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THERMAL ANALYSIS OF FLUORINE CONTAINING GELS AND PRECURSORS OF HIGH SILICA ZEOLITES

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By means of simultaneous DTA-, TG- and DTG-technique, the silicate gels and the MFI crystals obtained from these gels have been investigated. The gels have been prepared in presence and in absence of tetrapropylammonium cation (TPA^+) and with Li^+, Na^+, NH_4^+ and K^+ fluorides. In absence of TPA^+ no thermal effects have been observed in Li^+- and Na^+-gels. The effects observed in the NH_4^+-gel stem from a decomposition and release of inorganic phases: SiF_4, NH_4F, NH_3. The DTA/DTG effects in the TPA^+ containing gels and in the MFI crystals of monodisperse size are attributed to the decomposition of TPA^+ cation. It can be concluded from these effects that the interaction between the gels and the TPA^+ cation is rather weak. The interaction between TPA^+ and MFI crystals obtained in fluoride medium is stronger than the interaction with crystals obtained from alkaline media. Similar thermal effects are obtained after grinding the long crystals to those having a large distribution of crystal sizes.

Keywords: fluorine containing gels, high silica zeolites

Introduction

The development of the syntheses in presence of fluoride ions allows one to obtain zeolites in a much wider *pH* range than in alkaline media [1]. The so-obtained zeolite crystals exhibit a regular morphology and larger than usual crystal sizes. F^- ions solubilize the reactants, take part in polycondensation processes and crystallization. Several zeolites and their Al-free end-members of MFI, MTT, MTN, TON, FER [1, 2], MEL and ZSM-48 [3] structures have been synthesized by the use of fluoride ions.

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The characterization of reaction gels and crystalline precursors is of a great importance for the studies of crystallization mechanism. The thermal analysis is particulary useful for the investigation of the interaction between organic and inorganic cations with the aluminosilicate gel [4, 5] and crystalline material [6–8].

In the present study we report the interaction between the tetrapropylammonium (TPA^+) cation and the silica gel prepared in a fluorine medium by means of thermal analysis, the influence of the inorganic cation type on the interaction between TPA^+ and the gel and also the use of thermal analysis for the crystalline product characterization.

Experimental

The initial general composition studied was [9]:

$$10MF–xTPABr–10SiO_2–330H_2O$$

where M=Li, Na, K, NH_4 and x=0 and 1.25

Fumed silica (research grade, Serva) was used as a silica source. The other reactants were pure TPABr (purum, Fluka), reagent grade Li^+, Na^+, K^+, NH_4^+ fluorides (all reagent grade, Carlo Erba). The reagents were mixed in the following order: silica, distilled water, TPABr solution, fluoride salt solution.
MFI-zeosilite samples have been prepared in modified Morey-type PTFE-lined 20 cm^3 autoclaves, without agitation at 170°C.

Simultaneous TG, DTG, DTA analyses of initial gels dried overnight at 100°C and the crystalline products were performed by Netzsch STA 429 equipped with a HP Vectra ES/12 computer. The weight losses and thermal effects due to the release of decomposition products under dry nitrogen atmosphere (flow rate 10 cm^3/min) were evaluated. The heating rate was 10 deg/min.

Results and discussion

The DTA/DTG curves of the silica gels prepared in presence of Li^+, Na^+, K^+ or NH_4^+ in absence of the TPA cation are presented in Fig. 1. No effects have been observed in the systems with Li^+ and Na^+ cations. The system with KF exhibits some crystallinity due to the presence of K_2SiF_6 and α-K_2SiO_2. The thermal effects observed at 430°C can be attributed to the decomposition of potassium hexafluorosilicate and the evolution of small amount of SiF_4. The

total weight loss in this sample was measured to be 7.6% (3.4% in the rage of 390°–650°C). This K^+-gel leads to cristobalite when heated at 500°C in air.

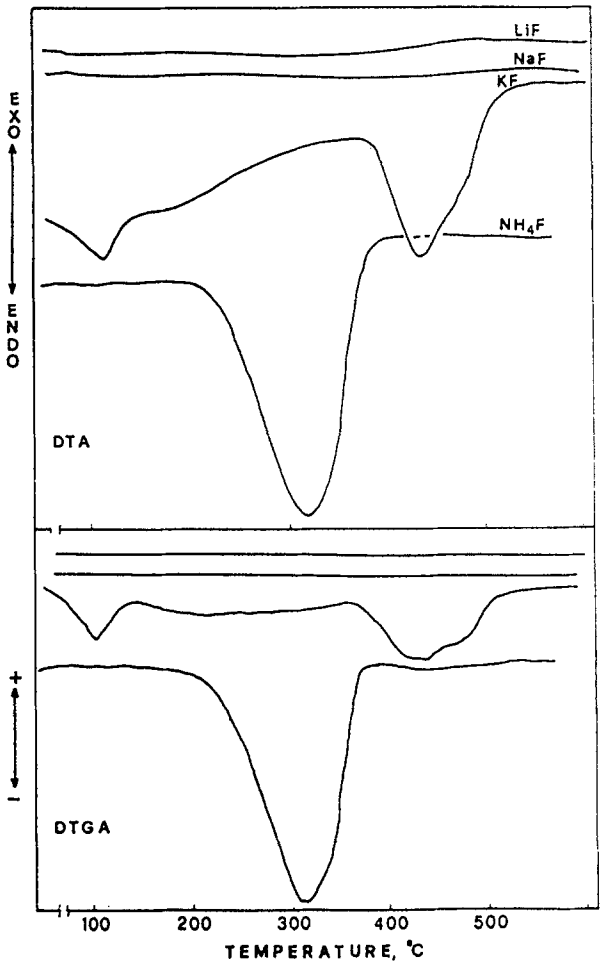

Fig. 1 DTA/DTG curves of the silica gels prepared in the presence of Li^+, Na^+, K^+ and NH_4^+ in absence of TPA^+ cation

The DTA thermal effect and simultaneous weight loss observed in the system with NH_4F results from the reaction of the silica gel with NH_4F. Indeed, the observed total weight loss (ca 42%) is in very good agreement with calculated one, (44%) based on the following formula:

$$10SiO_2+10NH_4F \rightarrow 9SiO_2+SiF_4\uparrow+6NH_4F\uparrow+4NH_3\uparrow+2H_2O\uparrow$$

The DTA/DTG curves of the TPA containing silica gels prepared in presence of alkaline metal fluorides are presented in Fig. 2.

The thermograms with Li^+ and Na^+ are similar to each other and show the same effects as in the previously reported system with OH^- [4]. A peak at about 110°C, detected on all four curves, is attributed to the phase transition of crystalline TPABr, precipitated on the surface of the solid phase during the drying process (TPABr dispersed on the surface).

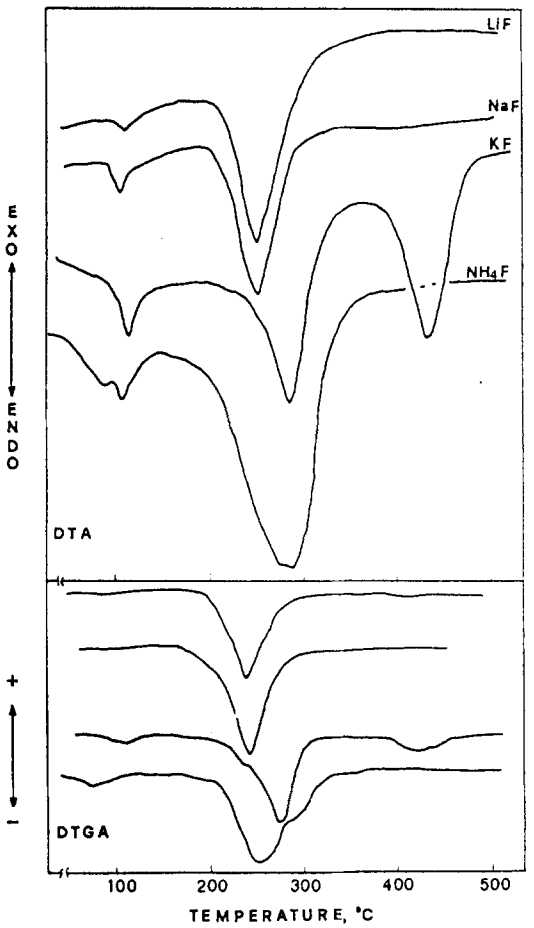

Fig. 2 DTA/DTG curves of the TPA^+ containing silica gels prepared in presence of different inorganic fluorides

In the K^+-gel this peak stems from the above mentioned effect and from an additional water loss (ca 4%).

The second DTA effect corresponds to the decomposition of the TPABr. The temperature of this effect (250°C) on DTA curves of Li^+, Na^+ and NH_4^+ -gels indicates that the interaction between the gel and the TPA^+ cations is weak. In the K^+-gel, the TPA^+ organic cation decomposes at a slightly higher temperature (280°C) and this is characteristic of bulkier crystalline TPABr [8]. The third DTA effect in the K^+-gel stems from the decomposition of the crystalline inorganic K_2SiF_6 phase (Fig. 1).

Figure 3 represents the DTA/DTG curves of the sonicated MFI crystals. The crystals obtained from Li^+-, Na^+- , NH_4^+ and K^+-gels are elongated and uniform in size of ca 60, 70, 95 and 70 μm, respectively.

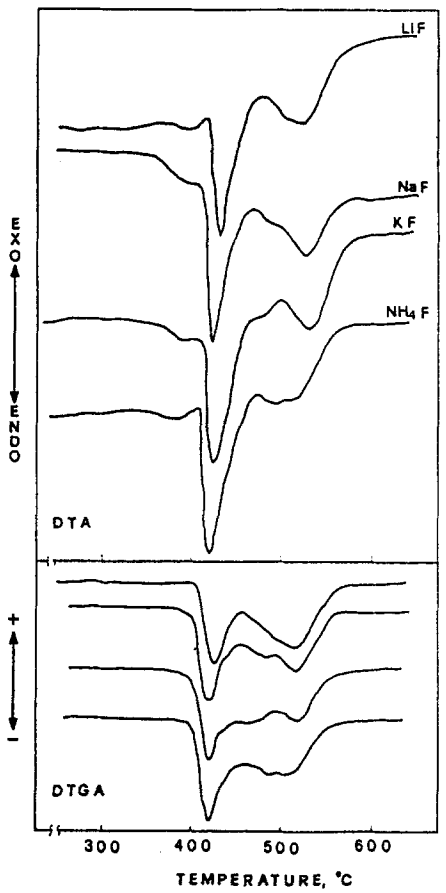

Fig. 3 DTA/DTG curves of the sonicated MFI crystals

The effects observed occur at higher temperature than in the MFI-silicates crystallized from alkaline media [6], as it was previously reported [10]. These effects have been attributed to the decomposition of the TPA^+ ions to tri- and dipropylamine and propylene with the succesive release of propylene and ammonia. Because the observed weight losses were in all samples larger than the theoretical ones (4TPA cations per one unit cell), the products released from the crystal decomposition have been analyzed [9]. Beside propylene and ammonia some amounts of hydrofluoric acid have also been detected.

The DTA/DTG curves of the MFI crystals obtained in presence of NH_4F in the as-synthesized form, slightly ground and finely ground are compared in Fig. 4 with those having a wide crystal size distribution (5–60 μm).

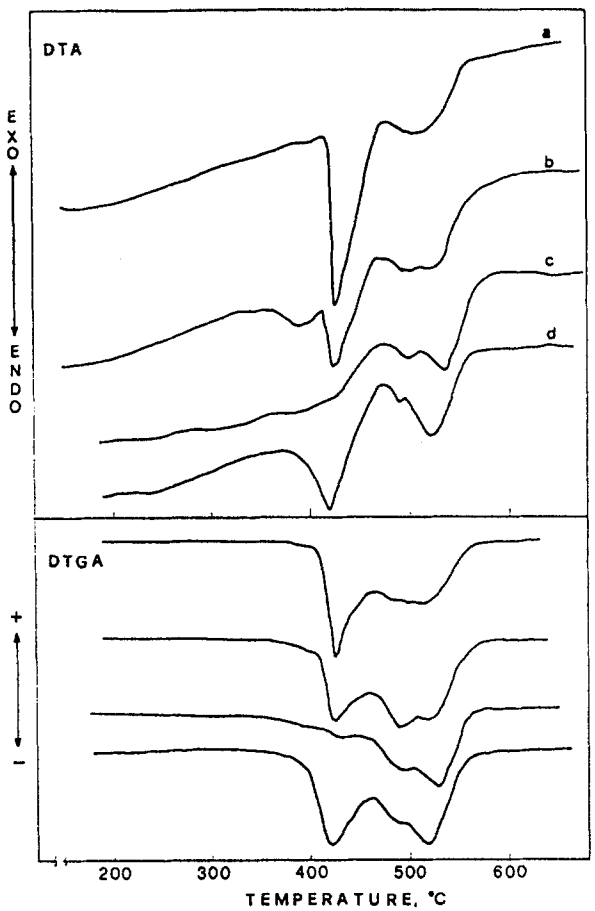

Fig. 4 DTA/DTG curves of the uniform MFI crystals obtained in presence of NH_4F: a) as synthesized, b) slightly ground, c) finely ground and d) MFI crystals obtained from a similar system but having a wide range of crystal size distribution (5–60 μm)

The more ground are the crystals (curves b and c), the smaller is the lower temperature DTA effect, which in the finely ground sample almost disappears. The release of the TPA^+ decomposition products from these crystals begins at lower temperature and in a milder form (smaller DTG effect) comparing to the as-synthesized sample. The total weight loss remains the same after the grinding. It can be seen from the curves that the second DTA and DTG temperature effects are shifted to higher temperatures. The DTA and DTG curves of small crystals (curve d), resemble that of slightly ground, long crystals (curve c). Thus, it can be concluded that after the first evolution of the decomposition products from the crystals, the remaining organics (tripropylamine, dipropylamine) are stronger stabilized in the small crystals than in the large ones.

Conclusions

The thermal analysis technique is very well suited to the gel and the final crystalline phases obtained in fluoride containing media. The DTA and DTG effects of the silicalite crystals are due to the decomposition of the TPA^+ ions occluded in the zeolite structure and to the release of their decomposition products. The characteristics of these effects depend on the size of the crystals.

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Zusammenfassung — Mittels simultaner DTA-, TG- und DTG-Techniken wurden Kieselgele und die MFI-Kristalle dieser Gele untersucht. Die Gele wurden in und ohne Gegenwart von Tetrapropylammoniumkationen (TPA^+) und mit Li^+-, Na^+-, NH_4^+ und Kaliumfluoriden hergestellt. Bei Abwesenheit von TPA^+ werden für Li^+- und Na^+-Gele keine thermischen Effekte beobachtet. Der bei NH_4^+-Gelen beobachtete Effekt ergibt sich

aus der Zersetzung und Abspaltung von anorganischen Phasen: SiF_4, NH_4F, NH_3. Die DTA/DTG-Effekte in TPA^+-haltigen Gelen und in den MFI-Kristallen monodispersen Ausmaes werden der Zersetzung des TPA^+-Kations zugeschrieben. Daraus kann man schlieen, da die Wechselwirkung zwischen den Gelen und dem TPA^+-Kation eher schwach ist. Die Wechselwirkung zwischen TPA^+ und MFI-Kristallen aus fluoridischen Medien ist strker als die Wechselwirkung mit Kristallen aus alkalischen Medien. Ähnliche thermische Effekts erhlt man, nachdem man die langen Kristalle zerkleinert und eine breite Kristallgrenverteilung erhlt.