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Note

THERMOGRAVIMETRIC MÖSSBAUER AND IR SPECTROSCOPIC AND OPTICAL REFLECTANCE STUDIES OF TRIS-(4,7-DIPHENYL-1,10-PHENANTHROLINE)-IRON(II) COMPLEX SUPPORTED ON SYNTHETIC ZEOLITE 3A

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Lunsford [1] has characterized the formation of many transition metal complexes in zeolite cavities. Others [2,3] have studied the thermochemical behaviour of zeolite inclusion complexes. Metals, especially the noble metals, and their complexes, supported on inert materials like zeolites have found wide-ranging uses in heterogeneous catalysis reactions.

The present paper deals with the study of the complex tris-(4,7-diphenyl-1,10-phenanthroline)–iron(II) in zeolite 3A ($K_{12}Al_{12}Si_{12}O_{48} \cdot 21\ H_2O$) supporting medium from thermogravimetric, IR and Mössbauer spectroscopic, and optical reflectance data. 4,7-Diphenyl-1,10-phenanthroline (bathophenanthroline) is a well known extracting agent for the spectrophotometric determination of Fe(II) ions [4]. The organic reagent forms a dark red 1:3 chelate with five-membered rings and fairly high stability with an absorption maximum at 533 μm.

Comparison of the complex-sorbed 3A with its preheated (~ 1073 K) form gives an indication of the thermal behaviour of the sorbed species. TG data have been used to evaluate the kinetic parameters and energies of activation of the thermochemical processes [5].

EXPERIMENTAL

A portion of synthetic zeolite 3A in powder form (Union Carbide Corp., U.S.A.) was first soaked and heated on a water bath with an ethanolic solution of the organic reagent, AnalaR bathophenanthroline. The zeolite was filtered and air-dried by means of an electric air-dryer. This sample was interacted with an aqueous solution of AnalaR iron(II) sulphate heptahydrate at the temperature of the water bath. The red complex formed gave the zeolite a light yellowish brown colour after sorption. The sorbed derivative was filtered from the supernate and air-dried on a filter paper by an electric air-dryer.

Thermogravimetric analysis was carried out at a heating rate of 10°C min^{-1}

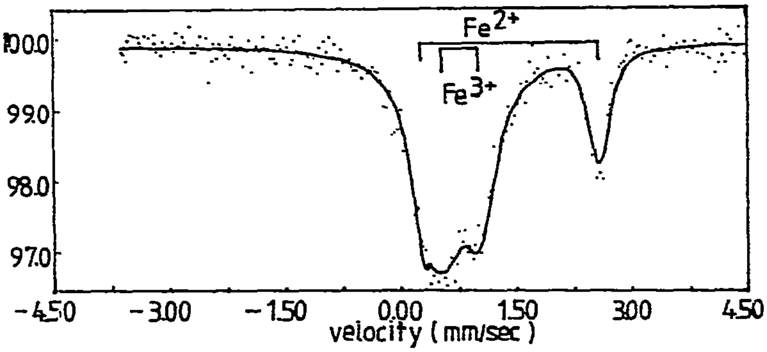

Fig. 1. Mössbauer spectrum of the complex-supported zeolite 3A.

TABLE 1

Mössbauer Parameters

IS [a] (mm s^{-1})	Half-line width at half height (mm s^{-1})	QS (mm s^{-1})	Relative area (%)
1.405(7) [b]	0.166(11)	2.317(13)	28.7(2.3)
0.759(8)	0.299(15)	0.467(13)	71.3(4.1)

[a] With respect to sodium nitroprusside.

[b] Figures in parentheses are standard deviations in terms of least significant figures.

between 293 K and 1073 K in air using a thermobalance supplied by the Fertilizer Corporation of India, Sindri. Optical reflectance studies were done in magnesium oxide using a VSU-2P type spectrophotometer between 200 and 1000 nm. IR spectra were obtained on a UR-10 Carl-Zeiss Jena spectrophotometer with 2 mg of the sample and 1 g of KBr between 4000 and 200 cm^{-1} frequencies. For these investigations the original complex-sorbed 3A and its residue left on the TG balance after heating to 1073 K were used. It was observed that the yellowish-brown colour of the sorbed derivative first became reddish-brown and then dark brown as a result of thermal changes. The Mössbauer spectra and the parameters obtained from the computer are with respect to sodium nitroprusside and reproduced in Fig. 1 and Table 1, respectively.

RESULTS AND DISCUSSION

Thermogravimetric data

The TG plot, as shown in Fig. 2, clearly distinguishes the thermal events. The zeolite sample begins to lose weight around 373 K and the first step loss proceeds till about 473 K mainly due to dehydration. Beyond 473 K and up to 633 K there are two distinct, yet almost similar rate of weight-loss steps. Coördinated water molecules are lost followed by decomposition of the hydroxo-iron complex, leaving an orange coloured residue which is stable up to 753 K. The horizontal in the TG plot confirms this fact. This residue is almost totally the oxidized Fe(III) complex of bathophenanthroline, which starts to decompose, with burning of the organic constituent, fom about 753 K and this process continues till about 813 K. No more weight-loss steps are obtained till 1073 K. The dark brown residue beyond 813 K. is mainly Fe(III) oxide with a little carbide. The 5.2% weight loss, in the temperature range 753 K–813 K, corresponds to decomposition of the complex and sedimenta-

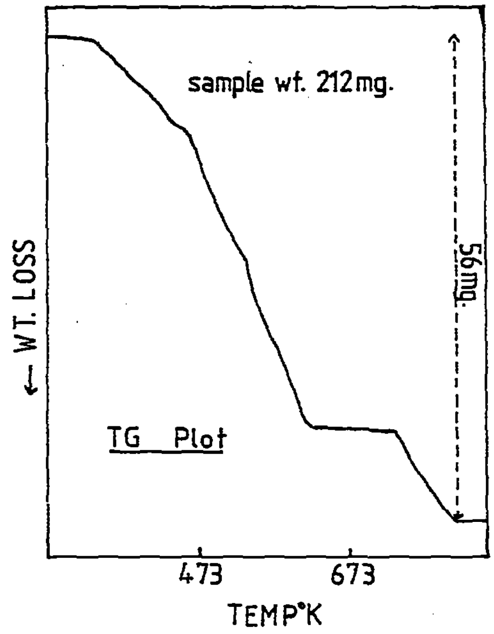

Fig. 2. TG plot of tris(bathophenanthroline)–iron(II) complex on zeolite 3A.

TABLE 2

Weight loss steps and kinetic parameters of thermochemical processes

Total wt. loss (%)	Wt. loss steps with temp. range and % loss	Rates of reaction ($\times 10^{-2}$ min^{-1})	Activation energy (kJ mole^{-1})	Thermochemical processes
26.4	1. 373–473 K; 4.7	5.1	27.1	Mainly dehydration and preliminary decomposition of hydroxo-complex.
	2. 473–553 K; 7.1	5.1	43.8	
	3. 553–633 K; 9.4	5.1	72.0	
	4. 753–813 K; 5.2	4.5	192.3	Partial decomposition of complex followed by sedimentation of mixed residue.

tion of a complex residue of mainly Fe(III) oxide. The first three weight-loss steps corresponding to 21.2% loss between 373 K and 633 K are due to both dehydration and preliminary decomposition.

Non-linear plots are obtained for $n = 1$, 2 and 3 for $\log_e[-(1-\alpha)^{1/n}]$ vs. time values. Almost uniformly similar rate constants are evaluated from these plots over the temperature ranges 373 K–473 K, 473 K–553 K, 553 K–633 K, and 753 K–813 K. Straight lines are obtained over the same temperature ranges when $\log_e\{\log_e[-(1-\alpha)^{1/n}/T^2]\}$ values are plotted against $10^3/T$ values, indicating first-order thermochemical processes due to dehydration, decomposition and oxidation. Table 2 includes the thermal data and kinetic parameters of the thermal events as calculated from these plots for $n = 2$.

Optical Reflectance Data

The absorbance vs. wavelength (nm) plots of the sorbed derivative of zeolite 3A and its preheated residue (Fig. 3) show that both the samples exhibit absorbance maxima at 400 nm. However, only a slight variation in absorbance data is observed between 400 and 460 nm in the case of the preheated residue. This may be attributed to the sedimented residue in the zeolite cavities after the decomposition of the sorbed bathophenanthroline complex beyond 753 K.

IR Spectroscopic Data

Schilt and Taylor [6], in their investigations of 1,10-phenanthroline complexes of many metal perchlorates found that intense bands were obtained at 724, 846, 1085 and 1431 cm^{-1} for tris-(1,10-phenanthroline)–Fe(II) complex. These bands are

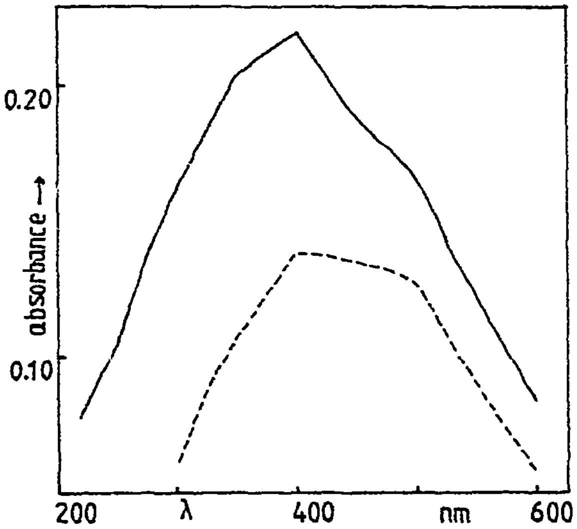

Fig. 3. Absorbance vs. wavelength (nm) for ————, the complex-supported zeolite 3A before heating and - - - - - -, its preheated form.

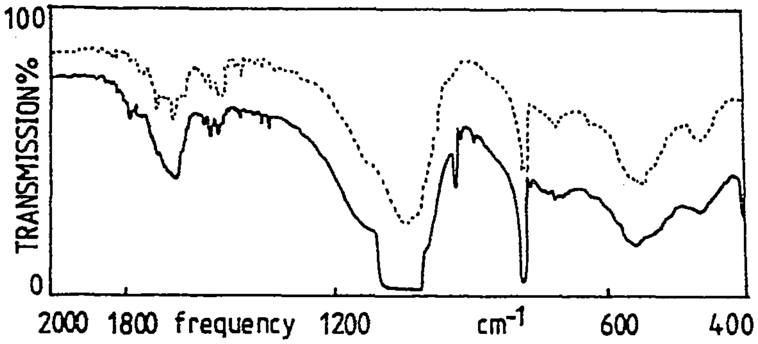

Fig. 4. IR spectra of ———, the complex-supported zeolite 3A and - - - - - -, its preheated form.

clearly observed in the IR spectra of the tris-(bathophenanthroline)–Fe(II) complex-sorbed zeolite 3A (bold line plot in Fig. 4) with slight variation in the intensity of the band around 1431 cm^{-1}. The band around 846 cm^{-1} disappears in the case of the preheated residue (broken line plot in Fig. 4). This shows partial decomposition of the organic reagent. The sorbed derivative of zeolite 3A prior to heating shows broadening of the band around 1000 cm^{-1} due to stretching vibrations of Si–O. This suggests at least partial chemisorption of the complex species in the zeolite pores.

Mössbauer Spectroscopic Data

The presence of both Fe(II) and Fe(III) is indicated in the Mössbauer spectra obtained at room temperature. Small quantities of Fe(III) can be due to the presence of the hydroxo-complex in aqueous medium and partial oxidation of Fe(II) complex to Fe(III) form as follows

$$[\mathrm{Fe(II)(bathophen)_3}] - e = [\mathrm{Fe(III)(bathophen)_3}]$$

Mössbauer data fail to specify if both the iron species are in or on the zeolite. However, thermal data, combined with the IR spectra and optical reflectance plot of the preheated sorbed derivative, indicate at least partial chemisorption. While most of the mixed residue as a result of thermal action forms a sediment on the zeolite surface, partial inclusion occurs in the zeolite cavities. The zeolite remains stable even after heating to 1073 K.

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