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Note

THERMOGRAVIMETRIC STUDIES OF PYRIDINIUM CHLOROCHROMATE REAGENT SUPPORTED ON SYNTHETIC ZEOLITE 3A

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Pyridinium chlorochromate has been found to be quite useful as an oxidant in organic syntheses [1–4]. This reagent, $C_5H_5NH^+CrO_3Cl^-$, is safely prepared by the addition of pyridine to a solution of chromium(VI) oxide in 6 M hydrochloric acid followed by filtration. The yellow orange product is stable in air. It was used in dichloromethane solvent to prepare an adsorbed derivative in the supporting medium of synthetic zeolite 3A in powder form, and the thermal behaviour of the derivative was investigated by TG and IR spectral analyses. The yellow adsorbed derivative was heated at a regulated speed in air up to 1073 K and its TG behaviour was compared with an adsorbed sample prepared with the solvent dichloromethane on the zeolite support. The IR spectra of the two adsorbed samples were recorded in KBr between 5000 and 650 cm^{-1}, and comparisons were made with the IR spectra of the preheated residues of the original samples after twice heating up to 1073 K.

The kinetic parameters derived from the TG data of the adsorbed samples along with their preheated residues and the IR spectral bands are summarized in Table 1.

EXPERIMENTAL

Details of sample preparation using synthetic zeolite 3A ($K_{12}Al_{12}Si_{12}O_{48} \cdot 21\ H_2O$) have been reported previously [5]. The TG data were recorded on a thermobalance provided by FCIL, Sindri, at a heating rate of 10°C min^{-1}. The residues obtained after the initial heating up to 1073 K were once again used for TG analysis, giving second residues. These TG plots are shown in Figs. 1 and 2. The IR spectra of the six samples, including the original and preheated residues, were recorded on a Spektromom 2000 spectrophotometer in KBr pellets and are shown in Figs. 3 and 4.

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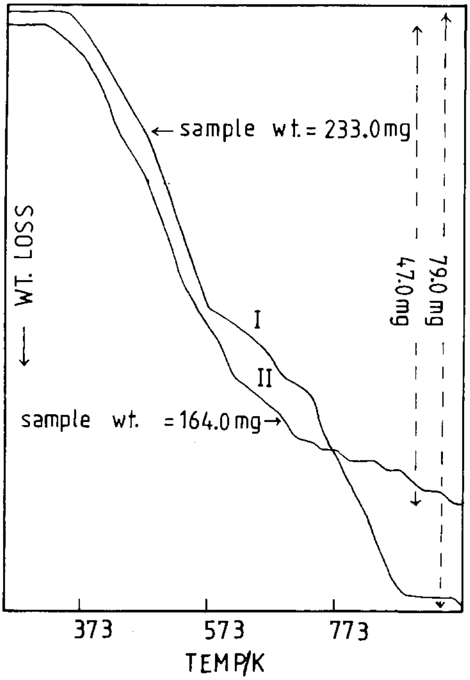
TABLE 1

TG data, kinetic parameters of thermochemical processes and IR spectral data

Zeolite	Wt. loss (%)	Temp. limits (K)	Rate of reaction from g(α) vs. time plots ($\times 10^{-2}$ min^{-1})			Activation energy from ln[g(α)/T^2] vs. 1000/T plots (kJ mole^{-1})			IR bands (cm^{-1})
			$n = 1$	$n = 2$	$n = 3$	$n = 1$	$n = 2$	$n = 3$	
Pyridinium chlorochromate adsorbed 3A (yellow)	17.6	333–573	15.5	5.3	3.2	45.1	30.8	26.0	3300, 1650, 1440sh, 1000, 780sh
	4.7	573–733	1.5	1.0	0.81	45.9	34.7	31.7	
	11.6	733–893	2.6	3.4	3.3	329.2	173.7	125.3	
	0.4	953–973							
Preheated 1st residue	2.6	573–673	7.0	3.3	2.2	71.8	46.9	39.5	3200, 1640, 1000
	8.3	Many other small steps below 573 and above 673							

Preheated 2nd residue									3000, 1580, 940
Dichloro-methane adsorbed 3A (white)	3.1	333–393	26.8	7.8	4.3	36.0	24.8	21.1	3300, 2300–1920, 1400sh, 1000
	7.9	393–493	12.8	5.1	5.3	48.2	32.5	27.2	
	12.8	493–693	3.9	2.7	2.0	71.6	46.8	38.7	
	1.2	693–713	2.5	3.0	2.5	157.1	95.2	71.4	
	4.3	Other minor steps beyond 713							
Preheated 1st residue	10.2	473–613	9.9	5.2	3.6	87.6	53.1	42.8	3300, 1640, 1000
	8.5	Other small steps below 473 and above 613							
Preheated 2nd residue									3200, 1640, 1000



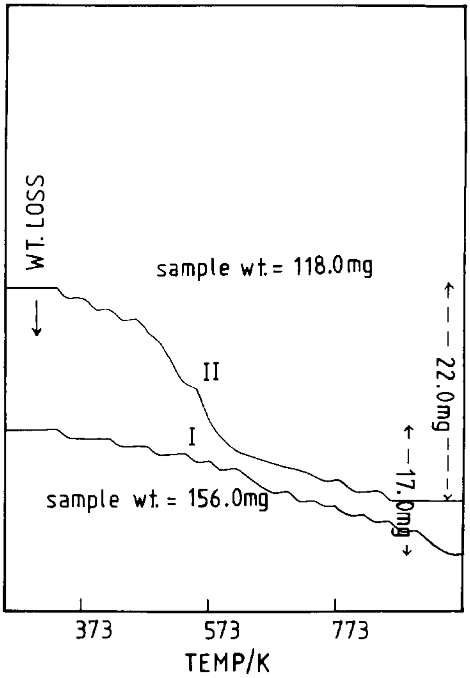


Fig. 1. TG plots of: I, pyridinium chlorochromate adsorbed derivative of zeolite 3A; and II, dichloromethane adsorbed zeolite 3A.

Fig. 2. TG plots of: I, the preheated yellow derivative; and II, the preheated white derivative of zeolite 3A.

RESULTS AND DISCUSSION

The TG plot of the air-dried pyridinium chlorochromate adsorbed zeolite 3A (yellow) shows mainly four major thermal events due to the loss of

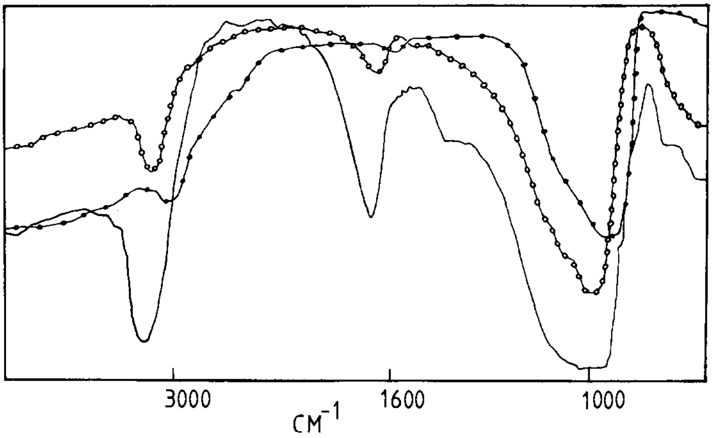


Fig. 3. IR spectra of: (————) the original yellow adsorbed zeolite 3A; (–O–O–) its first preheated residue; and (–●–●–) its second preheated residue.

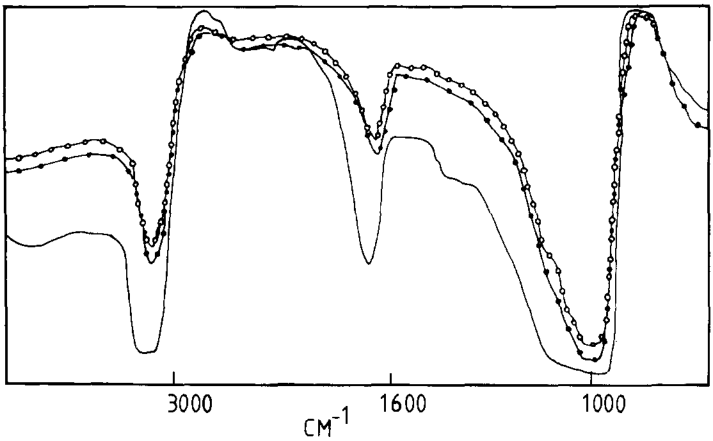


Fig. 4. IR spectra of: (———) the original white adsorbed zeolite 3A; (–O–O–) its first preheated residue; and (–●–●–) its second preheated residue.

organic solvent, dichloromethane, and physically adsorbed water up to 573 K, further dehydration and decomposition of adsorbed species up to and beyond 733 K. The third major event can be further resolved on the basis of kinetic parameters over two successive temperature limits, 733–833 K and 833–893 K. Due to a continuous weight loss step sequence, the different thermochemical processes are not easily distinguishable. The distinction is possible only due to differing kinetics evaluated from TG data. But the last weight loss of 0.4% occurs after an interval of 70°C and proceeds till 973 K due to residual desorption.

The first residue obtained after heating the yellow derivative up to 1073 K behaves quite differently on further TG analysis, with a continuous weight loss sequence only between 573 and 673 K. The weight loss attributed to dehydration and desorption takes place also over short ranges of temperature and in a number of small steps below 573 K and above 673 K. This typical thermal behaviour of the preheated residue is comparable with the preheated residue obtained with the adsorbed derivative formed after interaction of Ni(II) and Fast Sulphon Black F [6]. However, the zeolite derivatives are stable even after heating them twice up to 1073 K. A new inclusion complex with mainly CrO_3 is the final product of the thermochemical processes.

The dichloromethane adsorbed zeolite 3A sample also exhibits continuous weight loss steps up to 713 K, and the four events distinguishable from the kinetic parameters are due mainly to dehydration. The solvent is quite volatile. Beyond 713 K there are small weight loss steps (at least five) due to resultant structural changes brought about by heating. The adsorption of the organic solvent gives rise to this characteristic thermal behaviour of multi-step weight loss over short ranges of temperature. The adsorption of both the yellow organic reagent in dichloromethane and the solvent by itself and the subsequent thermal action result in changes in the aluminosilicate framework of the zeolite adsorbent and this fact is corroborated in the IR spectra of the adsorbed and their preheated samples.

The decrease in intensities of IR absorption bands at 3400 cm^{-1} and 1640 cm^{-1} and clear shifts towards lower frequencies as a result of heating the adsorbed derivatives repeatedly indicate structural changes. The absorption band at 1000 cm^{-1} is related to the Si/Al ratio in the zeolite framework [7] and a decrease in this frequency is mainly due to the increase in aluminium in the aluminosilicate tetrahedra. Adsorption of pyridinium chlorochromate reagent gives rise to shoulders around 1440 cm^{-1} and 780 cm^{-1} in the IR spectra and a broad shallow band appears in the solvent adsorbed sample around 2300–1920 cm^{-1}. These bands disappear on heating and signify external linkages of the adsorbed species in the zeolite adsorbent.

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