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THERMAL ANALYSIS OF ZEOLITE ZSM–5 PRECURSORS WITH DIFFERENT Si/Al RATIOS

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The thermal analysis of crystalline zeolite ZSM–5 precurcors with different Si/Al ratios was carried out in a nitrogen atmosphere. Different interactions between tetrapropylammonium species and the zeolitic environment were evidenced, depending on the Al content of the crystalline precursors. The results support the mechanism of ZSM–5 formation through a condensation process from the liquid phase.

Zeolite ZSM–5 is generally synthesized by hydrothermal crystallization of aluminosilicate gels. Though it has also been prepared in the absence of organic base or cation [1], tetrapropylammonium (TPA) is usually employed in the synthesis process. The interactions between the TPA species and aluminosilicate gels have been characterized and the templating role of some of these species has been evidenced [2]. Through several stages of the crystallization process, a crystalline zeolite form is obtained, containing TPA ions occluded in the framework [3]. The transformation to the desired cation-exchanged form of ZSM–5 to be used as catalyst necessitates the removal by thermal decomposition of the TPA cations present in the structure. Moreover, the residual gel normally present in the synthesized products can influence the catalytic properties of ZSM–5 crystals [4]. In this paper, the decomposition of zeolite ZSM–5 precursors has been investigated through thermal analysis techniques.

Experimental

A series of ZSM–5 samples were synthesized from the system: $4Na_2O$–8TPABr–xAl_2O_3–$100SiO_2$–$1100H_2O$, with x ranging from 0 to 4. The reaction temperature and time were always 170° and 48 h, respectively. The TPA-zeolites were characterized for their crystalline nature by means of X-ray

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diffraction. A fraction of each synthesis product was purified by ultrasound treatment to separate pure crystals from the residual gel. The effectiveness of ultrasound treatment was checked through SEM analysis. The ZSM–5 precursors dried at 100° in air overnight were characterized through thermal analysis: simultaneous thermogravimetric (TG), differential thermogravimetric (DTGA) and differential thermal analysis (DTA) were carried out with an automatic thermal analyzer (Netzsch Model STA 409) under a dry nitrogen atmosphere. The following experimental conditions were used: sample weight 100 mg; sample holder, platinum crucible; temperature range 25–700°; heating rate 10 deg min^{-1}; flow-rate 15 cm^3 min^{-1}.

Results and discussion

The chemical compositions of the zeolite ZSM–5 precursors synthesized as described previously are given in Table 1. Comparison of the Si/Al ratios in the starting system and in the zeolite ZSM–5 precursors evidences a difference which increase at lower ratios. Moreover, the total TPA content evaluated from TG analysis ranges from 3.4 to 3.9 molecules per unit cell. The TPA content increases with the Si/Al ratio in the zeolite.

The DTA curves for purified ZSM–5 precursor crystals are presented in Fig. 1. Three different endothermic peaks are observed in the temperature range 320–600°. These effects result from the Hofmann degradation reactions [5], by which the TPA cations are removed in a nitrogen atmosphere. The small peak with maximum at 350° is due to the decomposition of "surface" TPA occluded in the zeolite framework or in the crystal defects. The intensity of this peak increases with the Si/Al ratio in the crystals, probably because a higher Si/Al ratio favours the formation of defects, as detected by ^{29}Si MAS–NMR techniques. The presence of

Table 1 Chemical composition (number of respective ions per unit cell) of crystalline ZSM–5 zeolite precurcors after ultrasound treatment (x = Al content in the synthesis system)

x	Na, u.c.	TPA, u.c.	Al, u.c.
0.0	1.29	3.85	—
0.1	1.22	3.88	0.10
0.2	1.38	3.89	0.20
0.3	1.40	3.83	0.25
0.5	1.21	3.70	0.37
1.0	1.20	3.73	0.71
2.0	1.26	3.54	1.16
4.0	1.40	3.40	2.10

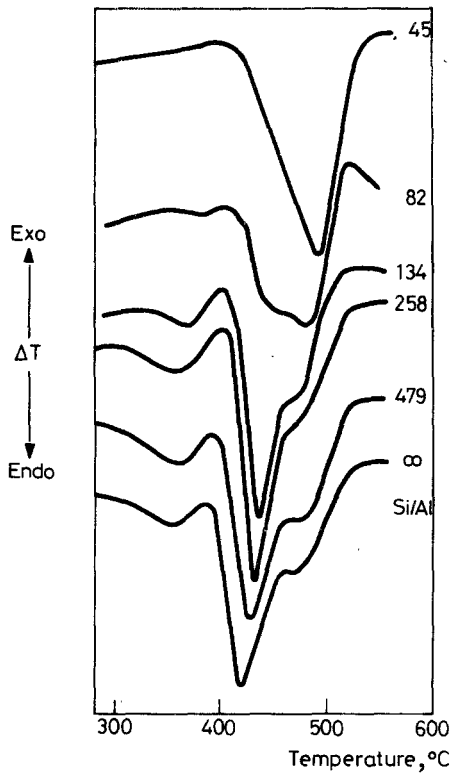

Fig. 1 DTA curves for the decomposition in nitrogen flow of ZSM–5 zeolite precursors with different Si/Al ratio

"surface" TPA occluded in the zeolite is in accordance with a mechanism of zeolite formation through condensation from the liquid phase [3]. The main endothermic effect is observed in the range 380–550°. This takes place in two steps: the first has a peak temperature increasing with decreasing Si/Al ratio (415–430°). The intensity of this peak is lower at higher Al content, while the second signal (470–485°) becomes stronger. These effects are attributed to the decomposition of TPA not linked and linked, respectively to Al atoms of the zeolite structure. On the other hand, the presence of different TPA species interacting with the zeolitic environment is confirmed by the observation that, for all the synthesized precursors, there is an excess of positive charges over Al (Table 1). Therefore, a fraction of the total TPA cannot be related to the presence of Al. A possible reason for the relative DTA signal involves interaction with the negative OH^- groups in the channels and with SiO^- groups resulting from structure defects. The lower peak temperatures exhibited by silicalite precursors confirm that the presence of

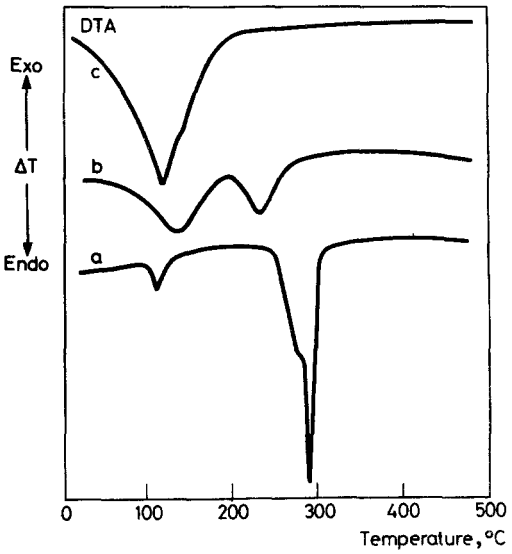

Fig. 2 DTA curves for the decomposition of TPABr (a), dried hydrogel from the synthesis system at $x=0.5$ (b) and hydrogel after filtering and washing (c)

structural Al results in a higher thermal stability of TPA cations in zeolite ZSM–5. In the case of silicalite precursors, the second thermal effect at 465° can be attributed to the interactions of TPA cations with SiO^- groups resulting from structure defects.

Further confirmation of the stabilization of TPA species in zeolite ZSM–5 is given by the DTA curves of TPABr (Fig. 2). The weak signal at 115° has been attributed to a phase transition of crystalline TPABr [2]. The second endothermic effect, at 275–290°, corresponds to the thermal decomposition of TPABr, through a reaction path evidenced by Parker [5]. This temperature is much lower than that we observed for zeolite ZSM–5 precursors, indicating the strong dependence of the stability of TPA species on their environment.

The DTA curve of the dried hydrogel used to carry out the synthesis ($x=0.5$) is also given in Fig. 2 (curve b). The observed endothermic effects are in the temperature range 60–280°. The first peak, at a temperature lower than 150°, is due to further dehydration of the gel. The second signal is attributed to TPA species adsorbed on the gel surface. In fact, the peak temperature did not depend on the Al content of the gel. Moreover, the DTA curve of gel filtered and washed after the synthesis did not show the second endothermic effect (Fig. 2c). Therefore, if TPA is only adsorbed and not chemically linked to the gel, this means that the mechanism

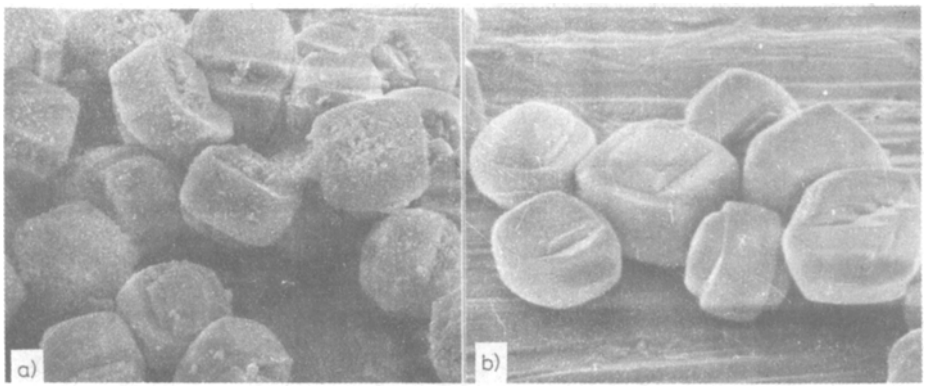

Fig. 3 SEM micrographs of as-synthesized crystalline ZSM–5 precursors ($x=0.3$ in the synthesis system) before (a) and after (b) ultrasounds treatment

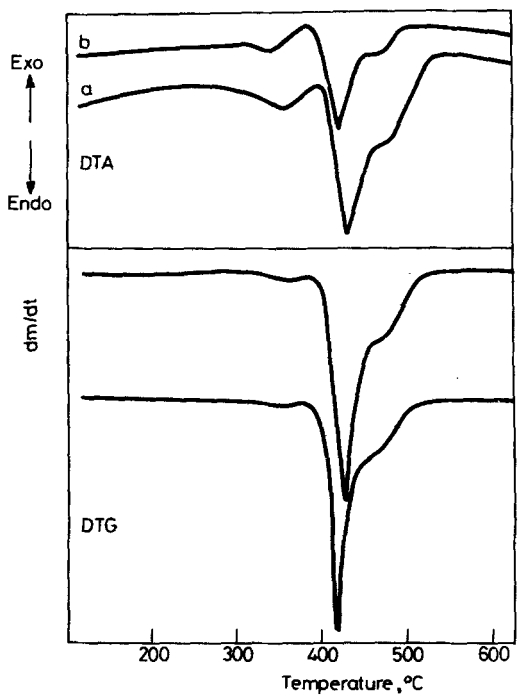

Fig. 4 DTA and DTG curves for the decomposition of crystalline silicalite precursor ($x=0$ in the synthesis system) before (a) and after (b) ultrasounds treatment

of zeolite ZSM–5 synthesis involves a process of condensation from the liquid phase [3].

The effect of ultrasound treatment on the residual gel was also investigated. Typical SEM micrographs of crystalline zeolite ZSM–5 precursors are reported in Fig. 3. Comparison of the crystals before and after treatment demonstrates that they are effectively purified from residual gel present on the crystal surface. Nevertheless, the DTA and DTG curves reported in Fig. 4 for samples as synthesized and after ultrasound treatment did not exhibit significant differences which could be related to the presence of gel. This can due to the low concentration and the smaller thermal effects of the gel with respect to the crystalline phase.

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Zusammenfassung — Thermische Analysen kristalliner Zeolith- (ZSM–5) Vorprodukte mit unterschiedlichen Verhältnissen Si/Al wurden in Stickstoffatmosphäre ausgeführt. Verschiedene Wechselwirkungen zwischen den Tetrapropylammonium-Spezies und ihrer zeolithischen Umgebung wurden nachgewiesen, die vom Aluminiumgehalt der kristallinen Vorprodukte abhängen. Die Ergebnisse sprechen für einen Bildungsmechanismus des ZSM–5 über einen Kondensationsprozess aus der flüssigen Phase.

Резюме — В атмосфере азота проведен термический анализ исходных кристаллических соединений для цеолита ZSM–5 с различным соотношением кремния и алюминия. Доказаны различные взаимодействия между тетрапропиламмонием и цеолитным остовом в зависимости от содержания алюминия в исходных кристаллических веществах. Полученные результаты поддерживают механизм образования цеолита ZSM–5 путем конденсации из жидкой фазы.