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Note

THERMOGRAVIMETRIC AND IR SPECTROSCOPIC STUDIES OF TRICRESYL PHOSPHATE-SORBED ZEOLITE 3A

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The thermochemical behaviour of zeolite inclusion complexes has been studied by Petranovic and Susic [1]. It has been found that salt inclusion into channels and cages of a zeolite can lead to modification of the properties: an increase in cationic capacity, the introduction of new anionic species, a change in the amount of zeolitic water, and also a change in the structure, depending upon the included component.

This work is devoted to a study of the thermal behaviour of phosphate inclusion species of zeolite 3A (Union Carbide Corporation, U.S.A.; lot No. 3340030044). While earlier workers [1] studied the thermal behaviour of electrolytes, in the present study a non-electrolyte such as tricresylphosphate (TCP) has been used for the preparation of sorbed derivatives. In an earlier communication [2] the author reported the kinetics of the joint desorption of water and TCP from synthetic zeolites 4A and 13X, which were in 0.5 mm pellet form, evaluated from TG data. The thermochemical behaviour of zeolite 3A in powder form is distinct from the pellet forms of the other two zeolites with the same sorbate. TG data have been used to determine the kinetic parameters of the thermal processes. The nature of the interaction between the sorbate molecules and the zeolite, and the thermal stability of the sorbed derivative have been characterized by IR spectra of the sample before and after heating on a Bunsen burner.

EXPERIMENTAL

In contact with excess tricresylphosphate, the zeolite 3A turned into a greyish colloidal mass. On filtering off the excess TCP, air-drying and soaking on a filter paper, a waxy solid resulted. A portion of this sample was heated on a Bunsen burner in a nickel crucible for several hours. As soon as heating commenced, evolution of TCP became apparent from the vapours accompanied by the sintering of the solid mass. Heating another portion of the TCP-sorbed derivative with a saturated solution of ammonium chloride led to complete separation of the sorbate from the zeolite, as evident from the IR spectra of this sample. All the three samples, the air-dried, preheated and ammonium chloride reacted, were subjected to TG analysis in air up to 1073 K at a heating rate of 10°C min^{-1}. These samples and their residues remaining in the TG balance (supplied by the Fertilizer Corporation of India) after heating to 1073 K were used for IR studies in nujol between 5000 and 650 cm^{-1} with a Spektromom 2000 IR Spectrophotometer.

RESULTS AND DISCUSSION

Thermogravimetric data

The TG plots of the TCP-sorbed 3A zeolite (Plot I) and its preheated form (Plot II) are shown in Fig. 1. It is clear that in both cases the loss of weight occurs at varying rates below and above the boiling point of the sorbate (537 K). The thermal events taking place are dehydration up to about 530 K and desorption beyond this. The extent of sorption is very high and is about 10% higher than the sorption capacity of zeolites in pellet form. The behaviour of the preheated sample shows that even after prolonged heating the sorbate is retained by the zeolite to the extent of about 4%. Higher temperature dehydration beyond 573 K does not occur in this case [3], as the TG plots exhibit only two-step weight losses. This additional dehydration step was found in the case of both 4A and 13X in pellet form. Desorption of TCP takes place at a rapid rate in the air-dried sorbed sample. In the case of the preheated sample dehydration and desorption occur at a similar rate. The slower rate of desorption of TCP in the preheated sample establishes the fact that the sorbate is more closely held by chemisorption in the crystal lattice.

Non-linear plots are obtained for $n = 1$, 2 and 3 for $\log_e[-(1-\alpha)^{1/n}]$ vs. time, with points of inflexion at 513 K and 533 K, respectively, for the air-

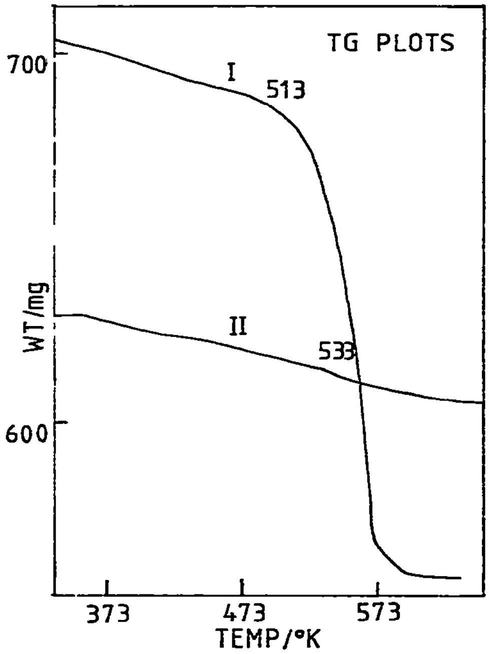

Fig. 1. TG plots of (I) tricresyl phosphate-sorbed zeolite 3A and (II) its preheated form.

dried and preheated samples. However, linear plots for first-order reactions are obtained for these samples for $\log_e[\log_e - (1 - \alpha)^{1/n}]$ vs. $1000/T$ over two different temperature ranges, e.g. 353—513 K and 513—613 K for the air-dried and 373—533 K and 533—653 K for the preheated samples. Dehydration and desorption of TCP can thus be distinguished as two different thermal events. The rates of reaction and activation energies of these thermochemical processes for $n = 2$ are tabulated in Table 1. The calculations are based on the methods suggested by Dollimore [4] and Karkhanavala and co-workers [5].

Infrared spectroscopic data

Figures 2 and 3 show the IR spectra of TCP-sorbed 3A and its preheated forms (continuous lines), and those of their residues remaining after TG treatment up to 1073 K (broken lines). The thermochemical behaviour of the TCP-sorbed and its preheated variety becomes quite clear from these spectra. The presence of $\nu(P = 0)$ bands are observed between 1300 and 1240 cm^{-1} and 1200 and 1170 cm^{-1} in Fig. 1 and shoulders around 1220 and 1180 cm^{-1} in Fig. 2. These bands disappear in the spectra of the residues of both the samples after heating to 1073 K. The preheated, granular variety of TCP-sorbed 3A retains a part of the sorbate which is lost at around 653 K. At this temperature collapse of the crystal lattice begins for the preheated sample. This is confirmed by the disappearance of IR bands at lower frequencies beyond 1200 cm^{-1} which are assigned to Si—O and Al—O bond vibrations [6]. Broadening and shifting of vibration bands around 3400 cm^{-1} and 1000 cm^{-1} suggest hydrogen bonding and changes in the aluminosilicate lattice structure of 3A as a result of the chemisorption of TCP. While sudden heating resulting in rapid evolution of TCP makes the sorbed sample granular and permits partial retention of the sorbate in the crystal lattice of

TABLE 1

Zeolite and composition $[A = (AlO_2)_{12}(SiO_2)_{12}]$	Total wt. loss (%)	Temp. of max. loss (K)	Wt. loss steps (%) time/temp.	Rates of reaction ($\times 10^{-2}$ min^{-1})	Activation energy (kJ $mole^{-1}$)
TCP-sorbed 3A $K_{12}A \cdot 9.6\ H_2O \cdot 3.66$ TCP $K_{12}A \cdot 3.66$ TCP (1st step)	46.8	513—573	7.4 up to 24 min/513 K	4.4	25.1
$K_{12}A$ (2nd step)			39.4 up to 34 min/613 K	16.0	226.3
Preheated TCP-sorbed 3A $K_{12}A \cdot 7.9\ H_2O \cdot 0.23$ TCP $K_{12}A \cdot 0.23$ TCP (1st step)	10.1		6.1 up to 26 min/533 K	5.4	42.9
$K_{12}A$ (2nd step)			4.0 up to 38 min/653 K	5.0	80.6

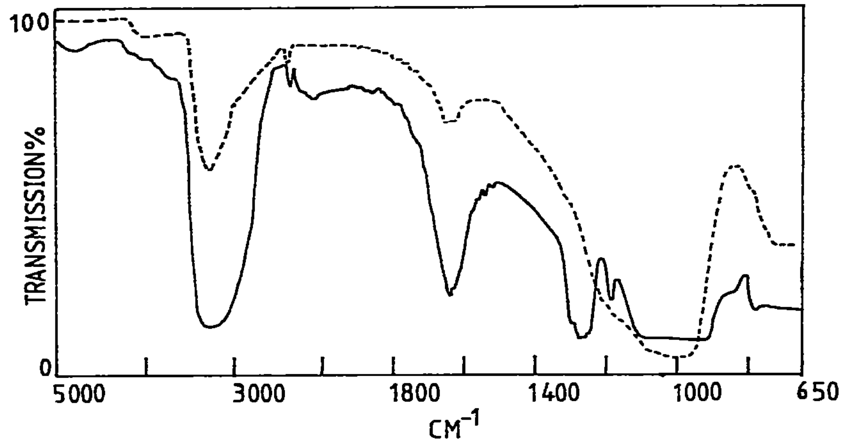

Fig. 2. IR spectra of tricresylphosphate-sorbed zeolite 3A (solid line) and its preheated (~1073 K) residue (broken line). The peaks due to nujol have been eliminated.

the sorbent, a gradual and slow rate of heating at 10°C min^{-1} on a TG balance allows complete desorption. The preheated granular form of the sorbed zeolite is much less stable compared with the air-dried sample. This fact is established from the IR spectra of the two residues remaining after heating up to 1073 K. The IR spectra of the sorbed zeolite sample which was heated with saturated aqueous NH_4Cl solution shows complete absence of $P = 0$ frequencies. The included phosphate can therefore be displaced by treatment with an electrolyte.

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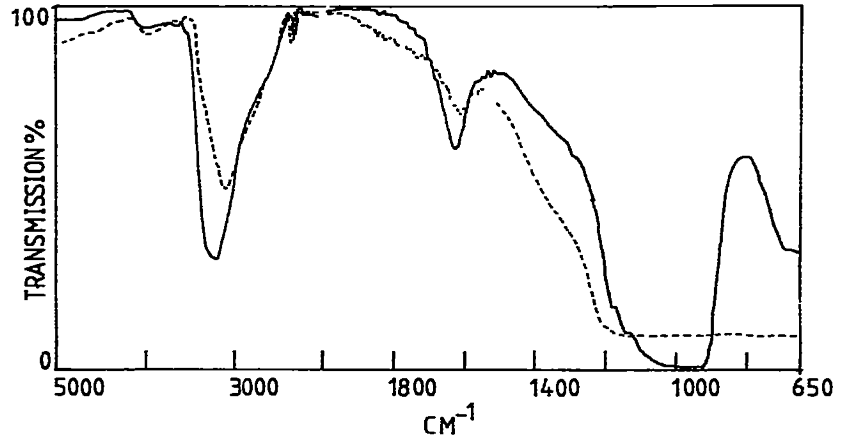

Fig. 3. IR spectra of preheated tricresylphosphate-sorbed zeolite 3A (solid line) and its preheated (~1073 K) residue (broken line). The peaks due to nujol have been eliminated.

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