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Note

DETERMINATION OF THE KINETIC PARAMETERS OF THE DEHYDRATION AND DECOMPOSITION PROCESSES OF THE SODIUM TETRAPHENYL BORON-SORBED DERIVATIVE OF ZEOLITE 3A BY THERMOGRAVIMETRIC METHOD

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Many earlier workers [1–3] have used thermoanalytical techniques to investigate reaction rates and evaluate the energy of activation of solid state reactions. These techniques were recently extended to the study of zeolite inclusion complexes [4–6]. The open structure of zeolites permits sorption of many species resulting in inclusion derivatives. These derivatives are quite capable of altering the basic properties of the sorbent zeolite. The present work is devoted to the study of the dehydration and decomposition processes of the sodium tetraphenyl boron-sorbed derivative of commercial zeolite 3A $[K_{12}Al_{12}Si_{12}O_{48} \cdot 21\ H_2O]$ in powder form and evaluation of their kinetic parameters. Additional information, obtained from IR spectroscopic studies of the zeolite derivative, have also been incorporated.

EXPERIMENTAL

Commercial zeolite 3A, as obtained from Union Carbide Corporation, U.S.A., was interacted with the complex sodium tetraphenyl boron in aqueous medium at the temperature of the water bath. The resultant product was filtered and air-dried by means of an electric air-dryer. A portion of the dry product was heated in a nickel crucible on a bunsen burner for several hours. TG data of this product, before and after heating, were recorded in air up to 1073 K, at a heating rate of 10°C min^{-1}, using a thermobalance supplied by the Fertilizer Corporation of India, Sindri. IR spectra were recorded for the two zeolites using a Spektromom 2000 spectrophotometer between 5000 and 650 cm^{-1} in KBr. Figures 1–3 show the TG plots, plots for $\log_e[g(\alpha)/T^2]$ vs. 1000/T and the IR spectra of the zeolite samples before and after heating.

RESULTS AND DISCUSSION

Thermogravimetric data

The air-dried sample of zeolite 3A starts to lose water around 353 K and dehydration proceeds in three successive steps up to 613 K. An abrupt, fast rate of

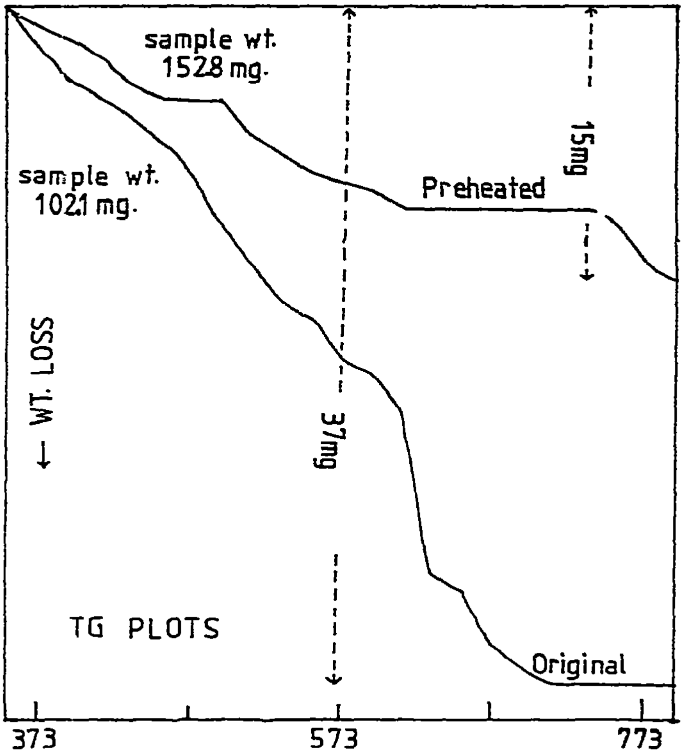

Fig. 1. TG plots of sodium tetraphenyl boron-interacted zeolite 3A and its preheated form.

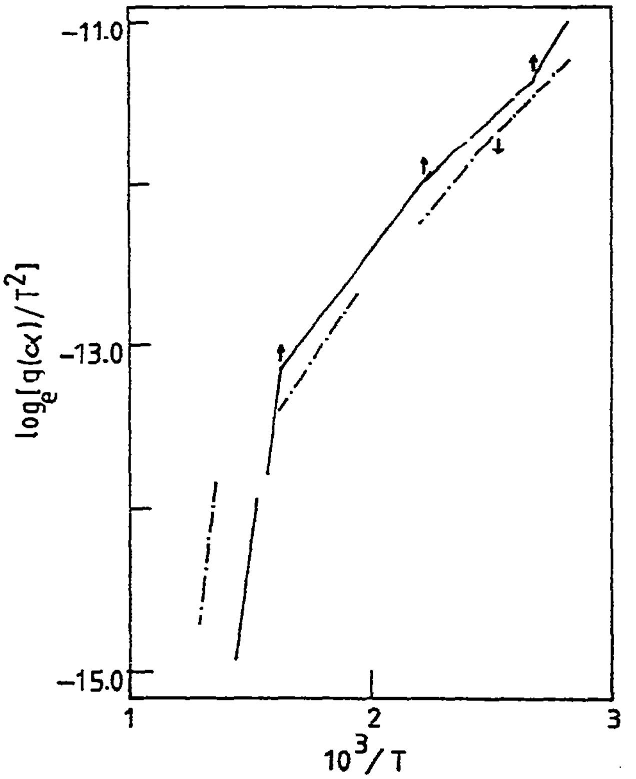

Fig. 2. Plots for calculating the energy of activation. ————, Original interacted zeolite; —·—·—·, preheated form.

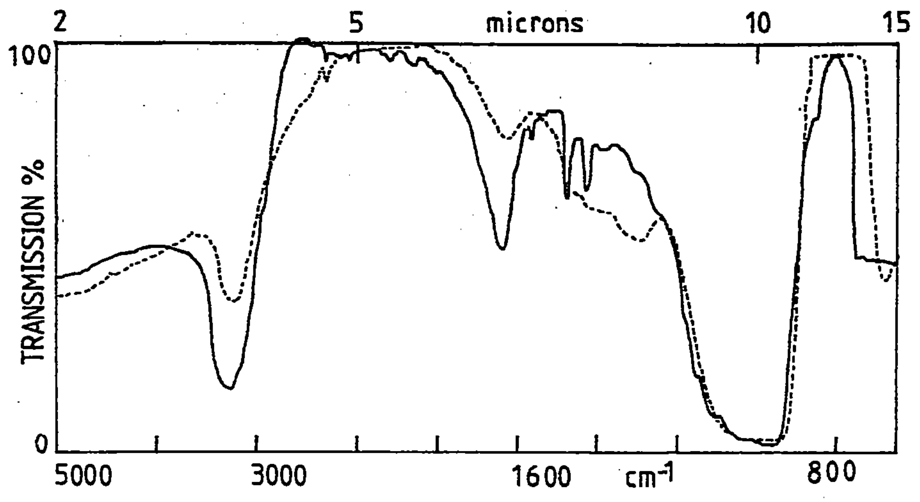

Fig. 3. IR spectra of ————, sodium tetraphenyl boron-interacted zeolite 3A and - - - - - -, its preheated form.

weight-loss step is observed between 613 and 633 K for the first-stage of decomposition of the sorbed sodium tetraphenyl boron. This is followed by a weight loss of the residual decomposition product between 653 and 713 K in the second stage. No further thermal events occur till 1073 K. The three-step dehydration process results in a 21.7% weight loss, while the two-step decomposition accounts for 14.5% weight loss.

Whereas the TG plot of the sorbed derivative before heating is rather complex, that for the preheated sample is easier to resolve and enables a clearer understanding of the various thermal events. Dehydration gives rise to two distinct steps of weight loss, between 353 and 453 K and then 513–613 K. Higher temperature dehydration suggests the presence of more closely held water molecules. The dehydrated residue is thermally stable till about 733 K when decomposition of included species takes place. Prior heating, having caused the burning of the organic constituents, allows sedimentation of the more closely held decomposition product in the pores of the zeolite. While the decomposition product of the first step in the original sorbed derivative decomposes further at a much lower temperature (about 653 K) the included residue decomposes at a later stage (733 K). In the case of the original zeolite all thermal events stop at around 713 K but the preheated sample, though exhibiting thermal stability till 733 K, permits the decomposition of the included species beyond this temperature. In the original zeolite, apart from dehydration, the thermal events can be visualized as the conversion of sodium tetraphenyl boron to first, sodium metaborate, followed almost immediately by at least partial decomposition of metaborate to sodium(I) and boron(III) oxides. This is confirmed by the high values of activation energy for the decomposition. The preheated sample with included species of metaborate decomposes to the mixed oxides of sodium and boron at a higher temperature, resulting in a higher value of energy of activation.

TABLE 1

Thermal data and kinetic parameters of sodium tetraphenyl boron-interacted zeolites 3A

Zeolite	Wt. loss (%)	Temp. (K)	Time (min)	Reaction rates ($\times 10^{-2}$ min^{-1})	Activation energy (kJ mole^{-1})	Thermochemical processes
$Na[B(C_6H_5)_4]$ -interacted 3A Derivative	9.2	353–453	18	7.6	31.0	Dehydration[a]
	12.5	453–613	34	3.3	38.4	Dehydration
	8.7	613–633	36	14.5	224.6	Decomposition
	5.8	653–713	44	5.5	207.3	Decomposition
Preheated 3A derivative	3.7	353–453	18	6.7	31.0	Dehydration
	3.7	513–613	34	2.9	42.8	Dehydration
	2.4	733–793	52	7.3	239.3	Decomposition

[a] Combination of the first two steps.

Wendlandt [7,8] in his earlier studies of metal tetraphenyl boron compounds, reported that the tetraphenyl borates start to decompose around 538 K. However, further decomposition of potassium metaborate was not observed by him.

Thermal data and kinetic parameters as determined from plots of $g(\alpha)$ vs. time and $\log_e[g(\alpha)/T^2]$ vs. $1000/T$ for $n = 2$ are given in Table 1. While non-linear plots for $n = 1$, 2 and 3 were obtained over different temperature ranges for $g(\alpha)$ vs. time, straight lines, indicating first-order reactions, were obtained for $\log_e[g(\alpha)/T^2]$ vs. $1000/T$ plots.

IR spectroscopic data

The IR spectra of the original sorbed derivative and its preheated form are shown in Fig. 3. Apart from exhibiting three prominent peaks around 3300, 1640 and 1000 cm^{-1} for lattice water and Si–O vibrations, respectively, the original zeolite also shows peaks around 1560, 1480 and 1420 cm^{-1} for skeletal vibrations, involving C–C stretching within the benzene ring. The presence of the tetraphenyl boron complex is thereby indicated in the interacted zeolite. These peaks are not found in the IR spectra of the preheated zeolite although shoulders appear around 1480 and 1420 cm^{-1}. However, a new broad but weak peak appears around 1300 cm^{-1} in the IR spectra of the preheated sample. This is due to absorbed metaborate in the zeolite pores.

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