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TGA–DTA study on calcination of zeolitic catalysts[1]

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Abstract

Template decomposition upon calcination of EMO and EMT zeolites has been studied using thermal analysis techniques. For both samples, desorption of water occurs below 200°C and template decomposition at 250–450°C. It is concluded that the template decomposition in EMO and EMT zeolites is relatively slow and is not structure-sensitive; it is accompanied by rapid desorption of the products, XRD studies on the calcined samples show no decrease in their crystallinity. However, both NMR- and IR-spectroscopy indicate partial distortion of the framework and formation of Lewis acid sites. A non-destructive activation of zeolites prepared with organic templates is proposed. © 1997 Elsevier Science B.V.

Keywords: Faujasites; Template decomposition; Thermal analysis of zeolites

1. Introduction

Zeolites are porous inorganic materials which find their major industrial applications in selective adsorption, separation and catalysis [1]. Much progress in preparation of zeolites has been achieved since the early 1960's owing to the employment of organic structure-directing agents (templates) such as amines, ethers and alcohols [2,3]. A number of novel zeolite structure types with specifically tailored properties and composition have been synthesized in recent years [4,5]. For instance, EMT (hexagonal Y zeolite, EMT structure type) and EMO (cubic Y. FAU structure type) zeolites, which belong to the faujasite family, have been prepared with 18-crown-6 and 15-crown-5 ethers, respectively [6,7]. Activation and regeneration of these materials, prior to their use as catalysts, involve high-temperature treatment (500–700°C) in the presence of oxygen. Although zeolites are rather stable materials, optimization of the calcination procedure is required to prevent structural degradation.

In the present paper, template decomposition on calcination of EMO and EMT zeolites is studied using TGA–DTA and TGA–FTIR. Structural changes of the catalysts are monitored by employing X-ray diffraction, NMR- and IR-spectroscopy. The mechanism of template decomposition is discussed and a non-destructive activation procedure is proposed.

2. Experimental

2.1. Materials

EMO (Si/Al = 3.8) and EMT (Si/Al = 3.65) zeolites provided by Elf Antar (France) had been synthesized according to the procedure described in [6,7]. When required, fivefold ion-exchange was carried out using 1.5 M $(NH_4)_2SO_4$ at 60°C.

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2.2. TGA–DTA

Thermal analysis of the samples was carried out on a TA SDT 2960 instrument. A zeolite sample (2–45 mg) was heated to the desired temperature (400–1200°C) at 1–20°C/min in a flow of nitrogen or air. Aluminium oxide was used as a reference in some experiments.

2.3. XRD

All samples were hydrated over saturated $CaCl_2$ solution for 24 h. Crystallinity of the powdered zeolites was determined by comparing peak intensities (2θ range from 10 to 35°) with those of the initial uncalcined zeolites. X-ray patterns were collected using a Philips diffractometer scanning at 1°/min.

2.4. NMR

^{27}Al and ^{29}Si MAS NMR spectra of the hydrated samples were obtained at room temperature using a Bruker MSL 400 NMR spectrometer. TMS and an aqueous solution of $Al(NO_3)_3$ were used as references.

2.5. FTIR

The presence of the Lewis and Brönsted acid sites was detected using pyridine (Py) adsorption at 150°C. Prior to the IR experiments, all samples were calcined and ion-exchanged. IR-spectra of self-supported zeolite discs were collected at a resolution of 2 cm^{-1} using a Nicolet Magna 550 FTIR instrument.

3. Results and discussion

Zeolites are crystalline microporous molecular sieves, and therefore, both water and organic molecules are 'trapped' in the pore system of uncalcined EMO and EMT materials. Thermal analysis of EMT and EMO under a flow of nitrogen reveals desorption of the water and organics in two stages, at 50–200°C and 250–400°C (Figs. 1 and 2). Low intensity exothermic peaks at 1050–1070°C correspond to the structural collapse of the zeolites (Table 1). In freshly prepared zeolites, NMR and XRD studies have shown [8,9], that crown ethers used in the synthesis are intact within the zeolite pores with each template molecule occupying one big cage. These bulky molecules cannot escape from the zeolite pores, their decomposition occurs at 250–400°C, followed by rapid desorption of the fragments.

The pore structure of EMO (FAU structure type) zeolite contains a network of uniform supercages, whereas the presence of modified supercages, the so-called 'hypercages' and 'hypocages', are characteristic of EMT [10]. Structural differences of these

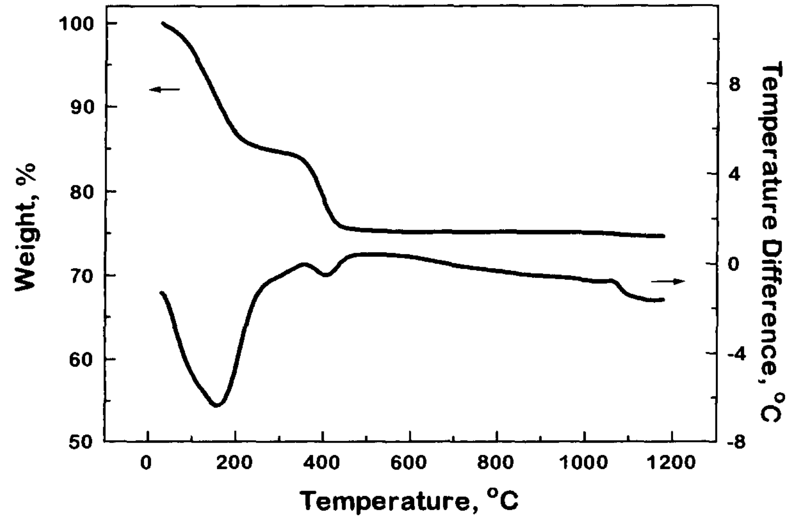

Fig. 1. Thermal analysis of uncalcined EMO zeolite in nitrogen at 20°C/min, sample weight 43 mg.

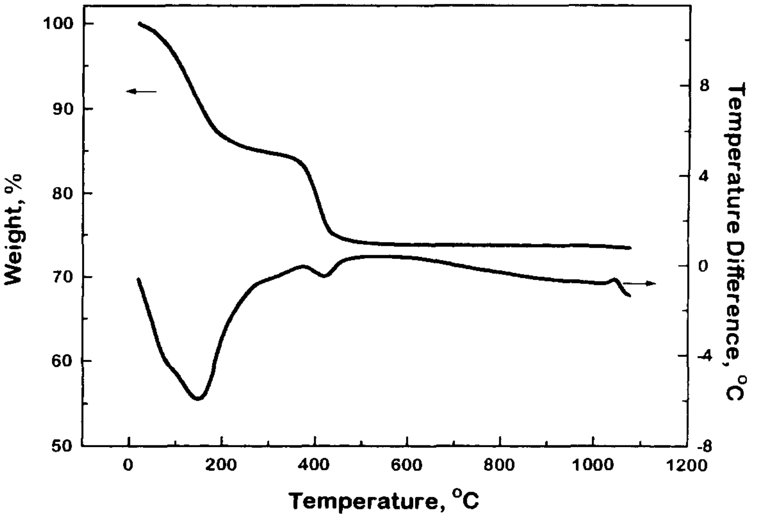

Fig. 2. Thermal analysis of uncalcined EMT zeolite in nitrogen at 20°C/min, sample weight 40 mg.

Table 1
Thermal analysis of EMO and EMT zeolites in nitrogen

Sample	H_2O desorption		Template desorption		Amorphisation temperature (°C)
	Weight loss (%)	Temperature (°C)	Weight loss (%)	Temperature (°C)	
EMO	15.3	25–200	9.9	250–450	1073
EMT	15.2	25–200	11.0	250–450	1051

zeolites could affect template decomposition. Indeed, according to [9], in the EMT zeolite 18-crown-6 ether molecules equally populate cages of both types. One can expect, therefore, to find two stages in TGA experiments reflecting desorption of the crown ether from different locations. Fig. 3 presents DTGA traces of the uncalcined EMT obtained at 1 and 20°C/min. Both curves show a single symmetrical peak corresponding to the template decomposition at 370–400°C. The weight loss between 300 and 450°C, viz. 11%, is in agreement with the results reported in [11] and corresponds to the removal of 3.5 crown ether molecules per unit cell (there are 2 'hypercages' and 2 'hypocages' per unit cell of EMT). FTIR analysis of the evolved gases shows only desorption of water below 200°C. Acetaldehyde, dioxane, ethylene and carbon monoxide are identified as major decomposition products on both the samples at 250–400°C.

Thus, we conclude that the template decomposition in EMO and EMT zeolites is relatively slow and is structure-insensitive, it is accompanied by rapid desorption of the products. The desorption pattern can be changed if acid sites are introduced into the zeolites by means of ion-exchange. In this case, ethylene is polymerised rather than desorbed, subsequently forming 3 wt% of coke which can be removed only via calcination in the presence of oxygen.

Fig. 4 presents thermal analysis results for EMT and EMO obtained at a temperature ramp of 10°C/min in air. Although the sample weight is ~2 mg for both zeolites, the DTA traces show intense exothermic peaks due to template combustion in air at 210°C. As in nitrogen, dehydration of the samples occurs below 200°C. If template decomposition is first carried out in nitrogen at 450°C, the following DTA run in air shows no exothermic peak.

To evaluate the impact of template burning on the zeolite structure, two series of samples (~2 g) have been prepared. In the first series, samples (EMO-A and EMT-A) have been subjected to calcination in air to 550°C at 5°C/min. Samples from the second series

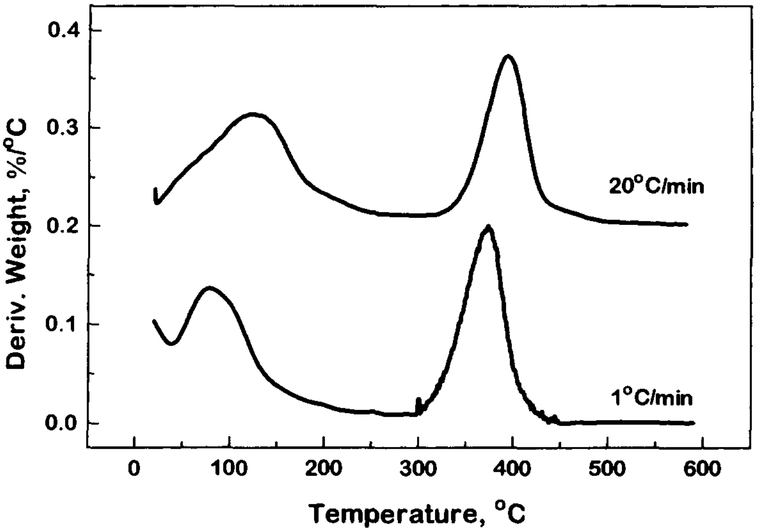

Fig. 3. High resolution TGA of uncalcined EMT zeolite in nitrogen at 1 and 20°C/min, sample weight 8 mg.

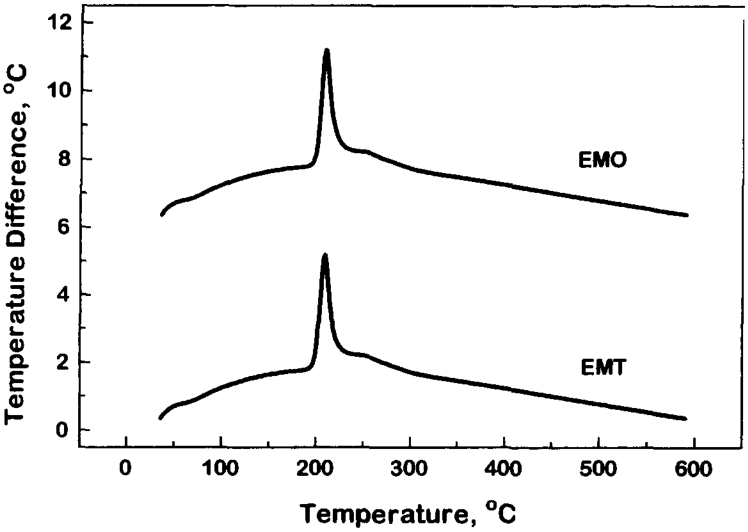

Fig. 4. DTA of uncalcined EMO and EMT zeolites in air at 10°C/min, samples weight 2 mg.

(EMO-B and EMT-B) have been pre-treated in nitrogen at 400°C followed by activation in air at 550°C. Activation in nitrogen leads to desorption of the organic templates (an endothermic process) from the samples in contrast to template burning in air (an exothermic process which might result in structure degradation). According to our XRD results, after calcination in air (550°C) there is no decrease in crystallinity for all four samples – this is not surprising since the amorphisation temperature for EMO and EMT is ca. 1000°C. However, both NMR- and IR-spectroscopy indicate partial distortion of Al in the framework. ^{27}Al NMR-spectra of EMO-A and EMT-A demonstrate noticeable broadening of the signal from tetrahedral Al (δ = 58–60 ppm [12]) compared to the uncalcined samples, which indicates the lowered symmetry of the framework Al. Generation of Lewis acid sites is also evident from the IR-spectra of

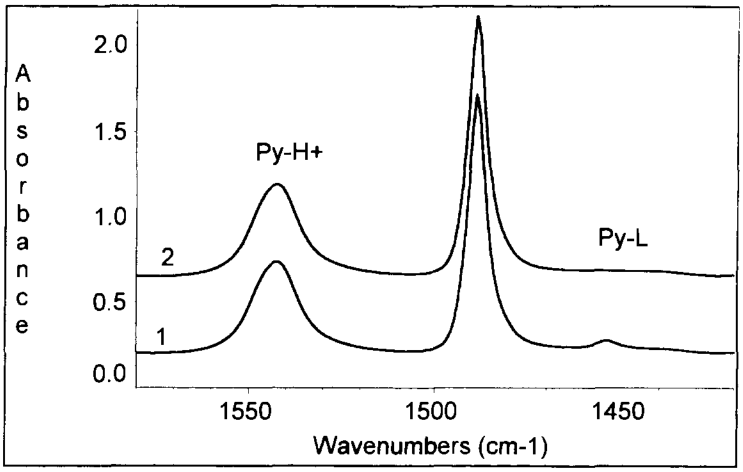

Fig. 5. IR-spectra of pyridine adsorbed on (1) EMT-A and (2) EMT-B samples at 150°C.

pyridine adsorbed on EMT-A sample at 150°C (Fig. 5). The weak band at 1450 cm^{-1} is due to the pyridine interacting with the Lewis sites [13], formed during fast calcination of the sample in air. The effect of this pre-treatment on zeolites is twofold. Firstly, excessive overheating during template combustion can lead to local distortion of the lattice and formation of defects. Secondly, water formed in this process can, at high temperature, partially hydrolize the zeolite framework, resulting in hydrothermal dealumination [14]. Both the formation of Lewis acid sites and local distortion of the zeolite framework, which is not observed for samples pre-treated in nitrogen, can degenerate performance of the catalysts in some applications. It should be noted that both effects are enhanced as calcination is performed on a larger scale.

We conclude, therefore, that a non-destructive template removal from EMT and EMO zeolites, in the as-made zeolites, requires heating in nitrogen at 400–450°C, followed by calcination in air to 550°C.

4. Conclusions

Thermal analysis of uncalcined EMT and EMO reveals desorption of the water below 200°C and template decomposition at 250–400°C. Template destruction results in the formation of acetaldehyde, dioxane, ethylene and carbon monoxide and is followed by rapid desorption of the fragments. XRD studies of the calcined samples show no decrease in their crystallinity. However, both NMR- and IR-spectroscopy indicate partial distortion of the framework and formation of the Lewis acid sites. A non-destructive activation of zeolites prepared with organic templates should include pre-treatment in nitrogen at moderate temperature.

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