Studies on Cu-EDTA adsorbed Dealuminated Scolecite

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Dealumination of natural zeolite scolecite has been done by strong HCl treatment. Aluminium is removed from the framework in soluble Al-EDTA form. Si/Al ratio increases from 1.56 to 3.05. Interaction of metal (Cu) and ligand (EDTA) on dealuminated scolecite has been done at suitable pH yielding Cu-EDTA complex on dealuminated scolecite phase. Dealuminated scolecite shows improved thermal stability and reasonably good crystallinity with slight change in lattice parameters.

Zeolites have been applied as heterogenous catalysts[1-4]. Their unique channel dimensions (pore diameter, <10 Å), thermal stability, non-reactive nature and cation-exchange and cation-selective properties lead to important catalytic activity[5] which makes them particularly useful to the oil and petrochemical industries. Zeolite encapsulated organometallic complexes represent a unique class of immobilised and heterogenised coordination compounds[6]. Extensive work has already been reported on dealumination, decationisation of zeolite[7] while enough literature is also available on ligand and coordination compounds supported on zeolite phases[8]. However, combined interaction of ligands and metal ions in strong acids (for dealumination) followed by ammoniation is not much known. Scolecite is natural fibrous zeolite with a chemical composition $Ca_8(AlO_2)_{16}(SiO_2)_{24}.24H_2O$. Scolecite has been used as catalyst for Cumene cracking[9] and as adsorbent for food dyes[10].

In the present work structural modifications of natural zeolite scolecite has been carried out by dealumination and Cu-EDTA complex interaction followed by ammoniation, keeping in view that such interacted scolecite derivatives have wide spread catalytic and adsorption applications.

Results and Discussion

Chemical analysis of the derivatives (Table 1) shows the extent of dealumination of zeolite phase. Strong acid treatment resulted in removal of aluminium from the frame

TABLE 1—ELEMENTAL ANALYSIS DATA

Sample	Ca wt%	Al wt%	Si wt%	NH$_4$ wt%	EDTA wt%	Metal wt%	Si/Al (molar ratio)
Scolecite[a]	10.21	13.75	21.47	–	–	–	1.56
Cu-EDTA-NH$_4$-scolecite[b]	1.31	7.18	24.12	2.20	6.50	1.08	3.23

[a]Sample is colourless; relative density = 2.30; refractive index = 1.532.

[b]Sample is blue coloured, relative density = 3.45; refractive index = 1.524.

work and finally out of zeolite structure in a soluble Al(EDTA) form due to the presence of excess EDTA in the solution[11]. The possible mechanism is reported as[12]

$$X\ H_4\ EDTA + Ca(AlO_2)(SiO_2)_y \rightarrow$$
$$X\ Ca\ Al\ EDTA.H_2O + Ca(AlO_2)_{1-x}(SiO_2)_y + H_2O$$
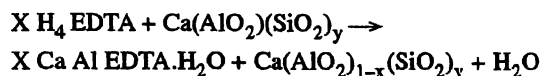
where, $x \leq 1$ and $y \geq 2.5$.

The analytical data of original scolecite and dealuminated Cu-EDTA and ammonium interacted samples show the decreased calcium content of the sample and its conversion into ammonium form. Analytical data also show significant metal and EDTA content in the prepared derivative of scolecite. The copper and EDTA contents of the prepared sample are in 1 : 1 molar ratio, thereby confirming formation of Cu-EDTA complex. The initial Si/Al molar ratio of 1.56 increased to 3.23 in the prepared sample confirming the more siliceous nature of the prepared sample. The emperical formula of the prepared sample derived on the basis of elemental analysis is

$$Cu_{0.53}EDTA_{0.55}(NH_4)_{3.80}Ca_{1.03}Al_{8.36}Si_{26.98}O_{68.86}.nH_2O.$$
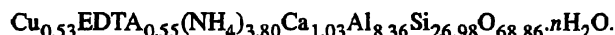
The original scolecite in pure condition is colourless. The prepared sample (Cu-EDTA-NH$_4$-scolecite) is blue in colour, due to the Cu-EDTA incorporation. The presence of aqueous ammonia intensifies the colour of the sample. The observed density of the untreated sample is 2.30, which increases to 3.45 in Cu-EDTA-NH$_4$-scolecite. The density of the zeolite phase is generally reported to be decreased after dealumination[13]. Increased density of the present derivative even after its significant dealumination is due to the incorporation of Cu-EDTA complex in zeolite. The refractive index of the original scolecite is observed to be slightly decreased in the treated derivative. This decrease is also an evidence of framework dealumination[14].

Ir studies : The ir absorption spectrum of Cu-EDTA-NH$_4$-scolecite consists of all the characteristic bands of the zeolite scolecite along with coordinated water[15]. The bands due to ammonia have also been observed (Table 2). The spectrum also shows several prominent absorption characteristics for EDTA complex of Cu^{2+}[16]. The OH stretching region of the spectrum shows bands at 3 755–3 400 cm^{-1}. The band at 3 755 cm^{-1} is attributed to silanol band (Si-OH modes). The medium intensity band at 3 660 cm^{-1} reflects the degree of dealumination[17]. In vibrational

region of the spectrum, the bands show higher frequency shift in comparison to the original scolecite. This is due to dealumination of zeolite structure. In this region, the most intense band is observed at 1 045 cm^{-1}. In comparison to original scolecite, this band has been found to be shifted by 10 cm^{-1} towards higher frequency side. This band is also reported sensitive to Si/Al ratio[18]. This higher frequency shift of the bands is due to increase in silica content in the treated derivative, as reported earlier[19].

TABLE 2–INFRARED ABSORPTION DATA (cm^{-1})

Assignment	Scolecite	Cu-EDTA-NH$_4$-scolecite
νOH	3 440	3 440
δH-O-H	1 640	1 640
ν_{asymm} (T-O)	1 035	1 045
ν_{symm} (T-O)	700	728
Double ring	580	600
δ(T-O)	440	445
Pore opening	370	–
$\nu \equiv$CH	–	3 170
ν-(Si-OH) modes	–	3 755
ν-(Al-OH) modes	–	3 660
ν-NH$_4^+$	–	2 990
δ_a -NH$_4^+$	–	1 485
δ_s-NH$_4^+$	–	1 430
ν(COO-M)	–	1 750
ν(COO-H)	–	1 660

Thermogravimetric analysis : The thermogravimetric data of the samples are summed up in Table 3. The prepared derivative shows three weight-loss steps with 16.6 wt% total loss. The first weight-loss step is fast and exists from 40 to 160° showing 6.40 wt% loss, which is due to the loss of physically adsorbed water. This significant weight-loss shows that the water adsorption capacity is increased in the Cu-EDTA-NH$_4$-scolecite derivative due to

TABLE 3–THERMOGRAVIMETRIC DATA

Sample	Total wt.-loss wt(%)	wt.-loss wt(%)	Temp. range °C	Rate of loss %/min
Scolecite	14.50	4.0	30–130	0.40
		4.0	160–275	0.34
		3.5	330–400	0.50
		3.0	400–660	0.12
Cu-EDTA-NH$_4$- scolecite	16.6	6.40	40–160	0.53
		7.00	160–520	0.19
		3.20	540–700	0.20

dealumination. It can be assumed that external surface increases due to dealumination process by the possible creation or fissures (defect sites) in the crystal[20]. The second weight-loss step of 7.00 wt% loss varies from 160 to 520°, which is due to the desorption of ammonia and decompo-

sition of Cu-EDTA complex. This is in good agreement with the work reported earlier that ammonia desorption takes place from 200 to 550° and EDTA decomposes between 150 and 400° depending on its derivatives[21]. The third weight-loss step at 540–700° corresponds to elimination of water molecules, i.e. elimination of structural hydroxyl groups by dehydroxylation. This weight-loss is comparatively more than that observed in the original scolecite. It indicates the formation of additional hydroxyl groups due to deammoniation of the derivatives. These hydroxyl groups are finally liberated with the original hydroxyl groups during dehydroxylation process in a temperature range 440–900° as reported earlier[22].

X-Ray diffraction studies : Using the X-ray diffraction data the unit cell dimensions and crystallinity of the acid-dealuminated Cu-EDTA-NH$_4$-scolecite derivative have been determined. Indexing of the *d*-spacing values clearly indicates the monoclinic system for the prepared derivative. The crystallinity of original scolecite was found to be affected after the treatment. Cu-EDTA-NH$_4$-scolecite sample shows significant loss of peak intensity and also the decrease in number of diffraction peaks in comparison to original scolecite. It is evident from Table 4 that the lattice parameters *a* and *c* remain same as in the original scolecite whereas the lattice parameter *b* shows reduction. Due to this, unit cell shrinkage occurs in dealuminated derivative[23]. The loss of crystallinity[24] is related with production of defect structure.

TABLE 4–STRUCTURAL DATA (BY X-RAY DIFFRACTION)

	Scolecite	Cu-EDTA-NH$_4$- scolecite
Crystal system	Monoclinic	Monoclinic
Lattice constants :		
a	9.848 Å	9.848 Å
b	19.978 Å	18.988 Å
c	6.522 Å	6.522 Å
β	110°	110°

Conclusions : The systematic modifications of molecular sieve zeolite by dealumination and metal complexes adsorption alters their properties in ways that can be advantageously explored for its applications as catalyst and adsorbent. The controlled dealumination of natural zeolite scolecite with concentrated HCl acid provides scolecite of the desired aluminium deficiency. Increase in density values and colour change confirms the incorporation of Cu-EDTA complex with the scolecite framework. Elemental analysis confirm that Si/Al molar ratio increases from 1.56 to 3.23 with about 50–60% framework dealumination. Shifting of the ir bands to higher frequency side and higher dehydroxylation loss in TGA also confirm dealumination

and structural modifications of natural zeolite scolecite. TGA also infers about the increased water sorption capacity of scolecite after dealumination which is due to increase in defect sites. X-Ray diffraction lines decreases due to production of defect structure after dealumination and unit cell parameter b is also reduced showing unit cell shrinkage due to dealumination of prepared Cu-EDTA-NH_4-scolecite derivative.

Experimental

The initial scolecite sample was fine white powder having composition $Ca_8(AlO_2)_{16}(SiO_2)_{24}.24H_2O$. The scolecite sample (10 g) was dissolved in 3 N HCl (100 ml) and the solution was heated for a few minutes.

A 0.15 M copper sulphate salt solution (10 ml) was mixed with EDTA solution (disodium salt, 20 ml) and acidic zeolite solution (50 ml). pH of the mixture was noted and it was shaken for 10 days. To it aqueous ammonia (sp. gr. 0.888) was added till the complete precipitation of the derivative. pH of the fluid was then increased from 1.75 to 6.9 during the NH_4OH treatment, and at the same time Cu^{2+} ions probably formed complex with EDTA while zeolite derivative separated out in its ammonium form. The precipitated sample was filtered and washed with hot redistilled water till the filtrate became free from the chloride ions, and dried at 70°.

The metal contents (Cu, Al, Ca) were determined by AES/ICP method. Silica content was estimated by difference, and N and carbon were estimated by a Perkin-Elmer analyser. Refractive index was measured by Abbe's refractometer and relative density of the sample determined by pycnometer. Infrared spectra (KBr) were recorded on a Perkin-Elmer spectrophotometer. Thermogravimetric analysis was carried out on a Perkin-Elmer thermal analyser at a heating rate of 10°/min in the temperature range 30–900°.

Acknowledgement

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