³⁺)X, respectively. Smith and Bailey (20) have recommended 1.61 and 1.75 Å as the distances to be used for pure Si-O and Al-O bond lengths, respectively. Jones (19) has proposed 1.603 and 1.761 Å as the corresponding distances. Eulenberger *et al.* (5) have stated that considerable differences up to approximately 0.1 Å occur between different (Si,Al)-O bond lengths of a particular tetrahedron. They emphasize further, that the O-(Si,Al)-O and particularly the (Si,Al)-O-(Si,Al) angles are more flexible and that for the latter, values between 120 and 180° have been observed. With the exception of the 1.53 Å distance

reported here for Ce³⁺X (see Table 3), all the results of this work fall within the rather broad limits specified by the above authors. Values of 1.76 and 1.53 Å for (Si,Al)-O distances in the same tetrahedrons were reported by Broussard and Shoemaker (3) for the 5A-type sieve. It is quite probable that such large variations in the (Si,Al)-O distances reported in the present paper could be due to the less accurate powder techniques and the resulting errors in least-squares refinement of the data. However, in some instances as indicated below, physical significance can be attached to these differences, thus indicating that some of them are probably real.

In all three cases studied the average of the four (Si,Al)-O distances of 1.63, 1.67, and 1.73 Å agreed within 2σ with the value of 1.676 reported by Jones (19) for feldspars of the same silicon:aluminum ratio.

Since the hydrated CeX sample studied in this work had previously been calcined after initial exchange and then exchanged with ammonium sulfate, it would not be proper to compare the results obtained for this sample with the cerium faujasite of Olson *et al.* (10) in which cerium ions, sodium, magnesium, and calcium ions were all present and the sample had undergone partial exchange only. One can however with some justification compare our (intermediately calcined) CeX hydrate with LaX hydrate which had undergone batch exchange only and had a 0.2-mole fraction of Na₂O per unit cell. In LaX hydrate Olson *et al.* found that per unit cell there were 12, 17, and 4 atoms in sites S2, S4, and S5, respectively, whereas in CeX hydrate there are 9.0 and 21.4 Ce atoms in sites 2 and 4, respectively. Since in LaX there were 33 cations whereas in CeX there were only 30 as determined by diffraction, the fact that no Ce³⁺ was found in site 5 could be easily explained by assuming that the difference is really due to a larger number of cations in the LaX case and to experimental error.

An unusual feature of the CeX hydrate structure is the close approach of the cerium ions in S2 to the O(3)s of the

TABLE 3
 FRAMEWORK INTERATOMIC DISTANCES AND ANGLES FOR CERIUM X ZEOLITES^a

Atom set	CeX · nH ₂ O	Ce ³⁺ X	(Ce ⁴⁺ , Ce ³⁺)X
Distances (Å)			
T-O(1.2)	1.71(6)	1.53(3)	1.67(5)
T-O(2.3)	1.70(9)	1.60(4)	1.73(6)
T-O(3.13)	1.77(8)	1.68(4)	1.68(4)
T-O(4.11)	1.74(6)	1.72(4)	1.61(4)
O(1)-O(2.15)	2.80(10)	2.64(5)	2.36(7)
O(1)-O(3.12)	3.21(8)	2.67(4)	2.84(6)
O(1)-O(4.17)	2.71(7)	2.75(4)	2.82(6)
O(2)-O(3.13)	2.70(10)	2.52(5)	2.88(7) ^b
O(2)-O(4.7)	2.57(10)	2.79(5)	2.79(6)
O(3)-(4.14)	2.75(8)	2.52(5)	2.50(5)
T-T(.6)	2.93(6)	2.78(3)	2.92(4)
Angles (°)			
T(.1)-O(1)-T(.5)	118.3(3.3)	131.6(2.1)	122.2(2.7)
T(.4)-O(2)-T(.3)	144.4(5.4)	152.9(2.6)	148.8(3.3)
T(.9)-O(3)-T(.8)	119.8(4.1)	144.6(2.4)	152.2(3.3)
T(.10)-O(4)-T(.11)	141.9(4.4)	165.4(2.8)	151.1(3.6)
O(1.2)-T-O(2.3)	110.6(3.8)	115.6(2.0)	87.8(2.4)
O(1.2)-T-O(3.13)	134.9(3.6)	112.8(1.9)	117.7(2.6)
O(1.2)-T-O(4.11)	103.6(3.3)	115.4(2.0)	119.0(2.7)
O(2.3)-T-O(3.13)	101.8(4.0)	100.4(2.0)	120.9(2.8)
O(2.3)-T-O(4.11)	96.6(3.9)	114.2(2.2)	112.8(2.8)
O(3.13)-T-O(4.11)	102.9(3.6)	95.5(2.0)	100.0(2.8) ^c

^a Atom designations are as follows: T is for silicon (aluminum). O(*M.N*) refers to the *M*th oxygen transformed by the *n*th symmetry element. The symmetry operations are: (1) *zyx*; (2) *yxz*; (3) *xzy*; (4) *zxy*; (5) $\bar{x}\bar{y}\bar{z}$; (6) $\bar{y}\bar{x}\bar{z}$; (7) *x*, 1/4 - *z*, 1/4 - *y*; (8) 1/4 - *z*, 1/4 - *y*, *x*; (9) 1/4 - *y*, 1/4 - *z*, *x*; (10) *y*, 1/4 - *z*, 1/4 - *x*; (11) 1/4 - *z*, *y*, 1/4 - *x*; (12) 1/4 - *x*, 1/4 - *y*, *z*; (13) *z*, 1/4 - *x*, 1/4 - *y*; (14) *x*, 1/4 - *y*, 1/4 - *z*; (15) 1/4 - *x*, *y*, 1/4 - *z*; (16) 3/4 + *x*, 3/4 + *y*, \bar{z} ; (17) 3/4 + *x*, 3/4 + *z*, \bar{y} ; (18) $\bar{x}\bar{z}\bar{y}$; (19) \bar{z} , 3/4 + *x*, 3/4 + *y*.

^b O(2)-O(3.16).

^c O(3.13)-T-O(4.11).

sodalite 6MR which opens into the D6MR. The distance of cerium to this oxygen is 2.19(9) Å and as compared to LaX hydrate represents a shift of 0.41 Å for the cerium ion along the body diagonal of the cubic cell toward site S1. Since this distance is 3.7 σ shorter than the other Ce-O distance in the structure, it is in the region of significance. Also, it is considerably less than the sum of the ionic radius of Ce³⁺ and the van der Waals radius of oxygen which is roughly 2.4 ± 0.1 Å. If S3 is actually occupied by 2 cerium ions/unit cell, the resulting repulsion could cause this shortening of the Ce(2)-O(3) distance.

Since S1 is occupied by water with a population parameter of 0.71, there are on

the average 11.4 water molecules/unit cell in these sites. Considering that there are 9 cerium ions/unit cell in S2 sites, the most likely distribution would be for a water molecule to be in S1 for each neighboring S2 site that is occupied.

Except for the shift in O(3) the framework coordinates for CeX hydrate are quite similar to those for LaX hydrate. It is significant that this shift in O(3) results in a lengthening of the Si-O(3) bond to 1.77 Å and hence giving support to the short Ce(2)-O(3) distance.

The cation positions observed for CeX calcined in a N₂ atmosphere are somewhat different from those found by Olson *et al.* (10) for LaX calcined in vacuum. They ob-

TABLE 4
NONFRAMEWORK ATOM INTERATOMIC DISTANCES AND ANGLES FOR CERIUM X ZEOLITES

Atom set ^a	CeX · nH ₂ O	Ce ³⁺ X	(Ce ⁴⁺ , Ce ³⁺)X
Distances (Å)			
O _w (1)–Ce(2)	2.53(3)		
O _w (1)–O(3.12)	3.02(5)		
Ce(1)–S2		2.812(8)	2.434(9)
Ce(1)–O(3.12)		2.74(3)	3.09(4)
Ce(2)–O(2)		2.91(4)	
Ce(2)–O(3.12)	2.19(9)	2.56(4)	2.66(6)
Ce(2)–O _w (2)		2.592(8)	2.954(9)
Ce(2)–O _w (3.14)	2.99(8)		
Ce(2)–Ce(2.12)		4.23(1)	4.82(2)
O _w (3)–O(2.12)	2.99(11)		
O _w (3)–Ce(4)	2.80(7)		
Ce(4)–O(4)	2.75(7)		
Ce(4)–O(2.12)	2.52(6)		
Angles (°)			
Ce(2)–O _w (1)–O(3.12)	45.5(1.4)		
Ce(2)–O _w (1)–O(3.16)	134.5(1.4)		
O(3.12)–O _w (1)–O(3.13)	76.2(1.8)		
O(3.12)–O _w (1)–O(3.19)	103.7(1.8)		
O(3.12)–Ce(1)–O(3.13)		90.2(1.0)	91.8(1.2)
O(3.12)–Ce(1)–O(3.19)		89.8(1.0)	88.2(1.2)
O(3.12)–Ce(1)–S2		125.2(0.7)	124.0(0.9)
O _w (1)–Ce(2)–O(3.12)	79.2(1.9)		
O _w (1)–Ce(2)–O _w (3.14)	137.0(1.8)		
O(3.12)–Ce(2)–O(3.13)	116.6(2.7)	98.8(1.1)	113.2(1.4)
O(3.12)–Ce(2)–O _w (3.14)	78.5(2.4)		
O _w (3.14)–Ce(2)–O _w (3.15)	72.5(2.0)		
S(1)–Ce(2)–O(3.12)		61.2(0.8)	74.5(1.0)
O(2)–Ce(2)–O(2.4)		107.8(1.0)	
O(2)–Ce(2)–S(1)		68.9(0.7)	
O(2)–Ce(2)–O(3.12)		130.1(1.0)	
O(2)–Ce(2)–O(3.13)		54.4(1.0)	
O(2)–Ce(2)–O _w (2)		111.1(0.7)	
O(3.12)–Ce(2)–O _w (2)		118.8(0.8)	105.5(1.0)
Ce(2)–O _w (2)–Ce(2.12)		109.5(0.3)	109.5(0.2)
Ce(4)–O _w (3)–Ce(2.14)	113.6(2.5)		
Ce(4)–O _w (3)–O(2.12)	51.6(2.0)		
O(2.12)–O _w (3)–O(2.13)	85.4(2.8)		
O _w (3)–Ce(4)–O(4)	78.8(2.0)		
O _w (3)–Ce(4)–O(2.12)	68.0(2.0)		
O(2.12)–Ce(4)–O(2.13)	106.8(2.6)		
O(4)–Ce(4)–O(2.12)	146.7(2.3)		
O(4)–Ce(4)–O(4.4)	116.3(1.9)		

^a Symmetry operations are the same as those designated in Table 3.

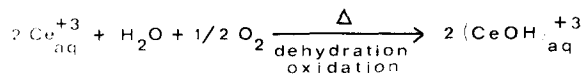
served that all the La³⁺ ions migrated to S2 sites upon calcination with a total of 30 lanthanum ions occupying the 32 possible sites/unit cell. For N₂ calcined CeX, which could also be termed Ce³⁺X, approximately 23 ions are in S2, 4 in S1, and 2.6 in S5. In

view of the errors which could exist due to the use of powder data instead of single crystal data, the occupancy of S5 is not certain. Smith *et al.* (9) found that in vacuum calcined LaY all 16 La³⁺ ions occupied S2 sites. One may wonder why this

difference in cation distribution occurs between materials which would be expected to have quite similar structures. Since in LaX S3 sites were occupied by water and in LaY both S3 and U sites are populated by an oxygen species, this difference in cationic distribution could be due to the lack of charge neutralizing hydroxyls or screening by water molecules in the CeX case. This lack of water or extra-framework oxygen is the result of performing the calcination in a nitrogen atmosphere which was generated by passing a stream of N₂ gas over the sample. This procedure thus removed all the steam produced from heating the initially hydrated sample and prevented the trapping of an oxygen species in site U. Calculations of the coulombic energy resulting from having three Ce³⁺ cations in each sodalite cage and considering only interactions of these ions with each other and with the net 36 oxygen atoms which serve as nearest neighbors show that indeed this distribution is a stable one, since there is a net attractive energy of 2.9 cal/sodalite unit. This calculation is based upon a rough model which divides the 88 available negative charges over the 384 available oxygen atoms: thus giving each oxygen atom a net negative charge of 0.229 *e*. Performing the same type of calculations for Smith's LaY, where now each oxygen would have net a negative charge of 0.142 *e*, indicates that a net repulsive force would exist without the hydroxyl ions at site U. In view of the above

over the eight available U positions. Since at least 50% of the cerium ions have been oxidized to the 4+ state, the charge density is higher in this case as compared to Ce³⁺X. One could rationalize the results by the following argument: since calcination was done in air in a muffle furnace, water was not excluded from site U as in the Ce³⁺X zeolite. These oxygen species which occupy the U positions along with the greater cationic separation compensate for the additional charge density and thus allow essentially the same cationic distribution. Electrostatic calculations of the type used above and assuming all cerium ions exist in the 4+ state, indicate again that a hydroxyl ion is necessary in U, since without it a net repulsive force results and with it a net attractive force exists. These results reemphasize the importance of electrostatic interactions and also give support to the proposal of Rabo *et al.* (8) that the presence of water or hydroxyl groups add to the structural stability of the sieve (LaY in their case) through the formation of a RE-OH (or O²⁻)-RE complex within the sodalite cages.

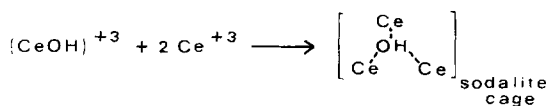
The following reactions could reflect the processes occurring during the calcination in air of the hydrated CeX zeolite: during calcination a dehydration and partial oxidation process take place. Due to the high charge of the oxidized cerium ion, it is highly probable that an ion of the type (CeOH)³⁺ will result. This process is described by the following scheme:



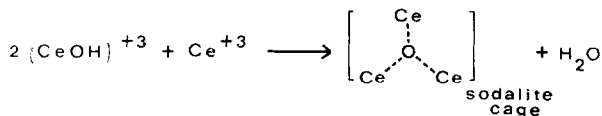
calculations one must assume that electrostatic considerations play an important role in determining the resulting cation distribution.

The cation distribution of CeX calcined in air is not much different from that of the N₂ calcined material. Since there are, per unit cell, 3.2 and 23.7 cations in S1 and S2 sites, the only difference is the lack of cerium ions in S5. On the average six non-framework oxygen atoms are distributed

As previously mentioned, the presence of hydrolyzed ionic species in faujasite type zeolites has been already indicated by Smith *et al.* (9) for LaY. The probability for the existence of such an ionic species will obviously increase with increasing positive charge of the cation. The (CeOH)³⁺ ions located in the sodalite cage could, in turn, interact with nonoxidized cerium ions, resulting in cerium-oxygen complexes, as shown in the following schemes:



or



The formation of $(\text{CeOH})^{2+}$ ions and their interaction with $(\text{CeOH})^{3+}$ ions should also be taken into consideration.

Since on the average there are only 3 cerium cations/sodalite cage in both these samples and $\frac{1}{4}$ or less cerium ion/D6MR, the most probable distribution would be for site S1 to be occupied by cerium when the corresponding S2 site is not. This distribution prevents any cerium to cerium distance of less than 4.2 Å.

The resemblance of Ce^{3+}X (N_2 calcined) to $(\text{Ce}^{4+}, \text{Ce}^{3+})\text{X}$ (air calcined) ends with the cationic distribution. As mentioned above, the greater cationic repulsion in the Ce^{4+} case, which resulted in an increase of the Ce—Ce distance from 4.23 Å in the N_2 calcined material to 4.82 Å in the air calcined case, is probably the cause of the large distortions which occurred in the faujasite framework. These distortions were of such a nature as to decrease the amount of puckering in the six-membered rings which comprise the sodalite cages and are shown in Fig. 4. The mutual repulsion of the Ce^{4+} ions can alternatively be described as a recession of these ions into the six-membered rings of the hexagonal prisms. The recession causes an opening of these rings as displayed by the increase of the O(3) to O(3) distance from 3.88 Å in Ce^{3+}X to 4.43 Å in $(\text{Ce}^{4+}, \text{Ce}^{3+})\text{X}$. The cerium ion in S2 is 1.23 Å from the plane of the three O(3) atoms in the N_2 calcined material and 0.88 Å in the air calcined material. Assuming a 1.40 Å radius for oxygen, the opening in the 6MR leading into the hexagonal prism, as measured by the effective opening defined by these three O(3) atoms, has increased from a radius of 0.8 to 1.16 Å. In addition, this shift in the O(3) position has resulted in a

lengthening of the cerium in S1 to O(3) distance to 3.09 Å.

In summary, this work has shown that the structures of the Ce^{3+}X sieves are somewhat different from that of La^{3+}X and that the cation positions observed for a particular sample depend upon the previous treatment of the sample. Also, as one would expect the structure of the sieve is altered significantly when the cerium is oxidized to the tetravalent state.

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