Asian Journal of Chemistry Vol. 9, No. 4 (1997), 752–757

Fe-EDTA Complex Supported on Aluminium-Deficient Scolecite

RASHMI JOSHI* and S.P. BANERJEE
Department of Chemistry
Dr. H.S. Gour University, Sagar-470 003, India

Highly dealuminated scolecite has been used to stabilize Fe-EDTA complex. Si/Al ratio of scolecite has been increased from 1.56 to 3.42 due to dealumination by mineral acid treatment. In-situ synthesis of Fe-EDTA complex on scolecite matrix has been proved on the basis of elemental analyses, infra-red spectroscopy, thermogravimetric and X-ray diffraction studies. Slight distortion in the symmetry of scolecite may be due to the chelate incorporation in the zeolite framework.

INTRODUCTION

The field of transition metal complexes in the zeolite matrices has been reviewed frequently.[1] Howe and Lunsford[2] synthesized complexes of Co(II) with ethylenediamine in zeolite cavities. Romanovsky *et al.*[3] have shown that faujasite supported phthalocyanine exhibit variety of marked catalytic properties. Recently dinitrogen complexes of rhodium have been synthesized on highly dealuminated Y-zeolite phase.[4]

Scolecite is a natural fibrous zeolite of natrolite group. It has been used as catalyst in Cumene-cracking.[5] The present study describes in detail the formation and properties of dealuminated and ammoniated scolecite products containing Fe-EDTA complex.

EXPERIMENTAL

The initial scolecite sample was fine white powder having composition $Ca_8(AlO_2)_{16}(SiO_2)_{24}\cdot 24H_2O$. The scolecite sample (10 g) was treated with 3 N HCl 100 mL and the solution was heated for a few minutes, then washed and dried.

A 0.15 M ferrous sulphate salt solution was mixed with EDTA solution and with acid treated zeolite. 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 Fe^{2+} ions probably formed

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*Address for correspondence: RRSSC/DOS, Post Box 439, Shankar Nagar, Nagpur-440 010, India.

complex with EDTA while zeolite derivative separated out in its ammonium form. Precipitated sample was filtered and washed with hot redistilled water till the filtrate became free from the chloride ions, and dried at 70°C.

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

RESULTS AND DISCUSSIONS

Strong acid treatment resulted in removal of aluminium from the framework and finally out of zeolite structure in a soluble Al (EDTA) form due to the presence of excess EDTA in the solution.[6] The possible mechanism is reported as:[7]

$$\begin{array}{c} xH_4\,EDTA + Ca(AlO_2)(SiO_2)_y \\ \downarrow \\ xCaAl\,EDTA{\cdot}H_2O + Ca(AlO_2)_{1-x}(SiO_2)_y + H_2O \end{array}$$

where $x \leq 1$ and $y \geq 2.5$

Table-1 shows the extent of dealumination of zeolite phase. The analytical data of original scolecite and dealuminated Fe-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 iron and EDTA contents of the prepared sample are in 1 : 1 molar ratio, thereby confirming formation of Fe-EDTA complex. The initial Si/Al molar ratio of 1.56 increased to 3.42 in the prepared sample confirming the more siliceous nature of prepared sample. The empirical formula of the prepared sample derived on the basis of elemental analysis is:

$$Fe_{0.67}EDTA_{0.73}NH_{4_{6.85}}Ca_{1.26}Al_{8.03}Si_{27.49}O_{71.25}{\cdot}nH_2O.$$

TABLE-1
ELEMENTAL ANALYSIS

S. No.	Sample	wt % Ca	Al	Si	NH_4	EDTA	Metal	Metal : EDTA (molar ratio)	Si/Al (molar ratio)
1[a]	Scolecite	10.21	13.75	21.47	—	—	—	—	1.56
2[b]	Fe-EDTA-NH_4-Scolecite	1.61	6.90	24.58	3.26	8.70	1.19	21.31 : 23.40	3.42

a. Sample is colourless; relative density = 2.30; refractive index = 1.532.
b. Sample is blue coloured, relative density = 2.60; refractive index = 1.518.

Physical studies

Original scolecite in pure condition is colourless. The prepared sample (Fe-EDTA-NH_4-scolecite) is brown in colour, due to the Fe-EDTA incorporation. Presence of aqueous ammonia intensifies the colour of the sample.

The observed density of the untreated is 2.30, which increases to 2.60 in Fe-EDTA-NH_4-scolecite. The density of the zeolite phase is generally reported to be decreased after dealumination.[8] Increased density of the present derivative even after its significant dealumination is becuase of Fe-EDTA complex incorporation in zeolite. The refractive index of the original scolecite is observed to be slightly decreased in treated derivative. This decrease in refractive index is also an evidence of framework dealumination.[9]

IR Studies

The IR absorption spectrum of Fe-EDTA-NH_4-scolecite consists of all the characteristic bands of the zeolite scolecite along with coordinated water.[10] The bands due to ammonia have also been observed (Table-2.) The IR spectrum also shows several prominent absorption characteristics for EDTA complex of Fe^{2+}.[11] The —OH stretching region of the spectrum shows bands between 3752 to 3400 cm^{-1}. The band at 3752 cm^{-1} is attributed to silanol band (Si—OH modes). The medium intensity band at 3690 cm^{-1} reflects the degree of dealumination.[12]

TABLE-2

INFRARED ABSORPTION DATA (cm^{-1})

Assignments	Scolecite	Fe-EDTA-NH_4-Scolecite
$\nu(OH)$	3440 br	3445 br
$\delta(H—O—H)$	1640 m	1640 m
$\nu_{Asym}(T—O)$	1035 m	1060 m
$\nu_{Sym}(T—O)$	700 m	720 w
Double ring	580 sh	590 sh
$\delta(T—O)$	440 m	449 m
Pore opening	370 m	—
$\nu(\equiv CH)$	—	3170 w
ν(Si—OH) modes	—	3752 m
ν(Al—OH) modes	—	3690 m
$\nu(NH_4^+)$	—	2992 m
$\delta_d(NH_4^+)$	—	1483 m
$\delta_s(NH_4^+)$	—	1430 m
$\nu(COO—M)$	—	1620 m
$\nu(COO—H)$	—	1650 m

br—broad, s—sharp, m—medium, w—weak, sh—shoulder

In vibrational region of the spectrum the bands are showing higher frequency shift in comparison to original scolecite. This is due to dealumination of zeolite structure. In this region of the spectrum the most intense band is observed at 1060 cm^{-1}. In comparison to orginal scolecite this band has been found to be shifted by 25 cm^{-1} towards higher frequency side. This band is also reported sensitive to Si/Al ratio.[13] This higher frequency shift of the bands is due to increase in silica content in treated derivative, as reported earlier.[14]

Thermogravimetric analysis

The thermogravimetic data of the samples are summed up in Table 3. The prepared derivative shows three weight loss steps with 24.5% wt. loss. The first weight loss step is fast and exists from 30-170°C showing 12% wt. loss. This wt. loss step is due to the loss of physically adsorbed water. This significant weight loss shows that the water adsorption capacity is increased in the Fe-EDTA-NH_4-scolecite derivative due to dealumination. It can be assumed that external surface increases due to dealumination process by the possible creation of fissures (defect sites) in the crystal.[15] The second weight loss step of 8.50% wt. loss varies from 170–430°C. The fast weight loss step is due to the desorption of ammonia and decomposition of Fe-EDTA complex. This is in good agreement with earlier reported work that ammonia desorption takes place from 200°C to 550°C and EDTA decomposes between 150° and 400°C depending on its derivatives.[16] The 3rd weight loss step lies between 430° to 680°C which corresponds to elimination of water molecules *i.e.* elemination of structural hydroxyl groups by dehydroxylation. This dehydroxylation weight loss is comparatively more than that observed in original scolecite. This 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°C as reported earlier by Benesi.[17]

TABLE-3
THERMOGRAVIMETRIC DATA

Sample	Total wt. loss wt (%)	wt. loss wt (%)	Temp. range (°C)	Rate of loss (%/min)
Scolecite	14.50	4.00	30–130	0.40
		4.00	160–275	0.34
		3.50	330–400	0.50
		3.00	400–660	0.12
Fe-EDTA-NH_4-Scolecite	24.50	12.00	130–170	0.86
		8.50	170–430	0.33
		4.00	430–680	0.16

X-Ray diffraction Studies

Using the X-ray diffraction data the unit cell dimensions and crystallinity of the acid dealuminated Fe-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. Fe-EDTA-NH_4 scolecite sample shows siginificant 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 original scolecite whereas the lattice parameter 'b' shows reduction. Due to this, unit cell shrinkage occurs in dealuminated derivative.[18] The loss of crystallinity[19] is related with production of defect structure.

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

	Scolecite	Fe-EDTA-NH_4-Scolecite
Crystal system	Monoclinic	Monoclinic
Lattice Constants:		
a	9.848 Å	9.848 Å
b	19.987 Å	18.739 Å
c	6.522 Å	6.522 Å
β	110°	110°

Conclusions

The systematic modifications of molecular sieve zeolite by dealumination and metal complex adsorption alters their properties in ways which 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 desired aluminium deficiency. Increase in density values and colour change confirms the incorporation of Fe-EDTA complex with the scolecite framework. Elemental analysis confirms 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 inferred about the increased water sorption capacity of scolecite after dealumination which is due to increase in defect sites. X-ray diffraction lines decreased due to production of defect structure after dealumination and unit cell parameter 'b' was also reduced showing unit cell shrinkage due to dealumination of prepared Fe-EDTA-NH_4 scolecite derivative.

ACKNOWLEDGEMENTS

The authors are thankful to Dr Nitin Labhsetwar for his help in the present work. Thanks are also due to R.S.I.C., Nagpur and R.S.I.C., IIT, Bombay for chemical analyses.

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(*Received:* 20 March 1997; *Accepted:* 2 June 1997) AJC-1288