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INFLUENCE OF DIFFUSIONAL BARRIERS ON THE THERMAL ANALYSIS OF THE ZEOLITE TON

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ABSTRACT

The thermal activation of samples of zeolite TON was studied by TG. Occlusion of ports by an amorphous lining raises the decomposition temperature of the template. This effect is attributed to an increased pressure of the products of the degradation reaction. The resulting limitations on the applicability of the Ozawa method to porous systems are discussed.

INTRODUCTION

The lattice porosity of the zeolites has been the object of extensive studies, as the main base on which the practical applications of the molecular sieves rest. Less attention was generally payed to extra-framework phenomena, like mesoporosity or surface phases, which can often control the accessibility of the ports, seriously modifying the properties of the sieve [1, 2].

The aim of this communication is to emphasize the role that the presence of an amorphous surface phase can exert on the decomposition pattern of the organic template which occupies the lattice porosity of the synthetic high-silica zeolites. Expecting the influence of the access limitations on the properties related to the internal surface to be maximal in the case of one-dimensional pore systems, we choosed for this study the zeolite TON (also known as ISI-1, KZ-2, Nu-10, θ-1, ZSM-22) whose channels, parallel to the axis c, present an oval section of 4.7x5.5 A.

EXPERIMENTAL AND METHODS

The synthesis of the zeolite TON has been widely described in the literature [3-5]. The samples we used have been obtained from reaction media containing triethylenetetramine or diethanolamine as

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templating agent A. The compositions of the reaction medium were in the range (4.2-4.7)Na_2O·(34-89)A·Al_2O_3·(56-79)SiO_2·(840-3750)H_2O·(0-50)NaCl. The syntheses were carried out in a stirred stainless-steel autoclave at temperatures between 150 and 170°C and crystallization time was never longer than 5 days.

Whether the synthesis is interrupted before complete conversion of the reactants or the crystallization is not congruent with the composition of the parent gel the silicoaluminate species still present in the reaction medium form an amorphous phase lining the zeolite crystals.

Our aim being the study of such a system, containing both zeolite and not-crystalline material, a major problem was the evaluation of the amorphous fraction. X-ray diffraction is a very questionable tool for this analysis and by this technique all the samples we used should have been considered fully crystalline zeolite.

In fact we evaluated the crystalline fraction from the amount of organic template in the solid. Our elemental analysis of the amorphous phase preceding the crystallization showed that the organic content of this phase is negligible in comparison with the organic content of the zeolite TON, in fair agreement with the results of Araya and Lowe [6]. Marler [7] demonstrated that the template fills the whole pore volume of the zeolite TON. By applying his calculation method to the known pore volume of 0.10 cm^3/g [5, 8] we were able to predict for a fully crystallized zeolite TON a triethylenetetramine content of 8.3% by weight and a diethanolamine content of 7.8%.

The organic content was evaluated by two independent techniques: TG measurements of the loss of weight following the initial dehydration peak and elemental analysis of the solid. The comparison between the two techniques allowed to evaluate the possible retention of organic components at high temperature.

The usual method for the determination of the cristallinity of zeolites, gas adsorption, was not well fitted for our system, being unable to discriminate between an amorphous material and a zeolite with occluded porosity. Once the crystalline fraction determined, we were able to use adsorption data to evaluate the extension of the port occlusion. Accessible pore volume was determined by nitrogen adsorption after activation of the sample at 600°C under flowing air during 10 hours.

TG experiments have been carried out using a Setaram TG85 thermobalance. Specimens of 30 mg have been heated from room temperature to 850°C. The heating rate was fairly constant between 100 and 800°C, and the heating curve was always well reproduced at given instrumental setting. The specimen was held in a corundum crucible under flowing air All zeolites studied were as-synthetized samples dried overnight in air at 75°C.

RESULTS AND DISCUSSION

The DTG traces of three samples prepared in triethylenetetramine media are reported in figure 1. The accessible pore volume of the samples was 0.03, 0.07 and 0.10 cm^3/g, respectively. The temperature of the different steps of weight loss decreased with the increase in pore volume. The loss of weight after dehydration corresponding to the maximum template content for all samples, the reduced pore availability of the first two samples must be attributed to a port plugging by a surface layer of limited mass.

The DTG traces of three samples prepared from diethanolamine media are reported in figure 2. The accessible pore volume of the samples was 0.01, 0.03 and 0.06 cm^3/g, respectively. The temperature of the DTG peaks decreased at increasing pore volume. The weight loss of the three samples after dehydration was 2.5, 3.8 and 4.8%, respectively. These values, always smaller than the maximum organic content, indicate that a significant mass of amorphous material is retained by the samples. If the crystalline fraction estimated from the amount of template is considered, the expected pore volume for the three samples should be 0.03, 0.05 and 0.06 cm^3/g, respectively. The reduction of crystalline fraction is not able to justify the reduced pore availability of the first two samples also when some retention of organic material at high temperature - evinced by elemental analysis - is taken into account. Hence evidences of pore plugging are convincing also in the case of the diethanolamine-synthetized samples.

The delay of the weight losses in the samples presenting port plugging can be easily explained. Surface lining, hindering the removal of the decomposition products generated inside the porosity, brings to an increase of their pressure. Hence the rate of the degradation reaction is reduced, in the same way in which any reversible reaction is influenced by the pressure of its gaseous products [9, 10].

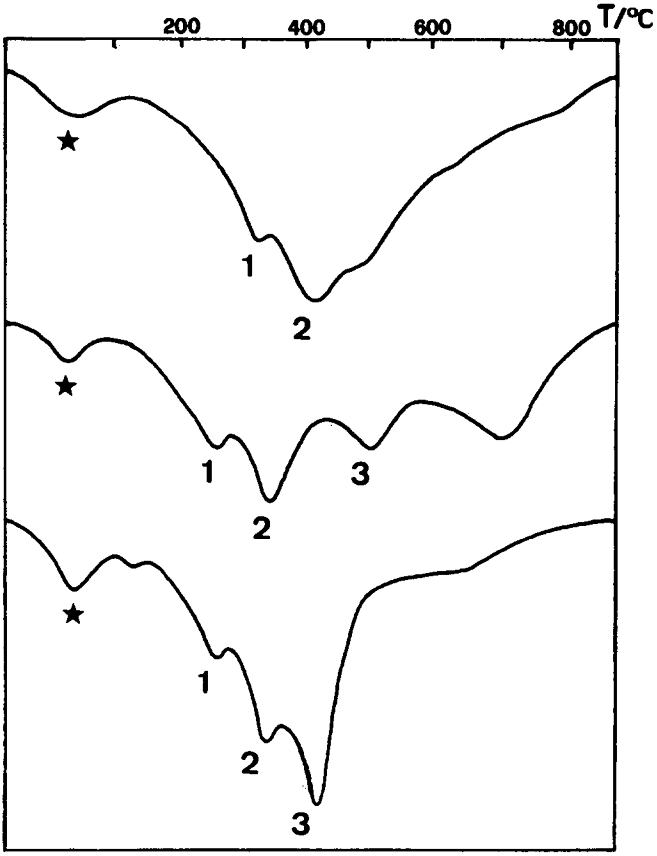

Fig. 1. DTG traces of samples of zeolite TON synthetized in the presence of triethylenetetramine. 30 mg of sample heated in flowing air at 20°/min. From top to bottom: samples of accessible pore volume 0.03, 0.07 and 0.10 cm³/g. Weight loss corresponding to the peak maximum: peak 1, 1.2%; peak 2, 3%; peak 3, 5% (after subtraction of the weight corresponding to the dehydration peak, *).

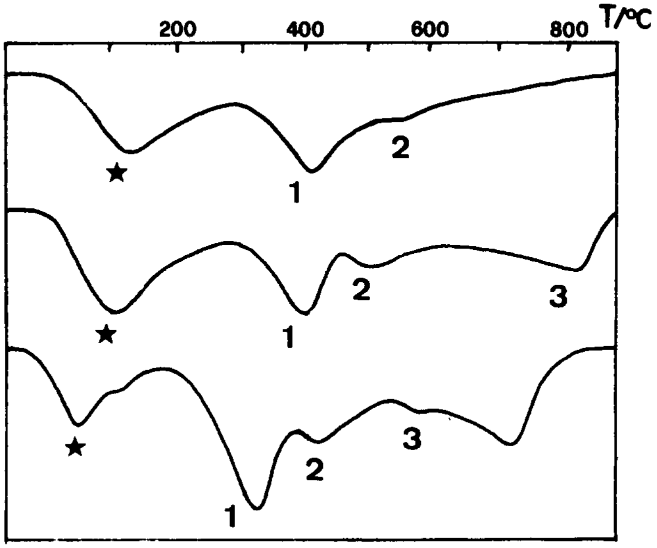

Fig. 2. DTG traces of samples of zeolite TON synthetized in the presence of diethanolamine. 30 mg of sample heated in flowing air at 20°/min. From top to bottom: samples of accessible pore volume 0.01, 0.03 and 0.06 cm³/g. Weight loss corresponding to the peak maximum: peak 1, 1%; peak 2, 2.1%; peak 3, 3.2% (after subtraction of the weight corresponding to the dehydration peak, *).

Some clues about the possible degradation mechanism of both templates are given by the elemental analysis of activated samples. While elemental analysis of the initial samples shows values of the ratio between carbon and nitrogen corresponding to the stoichiometry of the template used, the analysis of samples activated at 600°C shows lower carbon/nitrogen ratios. A triethylenetetramine-TON sample with a residual nitrogen content of 0.55% (by weight) presented a carbon content of 0.10%. In the case of the diethanolamine-TON at a residual nitrogen content of 1.65% corresponded a carbon content of 0.17%. This result suggests that the decomposition of triethylenetetramine and diethanolamine in the zeolite TON follows a dealkylation mechanism similar to the mechanism proposed for the decomposition of tetraalkylammonium cations in the zeolites of the ZSM-5 family [11].

Some discussion is deserved by the application to the thermal degradation of the templates of the method of Ozawa [12] for the determination of the activation energy. When porous systems are dealt with, some additional problems join to the usual limitations imposed to this kind of kinetic analysis by superpositions of phenomena and changes in the limiting steps with the variation of the heating rate. In the case of the decomposition of triethylenetetramine inside zeolite TON we applied the Ozawa procedure to the first degradation peak (marked as 1 on the curves of the figure 1) in order to minimize the superposition of different phenomena. With heating rates between 10 and 20 K min^{-1} for samples of accessible pore volume of 0.10, 0.07 and 0.03 cm^3/g the calculated energies of activation have been 103, 91 and 37 KJ/mol, respectively.

Fluid mechanics considerations easily account for the decrease of the Ozawa activation energy as a function of port plugging. In fact the pressure inside a channel with necked-down port should roughly increase with the square of the rate of gas emission. Hence each phenomenon increasing the rate of the decomposition - like an higher heating rate - would raise the pressure inside the channels, increasing the equilibrium temperature and slowing down the reaction. In this way a decrease of the activation energy calculated by the method of Ozawa should be expected in the presence of diffusional limitations also when no changes occur in the degradation mechanism. Hence this method, while allowing to detect the presence of diffusional barriers, is not suitable to estimate any absolute value of the activation energy of decomposition reactions occurring in a porous medium.

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