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THE THERMAL BEHAVIOR OF K-EXCHANGED FORMS OF NATROLITE *

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ABSTRACT

A series of K-exchanged forms of natrolite are easily obtained by treatment with KCl solution at room temperature for 1–62 days. The maximum degree of exchange of K is 91.94%. The thermal behavior of the exchanged forms is studied by DTA–TG and high temperature X-ray powder diffraction. The DTA curve of the exchanged form of the 91.94% sample exhibits a single large endotherm at 150 °C due to a one-step dehydration, showing the remarkable decrease in dehydration temperature compared with natrolite. The dehydrated phase of natrolite collapses at about 800 °C, while destruction of the dehydrated K-form occurs above 1000 °C. It is well recognized that the thermal stability of natrolite is increased by Na–K exchange.

INTRODUCTION

The thermal properties of natural natrolite have been studied by many workers [1–6]. However, data for the thermal behavior of cation-exchanged forms of natural natrolite are scanty, and so far as the writers know, only one paper has been published on this subject by Belitskiy [7], leaving many problems to be studied further.

In this note, the thermal behavior of the K-exchanged form of natrolite is briefly reported.

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* Dedicated to Professor Syûzô Seki in honor of his contribution to Calorimetry and Thermal Analysis.

EXPERIMENTAL

As a starting material, natrolite from Hashidate, Oomi-cho, Niigata Pref. was used. The sample was carefully purified by hand-picking under binoculars. Chemical analysis of the sample was performed by electron microprobe analysis (EPMA), giving the results in Table 1. X-ray powder data are shown in Table 2. Lattice parameters and cell volume obtained are: $a = 18.301(2)$ Å, $b = 18.636(3)$ Å, $c = 6.610(3)$ Å, $V = 2254(2)$ Å^3.

The K-exchanged natrolites were obtained as follows: 200 mg of the natrolite sample (under 200 mesh) was treated in 100 ml of 0.5 or 1 N KCl solution (pH 8–9) in a polyethylene bottle at 25°C for 1–62 days. The products were dried at 60°C, and then kept in a desiccator for at least 3 days in which relative humidity was maintained at about 55% by saturated $Mg(NO_3)_2$ solution, until they were subjected to subsequent measurements.

K, Na, Ca and Mg contents of all products were determined by atomic absorption spectroscopy.

DTA and TG curves were recorded with a Rigaku Thermoflex TG–DTA unit in static air, on a 15.0-mg sample at a programmed heating rate of 10 K min^{-1}. The sample was covered with 5.0 mg of calcined alumina.

High temperature X-ray powder patterns were obtained using a Rigaku Geigerflex D6C with a high temperature attachment.

The sample was heated in static air to a pre-determined temperature at a heating rate of 10 K min^{-1}, kept for an hour at that temperature, and then subjected to X-ray diffraction.

TABLE 1

Chemical composition of natrolite from Hashidate, Oomi-cho, Niigata Pref.

Compound	Wt.%	Atoms per unit cell	
SiO_2	46.44	Si	23.84
Al_2O_3	26.53	Al	16.05
Fe_2O_3	0.00	Fe^{3+}	0.00
MgO	0.00	Mg	0.00
CaO	0.13	Ca	0.07
K_2O	0.06	K	0.04
Na_2O	16.35	Na	14.26
H_2O	10.71	H_2O	18.34
Total	100.23	O	80

Si/Al = 1.485.

E (balance error) = −2.4%.

$$\left[E = \frac{(\mathrm{Al} + \mathrm{Fe}^{3+}) - \{\mathrm{Na} + \mathrm{K} + 2(\mathrm{Mg} + \mathrm{Ca})\}}{\{\mathrm{Na} + \mathrm{K} + 2(\mathrm{Mg} + \mathrm{Ca})\}} \times 100\%\right]$$

Analyzed by JEOL JXA 733 electron microprobe analyzer. Water content was obtained by TG. Correction was made by the method of Bence and Albee.

TABLE 2

X-ray powder data for natrolite and the K-exchanged form

h	k	l	Natrolite [a]		K-exchanged form [b]	
			d (Å)	I/I_0	d (Å)	I/I_0
2	2	0	6.528	100	6.920	100
1	1	1	5.883	22	5.883	4
0	4	0	4.662	25		
4	0	0	4.574	16		
1	3	1	4.375	41	4.489	12
3	1	1	4.349	39	4.457	12
2	4	0	4.150	32		
4	2	0	4.097	18	4.348	2
3	3	1	3.632	1		
4	4	0	3.262	11	3.461	20
1	5	1	3.194	19	3.324	9
5	1	1	3.151	24	3.275	8
2	0	2	3.087	12	3.081	20
2	6	0	2.940	16	3.126	6
6	2	0	2.900	7		
3	5	1	2.864	42	2.996	50
5	3	1	2.842	34	2.969	80
2	2	2			2.940	18
4	2	2	2.577	6	2.597	5
1	7	1	2.446	10	2.574	8
7	1	1	2.409	10	2.521	6
0	8	0	2.327	5	2.478	2
3	7	1	2.290	6		
8	0	0	2.284	10	2.412	2
0	6	2	2.259	4		
6	0	2	2.238	2		
8	2	0	2.219	2		
2	6	2	2.194	5	2.251	1
6	6	0	2.176	12	2.299	5
4	8	0	2.053	3	2.207	1
3	3	3	1.963	2	1.960	2
9	1	1	1.910	3	2.032	2
5	1	3	1.874	3		
2	10	0	1.826	5	1.943	2
5	3	3	1.803	5	1.818	2

[a] Hashidate, Oomi-cho, Niigata pref., Japan.

[b] Degree of K-exchange, 91.94%.

RESULTS AND DISCUSSION

Cation exchange treatment of natural natrolite has already been conducted by Hey [8], Belitskiy and Gabuda [9] and Belitskiy and Fedorov [10]. Hey [8] recognized a minor exchange with K- and Ag-solutions at room temperature. Belitskiy and Fedorov [10] investigated Na–K exchange with fused salts above 100 °C, and suggested the impossibility of K–Na exchange in a water solution between 0 and 100 °C. In the present exchange treatment, however, the K-exchanged forms, of which the degree of exchange of K was in the range 24.59–91.94%, were easily obtained. Here, the degree of K-exchange is expressed as $[K_2O/(Na_2O + K_2O + CaO + MgO)] \times 100\%$ (oxides, in moles).

X-ray powder data for the exchanged form (91.94%) are shown in Table 2, together with those of natural natrolite. Lattice parameters and cell volume obtained are: $a = 19.338(4)$ Å, $b = 19.810(6)$ Å, $c = 6.499(1)$ Å, $V = 2489(2)$ Å^3. Indexing and estimation of lattice parameters were performed based on the same space group, *Fdd*2, as natrolite. As is to be expected from the relative sizes of Na and K ions, the K-exchanged form has a considerably larger unit cell volume than natrolite; the change is chiefly in *a* and *b* axes. The expansion of the unit cell is 10.4%. The DTA curves of the seven exchanged forms (Curves B–H) are shown in Fig. 1, together with that of the original natrolite (Curve A). Curve A shows the typical DTA patterns of natrolite, having a large endotherm at 330 °C due to a one-step dehydration and a very small endotherm at 550 °C corresponding to the phase transition α- → β-metanatrolite. With increasing degree of K-exchange, the endotherm

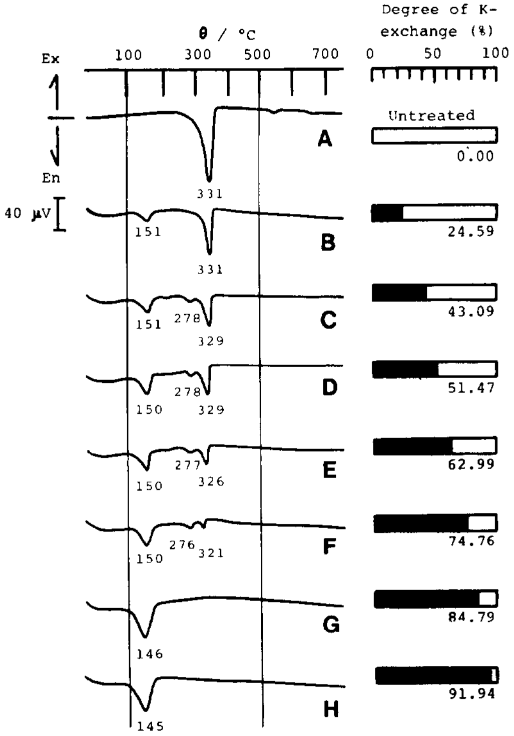

Fig. 1. DTA curves of natrolite and K-exchanged forms.

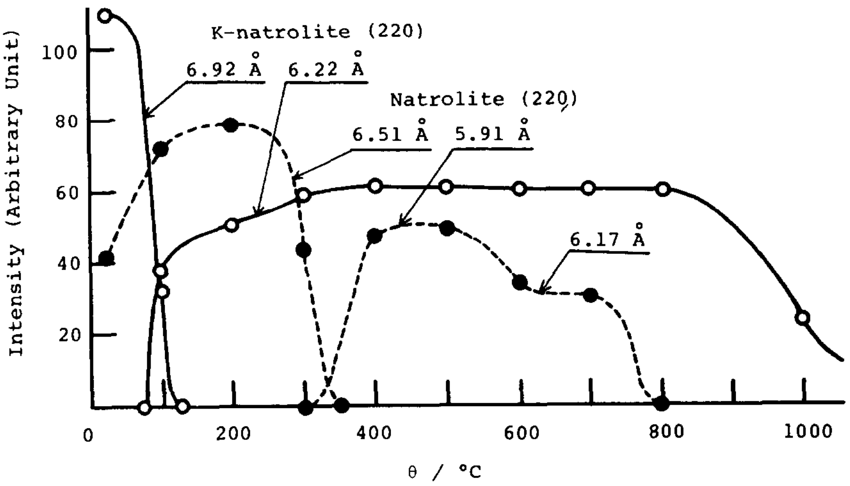

Fig. 2. The change in water content vs. degree of K-exchange.

at 330 °C has a diminished peak area, shifting slightly to a lower temperature, and a new endotherm at 150 °C begins to appear above 25%. The former peak disappears above 85%, with only the latter peak remaining. An additional small endotherm around 280 °C is recognized between 43 (Curve C) and 75% (Curve F). The above results indicate that the endotherm at 330 °C is caused by the loss of water molecules bonded to Na ions, while the 150 °C peak is due to the removal of water molecules coordinated around K ions. The considerable decrease in dehydration temperature of the K-exchanged form, when compared with natrolite, can be explained by the decreased bonding force of water molecules to cations resulting from the larger size of K than Na and the expansion of the framework.

The water content of the K-exchanged form decreases remarkably with increasing degree of K-exchange above 60%, as shown in Fig. 2. It is estimated that 2.50 water molecules are coordinated to 2 Na ions in the original natrolite under 55% of relative humidity, while 1.57 water molecules are bonded to 2 K ions in the K-exchanged form (91.94%). The behavior of decreasing water content with increasing ionic size of exchanged monovalent cation is also recognized in other zeolites (see, for example, ref. 11).

The results of high temperature X-ray powder diffraction are illustrated in Fig. 3. In this diagram, the strongest reflections (220) of both natrolite and the K-exchanged form (91.94%) are shown as a function of temperature. As shown in Fig. 3, the (220) reflection of natrolite ($d_{220} = 6.51$ Å) of the dehydrated form (α-metanatrolite) appears and becomes stronger with increasing temperature. The 5.91 Å reflection begins to shift above 500 °C, and reaches 6.17 Å at 600 °C, as a result of the transformation of α- to β-metanatrolite. The 6.17 Å reflection disappears at 800 °C. This result indicates that natrolite dehydrates above 300 °C, and the dehydrated phase

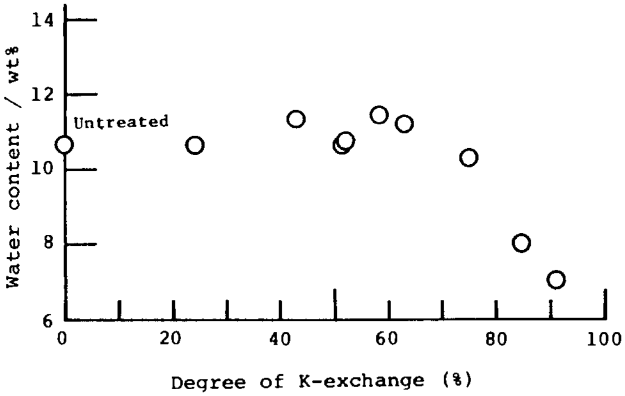

Fig. 3. The intensities of (220) reflections of both natrolite and the K-exchanged form (91.94%) as a function of temperature.

(β-phase) decomposes at 800 °C. In the case of the K-exchanged form, the intensity of the (220) reflection ($d_{220} = 6.92$ Å) decreases very abruptly around 100 °C, and at the same time a new reflection ($d = 6.22$ Å) appears. With increasing temperature, this reflection becomes gradually stronger up to 400 °C and persists above 1000 °C. This indicates that the exchanged form dehydrates at about 100 °C and the structure of the dehydrated phase is maintained up to a higher temperature than 1000 °C. Therefore, it is recognized that the thermal stability of natrolite is increased by K-exchange for Na.

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