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Study of the crystalline transformation of a ZSM-5 type zeolite by thermal treatments

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Changes in the framework of an ethanol-ZSM-5 type zeolite by thermal effects between 673 and 1173 K were investigated using the methods of thermal analysis, infrared, X-ray diffraction and scanning electron microscopy. Crystalline transformation of ZSM-5 into cristobalite at about 973 K was observed in either an air or nitrogen stream and using different heating programmes. The breakdown of the lattice is related to the thermal removal of some species of ethanol from the framework. Total removal of the organic promoter by washing with water prior to thermal treatment leads to a material in which the phase transition temperature is above 1173 K.

1. Introduction

Thermal stability of zeolites is an essential property for their use as catalysts, particularly in reactions at high temperatures. Furthermore, a great resistance to temperature is also required for the catalyst regeneration, especially during the burning-off of the coke deposited in the channels. Frequently, it is reported that ZSM-5 zeolite exhibits remarkable thermal stability due to its particular framework, consisting of a two-dimensional system of intersecting narrow channels, its unusually high SiO_2/Al_2O_3 ratio and the high density of the crystalline lattice [1]. Thus, Kulkarni *et al.* [2] found a temperature of framework decomposition above 1273 K for a TPA-ZSM-5. Nevertheless, the relatively limited studies reported on this topic seem to indicate that thermal stability can be dependent, to some extent, on the nature of the promoters used during the synthesis. Berak *et al.* [3] noticed that 100% crystalline ZSM-5 synthesized in the presence of surfactants loses 50% of its crystallinity at 1023 K. Tallon and Buckley [4] have also reported the relatively low stability of a ZSM-5 prepared with an amine template. On the contrary, Khusid *et al.* [5] concluded that hydrogen-forms obtained by different methods decompose at the same temperature, while the specific features of the pentasil geometry play a deciding role in the thermal stability of Na-ZSM-5.

Recently, we reported that when an ethanol Na-ZSM-5 is treated at 973 K in either an air or nitrogen stream it is transformed to cristobalite [6]. Here a more complete study is reported of the phenomenon observed, to elucidate whether it originated in the nature of the organic promoter used or in the method by which ethanol is removed from the framework. Thermal analysis (TA), X-ray diffraction (XRD), infrared spectroscopy (IR) and scanning electron microscopy (SEM) were used to characterize the as-made material and to gain information about the changes occurring in the thermally treated samples at different conditions.

2. Experimental procedure

An ethanol-Na-ZSM-5 type zeolite was provided by the Departamento de Ingenieria Química, Universidad Complutense de Madrid [7]. Its molar composition, determined by atomic absorption, was $1.2\,Na_2O \cdot Al_2O_3 \cdot 48SiO_2$.

Several samples of about 200 mg were treated in a thermobalance furnace in either air or nitrogen. In an *air stream*, each sample was treated at 823, 898, 973, 1073 and 1173 K (samples TA-1, -2, -3, -4 and -5, respectively) at a heating rate of $10\,K\,min^{-1}$. In a *nitrogen stream* the heating rate was $1\,K\,min^{-1}$ from room temperature to 973 K, with intermediate isothermal steps, for 60 h at 473, 498, 523, 573 and 623 K for each sample (samples TN-1, -2, -3, -4 and -5, respectively). Sample TN-6 was prepared with no isothermal step.

At 330, 353 and 371 K (samples TW-1, -2 and -3, respectively) were washed with water for 6 h. Sample TW-4 was washed as C-3, three times. After drying at 423 K, thermal treatment in an air stream was performed at 1073 K (at a heating rate of $10\,K\,min^{-1}$ from 423 K).

The thermal treatment time for all samples was 6 h at the final temperature.

Thermal analyses were carried out in a Mettler TA-3000 system, in a stream of either dried air or nitrogen ($100\,ml\,min^{-1}$) heating at either 1 or $10\,K\,min^{-1}$). Infrared spectra were obtained in a VR-20 Karl Zeiss spectrometer using the KBr technique. Diffraction patterns were obtained with a Phillips PV

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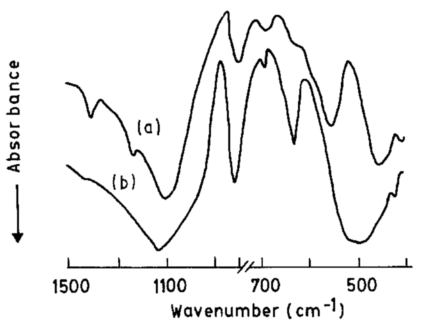

Figure 1 Infrared spectra of (a) the as-made zeolite, (b) samples TA-4 and TA-5.

1051 powder diffractometer, using Cu*K*α radiation at 40 kV and 20 mA, with slits of 1°, 0.1°. Micrographs were taken in an ISI-DS 130. The samples were placed on a carbon holder and gold-coated.

3. Results and discussion

3.1. Characterization of the synthesized zeolite

The infrared spectrum (Fig. 1a) shows the characteristic frequencies of pentasil group zeolites at 550, 590 and 1230 cm^{-1} [2, 8]. Other absorption bands observed are common to compounds including TO_4 tetrahedra in their structure. As amorphous silica is the main impurity, the optical density ratio between the 500 and 450 cm^{-1} bands is commonly used to estimate the purity of ZSM-5 zeolites [8, 9]. The calculated value (0.78) is indicative of a high-purity grade. This is also confirmed by XRD (Fig. 2a), showing the characteristic diffraction pattern of ZSM-5 zeolite [2, 10]. High crystallinity without amorphous material is suggested by the absence of a broad low baseline.

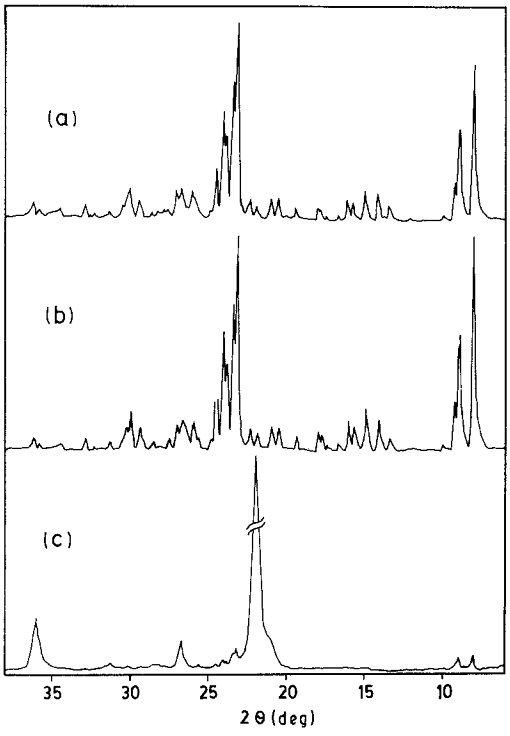

Figure 2 X-ray diffraction patterns of (a) the synthesized zeolite, (b) samples TA-1 and TA-2, (c) sample TA-3.

The micrograph in Fig. 3a shows that the zeolite is formed by well-defined single crystallites. Orthorhombic prisms of 9 to 15 μm crystal size may be observed, pointed at both ends by the [1 0 1] and [1 0 $\bar{1}$] planes, which frequently crystallize as penetration twins. Moreover, tabular-shaped crystal aggregates can be observed. These crystalline forms are similar to those reported for ZSM-5 type zeolites synthesized using other organic molecules [11, 12]. Some needle-type crystals which appear in the same micrograph could be perhaps of mordenite impurities.

The DTA curve in Fig. 4 shows one endothermal effect below 473 K related to water desorption, corresponding to 4.9% weight loss in the TG curve (Fig. 4). Between 543 and 723 K a strongly exothermic peak appears with the maximum about 653 K, attributed to combustion of the ethanol occluded in the zeolite channels during synthesis. This effect is accompanied by a 2.2% weight loss. Derouane *et al.* [13] found an exothermic maximum for TPA-ZSM-5 at somewhat higher temperature, but in a narrower interval (673 to 723 K). The insinuated shoulder close to 574 K and the more appreciable one between 833 and 898 K could be assigned to a further two possible steps of decomposition of the organic compound [14, 15]. At these temperatures, a very weak weight loss is only insinuated on the DTG curve. The two peaks observed at 1060 and 1100 K probably originated from modifications of the crystalline structure to form new phases.

3.2. Treatment in an air stream

In comparison with the as-made zeolite, diffraction patterns of samples TA-1 and TA-2 (Fig. 2b) show the expected modifications caused by removal of the organic promoter from the framework. The heights of both lines $2\theta = 7.95°$ and $2\theta = 8.8°$ increase while that of 23.0° and 23.25° remains rather unchanged. The doublet at $2\theta = 23.7°$ to 23.85° is now clearly observed, while a double peak at $2\theta = 24.3°$ is only insinuated. This is probably due to both the removal of ethanol molecules and the incipient transition from the orthorhombic symmetry to monoclinic [16].

The observed changes in samples calcined at 973 K and above are more intense. In TA-3 (see Fig. 2c) fundamental lines of ZSM-5 are still present, but their intensities are now very weak. Some very strong and well-defined signals appear instead, at $2\theta = 21.7°$ and 35.9°, indicating a very important crystalline transformation from ZSM-5 to cristobalite. Diffraction patterns of TA-4 and TA-5 show that the transformation was completed. Intensity changes in X-ray power diffraction patterns were mentioned by Araya and Lowe [17] when alcohol was removed by calcination from a synthesized hexane-1,6-diol-ZSM-5. However, no crystalline transformation was reported.

The phenomenon has also been proved by infrared measurement. Fundamental absorption bands of the pentasil framework gradually decrease as treatment temperatures increase, while the intensity of the SiO_2 tetrahedra bands rise. Samples calcined at 1073 and 1173 only give a signal of SiO_2, as shown in Fig. 1b.

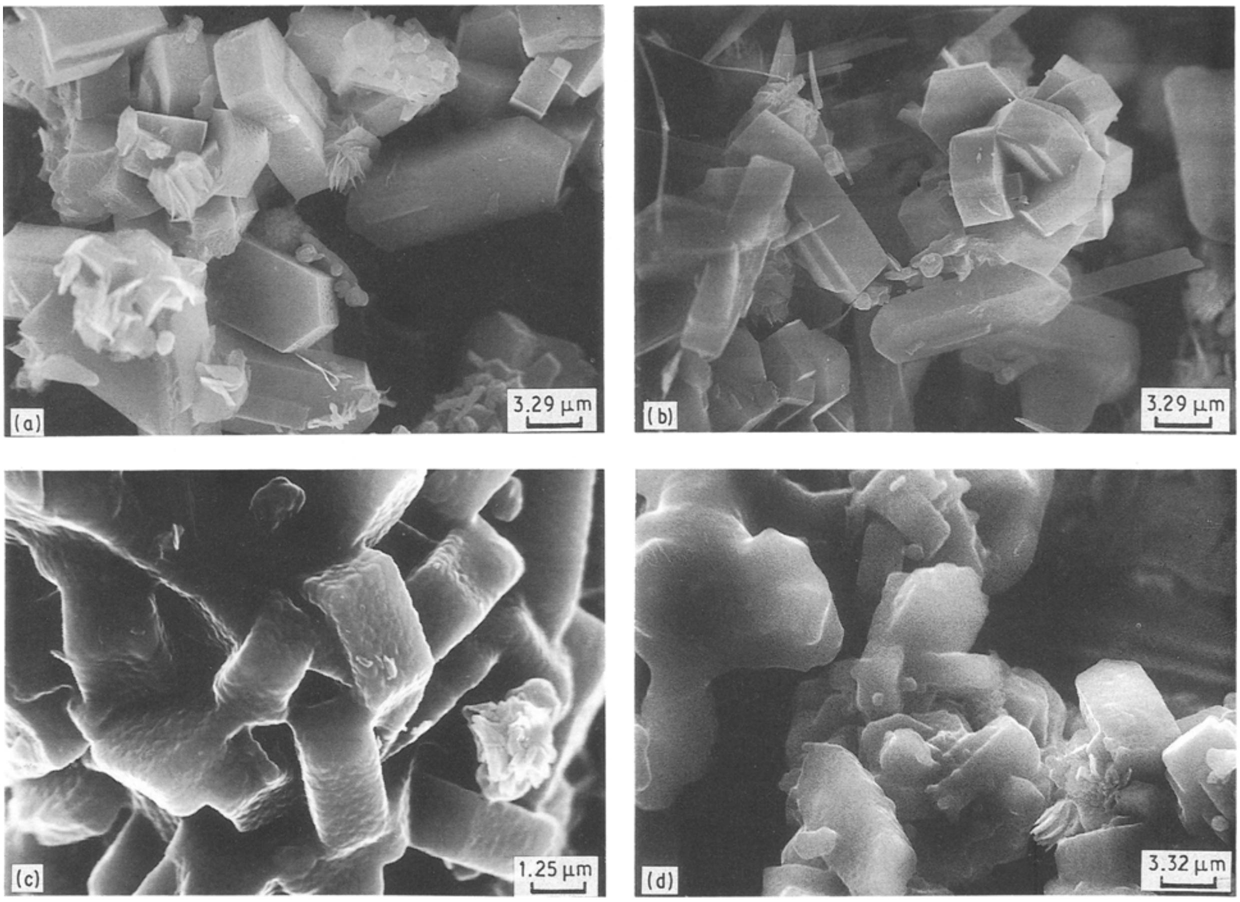

Figure 3 Photomicrographs of (a) the untreated ZSM-5, and of the samples calcined at (b) 973 K (TA-3), (c) 1073 K (TA-4) and (d) 1173 K (TA-5).

It is interesting to see by SEM the sequential transformation of the morphology of the crystals (Fig. 3). No appreciable changes were observed in TA-1 and TA-2, while in TA-3 the planes [1 0 1] of some orthorhombic prisms exhibit a rough appearance. In TA-4 and TA-5, crystals lose their well-defined edges and the surfaces become more rugged, as if they were softened and then welded. The result is the formation of agglomerates of greater size and non-crystalline external appearance. The big particles of sample TA-5 are like vitreous solids. Only some crystals resemble its primitive morphology. It must be pointed out that no micrograph shows cristobalite crystals, indicating that the crystalline transformation occurs in the inner of the crystals, keeping its primitive external morphology.

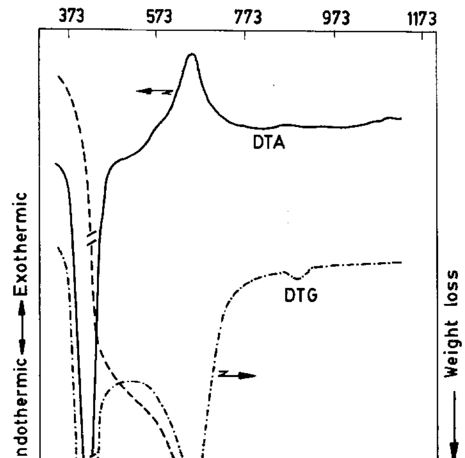

Figure 4 DTA, TG and DTG profiles of the as-made ZSM-5.

Khusid *et al.* [5] recently noticed the transformation of pentasil structure to cristobalite at 1263 to 1273 K in Na-ZSM-5 zeolites with Na_2O/Al_2O_3 ratios similar to the present ones and crystallinity grades of about 90%. In that case cristobalite was formed from the amorphized zeolite, while here direct crystalline transformation was observed without any appreciable intermediate amorphous phase.

At this point, two hypotheses can be considered in order to explain the lower temperature of transformation of the present well-crystallized zeolite.

1. It is related to the burn-off of ethanol which weakens the framework of the ZSM-5, in such a way that the break-down of the zeolite structure takes place at relatively low temperature. In any case, this temperature (973 K) is higher than that of the burn-off (673 K).
2. It is an intrinsic property derived from the use of ethanol as promoter in the synthesis step.

To analyse these hypotheses, two sets of experiments were performed under more controlled and milder conditions than the preceding ones, to remove

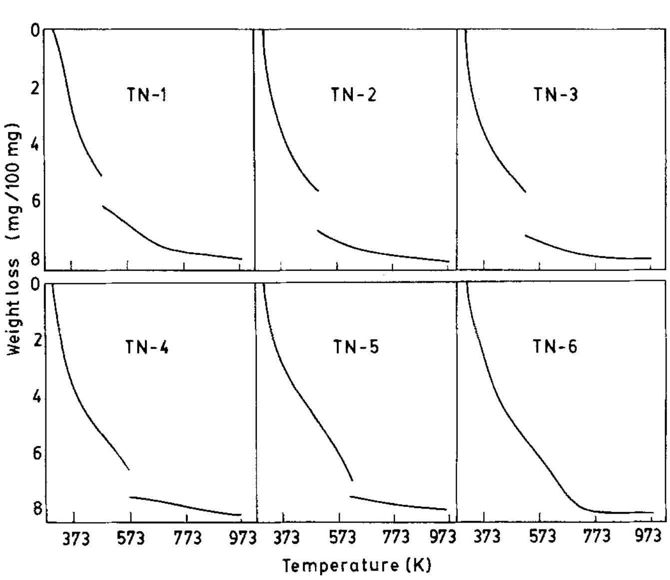

Figure 5 TG profiles of the samples treated in a nitrogen stream at different heating programmes.

ethanol as smoothly as possible. One involved heating in a nitrogen stream, and the other, washing the synthesized material with distilled water prior to calcination in air.

3.3. Treatment in a nitrogen stream

Fig. 5 shows the TG curves of the synthesized zeolite in a nitrogen stream at different heating programmes, from room temperature to 973 K (samples TN). The shape of such curves and the weight loss in the intermediate isothermal step illustrate the velocity of alcohol removal.

Diffraction patterns of all TN-samples show that transformation to cristobalite also took place. If the ratio between the characteristic diffraction peaks of both ZSM-5 ($2\Theta = 7.95°$; $I_z = 80\%$) and cristobalite ($2\Theta = 21.9°$; $I_c = 100\%$) is used to evaluate the extension of this phenomenon, the calculated values of I_z/I_c in Table I seem to indicate that such a ratio is independent of the way in which the alcohol is removed.

3.4. Samples washed with water

A peculiarity of alcohol-like templates is that they can be removed from the zeolite lattice, at least in part, by washing with water. This method was attempted in the preparation of TW-samples, prior to thermal treatment. Typical TG profiles, after stabilization of their weight at 423 K, are drawn in Fig. 6. The observed differences in weight loss in comparison to the TG curve of an unwashed sample, can be assigned to the different amounts of ethanol extracted with water. Only in sample TW-4 was all the organic material completely removed, as was verified by TG.

TABLE I Thermal removal of ethanol in nitrogen stream

Sample	T(K) isot.	$-\Delta W$(mg/100 mg)	I_z/I_c
TN-1	473	1.15	0.25
TN-2	498	1.45	0.21
TN-3	523	1.55	0.22
TN-4	573	1.00	0.26
TN-5	623	0.69	0.24
TN-6	—	—	0.25

Alter calcination at 1023 K for 6 h, diffraction patterns of TW-1, TW-2 and TW-3, denoted total crystalline transformation, while TW-4 remained unaltered. This last sample only exhibits this phase transition beyond 1173 K. At 1173 K, total transformation into cristobalite is already attained. No amorphous material was detected by XRD in any of the above cases.

The above results seem to indicate that the thermal stability of EtOH-NaZSM-5 is more dependent on the method used to remove alcohol from the framework, than on the use of ethanol itself to synthesize the zeolite. Contrary to normal findings with TPA-ZSM-5, in the present case thermal treatment cannot be used to remove the promoter. Only its removal by deep washing with water seems to lead to a thermally stable material at least up to 1173 K.

The different behaviour observed between TW-3 and TW-4 suggests the presence of two forms of ethanol inside the channels. The first, which is related to the ATD exothermal peak at 653 K, could be molecules occluded inside the pores. This form can be easily removed by washing and its burn-off does not

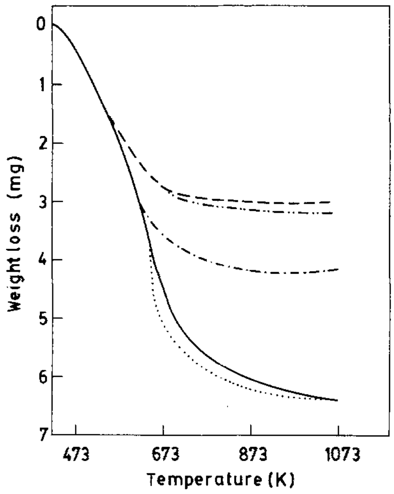

Figure 6 TG profiles of the samples washed with water: (—·—) TW-1 and TW-2, (—··—) TW-3, (– – –) TW-4, (——) unwashed sample, (···) TW-4 impregnated with ethanol.

seem to modify the structure. This is supported by the fact that when the stable sample TW-4 is impregnated with a large excess of ethanol and then again calcined at 1073 K, its structure remains stable. The TG profile of this sample in Fig. 6 shows that an amount of ethanol similar to that retained in the framework during the synthesis from the gel can refill the channels.

The second form of ethanol, which is related to the ATD peak at 833 to 898 K, could be associated with the framework aluminium sites. Its thermal removal, in either an air or nitrogen stream, seems to leave a weakened zeolitic structure which does not occur when it is removed by means of intensive washing with water. For TPA, this form would be TPA^+ counterions to aluminium negative centres, but at present nothing can be deduced about the nature of these ethanol species. Because ethanol is a weaker base than tetra-alkilammonium hydroxide, the formation of organic cations from it would require more electron-deficient sites than those necessary to form TAA^+. In fact, this exothermic effect was observed at lower temperatures than that reported for TPA [14, 15]. This could mean that ethanol entities are less strongly bound to the zeolite framework than TAA.

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