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THE SYNTHESIS OF LEVYNE-TYPE ZEOLITE STUDIED BY THERMAL ANALYSIS OF METHYLQUINUCLIDINE ALUMINOSILICATE GELS

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Abstract

DSC, TG and quadrupole mass spectrometer data concerning methylquinuclidinium iodide (MeQI), dried precursor gel, and crystalline levyne-type zeolite are discussed together with the thermal degradation of MeQI mixed with single inorganic components of the gel.

It is shown that MeQ^+ ions play a role in the organization of the gel structure.

Keywords: DSC, DTG, levynite, TG, thermal analysis, QTMD

Introduction

Although the levyne-type is one of the zeolites discovered (1862), its first synthesis in the presence of organic molecules was reported by Kerr only in 1969 [1]. Later other zeolites isostructural with levyne have been synthesized from systems containing organic compounds. All the templates used to obtain synthetic levyne-type zeolites have at least one cyclic substituent on the charged nitrogen [1–5]. The structure-directing and the space filling role of organic compounds in the formation of the framework of various zeolites is fairly well documented.

In studies of organo-zeolites, thermal analysis has been demonstrated to be an indispensable tool to characterize the intermediate and the final zeolitic phases [6]. The organization of tetralchylammonium aluminosilicate gels has been studied by thermal analysis supplemented by other spectroscopic techniques such as ^{13}C-NMR [7].

We report in this study the results obtained by thermal analysis and by quadrupole temperature programmed mass detector from the precursor gels contain-

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ing MeQI and the characterization of the crystalline levine-type zeolite. These results allowed us to form a hypothesis on the role played by MeQ^+ in the nucleation and crystal growth of the zeolite.

Experimental

The reaction gels and mixtures were prepared by combining appropriate amounts of 30% aqueous solution of NaOH (pellets RPE, Carlo Erba), MeQI obtained from quinuclidine (1-azabicyclo-(2.2.2.)octane, Aldrich) and iodomethane (Aldrich) according to methods described elsewhere [4, 8], $Al(OH)_3$ (dry gel, Pfaltz and Bauer), distilled water and SiO_2 (fumed silica, Serva). The gels and mixtures were dried at 100°C for 24 h to obtain a dry powder and then characterized after 48 h of ageing at room temperature.

The levyne-type zeolite was synthesized by heating at 150°C, in static conditions and in sealed teflon autclaves a gel with a batch composition characterized by the following molar ratios $4.5Na_2O$–$6MeQI$–Al_2O_3–$30SiO_2{\cdot}500H_2O$. More details on the synthesis and characterization of levyne-type zeolite from systems with different Na_2O and MeQI contents have been reported previously [9–11].

The nature and degree of crystallinity of the phases obtained were determined by X-ray powder diffraction using a Philips PW 1730/10 X-ray generator equipped with a PW 1050/70 vertical goniometer (CuK_α). Characterization by thermal analysis (DSC, TG and DTG) was carried out from room temperature to 900°C, using a Netzsch STA409 instrument. Adequate sensitivity in an air flow (15 ml min^{-1}) and at a heating rate of 10°C min^{-1} was obtained with a sample mass of about 10 mg. The volatiles evolved during the TG analysis were identified by TPD analysis carried out with a Carlo Erba QTMD (quadrupole thermal programmed mass detector). Identification was made from 1 to 150 a. m. u. (atomic mass units). The ion species signals, six selected ion species for each analysis, were followed as a function of the temperature. To identify all fragments each QTMD analysis was performed three times folllowing fragments with different a.m.u.

Results and discussion

The DSC curves for the levyne-type zeolite, prepared from the system $4.5Na_2O$–$6MeQI$–Al_2O_3–$30SiO_2$–$500H_2O$ are given in Fig. 1 together with the DSC curves of its precursor gel, of the pure MeQI and of the other mixtures studied. The corresponding DTG curves are presented in Fig. 2. The results of the thermal degradation followed by quadrupole temperature programmed mass dectector, are shown in Fig. 3. The courses of the DSC and of the corresponding DTG curves show that all thermal effects are connected with mass losses. In fact the same number of thermal effects are observed in the DSC and DTG curves.

The two effects observed in the DSC curve of pure MeQI (Fig. 1, curve A) the first endothermic and the second exothermic, are connected with the thermal degradation and subsequent combustion of the organic compound and correspond to only one effect in the DTG curve (Fig. 2, curve A).

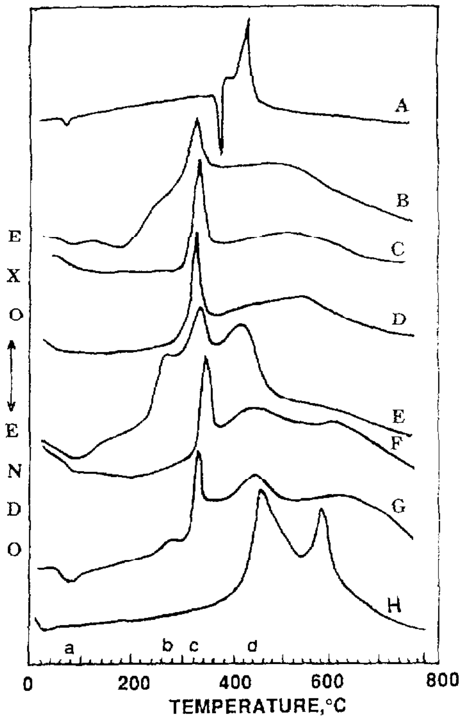

Fig. 1 DSC curves of the crystalline phases and amorphous mixtures studied. A=pure MeQI; B=$6MeQI–30Al_2O_3·500H_2O$; C=$6MeQI–30SiO_2·500H_2O$; D=$6MeQI–Al_2O_3–30SiO_2·500H_2O$; E=$6MeQI–30Al_2O_3–4.5Na_2O·500H_2O$; F=$6MeQI–30SiO_2–4.5Na_2O·500H_2O$; G=precursor to levynite $6MeQI–Al_2O_3–30SiO_2–4.5Na_2O·500H_2O$; H=pure levyne of composition $MeQ_{7.1}$ $Na_{0.9}$ $(Al_{3.5}Si_{50.5}O_{108})2.5H_2O$

The thermal degradation of organic matter incorporated inside the channels of the levyne-type zeolite (Fig. 1, curve H) shows two exothermic effects centred at 469 and 585°C, respectively and two mass losses corresponding to the two effects in the DTG curve (Fig. 2, curve H) centred at 469 and 580°C, respectively. In agreement with DSC and DTG results obtained for TMA and TEA zeolites and reported elsewhere [6–14] the loss occurs in two stages. The first one is connected with the DSC and DTG peak at 469°C corresponding to 10.26% of the total mass loss. The second one connected with the DSC and DTG peak at 585°C is equivalent to a loss of 11.01%. Both losses are due to degradation of the large or-

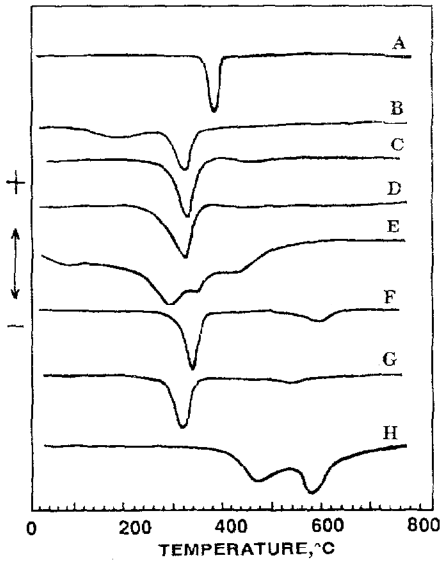

Fig. 2 DTG curves of the crystalline phases and amorphous mixtures studied. A=pure MeQI; B=$6MeQI–30Al_2O_3·500H_2O$; C=$6MeQI–30SiO_2·500H_2O$; D=$6MeQI–Al_2O_3–30SiO_2·500H_2O$; E=$6MeQI–30Al_2O_3–4.5Na_2O·500H_2O$; F=$6MeQI–30SiO_2–4.5Na_2O·500H_2O$; G=$6MeQI–Al_2O_3–30SiO_2–4.5Na_2O·500H_2O$; H=pure levyne

ganic molecules and combustion of the small fragments. Iodide ion is not incorporated inside the zeolite channels because the corresponding QTMD analysis signal in Fig. 4 does not show any possible fragment containing iodide. Only small fragments are observed because the larger ones are not desorbed from the zeolitic channels. The degradation of MeQ followed by this technique is always observed at higher temperature (588°C) because the experimental conditions are different from those of the DSC and DTG experiments.

These results suggest that inside the zeolitic channels the MeQ^+ cation is the counterion to the framework $(SiOAl)^-$ or to negative charges of SiO^- defect groups. Indeed, the total MeQ^+ per unit cell is equal to 7.1 and 3.5 and 3.6 MeQ per unit cell are attributed, to the first and to the second loss, respectively.

The first loss is due to the decomposition of MeQ^+ ions which are linked to SiO^- defect groups and hence they are less stabilized. The second loss is due to the decomposition of MeQ^+ ions which neutralize the framework $(SiOAl)^-$ negative charges. Indeed, the amount corresponding to the second loss, 3.6 MeQ/u. c. corresponds exactly to 3.6 Al/u. c., the value determined by chemical analysis [12]. These MeQ^+ ions are better stabilized by the levynitic channels, hence their decomposition occurs at higher temperatures. Similar behaviour was shown for other organic cations occluded in zeolitic channels [15].

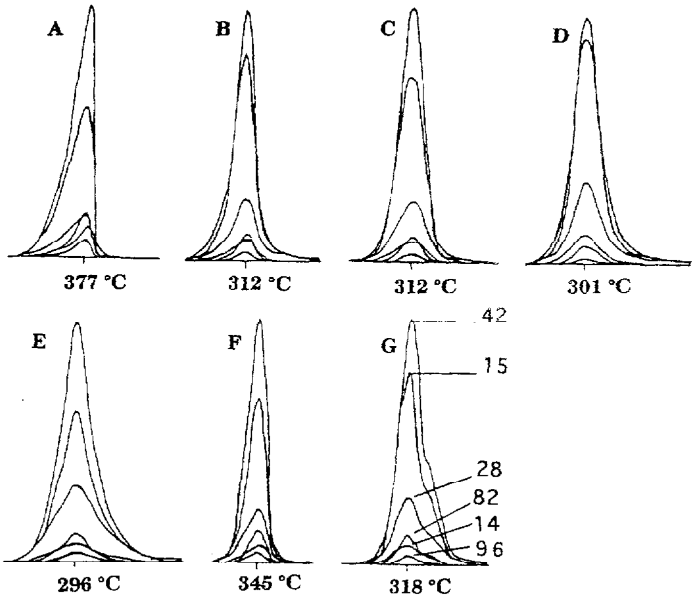

Fig. 3 QTMD spectra of the dry mixtures relative to 42, 15, 28, 82, 14, 96 a.m.u. A=pure MeQI; B=6MeQI–30Al_2O_3·500H_2O; C=6MeQI–30SiO_2·500H_2O; D=6MeQI–Al_2O_3–30SiO_2·500H_2O; E=6MeQI–30Al_2O_3–4.5Na_2O·500H_2O; F=6MeQI–30SiO_2–4.5Na_2O·500H_2O; G=precursor gel dry 6MeQI–Al_2O_3–30SiO_2–4.5Na_2O·500H_2O; H=pure levyne

The QTMD patterns of the unreacted dry mixtures are given in Fig. 3. Table 1 illustrates the different small species evolved during the TPD experiment.

Comparison of the DSC curve of the dried gel of the precursor to levyne zeolite (Fig. 1, curve G) and the DTG (Fig. 2, curve G) curves and the QTMD patterns in Fig. 3, curve G, suggests that MeQ^+ is partially linked to the aluminosilicate gel, and partially linked to iodide in this gel precursor to levyne zeolite. Indeed, Fig. 5 shows that when a complete QTMD analysis of the initial dry gel is made, the presence of iodine is also detected. Although the fragments detected in the QTMD analysis of the initial dried gel are similar to those observed for pure MeQI, their relative intensities are different (Table 1) [11] as are their temperatures of decomposition (Fig. 3). These results suggest that in the initial gel part of MeQ^+ being linked to the gel structure has a different thermal stability. On the other hand, the presence of peak **a** at 90°C (DSC pattern, Fig. 1 G), attributed to a reversible phase transition of MeQI, indicates that part of the organic cation is not linked to the aluminosilicate gel, but linked to iodide, forming small MeQI particles.

The peaks in the DSC curve and the corresponding DTG effects of the initial gel are attributed to the following effects: peak **b** is connected to the degradation

Table 1 Identification of the various small species evolved and their relative intensities detected in the TPD experiment

u.m.a.	Species	I/I_0		
		MeQI[a]	Initial gel[b]	Levyne[b]
14	CH_2	11.32	11.32	–
15	CH_3	68.86	79.53	322.77
17	OH/NH_3	1.44	185.17	368.59
28	C_2H_4	22.51	32.22	418.24
42	C_2NH_4	100	100	100
82	C_5NH_8	14.68	11.56	5.91
96	C_6NH_{12}	6.05	4.19	0.22
111	C_7NH_{13}	2.39	20.36	0.27
126	C_8NH_{16}	3.24	2.21	–
127	I	19.35	15.16	–

[a] Synthesized following the procedures in [11] and [14]

[b] The initial gel and the crystalline phase were obtained from the system $4.5Na_2O$–$6MeQI$–Al_2O_3–$30SiO_2 \cdot 500H_2O$

Table 2 Mass losses (% in mass) connected with the DSC and the DTG curves of Figs 1 and 2, respectively

Sample	Water loss	Peak **b** T=250°C	Peak **c** T=335°C	Peak **d** T=450°C
B	4.7	17.23	21.32	3.53
C	–	–	39.74	3.90
D	–	–	36.07	4.07
E	3.5	13.78	11.89	10.91
F	–	–	28.62	14.35
G	0.24	5.78	22.09	13.22

of MeQ^+ linked with the Al negative charge of the gel that contributes to the organization of the gel structure; peak **c** is attributed to the dry MeQI mono-dispersed on the surface of the dry solids. No differences are observed between the surfaces of SiO_2 and of Al_2O_3. The same effect is observed in both curves of mixtures C and D; peak **d** (detected between 414 and 494°C) could be due to the combustion of the organic compound residue stemming from the decomposition of MeQ^+ ions. The corresponding mass losses are given in Table 2. The affinity of MeQ^+ is higher toward the aluminate than toward the silicate anions. This behaviour is shown by the course of the DSC and DTG curves in Figs 1 and 2, respectively, where the degradation of the organic compound is observed at lower temperatures when Al_2O_3 is added to the batch.

Comparison of the DSC and DTG patterns of the original dry gel G and of the other dry mixtures (B–F) show that in the dry gel the organic compound is partially monodispersed on the surface of the dry gel (DSC peaks detected between 326 and 347°C) and is partially linked to the negative charge of the gel framework even in the presence of Al_2O_3 and Na^+ cation (DSC peaks detected between 220 and 269°C).

Figure 3 shows the QTMD spectra of the dry mixtures. The temperatures of decomposition follow the same sequence as that determined by the DSC curves. The decomposition temperature of pure MeQI is higher than those of the different dried gels, which vary from 296 to 345°C. The QTMD of all these samples are characteristic of the decomposition of MeQ^+, because the relative intensities of the m/e peaks at 96, 82 and 42 are very similar: the 42 a. m. u. peak is the most intense followed by the 15, 58, 82, 14 and the 96 a. m. u. peak.

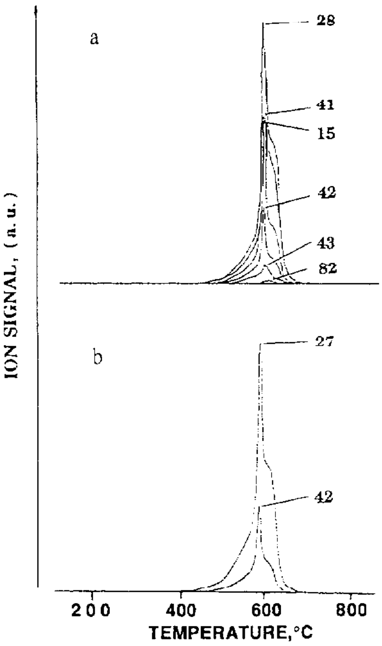

Fig. 4 QTMD spectra of levyne-type zeolite relative to 15, 27, 28, 41, 42, 43, 82. a.m.u. (sample H)

Figure 4a shows the fragments produced during the decomposition of MeQ^+ occluded in levynite crystals. The temperature of decomposition is high and the relative intensities of the various fragments are quite different from those observed for the dried gels. This is probably due to the higher temperature of de-

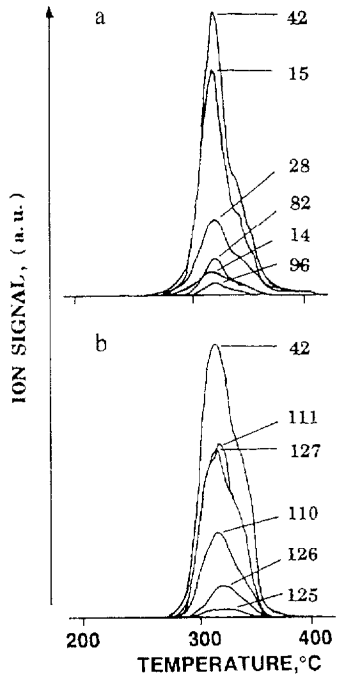

Fig. 5 QTMD spectra of the precursor dry gel G relative to 42, 15, 28, 82, 14, 96, 110, 111, 125, 126, 127 a.m.u.

composition where smaller fragments are formed in larger amounts. These data also suggest that MeQ^+ is not desorbed as such from the levynite channels, but only fragments of decomposition can be desorbed.

In order to prove the decomposition of MeQ^+ at this high temperature, another experiment was carried out where the fragments 27, 42, 111, 125, 126 and 127 a. m. u. were followed (Fig. 4b). The higher fragments 111, 125 and 126 would show the presence of MeQ^+, while the 127 a. m. u. is characteristic of iodine. The absence of the fragments of high a. m. u. shows clearly that MeQ^+ cannot be desorbed intact from the levynite channels and that iodine is not included in the final zeolitic samples. Moreover, comparison of the data of Fig. a and b shows the good reproducibility of the results.

Figure 5 shows the fragments detected during the decomposition of the dry gel G precursor to levynite crystals. In two different experiments where the 42 a. m. u. peak was taken as reference, both the interesting low and high a. m. u. peaks were identified. It is shown that iodine is detected at 127 a. m. u., the MeQ^+ ion at 126 a. m. u., the fragments 125 a. m. u. with one hydrogen less than MeQ^+ and also the 111 a. m. u. fragments, where MeQ^+ has lost a methyl group.

Conclusions

The above results show that methylquinuclidine is present in the gel as a monodispersed phase MeQI and as a cation linked to silicate and aluminate anions or as small MeQI particles. Moreover, similarly to TAA^+ cations, even in the presence of Na^+, MeQ^+ is not just a template cation but plays a role in the organization of the gel structure and then contributes to the nucleation of the levyne-type zeolite from the gel.

The MeQ^+ cations trapped inside the channels of the levyne-type zeolite are balanced by the negative charge of the framework or by SiO^- defect groups because iodide species are not detected in the mass spectra.

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