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THERMOANALYTICAL INVESTIGATION OF ZEOLITES AND RELATED COMPOUNDS

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ABSTRACT

Crystalline aluminosilicates and related compounds with zeolitic structures have found wide application as sorbents and catalysts. Thermal analysis provides the possibility of investigating and determining some of their characteristic properties, e.g., surface properties (acidity and adsorption capacity), thermal stability and even phase composition.

INTRODUCTION

Zeolites are crystalline aluminosilicates with a lattice containing tetrahedra of Si and Al atoms, each surrounded by four oxygen atoms. Their structure also includes cations of mostly alkali and/or alkaline earth metals, which balance the surplus negative charge of the AlO_4^- tetrahedra. These cations may be easily interchanged for others, including hydrogen ions. The lattice of a number of zeolites (of which many types are known, both as natural and synthetic products) forms well defined cavities of various sizes and shapes. Owing to their facility for specific interactions with the gas phase, zeolites have found wide application as sorbents and catalysts, especially where the acidity of their surface is of use. In addition to aluminosilicates, other crystalline compounds with similar properties and applications have recently been synthesized in which either aluminium or silicon is replaced by other elements, e.g., borosilicates and aluminophosphates.

In order to characterize individual zeolites, especially from the point of view of their behaviour during dehydration, their thermal stability and their acidic properties, various thermoanalytical techniques may be used.

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The thermal dehydration (dehydroxylation) of zeolites affects not only their surface properties, but also those of their crystal lattice. Siegel et al. [1] used thermomechanical analysis combined with high-temperature X-ray diffractography for the investigation of changes in the lattice parameters in a series of (Na, Ca)A zeolites during their dehydroxylation. The shrinkage of the lattice caused by the loss of water occurs at about 430 K, followed by an expansion step (between about 420 and 470 K) caused by the repulsive forces of the Na^+ ions after the loss of coordinated water. The significantly higher expansion in samples with a higher content of Ca^{2+} ions is interpreted by their prevailing localization in the six-membered rings of the lattice.

By further heating to higher temperature, a temperature is finally attained at which the zeolite lattice breaks down. This temperature (which characterizes the thermal stability of the zeolite) varies with the type of zeolite structure. Collela et al. [2] used the different thermal stabilities of phillipsite and chabazite for their thermogravimetric determination in zeolite-bearing rocks. After the irreversible dehydration of the possibly present amorphous hydrated phases at 240 °C they rehydrated the sample, then heated it to 350 °C, where the phillipsite structure broke down, and rehydrated the sample again. At 800 °C the chabazite structure was also destroyed. From the amount of water taken in by the sample during the rehydration steps the contents of both zeolites could be determined.

Fajnor and Kuchta [3] investigated a series of synthetic montmorillonites with various contents of Mg and/or Ca by DTA and TG. They characterized their samples by the magnitude of the temperature difference between the typical endothermic peak at about 1000 °C and the following endothermic peak (classification used previously with natural montmorillonites). The presence of small amounts of trioctahedral montmorillonite in the prevailingly dioctahedral samples was detected by the endothermic peak near 900 °C.

Thermal transformations taking place in NH_4A zeolites were investigated by Dondur and Rakič [4]. They performed simultaneous DTA and TG measurements in a flow of dry nitrogen. All their samples exhibited a broad endothermic peak near 200 °C accompanied by a significant mass loss; with samples containing at least eight NH_4^+ groups per unit cell of the zeolite a broad exothermic peak was also observed at higher temperatures, accompanied by a mass change of less than 1%. They also used IR spectroscopy and X-ray diffractography for samples heated to various temperatures. Both the dehydration and deammonization of the zeolites and the thermal decomposition of their structure followed by phase transformation (to sillimanite) were affected by the Na^+/NH_4^+ ratio in the sample.

Thermal stability is also an important characteristic of zeolites, especially of those which are used as catalysts. Experience obtained with various types of zeolites with different Si/Al ratios led to the conclusion that zeolites with a lower content of Al atoms in the lattice exhibit higher thermal stability. As a certain range of the Si/Al ratio is an inherent characteristic of every type of zeolite, many experiments have been carried out on the dealumination of zeolites, by which procedure the amount of Al atoms in the lattice is reduced, the structure remaining preserved.

Alsdorf et al. [5] investigated thermoanalytically the thermal stability of Y zeolites dealuminated either thermochemically or by extraction with ethylenediaminetetraacetic acid. The individual samples are also characterized by their sorption capacity for water and *n*-hexane. The stability and the adsorption capacities of less dealuminated samples (with up to about 50% of the original Al content) seem to be a function of the Al content only. With higher degrees of dealumination, however, the extraction of Al with EDTA seems to lead in some instances to samples with a relatively higher stability and adsorption capacity.

Another method of preparing zeolites with a higher ratio of Si to Al is their direct synthesis. These zeolites of the so-called ZSM type are prepared by hydrothermal synthesis from aluminosilicate hydrogels in the presence of alkali metal ions and of a structure-directing agent, e.g., tetraalkylammonium ions.

Gabelica et al. [6] investigated by DTA in nitrogen the termal decomposition of tetrapropylammonium ions differently incorporated into the framework of synthesized ZSM 5 zeolites. Whereas the endothermic peak at about 260 °C characterizes the decomposition of the tetrapropylammonium species not stabilized by the zeolite lattice (appearing also in the starting hydrogel), peaks appearing around 350 °C were attributed to the tetrapropylammonium ions partially located on the external surface of the particles, partially extending into the structure channels.

A group of peaks in the range between about 390 and 490 °C corresponds to the decomposition of even more stabilized tetrapropylammonium species, especially to those tetrapropylammonium ions which are in the positions of cations balancing the negative charge of the AlO_4^- units. These peaks shift clearly to higher temperatures when the degree of crystallinity of the sample increases.

Crystalline aluminophosphates, sometimes designated zeolites of the third generation, are prepared in a similar manner to the previously mentioned high-silica zeolites ("zeolites of the second generation"), i.e., hydrothermally in the presence of structure-directing agents (templates).

Bock et al. [7] investigated the effect of the method of preparation on the surface area, pore size and pore size distribution of the product. On the basis of a comparison between three differently prepared gels, obtained as the intermediate products of aluminophosphate synthesis, they claimed that a product of good quality, especially with a narrow pore size distribution, may be obtained only from a homogeneous, stoichiometrically well defined gel with a strongly coordinated template; such a gel is characterized by a DTG curve with well defined decomposition peaks of the individual compounds formed between the template and the aluminophosphate.

The acidic properties of the surface of zeolites are of great importance for their application as sorbents and catalysts. They are usually investigated by studying the adsorption of ammonia and of organic nitrogen-containing bases.

Auroux et al. [8] studied the influence of the impregnation of H-ZSM 5 with boric acid by the adsorption of NH_3 in a microcalorimeter. From their measurements it follows that the presence of boron [probably causing the replacement of OH groups by $OB(OH)_2$ groups] results in a significant decrease in the heat of adsorption of NH_3. This is caused by a decrease in the acidity and an increase in the heterogeneity of the surface accompanying the increase in the content of boron.

Another technique that gives the possibility of investigating the interaction between zeolites and gaseous bases (e.g., ammonia) is temperature-programmed desorption (TPD). Hunger and Hoffmann [9] investigated the possibility of a better resolution of two desorption peaks by a non-linear heating programme.

CONCLUSION

The aim of this paper was not only to summarize the relevant contributions published in the Proceedings of the Conference, but also to use these papers (thanks of the wide range of applications covered) as examples illustrating the possibilities and tendencies in the investigation of the individual characteristics of zeolites and related compounds. Interested readers may find more about these topics, e.g., in a review by Gabelica et al. [10] dealing especially with the application of combined thermoanalytical techniques in this field.

REFERENCES

1 H. Siegel, W. Schmitz, R. Schöllner and A. Dyer, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 93 (1985) 561.

2 C. Collela, M. Di Gennaro and R. Aiello, Proc. 8th ICTA '85, Bratislava, Suppl., p. 115.

3 V.Š. Fajnor and L. Kuchta, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 93 (1985) 549.

4 V. Dondur, V. Rakič, R. Dimitrijevič and D. Vučinić, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 93 (1985) 753.

5 E. Alsdorf, U. Lohse and M. Feist, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 93 (1985) 553.

6 Z. Gabelica, J.B. Nagy, P. Bodart and A. Nastro, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 93 (1985) 749.
7 J.A. Bock, J.D. Fellmann and H.G. Langer, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 579.
8 A. Auroux, M.B. Sayed and J.C. Védrine, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 93 (1985) 557.
9 B. Hunger and J. Hoffmann, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 189.
10 Z. Gabelica, B. Nagy, J. E.G. Derouane and J.P. Gilson, Clay Miner., 19 (1984) 803.