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STRUCTURAL STUDIES ON THORIUM(IV)-TITRIPLEX IV-INTERACTED 13X ZEOLITE

S. P. Banerjee

Chemistry Department, Dr. Harisingh Gour Vishwavidyalaya, Sagar 470003, India

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Abstract

A new zeolite derivative has been prepared by interacting Th(IV) and complexone in HCl medium and neutralising with aqueous ammonia. The amorphous and siliceous derivative showed a total mass loss of 29.25% in TG for stepwise dehydration, dehydroxylation and decomposition. Heats of reaction were 1167.6 J g^{-1} at 88.7°C and 75.167 J g^{-1} at 492.5°C for loss of volatile components and decomposition respectively. ^{29}Si and ^{27}Al MAS NMR spectra as well as XRD data of the derivative before and after calcination indicate presence of both four-coordinated and six-coordinated Al in varying ratios and the total loss of crystallinity.

Keywords: complexes, zeolite

Introduction

The naturally occurring isotope thorium-232 is the parent substance of the 4n series of radioactive elements. It is also the starting material for preparing fissionable material and is of prime importance in nuclear technology. Its fixation in zeolite support is useful in its disposal and control. The present study relates to the preparation of Th(IV)-Titriplex IV adsorbed derivative on a protonated, ammoniated and partially dealuminated 13X zeolite and studying its structural and thermal behaviour. In high *pH* range complexones form stable metal chelates and help in solubilization of the metals. This fact has been utilized to interact Th(IV) ions with Titriplex IV in strong mineral acid and an adsorbent and recovering the interacted derivative by ammoniation.

Experimental

Equal portions of AnalaR Th(IV)NO_3-tetrahydrate, complexone 1,2-diaminocyclohexane NNN'N'-tetraacetic acid-monohydrate (E. Merck, Germany) and synthetic zeolite 13X (Indian Petrochem. Corpn. Ltd.) were dissolved in

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AnalaR hydrochloric acid of specific gravity 1.18 and heated on a water bath. The viscous fluid turned dark yellow at first due to evolution of NO_x which soon cleared on continuous heating to give a colourless gel [1]. A white precipitate was obtained on cooling and neutralising by adding sufficient aqueous ammonia

Table 1 TG and DTG results

Sample wt./ mg	Total mass loss/%	Mass loss/% with temp. range/°C	Rate of mass loss/ mg min^{-1}	Peak temp./ °C
28.41	29.25	8.27; 28.0–100.0	0.326	74.5
		14.04; 100.0–256.5	0.255	122.5
		6.94; 260.0–499.0	0.083	317.5

Table 2 DSC and analytical results

Sample wt./ mg	ΔH Endo/mJ with temp. range/°C	ΔH/ J g^{-1}	Peak temp./ °C	Th/	C/ %	N/
16.75	19557; 25.0–330.0	1167.6	88.7	12.0	2.3215	0.3372
	1259.1; 410.0–600.0	75.167	492.5			

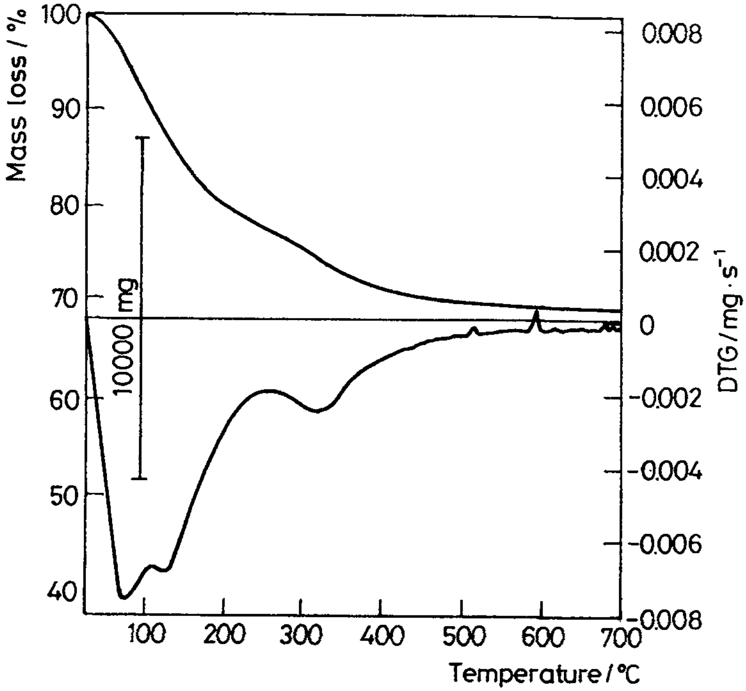

Fig. 1 TG and DTG plot of Th(IV)-Titriplex IV-interacted 13X zeolite between 25 and 700°C

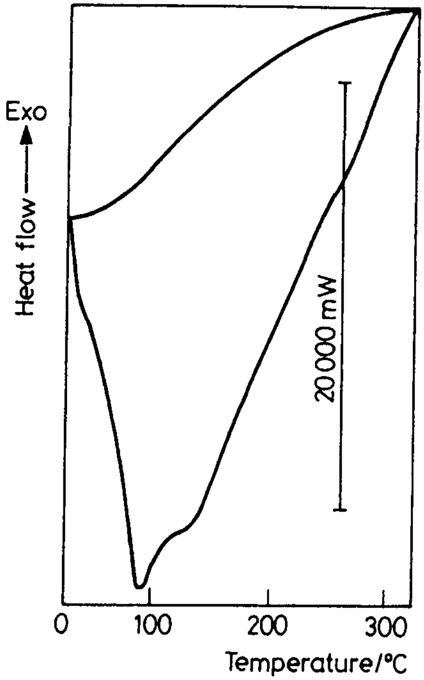

Fig. 2 DSC endotherm at 88.7°C between temperature range of 25 and 330°C

of specific gravity 0.888. The *pH* of the supernate after filtering off the white precipitate on a Whatman No.1 filter paper and washing with hot distilled water respectively, was just below 7. This greyish-white sample after air-drying was characterized by X-ray diffraction using Philips X-ray unit with PDP 11/23 computer and CuK_α radiation of 1.54060Å and 1.54439Å between 2θ angles 5° and 70°, thermal methods like TG, DTG and DSC using a Mettler TA3000 thermoanalyzer in static air at a heating rate of 10 deg·min^{-1} and MAS NMR by recording ^{29}Si ^{27}Al spectra at 9.4T on a Chemagnetics CMX-400 spectrometer. ^{29}Si spectra were recorded at 79.5 MHz with 2 μs (30°) pulses and 90 s recycle delays. ^{27}Al spectra were measured at 104.3 MHz with very short 0.6 μs (less than 10°) radiofrequency pulses and 0.3 s recycle delays. The rotors were spun in air at 4.5 kHz in a double-bearing probe head. ^{29}Si and ^{27}Al chemical shifts are quoted in ppm from external tetramethylsilane and $Al(H_2O)_6^{3+}$ respectively. Percentages of C, N and Th(IV) were determined using Carlo Erba 1108 analyzer and spectrophotometric method with organic reagent thorin [2] at 545 nm and *pH* 0.62. The relevant data are reproduced in Tables 1 and 2 and the TG, DTG and DSC curves of the derivative and the ^{29}Si and ^{27}Al NMR spectra Figs 1–5.

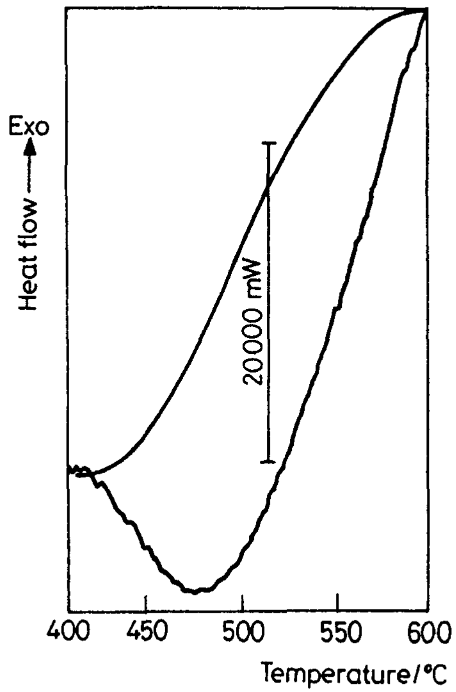

Fig. 3 DSC endotherm at 492.5°C between temperature range of 410 and 600°C

Results and discussion

On the basis of N% (0.3372) and C% (2.3215) the presence of Titriplex IV can be estimated to be between 0.044 and 0.05 mol. The derivative contains 12.0% of the heavy Th(IV) ions besides the complexone. The original zeolite 13X in strong mineral acid is expected to be in the protonated form after removal of Na(I) and partial dealumination could occur by the mechanism suggested by Lee and Rees [3]. Kerr [4] had removed aluminium directly from a synthetic sodium Y zeolite with EDTA as the complexing agent. The Th(IV)-Titriplex IV derivative prepared may, therefore, be a mixture of hydrated metal-complexone species with non-framework aluminium and the protonated dealuminated 13X zeolite [5]. Acid treatment and the Th(IV)-Titriplex IV interaction can lead to the collapse of the crystal structure of the original synthetic zeolite as confirmed by X-ray diffraction results. The diffractogram shows no crystalline peaks but only a low intensity hump around 2θ angle of 29°. It has been reported that a colloidal hydrous oxide, $ThO_2{\cdot}nH_2O$, is formed by keeping a mixture of thorium nitrate and ammonium hydroxide at 70°C for several hours [6]. Since the aqueous NH_3 added to neutralise the acid was not in excess the

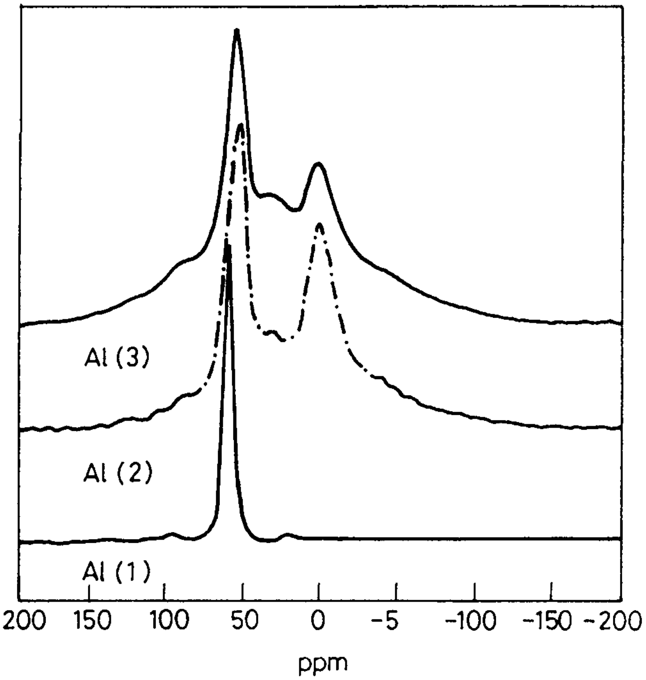

Fig. 4 ^{27}Al MASNMR spectra of (1) 13X zeolite, (2) Th(IV) derivative before and (3) after calcination

pH was not sufficiently high to form a stable complex. On the other hand neutralisation with ammonia produced sufficient heat of reaction to form the hydrous oxide. In acid solution with a *pH* value of upto 3 the following hydrolysis reaction is expected:

$$Th(NO_3)_4 + 2H_2O + 2H^+ \rightleftharpoons Th(OH)_2^{2+} + 4HNO_3$$

On ammoniation, at higher *pH*, similar species can also exist. Formation of polynuclear complexes with a chain structure of the type $Th[(OH)_3Th]_n^{(n+4)+}$ or $Th[^{O}_{OH}Th]_n^{(n+4)+}$ are also possible [7]. Similarly EDTA complexes (1:1) of metal ions with the charge +3 or higher are reported to partially hydrolyse in basic solution forming species like $M(OH)Y^{(5-Z)}$ or its dimer $M_2(OH)_2Y^{(10-2Z)}$. Considering reported behaviour of thorium complexes and the effect of acid treatment on zeolite the greyish-white derivative under investigation is a mixture of hydrous Th(IV)-Titriplex IV species supported on an amorphous protonated siliceous base. Thermal data obtained from TG and DTG studies can be due to dehydrogenation (mass loss=8.27% peak temp.=74.5°C), dehydration (14.04%; 122.5°C) and dehydroxylation (6.95%; 317.5°C). The DSC data between 25 and 330°C represent the combined phenomena upto 330°C with peak temperature of the endotherm 88.7°C and heat of reaction (Δ*H*) of 1167.6 J g^{-1}. The high temperature reaction between 410 and 600°C (endothermic peak at 492.5°C) with Δ*H* of 75.167 J g^{-1} is due to the decomposition of organometallic species leaving an off-white residue in thermal analysis. In 13X zeolite the aluminium present is totally four-coordinated. But in the derivative prepared with Th(IV) after interaction with Titriplex IV both tetrahedral (at 56.3 ppm) and octahedral aluminium (at 4.26 ppm) in the ratio ca. 1.7:1 have been confirmed. Calcination of this derivative alters this ratio considerably and six-coordinated aluminium tends to become four-coordinated. The peaks at 2.28 ppm (for octahedral aluminium) and 54.87 ppm (for tetrahedral aluminium) indicate this fact. A third peak, not very well defined, at 30.76 ppm and 32.76 ppm in the spectra of the calcined derivative and the original can be due to the non framework aluminium. The broad featureless ^{29}Si spectra for the two Th(IV) derivatives, before and after calcination, confirm as indicated by the XRD studies, that these are amorphous in nature.

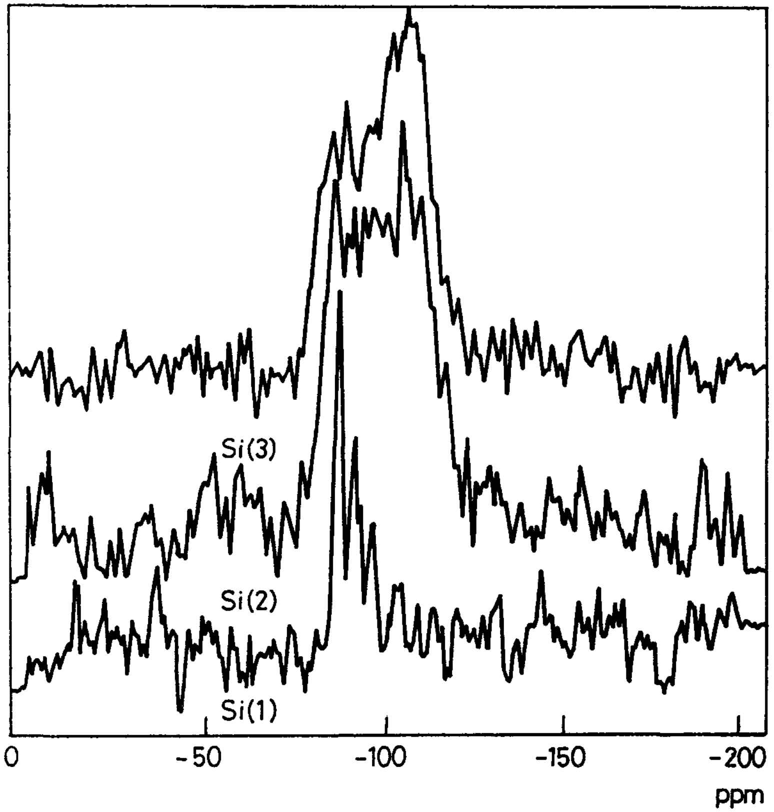

Fig. 5 ^{29}Si MASNMR spectra of (1) 13X zeolite, (2) Th(IV) derivative before and (3) after calcination

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