Syntheses of Sodium-Calcium Zeolites at Atmospheric Pressure and 80 °C. I. Reagents Used: Na_4SiO_4, $Al(OH)_3$, $Ca(NO_3)_2$

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Sodium-calcium zeolite minerals were synthesized in an electric oven at 80 °C for 1—5 weeks from suspensions of a suitable combination of the starting materials, which had a chemical composition of $2n Na_2O \cdot 2CaO \cdot Al_2O_3 \cdot n SiO_2 \cdot x H_2O$ ($4 \leqq n \leqq 20$, $x = 83$—610). All of the synthetic products were obtained as massive products in the gel. X-Ray and IR analyses and a quantitative analysis of the principal ingredients showed these massive products to be well-crystallized hydroxycancrinites which contained 0—4.9% calcium oxide.

Zeolite minerals have been studied for a long time and have been synthesized extensively by many investigators, because they have useful properties, such as ion-exchange and molecular-sieve. Barrer and his co-workers have reported that the crystallization from active gel of sodium and potassium aluminosilicates could occur at 100 °C or below, but less reactive materials (*e.g.*, calcium and lithium aluminosilicates) were crystallizable only above about 150 °C.[1,2] Most calcium zeolites including sodium-calcium zeolites have thus been far synthesized only above 150 °C. It is now well known, however, that the crystallization of zeolite minerals is considerably influenced by the particular combination of the starting materials. It is also known that either water or salt, singly or in combination, aids the formation of aluminosilicate.[3] If suitable combinations of the starting materials, including salts and excess water, are chosen, sodium-calcium zeolite minerals can therefore be expected to crystallize at atmospheric pressure and at temperatures lower than 150 °C.

Our aim is to examine the reactivity of the starting materials and to make clear what kinds of sodium-calcium zeolite minerals can be synthesized under these mild conditions. In this paper it is reported that the sodium-calcium hydroxycancrinite has been synthesized at 80 °C and under atmospheric pressure from a suspension of sodium silicate (ortho), aluminium hydroxide, and calcium nitrate.

Experimental

Reagents Used. *Sources*: *Silicon*: 1 mol dm^{-3} solution of sodium silicate (ortho); *Aluminium*: finely powdered aluminium hydroxide; *Calcium*: 1 mol dm^{-3} solution of calcium nitrate.

Synthetic Method. The starting materials, composed of $2n Na_2O \cdot 2CaO \cdot Al_2O_3 \cdot n SiO_2 \cdot x H_2O$ ($1 \leqq n \leqq 20$, $x = 83$—610), were prepared as follows. Aluminium hydroxide was stirred well into the source of silicon, and then a calcium nitrate solution was added slowly. After this mixture had been stirred enough, the suspensions finally obtained were placed in 100 cm^3 polyethylene bottles and allowed to stand overnight. These bottles were kept for 1—5 weeks in an electrically heated oven, thermostatically controlled at 80 ± 1 °C, and then the bottles were cooled in air. The reaction products were washed in hot water until the washings were free from alkali. Massive products present in the gel were separated from the gel by decantation and filtered off. All the products were air dried and powdered by the use of a porcelain mortar and 200-mesh sieves.

Analytical Apparatus and Method. *X-Ray*: A powder diffractometer (Rigaku Co.) was used with filtered Cu *Ka* radiation. It was operated at 30 kV; 15 mA; time constant, 1 s, and count range, 1000 cps.

IR: An infrared spectrophotometer of the JASCO DS701-G type was used. Samples were measured by the KBr-wafer method.

Quantitative Analysis of Principal Ingredients: The method of "Speedy Analysis of Silicate"[4] was used.

Results and Discussion

Sodium-calcium zeolite minerals have been synthesized from suspensions having the chemical composition of $2n Na_2O \cdot 2CaO \cdot Al_2O_3 \cdot n SiO_2 \cdot x H_2O$ ($1 \leqq n \leqq 20$, $x = 83$—610). They were obtained in three different states.

Two of them were in gel-like states (these will be referred to as "Gel 1" and "Gel 2" hereafter), while the other was in a massive form. The "Gel 1" minerals were obtained from suspensions with n values from 1 to 3. Mixtures of "Gel 2" and massive products were obtained from suspensions with n values from 4 to 20. X-Ray analysis revealed that the crystallinities of "Gel 1," "Gel 2," and the massive products were very low, low, and high respectively, as is shown in Fig. 1. We can also see in Fig. 1 that "Gel 2" has some peaks in

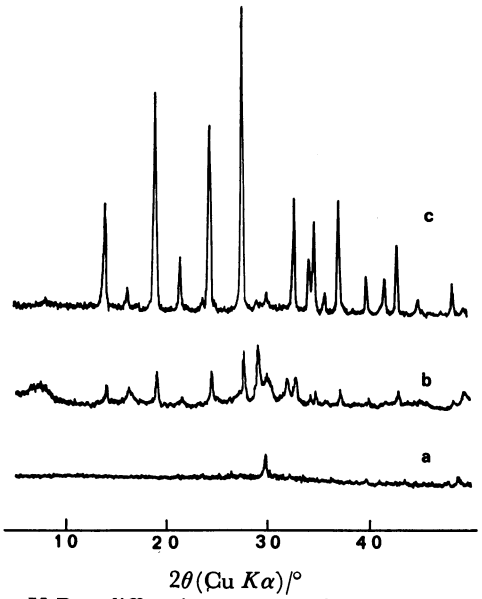

Fig. 1. X-Ray diffraction patterns of "Gel 1"(a), "Gel 2" (b), and massive product (c).

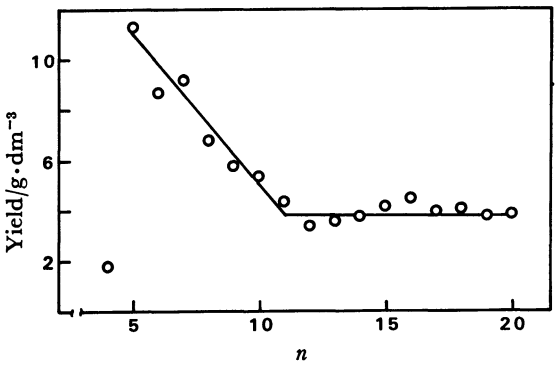

Fig. 2. The relation between the value of n and the yield of massive products.

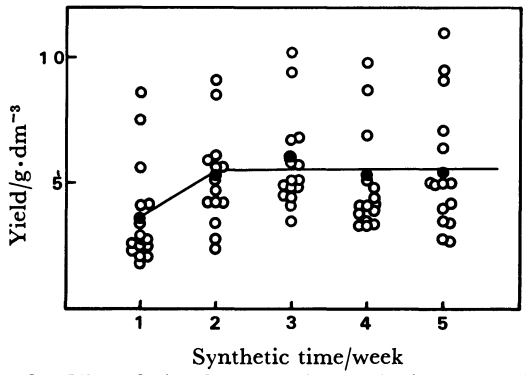

Fig. 3. The relation between the synthetic time and the yield of massive products.
●: The mean value of the yield.

Table 1. X-Ray powder-diffraction data for hydroxycancrinite

Natural cancrinite[a]			Massive product (hydroxy-cancrinite)		Synthetic hydroxy-cancrinite[b]	
hkl	*d*/Å	I/I_1	*d*/Å	I/I_1	*d*/Å	I/I_1
100	10.92	40				
110	6.23	5	6.46	33	6.30	65
200	5.45	5	5.57	7	5.46	14
101	4.64	90	4.75	68	4.60	66
210	4.11	15	4.21	19	4.12	15
			3.82	5	3.72	7
300	3.64	70	3.71	65	3.63	76
211	3.21	100	3.27	100	3.21	100
310	3.02	10	3.02	5	3.04	8
301	2.950	10			2.963	10
400	2.730	40	2.763	33	2.724	56
311	2.607	30	2.644	15	2.601	33
002	2.560	30	2.614	27	2.551	23
320,102	2.498	20	2.543	7	2.500	11
401	2.408	40	2.442	49	2.404	28
112	2.536	1				
202	2.321	1				
321	2.249	25	2.276	11	2.250	14
330,302	2.099	70	2.127	26	2.098	37
501,222	2.010	20	2.031	6		
132,331	1.953	2				
421	1.914	10				
420	1.868	20	1.895	15		

a) "Mineral Powder Diffraction File," (JCPDS International Diffraction Data 1980). b) Synthesis by Aoki and Abe. I/I_1: calculated from their pattern.

Table 2. IR data for hydroxycancrinite

Material	SiO_2/Al_2O_3	Asym. Stretch		Sym. Stretch		Dobl. Ring		T-O Bend		Pore Opening?	
Hydroxy-cancrinite	2	1095mw 1000s	1035msh 965msh	755w	680m	624m	567m	498mw 458m	429m	390mw	353wb
Massive product[a]	2.6	1115mw 997s	1035ms 965msh	820w 687m	757wsh 670wsh	624m	575m	500mw 462m	430m	390mw	346wb
Massive product[b]	2.6	1117mw 1002s	1037s 965s	820w 685m	760ws 669wsh	624m	575m	498mw 465m	428m	393mw	342wb
Massive product[c]		1120mw 990wsh	1040w 950s	820w 685m	668wsh	620m	573m	492mw 460m	422m	387mw	340w

a) n=20, synthetic time=5 weeks, CaO=0%. b) n=5, synthetic time=3 weeks, CaO=3.0%. c) n=5, synthetic time=1 week, starting materials involving sodium nitrate instead of calcium nitrate. s=strong, m=medium, w=weak, sh=shoulder, b=broad

addition to those of the massive products. "Gel 2" is possibly a mixture of the massive product and another material. As a result, we studied the massive products in detail.

The optimum conditions for the syntheses of massive products are determined from the n values and the synthetic-time dependence of the yield (g dm^{-1}) and the crystallinity. As may be seen from Figs. 2 and 3, the yield is more dependent on the n value than on the synthetic time. In Fig. 3, the data scatter widely because the yield is strongly dependent on the n value, and from the mean value of them it is clear that the yield becomes approximately constant after two weeks. On the other hand, the crystallinity becomes better with the increase in the synthetic time, but has little relation with the n value. From these examinations it may be concluded that the n values 5, 6, and 7 and a synthetic time of more than two weeks are the most suitable conditions for the synthesis.

We analyzed the massive products by means of X-Ray, IR, and quantitative analyses to ensure their identification. The X-Ray results are shown in Table 1. From Table 1, it is clear that the diffraction data of the massive product agree with those of cancrinite[5] and with those of the synthetic hydroxycancrinite reported by Aoki and Abe.[6]

The IR results are shown in Table 2. The data agree with those of the hydroxycancrinite reported

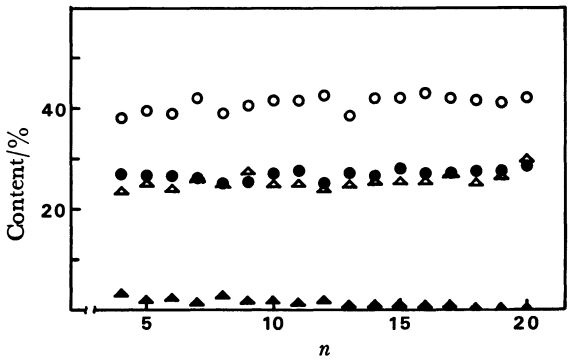

Fig. 4. The relation between the value n in starting materials and quantity of ingredients of massive products.
○: SiO_2, ●: Al_2O_3, △: Na_2O, ▲: CaO.

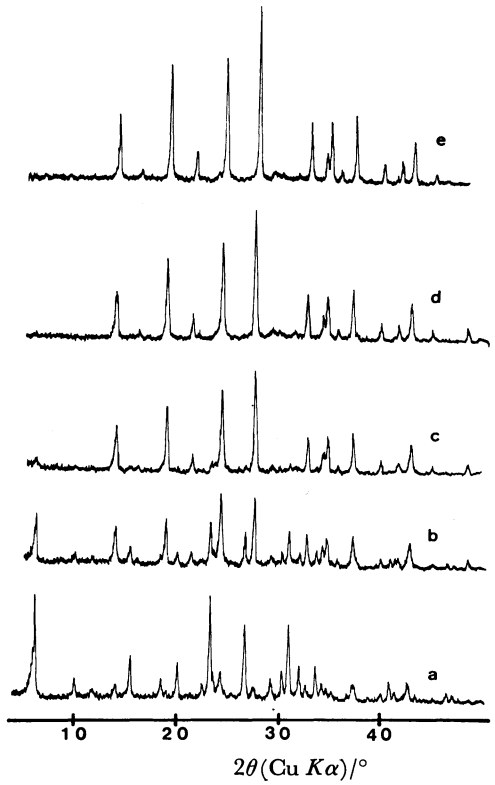

Fig. 5. X-Ray diffraction patterns of massive products which were synthesized in 1 d run (a), 2 d run (b), 3 d run (c), 4 d run (d), 5 d run (e).

previously,[7] except for small differences in the regions of 950—1200 and 750—820 cm^{-1} caused by asymmetric and symmetric stretching.

The amounts of the ingredients in massive products as a function of the n value have been determined by quantitative analysis, they are shown in Fig. 4. The dependence of the quantity of the ingredients on the n value is rather weak. Calcium oxide of 0.2—4.0% has been detected in all massive products except for those obtained by synthetic times between 4 and 5 weeks and when the n value equals 20. The mean values of the contents of Na_2O, CaO, Al_2O_3, and SiO_2 for 84 products are 27.5%, 1.5%, 26.7%, and 40.9% respectively. The experimental formula determined by the use of these values is $Na_9Ca_{0.25}Al_5Si_7O_{24}(NO_3)_{4.5}\cdot xH_2O$. The existence of the NO_3^- ion in this formula is deduced from the IR data, which has two characteristic absorption bands caused by the NO_3^- ion at 1384 and 820 cm^{-1}. In this deduction of the existence of the NO_3^- ion, we also referred to the report by Guth.[8] The experimental formula determined here agrees with that of cancrinite. From these three analyses, the massive products obtained here are identified as examples of hydroxycancrinite.

Table 3. X-Ray powder-diffraction data for massive products synthesized for shorter synthetic times

1 d Run		2 d Run		3 d Run	
d/Å	I/I_1	d/Å	I/I_1	d/Å	I/I_1
14.98	100	15.24	85		
9.03		9.11			
7.69					
7.46		6.46		6.46	35
5.83		5.87		5.57	5
4.87					
		4.77	69	4.75	67
4.48		4.48			
		4.21		4.19	16
4.00					
3.85	100	3.84			
		3.82		3.82	5
3.69		3.71	100	3.69	65
3.38	79	3.38			
		3.27	96	3.27	100
3.08		3.08		3.07	5
2.969		2.979		3.02	5
2.912	64	2.912			
2.814		2.823			
2.763		2.772		2.763	38
		2.691			
2.644		2.644		2.644	16
		2.614		2.607	29
				2.536	6
2.430		2.442		2.442	37
2.222		2.222		2.281	13
		2.196		2.186	13
2.132		2.127		2.127	25
				2.031	6
				1.895	10

Comparing with the conditions of the conventional synthetic way of hydroxycancrinite, such as a temperature higher than 80 °C and the limited n value of the starting materials, it is remarkable that only hydroxycancrinite has been synthesized over such a wide range of n values as n=4—20 and under such mild conditions as 80 °C and the atmospheric pressure used in this study. This suggests that the present combination of starting materials is especially effective in the synthesis of hydroxycancrinite. It seemed, therefore, that it would be to make clear the facility and characteristics of the present combination of starting materials. Thus, we have performed the following experiments using the most suitable n values 5, 6, and 7.

First we made experiments at shorter synthetic times in order to elucidate the initial crystallization. The

Table 4. X-Ray powder-diffraction data for synthetic results from the starting materials without calcium nitrate

1 d Run		2 d Run	
d/Å	I/I_1	d/Å	I/I_1
14.98	(1)		
9.03			
6.46		6.46	44
5.83			
		4.72	53
4.48			
		4.19	17
3.85	(3)		
3.71	(4)	3.68	100
3.38	(2)		
		3.27	81
3.08			
2.974			
2.912			
2.867			
2.814			
		2.755	33
2.698			
2.614		2.607	39
2.270			
2.132			
		2.122	39
1.941			

Table 5. X-Ray powder-diffraction data for the synthetic results from starting materials containing sodium nitrate instead of calcium nitrate

1 d Run		2 d Run		3 d Run	
d/Å	I/I_1	d/Å	I/I_1	d/Å	I/I_1
14.98	(1)	14.98	100		
9.03		9.03			
7.69		7.69			
		6.42		6.46	30
5.76		5.76		5.57	6
		4.87			
		4.72		4.77	67
4.46		4.46			
				4.19	18
3.85	(2)	3.85	61	3.80	6
		3.69		3.71	56
3.36	(3)	3.36	64		
		3.25		3.27	100
3.08		3.08			
2.919	(4)	2.967		3.02	4
2.876		2.912			
2.814		2.814			
		2.755		2.763	22
2.683		2.683			
				2.644	15
				2.607	26
				2.536	7
		2.430		2.442	34
				2.276	10
2.227		2.222		2.186	10
2.137					
				2.122	21
				2.031	4
				1.895	8

results are shown in Table 3 and Fig. 5. In a one-day run, a faujasite-type zeolite with a strong peak at nearly d(Å)=14.73 was synthesized. In a two-day run, a mixture of the faujasite-type zeolite and hydroxycancrinite was detected. From the four-day run, only hydroxycancrinite was observed in the X-Ray diffraction pattern. From these results, it is clear that the hydroxycancrnite has been synthesized almost completely in such a short time as four days under these mild conditions.

Secondly, we examined the effect of calcium salts on the crystallization. The results of the synthesis without calcium nitrate are shown in Table 4. As may be seen in Table 4, only the faujasite-type zeolite was synthesized in a one-day run. From the second-day run, the zeolite was changed from the faujasite-type into a mixture of sodalite-type zeolite and hydroxycancrinite. The crystallinities of these zeolites were very low. Therefore, we can guess that calcium nitrate as a calcium source plays a very important role in the formation of hydroxycancrinite. It had been believed that the existence of calcium would tend to hinder the formation of the aluminosilicate framework under mild conditions. Our experiment, however, revealed that if the $CaO/(CaO+Na_2O)$ ratio is limited within the range between 0.05—0.2, calcium tends to promote the formation of zeolite.

Lastly, we performed a synthesis experiment using sodium nitrate instead of calcium nitrate in order to make sure of the role of the NO_3^- ion. The results shown in Table 5 are almost the same as those in Table 3, thus indicative that calcium nitrate and sodium nitrate lead to the same effect. Therefore, it is confirmed that the characteristics of the present combination of starting materials are mainly due to the NO_3^- ion. This result is consistent with the report by Guth,[8] who pointed out that AO_m^{n-} favored the hexagonal derivation of cancrinite.

The success of the present synthesis suggests the possibility of preparing other sodium-calcium zeolite minerals under mild conditions if suitable combinations of starting materials are chosen.

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