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Note

THERMOGRAVIMETRIC, IR SPECTROSCOPIC AND X-RAY DIFFRACTION STUDIES OF FURIL α-DIOXIME–NICKEL(II) COMPLEX SUPPORTED ON SYNTHETIC ZEOLITE 3A

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Soule [1] was among the first to use furil α-dioxime reagent for estimating nickel(II) in the form of a stable chelate. The present work deals with this chelate-forming reaction supported on synthetic zeolite 3A in powder form so as to characterize the desorption phenomena of the new derivative by TG analysis and structural elucidation by IR spectroscopic and X-ray diffraction methods. Similar studies of complex-sorbed derivatives of zeolite 3A have been reported recently [2,3].

EXPERIMENTAL

An aqueous solution of nickel(II) sulphate heptahydrate was interacted with an alcoholic solution of the organic reagent, furil α-dioxime, in the supporting medium of synthetic zeolite 3A ($K_{12}Al_{12}Si_{12}O_{48} \cdot 21\ H_2O$) over a water bath. After filtering and air-drying (~ 100°C) the new reddish-yellow derivative was subjected to TG analysis on a DuPont 900 thermal analyzer at a heating rate of 10°C min^{-1} up to 500 °C. The TG plot is shown in Fig. 1 and the relevant thermal data are given in Table 1. The IR spectra of this derivative and the residue after heating to 500°C were recorded on a UR-10 Carl-Zeiss Jena spectrophotometer using 2 mg of the samples and 1 g

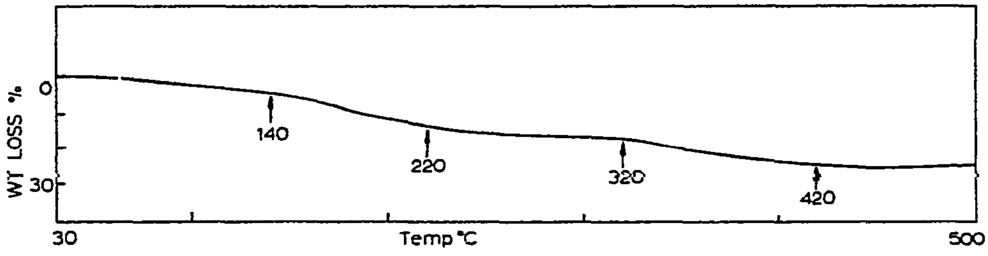

Fig. 1. TG plot of (furil α-dioxime)$_2$Ni(II) complex supported on zeolite 3A. Sample weight = 12 mg.

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TABLE 1

TG data and kinetic parameters for (furil α-dioxime)$_2$Ni(II)-zeolite 3A

Temp. range (K)	Wt. loss (%)	Rate constants ($\times 10^{-2}$ min^{-1})		Activation energy (kJ mole^{-1})	
		$n=1$	$n=2$	$n=1$	$n=2$
333–413	5	17.4	5.5	33.0	23.4
413–493	9	15 6	7 6	75.9	46.7
493–593	3	1 9	1.5	45.4	33.0
593–683	7	3.4	4.2	197.0	110.1

of KBr between 4000 and 400 cm^{-1}. The spectra are reproduced in Fig. 2. The X-ray diffractogram of the chelate sorbed on zeolite 3A was obtained at a scanning speed of 2° cm^{-1} and chart speed of 2 cm min^{-1} with copper target and a range of 2×10^3 c s^{-1}. Intensities and d spacings with respect to

TABLE 2

X-Ray data for (furil α-dioxime)$_2$Ni(II)-zeolite 3A

Data from ref. 7			This work	
d(Å)	I/I_{max}	hkl	d(Å)	I[a]
12 15	100	100	12.28	vs
			10.78	w
8 78	30	110		
7.15	30	111	7.14	w
	5	210		
	20	211		
	2	220		
4 11	80	300	4.11	m
3 91	90	310	3.90	w
3.72	10	311	3.71	vs
3.42	80	320	3.43	w
3.30	10	321	3.30	s
3 10	70	400	3 08	w
3.00	70	322	2.99	s
2.89	20	330	2.90	w
2.76	20	420	2.76	w
2.69	15	421	2.68	w
2.52	50	422	2.52	w
		430		
		431		
2.40	70	333	2.41	w

[a] vs = very strong; s = strong; w = weak; m = medium.

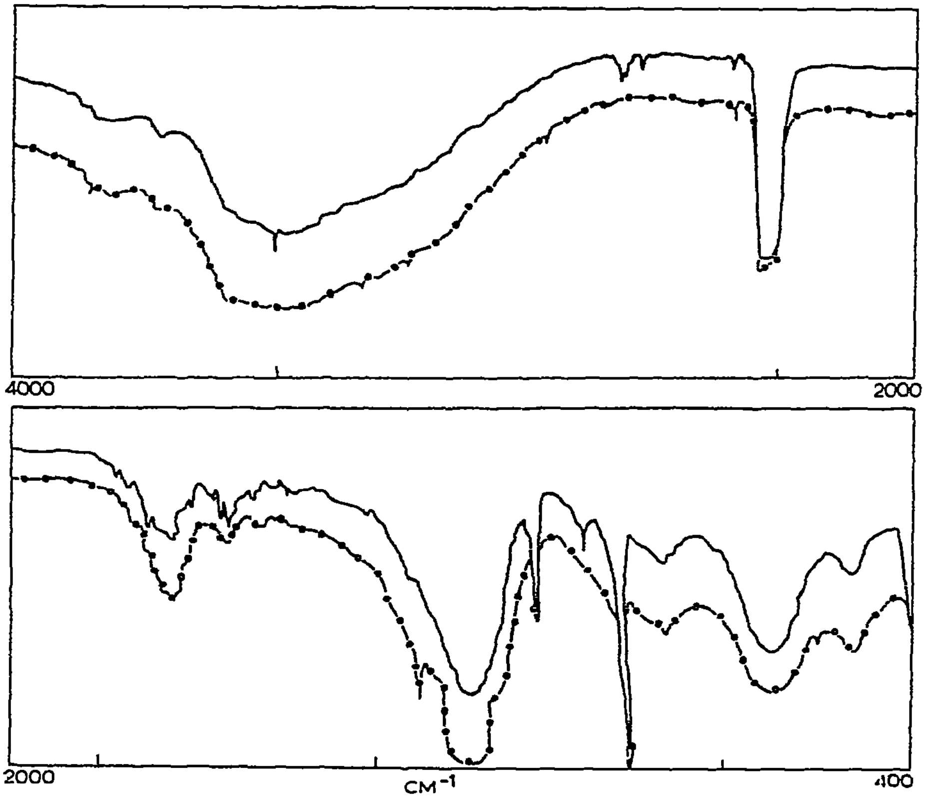

Fig. 2. IR spectra of the derivative (———) and the residue after heating to 500°C (·—·—·).

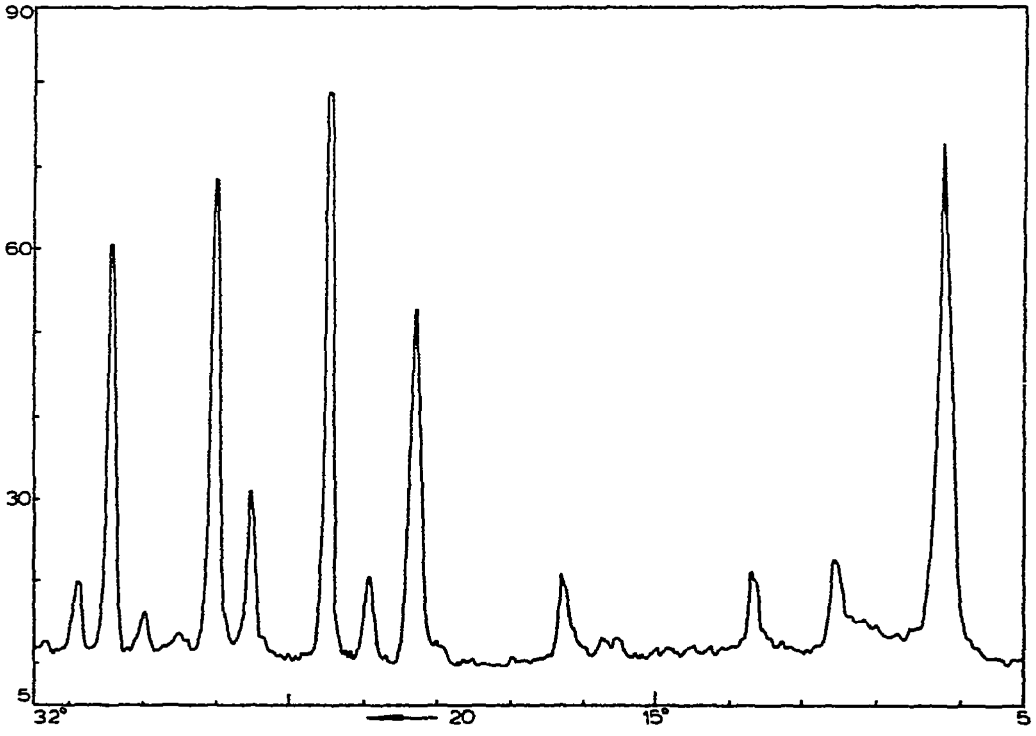

Fig. 3. Part of the X-ray diffractogram of the chelate sorbed on zeolite 3A.

CuK_α radiation of wavelength 1.5418 Å from 2θ values were tabulated from this diffractogram (Fig. 3) and are given in Table 2.

An air-dried sample of the chelate supported zeolite was strongly heated in a nickel crucible for several hours which resulted in a very light greyish residue. This residue and the original sorbed derivative were dissolved (50 mg in 40 ml) in dilute nitric acid solution and their optical densities were recorded against wavelength (nm) on a photoelectric spectrophotometer.

RESULTS AND DISCUSSION

The thermal behaviour of both nickel sulphate heptahydrate and (furil α-dioxime)$_2$ nickel(II) chelate has been reported by earlier workers [4–6]. For the heptahydrate, dehydration occurred in several steps at lower temperatures, and decomposition and oxide formation occurred only above 700°C. The Ni(II) chelate, however, decomposed around 100°C and gave the metallic oxide around 950°C. The thermal behaviour of the present sample is somewhat different. The TG plot of the (furil α-dioxime)$_2$Ni(II) chelate sorbed on zeolite 3A exhibits weight-loss steps from 60°C, with three clear breaks at 140, 220 and 320°C. First, loss of water and alcoholic solvent takes place, followed by partial decomposition of the chelate and further dehydration and decomposition. The kinetic parameters of these thermal events, calculated for $n = 1$ and 2, and weight-loss (%) steps are tabulated in Table 1. Part of the chelate remains as the included species in the zeolite supporting medium when heated gradually at 10°C min^{-1} up to 500°C. The IR spectra of the residue remaining on the TG balance show characteristics identical with the original sorbed sample and confirm the presence of the chelate in both. The strong band around 2340 cm^{-1} is attributed to OH stretching, as found in nickel(DMG)$_2$ chelate [6]. The stretching of the already broad peak at 3400 cm^{-1} indicates hydrogen bonding. The almost square and well-shaped band, especially in the case of the preheated zeolite, suggests inclusion in the aluminosilicate cage.

When the chelate sorbed on zeolite 3A is heated strongly over a burner, decomposition is more extensive and more or less complete. Spectrophotometric studies show that the λ_{max} of the original unheated sample shifts from 410 nm (violet region) to 520 nm (green region) in the case of the preheated sample. This shift is an indication of the nature of the thermochemical change in the sorbed derivative as a result of direct heating. The optical density of the preheated sample is considerably reduced as compared to that for the original derivative. At 410 nm it is about one-ninth of the value for the unheated sample.

X-ray diffraction powder patterns of synthetic zeolite 3A and its Ni(II)-exchanged form have been determined earlier [7]. The X-ray data obtained in the case of the (furil α-dioxime)$_2$Ni(II)-chelate sorbed on zeolite 3A are compared with those found earlier for Ni(II)-zeolite 3A. Differences in these data could be ascribed to structural changes brought about by the included species of the nickel chelate in zeolite 3A.

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