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THERMAL ANALYSIS OF SYNTHETIC (NEAR-CHABAZITE) ZEOLITES WITH DIFFERENT Si/Al RATIOS

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ABSTRACT

The thermal behaviour of synthetic K–G type zeolites (near-chabazites of Barrer) depends on their chemical composition. Samples with a Si/Si+Al fraction between 0.5 and 0.55 and consequently with a high potassium content, show a limited reversible dehydration between room temperature and 180°C. Above 180°C, after breakdown of the crystal structure, irreversible dehydration proceeds readily, with a sharp maximum near 270°C.

Samples with a Si/Si+Al fraction greater than 0.57 and a lower potassium content dehydrate continuously over the whole range between room temperature and 450°C.

INTRODUCTION

In 1956 Barrer and Baynham[1] synthesized a novel zeolite K–G which, according to its X-ray powder pattern, was identified as a chabazite-like phase (near-chabazite). The composition of different preparations varied between $K_2O \cdot Al_2O_3 \cdot 2.3SiO_2 \cdot nH_2O$ and $K_2O \cdot Al_2O_3 \cdot 4.15SiO_2 \cdot nH_2O$. In a systematic investigation of the system K_2O–Al_2O_3–SiO_2–H_2O, Zhdanov and Ovsepyan[2] found that K–G even crystallized with a SiO_2/Al_2O_3 ratio as low as 2.0. K–G with the same SiO_2/Al_2O_3 ratio was also obtained from the reaction of kaolinite with potassium hydroxide solutions[3].

Although the X-ray powder patterns of the different products are very similar, it turned out that various properties, especially the ion-exchange behaviour, differ markedly[4].

In order to get a classification on an easily reproducible basis, 25 samples of K–G, with silica to alumina ratios between 2.0 and 3.4, were prepared and studied with simultaneous DTA, TG and DTG and in some cases with simultaneous X-ray and TG.

EXPERIMENTAL

K–G were synthesized from pure aluminum metal, tetramethoxysilane and potassium hydroxide. The different components were calculated on the basis of the crystallization fields of Zhdanov and Ovsepyan[2]. Aluminum metal was dissolved in a potassium hydroxide solution of appropriate concentration. After complete dissolution, the tetramethoxysilane was added and the mixture was vigorously shaken to a homogeneous dispersion. The reaction mixtures were placed in polypropylene tubes, which were sealed and rotated in an oven at 90°C. After crystallization the products were separated from the mother liquor, washed three times with de-ionized water, dried and equilibrated over a saturated calcium nitrate solution at room temperature (50% relative humidity). X-ray powder photographs were taken with a Guinier–De Wolff camera and CuKα radiation. The chemical composition was determined by standard methods. For the preparation of ion-exchanged forms, the samples were treated three times with 1 M solutions of the respective ions at room temperature or at 80°C. Scanning electron micrographs were taken in order to compare the crystallite shape of different samples and to study the morphological changes undergone during outgassing and recrystallization at elevated temperatures.

The DTA and TG curves were recorded simultaneously with a Mettler thermoanalyzer I, the conditions being as follows: sample weight, 100 mg; reference sample, ignited kaolinite, 100 mg; heating rate, 10°C min^{-1}; atmosphere, dried air, 1.9 l h^{-1}; sensitivity, 50 μV.

RESULTS AND DISCUSSION

In Table 1 nine representative samples are listed and in Table 2 the X-ray powder patterns of a low and a high silica sample are given.

Dehydration

On the basis of the dehydration behaviour, which can be followed most easily by DTG, the samples may be divided into two classes:

$$\text{Class A: with } \frac{\mathrm{Si}}{\mathrm{Si+Al}} > 0.57 \quad \text{or} \quad \frac{\mathrm{SiO_2}}{\mathrm{Al_2O_3}} > 2.7$$

$$\text{Class B: with } \frac{\mathrm{Si}}{\mathrm{Si+Al}} = 0.5\text{–}0.55 \quad \text{or} \quad \frac{\mathrm{SiO_2}}{\mathrm{Al_2O_3}} = 2.0\text{–}2.5$$

Class A samples dehydrate smoothly and continuously over a wide range of temperature. The DTG curve is nearly symmetrical with an even maximum between 130 and 260°C (Fig. 1, curve A). The behaviour is in accordance with natural chabazite[5], whose Si/Si+Al fraction is between 0.65 and 0.70. The simultaneous thermal and X-ray investigation[6] shows, that the crystals retain their basic crystal structure over the entire range of dehydration. They are rendered X-ray amorphous between 600 and 920°C. Heating to 500°C does not alter the external appearance of the crystallite balls (Fig. 2)

Class B samples dehydrate in two steps. The DTG curve is unsymmetrical; it shows a shoulder near 100°C and proceeds to a relatively sharp maximum between 260 and 270°C (Fig. 1, curve B). Borthakur et al.[7] have proposed that such irregularities may be due to non-zeolitic impurities or to mixtures of zeolites with different pore size. However, no impurities can be traced in the X-ray photographs nor on the scanning electron micrographs.

TABLE 1

CHEMICAL COMPOSITION OF SOME SYNTHETIC K–G; GENERAL FORMULA: $K_{18-x}[Al_{18-x}Si_{18+x}O_{72}]\cdot mH_2O$

Sample No.	*K*	*Al*	*Si*	*O*	*H_2O*	$\frac{Si}{Si+Al}$
03-65	18	18	18	72	33	0.50
20-05	17.5	17.5	18.5	72	33	0.515
20-06	17	17	19	72	33	0.53
20-08	16.5	16.5	19.5	72	33	0.54
20-10	15.5	15.5	20.5	72	34	0.57
31-01	15	15	21	72	34	0.585
20-13	15	15	21	72	35	0.585
20-14	14	14	22	72	35	0.61
00-16	13.5	13.5	22.5	72	35	0.625

TABLE 2

X-RAY POWDER PATTERNS OF A LOW SILICON (03-65) AND A HIGH SILICON (00-16) SAMPLE COMPARED WITH POTASSIUM FORM OF NATURAL CHABAZITE

03-65		*00-16*		*natural chabazite*[1]	
d (Å)	*I*	*d (Å)*	*I*	*d (Å)*	*I*
9.46	ms d	9.47	ms	9.47	vs
6.85	s	6.85	m	6.93	mw
				5.55	m
5.27	m	5.16	m	5.02	m
4.32	m	4.32	m	4.32	s
3.95	m	3.96	m	3.89	ms
3.43	m	3.43	m	3.57	ms
				3.34	ms
3.16	w	3.14	w	3.16	mw
2.92	vs	2.93	vs	2.91	vs
2.59	m	2.59	m	2.59	m
2.32	w	2.32	w		
2.29	s	2.29	ms	2.30	m
2.19	m	2.16	w		
2.09	m	2.08	m	2.08	m
1.90	w	1.91	w	1.87	m
1.84	s	1.83	m	1.80	s
1.71	s	1.72	s	1.72	ms

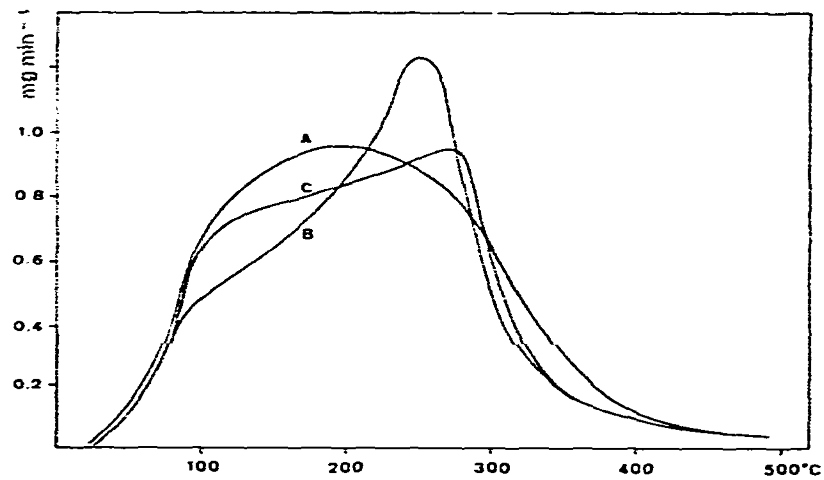


Fig. 1. DTG curves of 3 selected K–G samples. Curve A = No. 20-13; curve B = No. 03-65; curve C = No. 20-10.

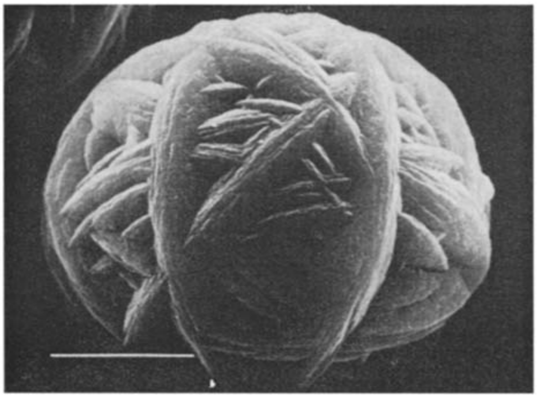


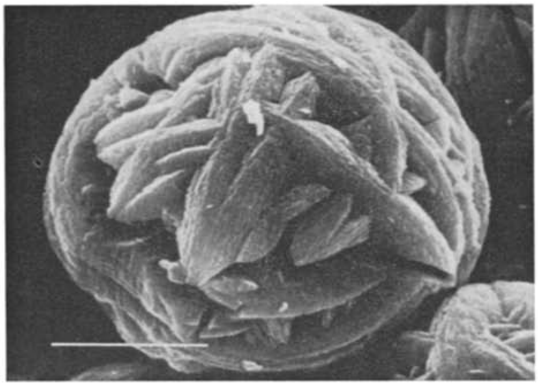
Fig. 2. Crystallite ball of sample 31-01, heated to 550°C for 2 h. White line marks 5 μm.

The simultaneous thermal and X-ray analysis indicates that the crystal structure of class B sample collapses between 180 and 190°C, i.e., just before the onset of the DTG maximum. Due to the denser population of potassium ions in the structural voids and pores, the release of zeolitic water below 200°C is impeded, as compared with class A samples. Beyond 200°C the energy of the water molecules becomes high enough to overcome the "ion barrier" which, in addition, may be rendered ineffective by the structural disintegration. Subsequently the remaining water is released nearly at once leading to an unusually sharp DTG maximum near 270°C.

Samples with a Si/Si+Al fraction between 0.55 and 0.57 show intermediate properties (Fig. 1, curve C).

Recrystallization

The external appearance of the crystallite balls of class A as well as of class B samples do not change appreciably upon breakdown of the crystal structure. However, when the samples are heated above 500°C small fissures appear at the contact zones between the intergrown platelets, broadening constantly with increasing temperature (Fig. 3).



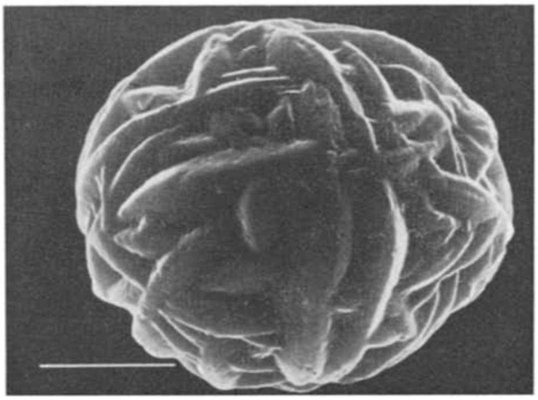


Fig. 3 (left). Crystallite ball of sample 31-01, heated to 1000°C for 2 hours. White line marks 5 μm.

Fig. 4 (right). Crystallite ball of sample 03-65, after recrystallization into kaliophilite at 1145°C. White line marks 5 μm.

Above 1000°C, class B samples recrystallize readily into kaliophilite, exhibiting a sharp exothermic peak (Fig. 6). The peak temperature increases with decreasing aluminum content. Only limited sintering takes place up to 1250°C (Fig. 4).

Class A samples start to sinter at about 1000°C (Fig. 5). They recrystallize over a wide range of temperature giving rise to a low and broad exothermic peak (Fig. 6). Beside kaliophilite, leucite appears as a new product, replacing the former progressi-

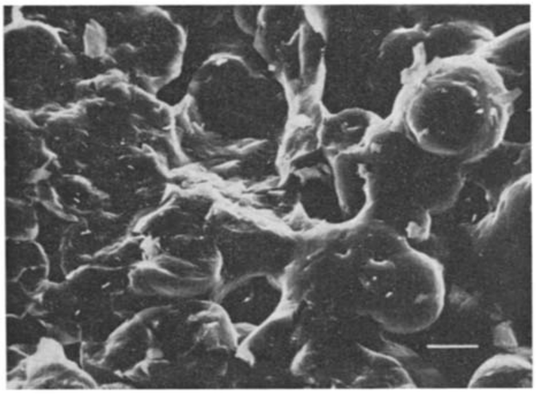


Fig. 5. Sintered product of sample 31-01, heated to 1250°C for 1 h. The X-ray analysis shows this product to consists of a mixture of kaliophilite and leucite. White line marks 10 μm.

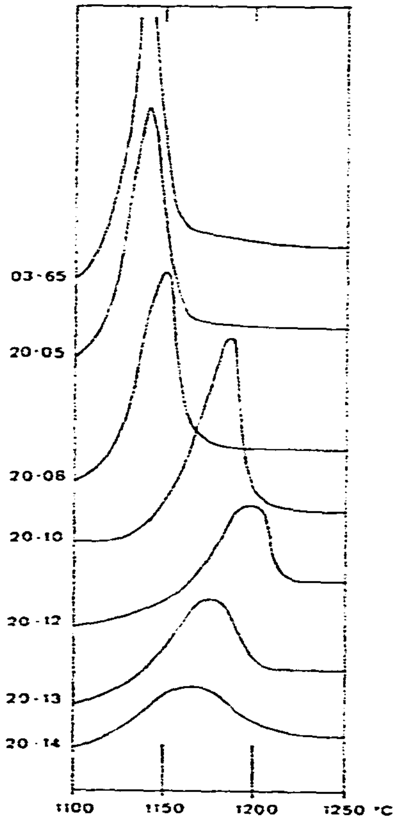


Fig. 6. DTA curves (recrystallization range) of 7 selected K–G samples.

vely with increasing Si/Si+Al fraction in the original sample. The peak temperature of the reaction decreases as the Si/Si+Al fraction approaches the ideal composition of leucite.

Sodium forms of K–G recrystallize into nepheline and calcium forms into anorthite, irrespective of the original composition. Surplus silica, in samples with a Si/Si+Al fraction greater than 0.5, is segregated. It effects a partial or even complete vitrification of the product.

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