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Short Communication

DIELECTRIC DIFFERENTIAL THERMAL ANALYSIS
IX. The role of guest molecules

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The present paper deals with the role of guest molecules in the moleculer sieves systems.

The category of porous crystals, which include zeolites, fedspathoids, clathrates, molecular sieves, pillared clays, Werner compounds, etc. [1], consist of host lattices with channel systems freely accessible to molecules of appropriate size and shape, and of compounds whose structures include well-defined cavities. These porous crystals have the property of being able to accommodate guest molecules.

The present paper considers six molecular sieves: ZSM-5, $AlPO_4$-5, FAPO-5, CoAPO-5, MnAPO-5 and ZnAPO-5, as representatives of this class of compounds. The first of them crystallizes in the MFI structure type and the others in the AFI structure type [2], and they include as guest molecules TBA and TEA, respectively (to be accurate, water is a guest molecule too, but it interacts with the host lattice fundamentally through physical forces).

In the molecular sieves studied here, the guest molecule is introduced as a template agent during the synthesis [3, 4] and both TBA and TEA are structurally intact in the molecular sieve channels [2–4].

The thermal behavior of the molecular sieves studied here indicates that the guest molecules are desorbed at about 300° to 500°C for MFI and from 500° to 720°C for AFI [5, 6].

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In the present paper, we report the dielectric thermograms of the above molecular sieves and discuss the role of guest molecules in thermodielectric analysis.

ZSM-5 was synthesized from highly reactive aluminosilicate gels by adding quaternary ammonium ions (TBAOH). The gels were crystallized in teflon-lined autoclaves at 150°C for 5 days, using a modification of the literature method [7].

Synthesis gels for MAPO-5 (M: Fe, Co, Mn and Zn) were prepared by using modifications of previously described methods [8,9].The template was in all cases TEA and gels were crystallized in teflon-lined autoclaves at 200°C for 1 day. $AlPO_4$-5 was synthesized similarly, but in the absence of the added metal.

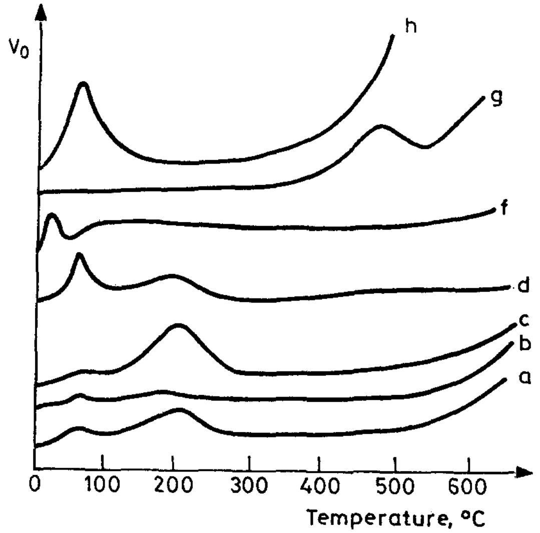

Fig. 1 Thermodielectric curves of: CoAPO-5 (*a*), FAPO-5 (*b*) ZnAPO-5 (*c*), MnAPO-5 (*d*), $AlPO_4$-5 (*f*), ZSM-5 (*g*) and non-crystallized product (*h*)

The reactives used for ZSM-5 were active sodium silicate (27% SiO_2, 8% Na_2O), $Al_2(SO_4)_3$ (Merck), H_2SO_4 (98%, BDH) and TBAOH (40%, BDH); for MAPO we used alumina (Merck), H_3PO_4 (85%, BDH), $CoSO_4 \cdot 9H_2O$, $ZnSO_4$, $MnSO_4 \cdot 4H_2O$ (BDH), $FeSO_4 \cdot 5H_2O$ (Fluka and TEA (BDH).

In the characterization the elemental and phase compositions were controlled. The synthesis efficiency was close to 100%. The Si/Al ratio in ZSM-5 was about 30, and the weight per cent of metal in MAPO-5 was in all cases around 1%.

Thermoelectrical curves were obtained in a thermodielectric analyser described previously [10] and are reported in Fig. 1. Besides the well-known water desorption peak this Figure clearly shows (curves *a-f*) a second one at higher temperature, i.e. at around 200°C, for the AFI molecular sieves and at around 470°C for the MFI molecular sieve. These peaks can be ascribed to amine desorption, i.e. TEA for AFI and TBA for MFI. The presence of this thermal effect in molecular sieves is a new example of the possibilities of thermodielectric analysis as an analytical tool, enlarging the number of peaks which can be recognized in a thermoelectric curve. As an application of this finding, it can be seen in Fig. 1 that curve *g* does not exhibit this peak and it corresponds to a non-crystallized product of a ZSM-5 synthesis gel. This indicates that when ZSM-5 is not formed the effect corresponding to TBA desorption is not present in the curve and only a water peak is observed, which is not present in the ZSM-5 curve because of its hydrophobicity.

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