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STRUCTURAL INFORMATION DERIVED FROM TEMPLATE DECOMPOSITION IN NEW TYPES OF ZEOLITES

I. Thermal analytical study on as-synthesized Ga-ZSM-5

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The crystallization of Ga-ZSM-5 zeolites and the incorporation of gallium into the framework were investigated by means of TG-DTA measurements. Special attention was paid to the decomposition of the embedded template, which was followed by the observation of coke formed in particular on the external surface of the crystals. A semiquantitative relation was found between the maximum temperature of template decomposition and the Si/Ga ratio in the framework. The amount of embedded template depended on both the zeolite content of the sample and the Si/Ga ratio in the framework. The apparent velocity of desorption of products resulting from the decomposed template, and the coke/template ratio, were sensitive to the crystallinity of the Ga-ZSM-5 samples.

Introduction

Thermal analysis reveals information concerning the structure and stability of zeolites, which is important for the application of these materials in industrial processes such as catalysis and adsorption. This method has already been successfully applied to obtain data on phase changes during Ostwald ageing, on thermal stability, on cation location and on template decomposition [1–6].

Despite these possibilities, thermal analysis plays only a minor role in the characterization of zeolites and synthesis products. It is used mainly as a 'fingerpring' method. Especially the investigation of the new generations of zeolites based on silicon-rich (ZSM) and metal-modified alumophosphate frameworks (AlPO, SAPO, MAPSO) opens up new possibilities for the application of thermal analysis. In most cases, these new types of zeolites are

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synthesized in the presence of organic molecules, so-called templates, which are embedded into the channels and cavities of the zeolite structure. The thermal behaviour of these molecules also reveals new information about the physicochemical properties of the sample under consideration.

In this work, we start with an investigation of Ga-ZSM-5 zeolites containing tetrapropylammonium bromide as template. In the case of ZSM zeolites, the following information is desired:

- qualitative proof of the isomorphous substitution of silicon by other metals (M) within the zeolitic framework,
- quantitative determination of the Si/M ratio in the framework,
- data on the course of crystallization,
- identification of the zeolite, the zeolite content and the phase composition.

Experimental

Synthesis

The zeolite samples were hydrothermally crystallized at 170°C from gels of the overall composition: $15Na_2O * 2Ga_2O_3 * 100SiO_2 * 13TPABr * 4400H_2O$, using tetrapropylammonium bromide (TPABr) as template, sodium hydroxide, sodium gallate and silica sol.

Thermal analysis

TG-DTA measurements were carried out with a MOM derivatograph, using alumina sample holders containing about 100 mg of sample. The rate of heating was 5 deg/min in air.

Results

Isomorphous substitution

The most interesting question characterizing high silica zeolites such as pentasils (ZSM-5) is whether isomorphous substitution of framework silicon atoms by atoms of other elements occurs or not. First, an assignment of the thermal effects observed in the TG-DTA curves is necessary. In general, four distinct DTA peaks accompanied by corresponding losses in weight are observed (Fig. 1). They are assigned to the following processes:

I. water desorption from zeolite pores at about 100°C,

II. decomposition and oxidation of the embedded template between 360° and 450°C,

III. oxidation of coke resulting from the template above 500°C, and

IV. dehydroxylation of hydroxyl groups from lattice defect sites between 600° and 700°C.

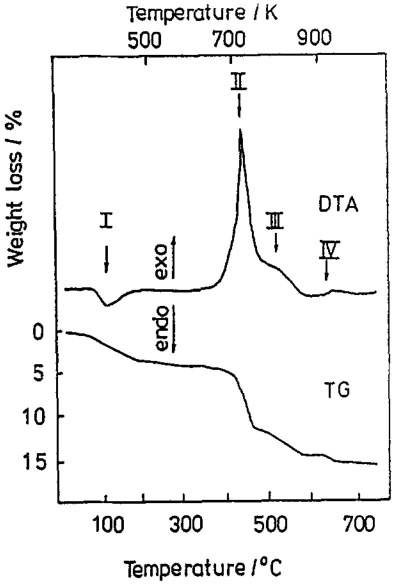

Fig. 1 Thermal behaviour of Ga-ZSM-5 (Si/Ga = 20) in air

Figure 2 shows the DTA curves obtained from silicalite, the pure silica analogue of the ZSM-5 zeolite, and the gallium-containing ZSM-5 sample in the as-synthesized, i.e. template-containing form. The maximum temperature of water desorption lies at 100°C. However, this process occurs over a wide temperature interval, between about 70° and 200°C indicating the weak, heterogeneous bonding of water within the as-synthesized samples.

In contrast, the template decomposition proceeds very rapidly. In comparison with silicalite, a marked temperature increase of peak II by about 85 deg is observed in the case of Ga-ZSM-5 (Fig. 2). This is a sure indication of the incorporation of gallium into the lattice. The temperature increase is presumed to be a result of the additional contribution of the ionic interaction to the template lattice interaction energy.

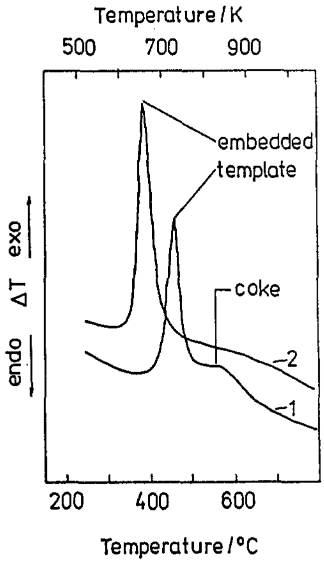

Fig. 2 Influence of the isomorphous substitution of silicon by gallium in the framework on the DTA curves of 1– Ga-ZSM-5 and 2– silcalite

The oxidation of coke originating from acidic cracking of the decomposed template (like propene) on the external surface of the zeolite crystals is slow. A maximum temperature is difficult to determine. When the DTA curve obtained from silicalite is compared with that of Ga-ZSM-5, it is obvious that the formation of coke is related to the incorporation of gallium. As a consequence of its neutral framework, silicalite does not contain acid centres. Accordingly, it exhibits no catalytic activity and no coke is formed. In this connection, samples with incorporated elements differ from those containing only neutral frameworks (silicon can also be substituted by atoms of the same charge, e.g. Ge^{4+} or $2Si^{4+}$ by $1Al^{3+}$ and $1P^{5+}$).

Ga content of the framework

A study was made of whether quantitative information about the isomorphous substitution could also be derived from measurements on samples synthesized with different gallium contents (Fig. 3). A proportional increase in the maximum temperature of template decomposition with increasing gallium content of the sample is observed. At the same time, the template content decreases linearly. This indicated that, with increasing gallium content of the starting synthesis gel, the amount of gallium incorporated into the framework increases, but only to a total gallium content of 4 Ga/u.c. If the overall gallium content exceeds this maximum value, no further increase occurs in the maximum temperature of template decomposition. Additionally, the template content remains constant, as seen in Fig. 3.

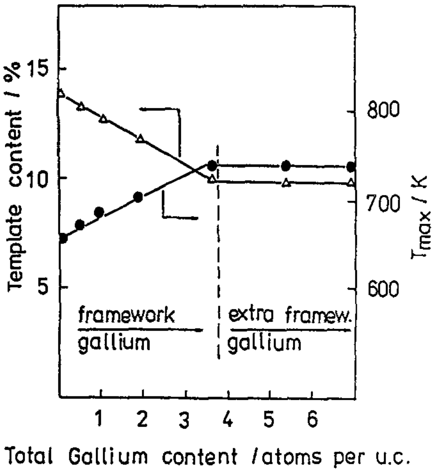

Fig. 3 Dependence of the template content and the maximum temperature of template decomposition (T_{max}) on the total gallium content of Ga-ZSM-5

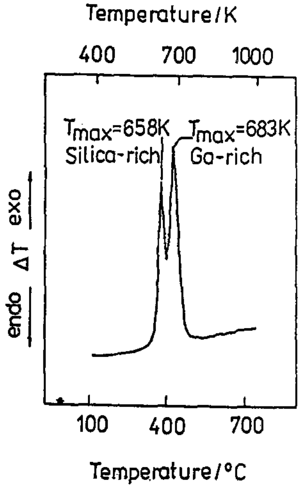

Fig. 4 Splitting of the DTA template decomposition peak due to heterogeneous Ga-distribution in the sample

The DTA curves do not exhibit a single template decomposition peak in all cases. Surprisingly, in some cases a splitting of this peak is observed (Fig. 4). As the maximum temperature of peak II refers to a certain Si/Ga ratio of the framework, the samples are expected to be heterogneneous with respect to this property.

The course of crystallization

DTA curves obtained after different times of crystallization are shown in Fig. 6. After a nucleation time of about 5 hrs, the crystallization of the zeolite starts rapidly. The onset of crystallization can be easily detected via the occurrence of the template peak at 468°C. The intensity of this peak increases very rapidly and its position remains constant as the time of crystallization is prolonged to 10hrs. Thus, the Si/Ga ratio of the sample remains nearly unchanged during the period of crystal growth. At the same time, the template content of the zeolite sample increases. After 10 to 24 hrs, it reaches the value expected for ZSM-5 zeolites (4 TPS/u.c.). As the Si/Ga ratio is constant, this increase is due to the higher zeolite content of the sample. The increase in the template content and the increase in the XRD peak intensity of the samples are nearly identical Fig. 5.

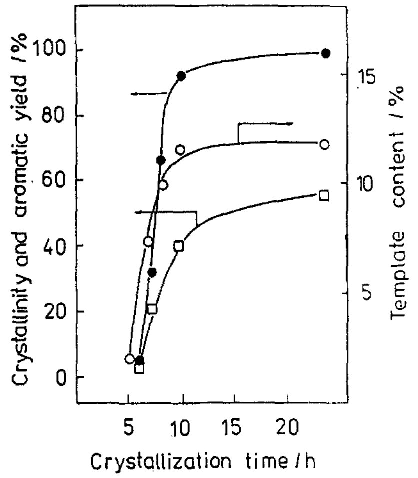

Fig. 5 XRD crystallinity (●), template content (o) and aromatic yield (□) *vs.* crystallization time

Coke formation

The decomposition of the template is accompanied by the formation of 'coke'. With prolongation of the time of crystallization between 5 and 8 hrs, the amount of coke formed increases (Table 1). This result correlates with the increasing zeolite content of the samples. On the other hand, if the time of crystallization exceeds 8 hrs, the tendency to coke formation decreases.

Table 1 Characteristic thermal data of as-synth. Ga-ZSM-5 (Si/Ga = 25) samples crystallized for different length of time

Crystallization time / h	Velocity of template desorption / mg / min.	Coke / template ratio	Max. temperature of template oxidation / K	Coke content/ % per sample	Velocity of coke oxidation / mg / min
5	–	–	723	1.1	0.07
6	–	–	738	1.5	0.07
7	–	–	–	2.0	–
8	0.57	0.45	733	4.0	0.166
10	0.73	0.38	733	4.0	0.156
24	1.0	0.36	738	4.0	0.2
48	1.25	0.34	738	4.0	0.14
96	1.38	0.16	753	4.0	–

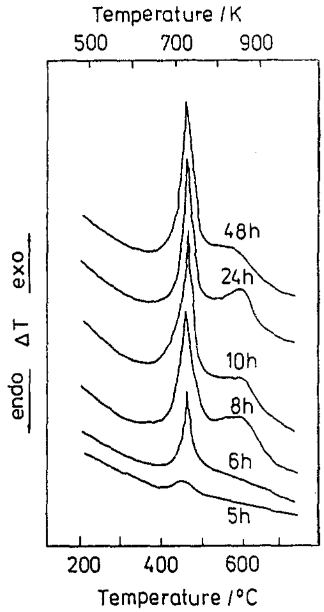

Fig. 6 DTA analysis of Ga-ZSM-5 (Si/Ga = 25) in dependence on the time of crystallization

This is expressed in the falling coke/template ratio, although the acidity is maintained. The velocity of coke oxidation simultaneously increases. This behaviour is reflected in the variation in intensity of peak III in the DTA curves of the corresponding samples Fig.6.

It is assumed that these changes are caused by differences in the nature of the external surface of the crystals. At the onset of crystallization, this surface seems to be 'rough', leading to an increased contact time of the decomposition products with active centres. This idea is confirmed by the marked increase in the velocity of template desorption with increasing time of crystallization. At the same time, the maximum temperature of template decomposition indicates unchanged template bonding in the samples.

The change in the velocity of coke oxidation can be a result of the different nature of the coke. The ESR spectra of coked samples were measured to elucidate this question. It is well known that catalysts containing coke products show a radical signal, the line width of which depends on the kind of coke present in the pores or on the surface. This is also the case for the samples under discussion. The sepctra measured after vacuum dehydration at 50°C show that the line width of the single line characteristic of coke decreases from about 10 G to 7 G with increasing time of crystallization.

This could be interpreted by suggesting that the aromatic character of the coke decreases with increasing time of crystallization.

Discussion

The increase in the maximum temperature of template decomposition in the case of gallium-containing samples is clearly connected with the additional contribution of an ionic interaction. Indeed, with increasing gallium content, the lattice charge is increased, because the uncharged $SiO_{4/2}$ units are replaced by negatively charged $GaO^{-}_{4/2}$ units. The template is positively charged. This result is supported by the appearance of catalytic activity in the case of gallium-containing samples and the observed formation of coke. Both are connected with Brönsted acid sites which originate from protons attached to the negatively charged framework. The neutral silicalite is catalytically inactive. Hence, the tendency to coke formation is very small. Just at the onset of crystallization, gallium is incorporated into the framework, as can be concluded from the increased template decomposition temperature in comparison with that of silicalite.

The proportional relationship between the gallium content of the lattice and the maximum temperature is expected, because the overall negative charge of the lattice is increased, but the template content remains constant or is slightly decreased. The temperature shift reflects the increasing contribution of the ionic template-lattice interaction to the stabilization energy.

In principle, the observed relationship would allow the quantitative determination of the gallium content of the framework. However, for this purpose the relation given in Fig. 3 is not sufficient. As the ammonia TPD reveals, only about half of the total gallium contained in the zeolite samples is really incorporated. Therefore, the temperature maxima observed may be not representative in detail of the Si/Ga ratio within the framework. Nevertheless, it allows the gallium incorporation to be followed semiquantitatively.

Obviously, in the case under consideration the incorporation is limited to about 2 Ga atoms per unit cell, although the total content given in Fig. 3 is about 4. An excess of gallium within the gel does not necessarily lead to a further increase in gallium incorporation. This finding is confirmed by NH_3 TPD measurements. In combination with chemical analysis, a quantitative subdivision into framework and nonframework gallium species is possible.

As theoretically expected, within silicalite about 4 molecules per unit cell of template are embedded into the lattice. It is noteworthy that the template content decreases with increasing gallium incorporation. This decrease is suggested to be a consequence of the lattice charge. In this case, hydrated sodium ions in the gel compete with the template for the negative charge on the surface of the growing crystals or precursors. However, the sodium ions are smaller and can therefore approach negative charges more closely at the surface of growing crystals. This means that the template content of the zeolites also contains information about the Si/Ga ratio of the framework. An excess amount of gallium (more than 4 Ga/u.c.) does not lead to a further decrease in the template content, supporting the above-mentioned conclusion of a limited gallium incorporation.

The zeolite content of the sample can be determined directly from the amount of template in the lattice, where all material containing zeolite subunits is enclosed. Furthermore, in the case of ZSM-5 crystallization, the change in the XRD intensity during the course of crystallization relates quantitatively to the zeolite content of the sample. This is an important result, because numerous factors affect the XRD intensity. The catalytic activity as a function of the time of crystallization shows the same behaviour, supporting the above conclusion. Last not least, the coke content increases with increasing zeolite content of the synthesis product. The formation of coke is closely connected with the number of acid centres, which increases with the zeolite content (the Si/Ga ratio is constant).

On the other hand, not only quantitative information concerning the zeolite content is attained. The investigations show qualitative changes in the crystallization products during the course of crystallization. The coke/template ratio is a measure of the catalytic activity, especially of the surface. This ratio is high for samples crystallized for short times and decreases significantly with increasing time of crystallization. Simultaneously, the velocity of template decomposition increases. However, the maximum temperature of template decomposition, which is a measure of the strength of template bonding in the lattice, remains constant. As the template bonding is not affected by the time of crystallization, we conclude that the observed effects are caused mainly by changes in the properties of the external surface of the crystals. From this finding, it is assumed that there may be a diffusional barrier on the external surface of the crystals, leading to an increased contact time of the template decomposition products with active centres. These could consist of nonframework gallium species. Diffusional measurements are necessary to support this idea.

Conclusion

The results presented show the great potential of thermal analysis in the characterization of new types of zeolites, which in most cases are prepared with template molecules. The TG-DTA curves contain important information about the products synthesized: the Si/Ga ratio of the framework, and the quality of the crystals with respect to the surface properties; they also allow the course of crystallization to be followed. Despite the advantage achieved, further work is necessary to quantify the observed relation between the maximum temperature of template decomposition and the Si/Ga ratio of the framework.

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Zusammenfassung — Die Kristallisation des siliziumreichen templathaltigen Zeoliths ZSM-5, modifiziert mit Gallium, wird mittels TG-DTA untersucht. Es wird ein Zusammenhang zwischen der Zersetzungstemperatur des Templats, dem Gehalt an Templat sowie der Koks-bildung aus den Templatzersetzungsprodukten und der isomorphen Substitution, dem Si/Ga-verhältnis sowie der Kristallinität der Zeolithproben gefunden.