

## Note

# Thermogravimetric, IR spectroscopic and X-ray diffraction studies of Cu(II)-interacted Deolite

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The commercial molecular sieve Deolite has been used as a dehydrating agent, but not for cation exchange or adsorption. The cation exchange studies of Deolite with K(I) and Ca(II) have already been carried out and reported [1]. The present paper describes an attempt to prepare the cation exchange derivative of Deolite with Cu(II) and to investigate this derivative by thermogravimetric, IR spectroscopic and X-ray diffraction methods.

## EXPERIMENTAL

The experimental details of the sample preparation using synthetic zeolite (Deolite) have been reported previously [2]). The composition was studied using a Shimadzu simultaneous X-ray fluorescence spectrophotometer. The TG analyses were performed on a Perkin–Elmer thermobalance, in air at a heating rate of  $150 \text{ K min}^{-1}$  upto 1173 K. IR spectra were recorded between 4000 and  $400 \text{ cm}^{-1}$  in KBr pellets and X-ray diffraction patterns were obtained between  $2\theta$  angles of 7 and  $60^\circ$ , using a Phillips PW1140 unit with a copper target. Most of the reflections were indexed for their (hkl) values using methods reported in the literature [3,4].

## RESULTS AND DISCUSSION

The analytical data for Deolite and its exchanged derivative are presented in Table 1.

Similar studies have been carried out for other synthetic zeolites [5–7]. The analytical data indicate an 80.71% exchange of sodium, expressed as  $\text{Na}_2\text{O}$ , from the original Deolite. The TG plots of the copper(II)-exchanged derivative give a total weight loss of 20.40%, of which the major steps of weight loss occur between 353 and 633 K. These steps can be attributed first to dehydration of physically adsorbed water, up to about 397 K, and then to loss of more closely held coordinated water molecules beyond 393 K; these steps are confirmed in the DTA and DTG plots. The DTA plot of this sample shows a very broad peak between the temperature limits mentioned

TABLE 1

Analytical data for composition (wt.%)

Zeolite	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	H <sub>2</sub> O	Si/Al	Exchange in terms of Na(I)
Deolite	41.82	22.59	14.00	1.08	20.51	1.67	—
Cu(II)-Deolite	41.95	24.55	3.51			1.51	80.71

TABLE 2

Thermal data for the copper-exchanged Deolite

Zeolite	Total weight loss	Wt. loss (%) at different temperatures	Rate of reaction (min <sup>-1</sup> )		Activation energy (kJ mol <sup>-1</sup> )	
			<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 1	<i>n</i> = 2
Copper(II)-Deolite	20.40	6.1 up to 393 K	$5.1 \times 10^{-1}$	$1.6 \times 10^{-1}$	65.0	39.3
		10.0 up to 573 K	$5.5 \times 10^{-2}$	$3.4 \times 10^{-2}$	56.8	37.4
		1.4 up to 633 K	$1.4 \times 10^{-2}$	$1.6 \times 10^{-2}$	70.1	46.2
		2.9 after 633 K	$2.7 \times 10^{-3}$	$3.5 \times 10^{-3}$	42.3	34.4

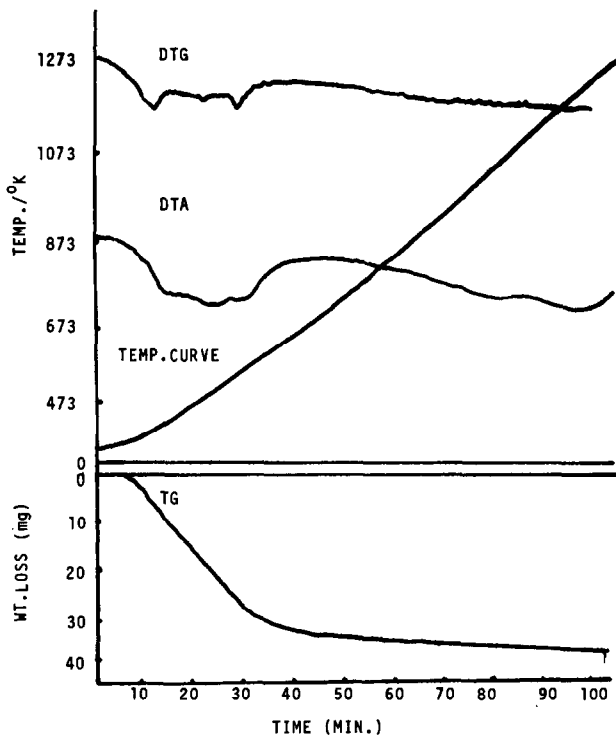


Fig. 1. Thermogram.

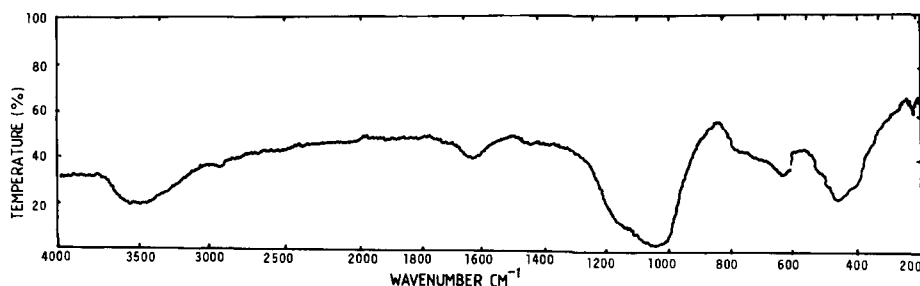


Fig. 2. IR spectra.

above, with two peaks at around 413 and 573 K, while the DTG plot also gives very well-defined peaks at these two temperatures. The weight loss beyond 573 K is the result of dehydration at a much slower rate; this is found at temperatures above 573 K in the case of most zeolites [8]. The

TABLE 3

Principal infrared frequencies ( $\text{cm}^{-1}$ )<sup>a</sup>

Original Deolite	Cu(II)-Deolite	Assignments
3620–3340(sb)	3600–3400(wb)	OH stretching
1630(s)	1620(s)	Sym. water bending
1000(sb)	1050–990(sb)	Asymmetric H–O stretching
650(s)	680(ms)	Symmetric H–O stretching
560(ms)	550(ms)	Double ring
440(sb)	420(s)	H–O bending

<sup>a</sup> Abbreviations: b, broad; m, medium; s, sharp; ms, medium sharp; w, weak.

TABLE 4

X-ray diffraction data for Cu(II)-Deolite

Peak	$d$ (Å)	$I/I_0 \times 100$	(hkl)
1	7.0810	20.0	(111)
2	5.7166	50.7	(210)
3	5.0107	10.8	(211)
4	4.3959	40.4	(220)
5	4.1140	10.8	(221) (300)
6	3.7855	50.7	(311)
7	3.3264	20.0	(320)
8	3.1865	20.0	(321)
9	2.8566	100.0	(410)
10	2.6749	20.3	(420)
11	2.5031	50.5	(422)
12	2.4422	10.9	(430)
13	2.3678	10.8	(511)
14	1.7744	20.0	(444)

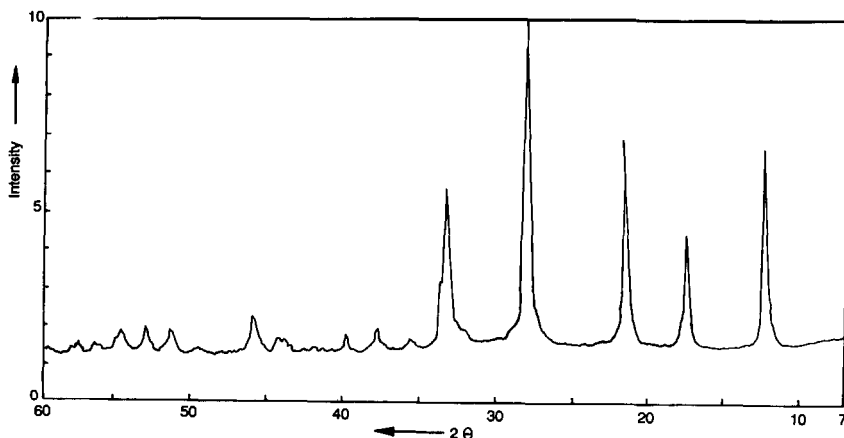


Fig. 3. X-ray diffractograms.

thermal data are listed in Table 2. The plots of  $-\log_e (1 - \alpha)^{1/n}$  against time are not linear for  $n = 1$  or 2, while the plots for  $-\log_e [g\alpha/T^2]$  against  $1000/T$  do yield straight lines, indicating first-order dehydration processes over a definite range of temperature (Fig. 1).

The IR spectrum of the exchanged derivative is identical to that of Deolite. Showing the common absorption bands for hydroxyl ( $3600\text{--}3500\text{ cm}^{-1}$ ), water molecules ( $1660\text{--}1600\text{ cm}^{-1}$ ) and the framework vibration of Deolite (below  $1300\text{ cm}^{-1}$ ) [9], see Fig. 2 and Table 3.

The X-ray diffraction powder patterns of Deolite have been reported earlier [1]. In the case of the Cu(II)-exchanged derivatives, the (100) and (110) reflections become completely diffused and indistinct although the crystalline structure is unaltered, see Table 4. The X-ray data show some similarities with the data reported for Cu(II)-exchanged zeolites [10], see Fig. 3.

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