ZEOLITE SYNTHESES FROM SUPERALKALINE REACTION MIXTURES*

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The synthesis of faujasite-type zeolite from superalkaline reaction mixtures are described. The contribution shows the influence of component K_2O added in the system Na_2O–Al_2O_3–SiO_2–H_2O with $H_2O/(K_2O + Na_2O) = 13-15$. The reaction course was investigated in the range $K_2O/(K_2O + Na_2O)$ from about 0·07 to 0·5. Under used conditions it is quite possible to isolate faujasite-type zeolite as a single crystalline phase. By means of IR spectroscopy, low SiO_2/Al_2O_3 ratios from 2·0 to 2·1 in the faujasite framework have been indicated. The low SiO_2/Al_2O_3 ratios are interpreted by a higher stability of the Si—O—Al— than the Si—O—Si— bond with increasing hydroxyl ion concentration.

In preceding papers[1–4] we reported on possibilities to synthesize fine-grained zeolite A (0·1 – 0·5 μm) from unusually superalkaline reaction mixtures with $H_2O/Na_2O = 13-15$. The initial solutions for such superalkaline reaction batches were obtained by alkaline decomposition and recycling processes of aluminium and/or silicon containing raw materials and waste products (e.g. brown-coal-flyashes, exhausted adsorbents and catalysts). Such solutions contain sodium as a predominant cation. However, also other cations can be enriched in the solutions, above all by recycling processes. In the case of sodium the mostly accompanying cation is potassium. According to the literature[5], potassium ions added to the reaction batch delay the formation of zeolite A in every case. The retardation effect of potassium ions on nucleation is caused by steric effects. The kind of zeolite which crystallizes from aqueous alkaline mixtures can be strongly influenced by the type of cation present. Comprehensive studies[6–9] have described the influence of potassium. The preparation of low-silica faujasites from a mixed sodium–potassium system has been published in ref.[10]. Our contribution deals with the influence of component K_2O added to the system Na_2O–Al_2O_3–SiO_2–H_2O in the $H_2O/(K_2O + Na_2O)$ molar ratio from 13 to 15. The reaction course was studied in the $K_2O/(K_2O + Na_2O)$ molar range from 0·07 up to 0·5.

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EXPERIMENTAL

The syntheses were carried out at a laboratory scale. Mixing and homogenization of aluminate (Na_2O-Al_2O_3-H_2O) and silicate (Na_2O-SiO_2-H_2O, K_2O-SiO_2-H_2O) solutions were carried out under continuous agitation. Both silicate and aluminate solutions were heated up to the reaction temperature before mixing. The zeolite crystallization was studied at temperatures from 40 to 60°C and with variation of alkaline and silicate concentrations in the mixture. The aluminate concentration was constant.

For kinetic studies, samples were withdrawn at certain intervals. The suspensions were separated in solid and mother liquor. The aluminosilicates were washed with hot deionized water and dried at 110°C. For characterization of both initial and reaction products, the following methods were used: *1*) chemical analysis, *2*) X-ray powder diffraction, *3*) IR-spectroscopy, *4*) water sorption.

RESULTS AND DISCUSSION

The zeolite crystallizations in dependence on both temperature and potassium content in the reaction batch are listed in the Table I. The results show that the crystallization in superalkaline reaction mixture is accelerated by temperature increase if the potassium content is the same. Potassium considerably influences the reaction

TABLE I

Beginning of zeolite crystallization in dependence on both temperature and $K_2O/(K_2O + Na_2O)$ molar ratio in the system K_2O-Na_2O-Al_2O_3-SiO_2-H_2O with $H_2O/(K_2O + Na_2O) = 13-15$ and $SiO_2/Al_2O_3 = 2$

Temperature °C	$K_2O/$ $/(K_2O + Na_2O)$	Beginning of crystallization h	Zeolite types
40	0	6	A
40	0·07	15	faujasite, (A)
40	0·14	24	faujasite
50	0	2·5	A
50	0·07	5	A
50	0·14	10	faujasite
50	0·28	24	faujasite
60	0	1	A
60	0·07	1·5	A
60	0·14	4	faujasite
60	0·28	8	faujasite
60	0·50	24	K-F

course. The beginning of the zeolite A crystallization is postponed to longer time by increasing $K_2O/(K_2O + Na_2O)$ molar ratio. The zeolite A formation is eventually quite prevented in favour of other crystalline phases, above all faujasite. Under conditions determined, it is quite possible to isolate faujasite-type zeolite as a single crystalline phase. The crystallization field obtained in dependence on the K_2O content and the reaction time at 50°C is displayed in Fig. 1. The increase of the potassium content in the mixture eventually leads to the formation of the edingtonite type K-F. This zeolite type is generally formed in alkaline systems with high K_2O contents[6-9].

The water sorption capacities of the synthesis products which contained faujasite-type zeolite as only crystalline phase amounted to 15–20%. Two commercial standards used for comparison (Grace GmbH) adsorbed about 25% of water.

In order to investigate the obtained SiO_2/Al_2O_3 molar ratio of the faujasite structures, IR spectroscopy was used. Substitution of the Al—O bonds by the significantly shorter Si—O bonds results in a shrinkage of the unit cell dimensions, in a bond-strength increase between the lattice components and, consequently, in a shift of the skeletal stretching vibrations to higher frequencies. Results on the Si/Al ratio in dependence on the skeletal vibrations were described in many papers e.g. ref.[11] and complied in ref.[12]. A linear correlation between the skeletal vibrations and the molar fraction of aluminium in the framework has been stated. The best correlation exists with the skeletal vibration from 970 to 1 100 cm^{-1}. We reproduced the correlation depicted in ref.[11] and used both correlations in order to determine the SiO_2/Al_2O_3 molar ratio in the faujasite structure obtained from superalkaline mixtures. The results showed, that the framework of all faujasites, prepared in superalkaline mixtures, consists of SiO_2/Al_2O_3 molar ratios from 2·0 up to 2·1. A representative

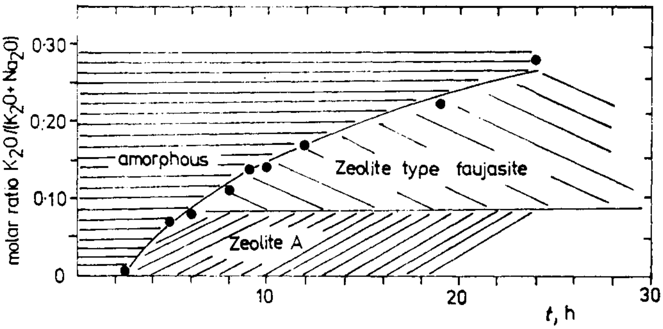

FIG. 1

Influence of the K_2O content in the reaction batch on the zeolite crystallization at 50°C. $SiO_2/Al_2O_3 = 2$

IR spectra of the crystallization sequence for zeolite type faujasite from an aluminosilicate gel are shown in Figs 2 and 3. The spectra were obtained on the solid phase separated from the solution and show the appearance of the structure sensitive bands near 560, 660, 750 and 1 020 cm^{-1} as faujasite formation proceeds. The absorption band near 850 cm^{-1} is assigned to a Si—OH bending vibration which decreases as crystallization of the faujasite structure proceeds. The band near 560 cm^{-1} assigned the stretching mode to the vibrations of the double 6-rings. Figure 3 shows both O-T-O stretching mode of the gel after 2 h (1 000 cm^{-1}) and the faujasite crystallized after 16 h (975 cm^{-1}).

The crystallization course was also studied by means of X-ray powder diffraction, water sorption (Fig. 4) and chemical analysis (Fig. 5). All these methods show an identical reaction sequence of the faujasite formation. First traces of faujasite were registered by X-ray powder diffraction after 9 h. A quantitative increase of the crystalline phase followed after 12 – 13 h.

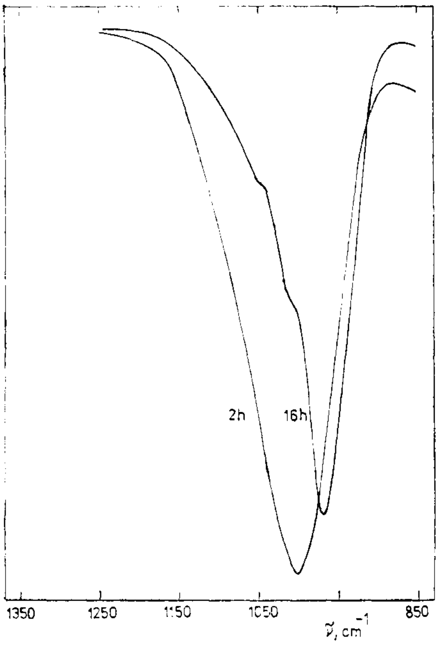

FIG. 2

IR spectra of the crystallization stages of faujasite-type zeolite in the range of skeletal vibrations. Reaction conditions as in Fig. 4, $SiO_2/Al_2O_3 = 2$

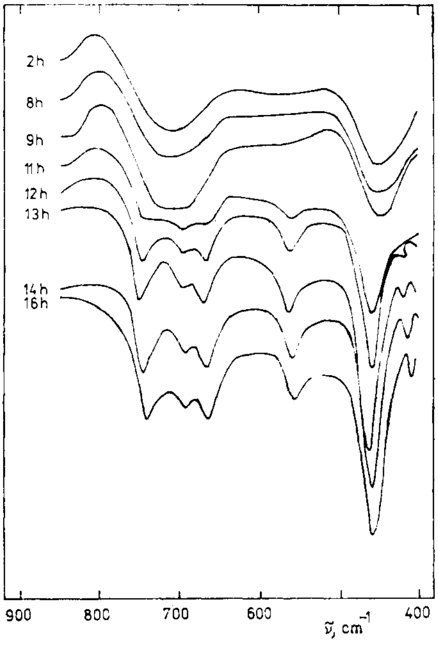

FIG. 3

Continuation from Fig. 2

Both Figs 2 and 3 show a shift of the band frequencies to lower wave numbers in the course of zeolite synthesis. This result indicates a decrease of the silicon fraction in the faujasite structure. That was examined by the repetition of the synthesis, but with SiO_2/Al_2O_3 molar ratio of 3 in the reaction mixture. Both reaction courses are shown in Figs 4 and 5. Both reaction courses are comparable. The identical IR spectra of the reaction mixture concerning the band frequencies, which are independent of the SiO_2/Al_2O_3 molar ratio in the reaction batch, are remarkable. The low Si/Al ratios are interpreted by a higher stability of the Si—O—Al— than the Si—O——Si— bond with increasing concentration of hydroxyl ion. A lower electrical negati-

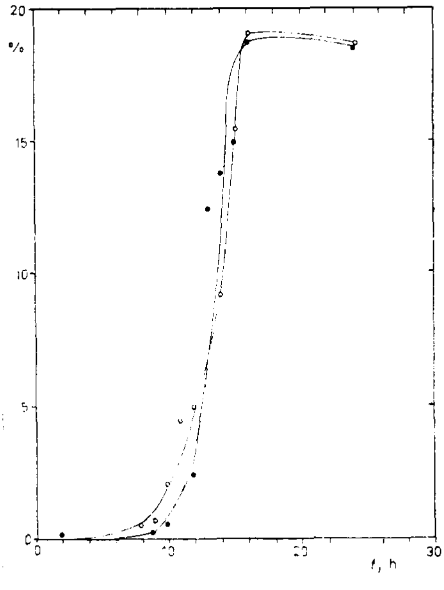

FIG. 4

Alteration of water sorption capacity (%) as a function of time during the synthesis of faujasite. Reaction conditions: 50°C, $H_2O/(K_2O + Na_2O) = 14·3$ and $K_2O/(K_2O + Na_2O) = 0·14$; ● $SiO_2/Al_2O_3 = 2$, ○ $SiO_2/Al_2O_3 = 3$

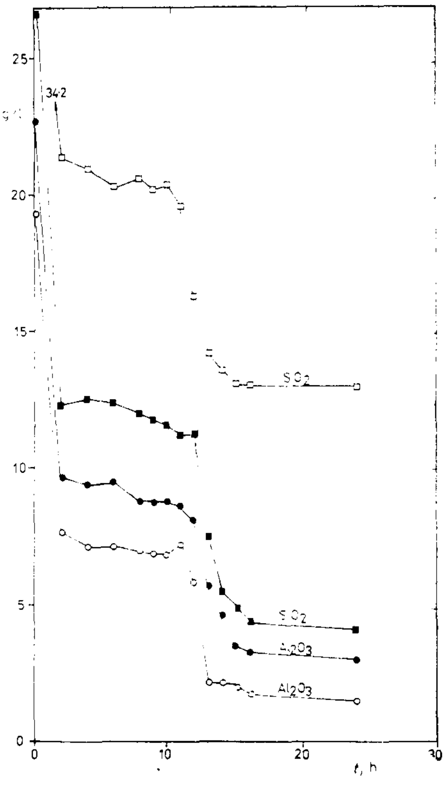

FIG. 5

Alteration of both Al_2O_3 and SiO_2 concentrations in mother liquor as a function of time during the faujasite syntheses in Fig. 4. ● ■ $SiO_2/Al_2O_3 = 2$, ○ □ $SiO_2/Al_2O_3 = 3$.

vity of aluminium results in a lower coordination unsaturation of silicon in links Si—O—Al and hence impedes the attack of bond Si—O by the hydroxide ion, formation of an intermediate pentacovalent complex with a silicon atom in the centre, and break of the bond. As a result, the equilibrium of the polycondensation reaction shifts towards formation of condensed aluminosilicate structures[13]. In comparison with commercial faujasite-type zeolites the low-silica faujasite is distinguished by higher ion exchange capacity. The investigations, including specification of the crystallization field of the above-mentioned system, will be continued.

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