

Note**CATALYTIC OXIDATION REACTION SUPPORTED ON SYNTHETIC ZEOLITE 3A. A STUDY BY MÖSSBAUER SPECTROSCOPIC, X-RAY DIFFRACTION, REFLECTANCE AND THERMOGRAVIMETRIC METHODS**

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(Received 25 March 1982)

3,3'-Dimethylnaphthidine is an useful redox indicator for zinc(II) vs. potassium hexacyanoferrate(II) titration. It has also been used in other redox titrimetric methods [1–3]. The oxidised form of the indicator has a purple-red colour and the reduced form is colourless. However, the colour change observed at the end-point is from purple-red to greyish-green owing to the presence of excess hexacyanoferrate ions. A solution of this indicator in glacial acetic acid was sorbed on synthetic zeolite 3A and interacted with aqueous potassium hexacyanoferrate(II) solution at the temperature of the water bath. The interaction resulted in the formation of a dark blue product resembling Prussian blue. The thermochemical behaviour of this new product on 3A has been reported on the basis of thermogravimetric analysis and X-ray diffraction and Mössbauer spectroscopic data obtained with it have been incorporated for its characterisation. Reflectance data of the new product before and after heating in a nickel crucible have been used for determining the nature of the thermochemical changes.

EXPERIMENTAL

A portion of zeolite 3A in powder form was first heated with 3,3'-dimethylnaphthidine, Analar, in glacial acetic acid on a water bath. The filtered and dried zeolite sample with the sorbed indicator was next treated with an aqueous potassium hexacyanoferrate(II) solution and heated once again on a water bath. An immediate colour change occurred resulting in the sedimentation of a dark blue product. This new zeolite derivative was filtered and dried in hot air from an air dryer. Simultaneously, the indicator solution in glacial acetic acid was similarly heated on a water bath with an aqueous

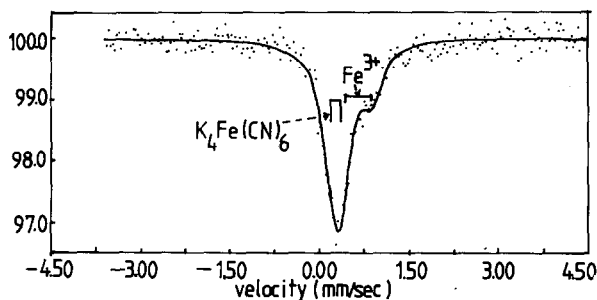


Fig. 1. Mössbauer spectra of DMN and $K_4Fe(CN)_6$ interacted zeolite 3A.

potassium hexacyanoferrate(II) solution. This interaction, however, did not produce the observed colour change in the presence of the zeolite support.

Mössbauer spectroscopic data of the dark blue product supported on zeolite 3A were obtained at room temperature and the parameters evaluated. Figure 1 and Table 1 show the Mössbauer spectra and the Mössbauer parameters of this new product. An X-ray diffractogram (Fig. 2) for this product was obtained at chart and scanning speeds of 2 cm min^{-1} and 2° min^{-1} , respectively, and a range of 400 c s^{-1} . The X-ray data evaluated from 2θ values with respect to CuK_α radiation of wavelength 1.5418 \AA are given in Table 2. The TG data of the indicator-sorbed zeolite and its potassium hexacyanoferrate(II)-interacted form were obtained on a Thermobalance supplied by FCIL, Sindri, at a heating rate of $10^\circ \text{C min}^{-1}$ in air. The two TG plots are reproduced in Fig. 3.

A part of the new product supported zeolite 3A was heated in a nickel crucible for several hours. The resultant dark brown residue, alongside the

TABLE 1

Mössbauer parameters

Isomer shift ** (mm sec^{-1})	Half line width at half height (mm sec^{-1})	Quadrupole shift (mm sec^{-1})	Relative area (%)
0.263 (9) *	0.166 (18)	0.160 (23)	57.8 (8.0)
0.647 (58)	0.266 (58)	0.439 (63)	42.2 (10.4)
	OR		
0.528 (26)	0.190 (32)	0.704 (40)	32.5 (6.3)
0.329 (9)	0.225 (24)	0.000 (0)	67.5 (7.8)

* Figures in parenthesis are standard deviations in terms of least significant figures.

** With respect to sodium nitroprusside.

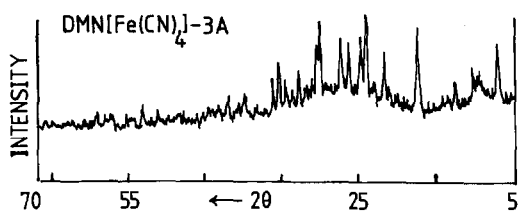


Fig. 2. X-Ray diffractogram of DMN and $K_4Fe(CN)_6$ interacted zeolite 3A.

original sample were both used for optical reflectance studies in magnesium oxide. The data were recorded on a VSU-2P type spectrophotometer between 200 and 1000 nm. The absorbance vs. wavelength plots are shown in Fig. 4. The iron content in the zeolite samples before and after heating were determined from their solutions in aqua regia on a Beckman Model 1272

TABLE 2

X-Ray data for zeolite 3A

Ref. 6			This work	
d (Å)	I/I_{max}	hkl	d (Å)	I
12.30	100	100	12.28	s
8.81	70	110	8.67	m
7.20	30	111	7.03	m
5.53	20	210	5.10	s
5.03	5	211	4.08	m
		220		
4.38	35	300		
3.73	60	311	3.68	vs
3.44	25	320	3.39	s
3.26	20	321	3.27	s
3.00	55	322	2.96	s
2.91	10	330	2.94	vs
2.77	25	420	2.75	s
		421		
2.63	10	332		
2.53	10	422	2.54	m
2.19	5	440	2.15	m
		442	2.10	w
1.92	10	443	1.91	w
1.86	5	630		
1.75	5	550	1.75	w
1.69	5	552	1.66	w

Atomic Absorption spectrophotometer and were found to be 7.46 and 6.47%, respectively.

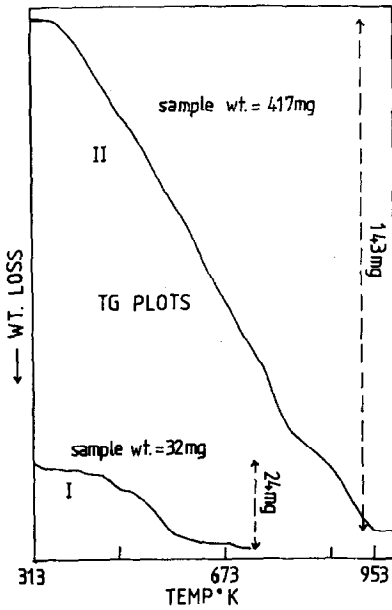


Fig. 3. TG plots for I, DMN sorbed zeolite 3A and II, its $K_4Fe(CN)_6$ interacted form.

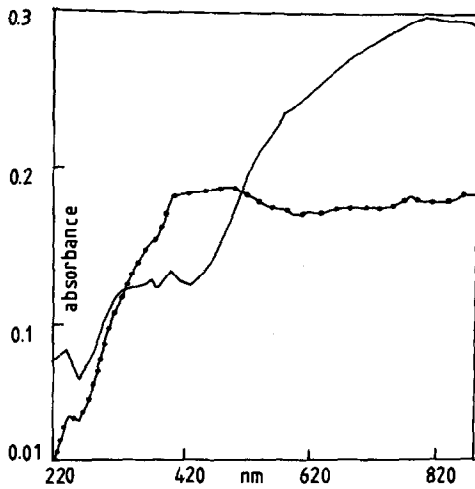
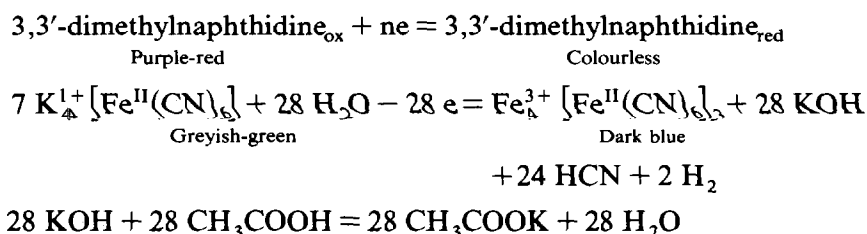


Fig. 4. Absorbance vs. wavelength (nm) plots. —, DMN and $K_4Fe(CN)_6$ interacted zeolite 3A; ●-●-●, preheated form.

RESULTS AND DISCUSSION

The investigations carried out on the zeolite derivative supporting the interacted species indicate that a new product with a composition similar to Prussian blue is formed as a result of catalytic oxidation of potassium hexacyanoferrate(II). The supporting medium of zeolite 3A with the sorbed redox indicator acts like an electron-exchanger bringing about this oxidation. The regular crystalline and internal porous structure of the zeolite permits the diffusion and interaction of the reactants leading to the formation of the dark blue pigment. Under similar conditions but without the zeolite, no Prussian blue is formed after the interaction between the oxidised form of 3,3'-dimethylnaphthidine and potassium hexacyanoferrate(II). The following mechanism for the zeolite supported reaction can be suggested.



The Mössbauer spectra of the zeolite support after the interaction of the sorbed indicator and potassium hexacyanoferrate(II) show the presence of both Fe(II) and Fe(III) forms as indicated by the asymmetric splitting of the spectra [4,5]. The d spacings and intensities obtained from the X-ray diffractogram of the zeolite sample have been compared with the X-ray data of zeolite 3A [6] in Table 2.

Of the d spacings found with the new zeolite derivative 7.03, 5.10, 3.68, 3.27, 2.96, 2.50, 2.15, 1.91, 1.73 are also found in the X-ray diffraction pattern of Fe(II)-exchanged zeolite 3A [6].

The presence of the redox indicator as sorbed species in the zeolite is indicated by the IR spectral data obtained from 5000 to 650 cm^{-1} in KBr. Strong bands at 3300, 1580 and 1480 cm^{-1} and weak ones at 1420 and 1360 cm^{-1} are visible owing to NH groups, C-H stretching and C=C stretching vibrations in the aromatic ring as well as C-H deformation and C-CH₃ group vibrations. A very prominent and broad band between 1300 and 840 cm^{-1} is found for the usual Si-O and Al-O bond vibrations.

The TG plot of the indicator-sorbed 3A exhibits two major weight loss steps, from 433 to 493 (15.6%) followed by 493 to 633 (46.9%). These steps can be attributed to dehydration and desorption of acetic acid. A further 3.1% weight loss occurs at 673 K due to the decomposition of dimethylnaphthidine. Minor weight loss steps are observed due to initial dehydration and

desorption of acetic acid around 373 and 393 K. The earlier weight loss steps account for 9.4% loss upto 413 K. The total loss of 75% indicates a very high degree of sorption. From the variations in the rate of weight loss four major events can be predicted for the zeolite sample supporting the products of the interaction with the indicator and potassium hexacyanoferrate(II). The first event, dehydration (6.0%) proceeds until 473 K. This is followed by a continuous weight loss step (16.6%) up to 713 K during which loss of acetic acid occurs and decomposition of the sorbed species commences. The third step, between 713 and 853 K, corresponds to the oxidation of the mixed products (7.0%). Decomposition of cyanogen (5.0%) proceeds from 853 K until a horizontal is obtained at 953 K. Due to the presence of other sorbed components the thermal behaviour of this zeolite derivative differs considerably from the known behaviours of potassium and other hexacyanoferrates [7-9].

There are three small peaks at 240, 370 and 400 nm in the absorbance vs. wavelength plot of the dark blue sorbed derivative of 3A before heating. There is a regular increase in the absorbance values from 435 and a maximum is attained at 800 nm. The plot represents a number of sorbed components in 3A. The plot obtained for the preheated sample shows the effect of thermal decomposition of the sorbed species and is quite different from the one obtained before heating. The two plots cross each other at 330 and 515 nm and in the two regions between 330 and 515 and beyond 515 nm the reflectance characteristics vary considerably.

The analytical data for iron in the two zeolite samples before and after heating indicate the formation of an insoluble iron compound as a result of heating. This residue can only be the oxide.

ACKNOWLEDGEMENT

The author is grateful to Dr. L.V.C. Rees of Imperial College of Science and Technology, London, for his assistance in the computation of the Mössbauer data.

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