

Structural studies of materials obtained by treating zeolite X with metal titriplex IV complexes

Sati Prasad Banerjee

Department of Chemistry, Dr H S Gour Vishwavidyalaya,
Sagar 470 003

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Synthetic zeolite 13X has been treated with conc HCl complexone Titriplex IV and metal ions like Tl(I) and oxovanadium(IV) before ammoniation to yield dark brown and white derivatives respectively. Structural studies of these derivatives before and after calcination have been carried out using XRD and ^{27}Al and ^{29}Si MAS NMR data with complimentary IR data. Thermal behaviour of these two derivatives have been reported on the basis of TG, DTG and DSC results and percentages of carbon and nitrogen obtained have been used to compute the extent of complexing agent present.

Treatment of zeolites with mineral acids or chelating agents causes dealumination of their aluminosilicate framework¹. On the other hand, ammonium ion exchange followed by heating (ultrastabilization) brings about dealumination accompanied by changes in the surface characteristics². Combined interaction of a chelating agent in strong mineral acid followed by ammoniation with a mixture of synthetic zeolite and metal ions is not widely known. This note reports the interaction of Tl(I) and oxovanadium (IV) with 1, 2-diaminocyclohexane NNN'N'-tetraacetic acid, a complexone commercially known as Titriplex IV, with synthetic zeolite X in the presence of conc HCl. The two solid derivatives were isolated from the resultant viscous fluids by neutralising the acid with aqueous ammonia. The Tl(I) and oxovanadium(IV)-treated derivatives were also calcined at 700-800°C in a muffle furnace. The two new derivatives with Tl(I) and oxovanadium(IV) species and their calcined residues have been characterised by several techniques. Thallium, and particularly thallous, solutions are highly toxic³. Vanadium-containing zeolites have been used to catalyze heterogeneous oxidation of sulphur dioxide. This study helps to establish the structures of the new potentially useful derivatives in the area of environmental protection and catalysis.

Experimental

Sample preparation

Equal quantities of synthetic zeolite 13X (IPCL), Titriplex IV (Merck, mol. formula $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_8 \cdot \text{H}_2\text{O}$) and VOSO_4 and TlNO_3 (AR grade) were mixed in 35% w/v HCl (AR) (sp. gravity = 1.18) and warmed. For oxovanadium(IV) derivative, a blue viscous fluid resulted while for Tl(I) derivative nitrous fumes were evolved, which was accompanied by the formation of a dark brown fluid. The fluids were treated with a sufficient amount of aq. ammonia (sp. gravity = 0.888; 32.5% w/v) to reprecipitate white and dark brown solids, respectively. These were filtered on Whatman No. 1 filter paper, washed thoroughly with hot distilled water and air dried. A portion of each derivative was next heated in a muffle furnace at 700-800°C for 3 h. A dirty white residue was obtained for oxovanadium(IV) and a mixed carbonaceous yellow refractory residue for Tl(I)-Titriplex IV derivative of zeolite X.

The new derivatives have been examined using TG, DTG and DSC using Mettler TA3000 thermal system, in static air and at a heating rate of 10 K min^{-1} , FTIR in KBr pellets in the range of 4000-400 cm^{-1} , XRD using CuK_α radiation between 2 θ angles of 5 and 50° and analysis of carbon and nitrogen with a Carlo Erba 1108 analyzer. Zeolite X interacted with Tl(I)-Titriplex IV and oxovanadium(IV)-Titriplex IV (Samples 1 and 2) produced samples 3 and 4 respectively after heating in the muffle furnace. Magic-angle-spinning (MAS) NMR spectra were recorded at 9.4T on a Chemagnetics CMX-400 spectrometer. ^{29}Si spectra were acquired at 79.5 MHz with 2 μs (30°) pulses and 90s recycle delays. ^{27}Al spectra (Fig. 1) were measured at 104.3 MHz with very short, 0.6 μs (less than 10°), radiofrequency pulses and 0.3s recycle delays. The rotors were spun in air at 4.5 KHz in a double-bearing probehead. ^{29}Si and ^{27}Al chemical shifts are quoted in ppm from external TMS and $\text{Al}(\text{H}_2\text{O})_6^{3+}$, respectively.

Results and discussion

The crystal structure of sample 1 is relatively less affected by the acid treatment and chelation. It shows 8 crystalline peaks with maximum peak intensity at d -value 3.04Å. Sample 1 on heating resulted in derivative 3 which shows 22 crystalline peaks with maximum peak intensity at $2\theta = 29.485^\circ$. Sample 2 exhibits amorphous characteristics with no clear

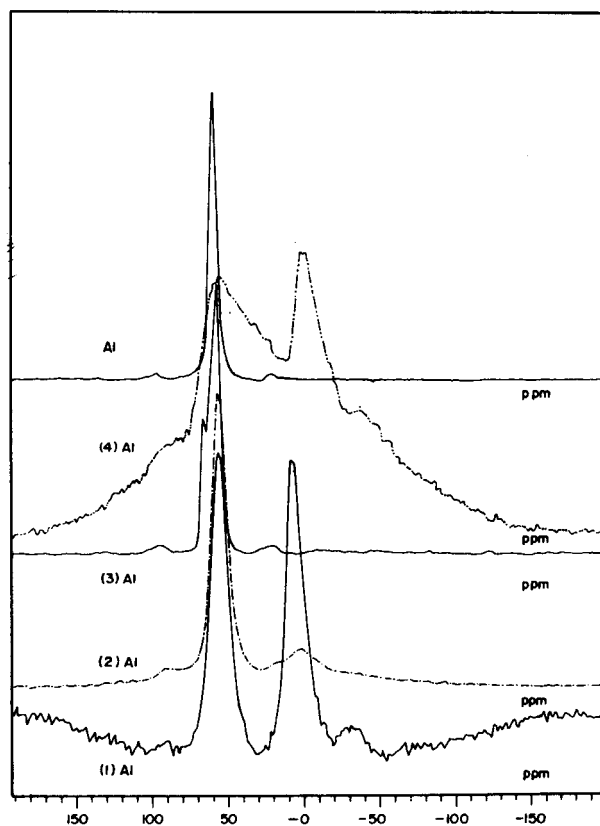


Fig. 1—MAS NMR spectra of ^{27}Al for 13X, (1) & (3) for sample 1 & 3; (2) & (4) for sample 2 & 4

peaks but only a hump-like diffraction pattern. Sample 4 obtained after heating sample 2 becomes partially crystalline with maximum peak intensity at $2\theta = 41.025^\circ$. All four samples are, however, quite different from the original zeolite X which showed well-defined intense peaks at $2\theta = 6.1250^\circ$, 23.3050° , 26.6500° and 30.9350° (Table 1).

The infrared spectra of zeolites show some characteristic features. Bands at $1000\text{--}1100\text{ cm}^{-1}$ and $400\text{--}500\text{ cm}^{-1}$ are assigned to asymmetric stretching and TO bending of the TO_4 unit, respectively. The IR absorption at $500\text{--}600\text{ cm}^{-1}$ is considered to be due to ring vibrations. Besides these basic features, all four samples show IR bands for high frequency and low frequency OH groups vibrations at $4000\text{--}3000\text{ cm}^{-1}$. Similarly all show IR bands for $>\text{CH}_2$ and Si-H at $2300\text{--}2900\text{ cm}^{-1}$. Sample 1 shows a band at 1416 cm^{-1} (CO_2) which disappears on heating in sample 3. In the case of sample 2, two bands appear at 1537 cm^{-1} and 1400 cm^{-1} for NH_3 and CO_2 respectively and the latter disappears due to heating in sample 4. Heating of sample 2 also brings about the appearance of the bands at 905 and 796 cm^{-1} corresponding to changes in the framework structure like further dealumination.

Table 1—X-ray diffraction data

Angle (2θ)	d -value α_1 (Å)	d -value α_2 (Å)	Relative intensity (%)	Sample
20.705	4.2865	4.2970	7.3	Sample 1
29.390	3.0366	3.0441	100.0	
34.155	2.6231	2.6295	36.3	
36.180	2.4808	2.4869	4.5	
40.210	2.2409	2.2464	3.3	
43.910	2.0603	2.0654	6.0	
47.330	1.9191	1.9238	2.5	
49.060	1.8554	1.8600	31.0	
12.030	7.3510	7.3691	5.2	Sample 3 (calcined Sample 1)
14.440	6.1291	6.1442	8.2	
16.090	5.5041	5.5176	16.7	
17.605	5.0337	5.0461	1.5	
19.085	4.6465	4.6580	11.3	
20.425	4.3446	4.3553	21.5	
23.865	3.7256	3.7348	9.9	
24.625	3.6123	3.6212	27.7	
25.060	3.5506	3.5593	41.0	
26.080	3.4140	3.4224	79.7	
26.965	3.3039	3.3120	87.9	
27.905	3.1947	3.2026	25.2	
28.335	3.1472	3.1549	37.9	Sample 2
28.960	3.0807	3.0883	49.8	
29.485	3.0270	3.0345	100.0	
30.895	2.8920	2.8991	37.1	
31.320	2.8537	2.8607	36.7	
33.425	2.6787	2.6852	24.1	
34.130	2.6249	2.6314	22.1	
34.920	2.5673	2.5736	15.3	
36.280	2.4741	2.4802	8.1	
37.080	2.4226	2.4285	10.6	
37.780	2.3793	2.3851	35.4	
38.405	2.3420	2.3478	9.1	
39.200	2.2963	2.3020	11.3	Sample 4 (calcined Sample 2)
39.850	2.2603	2.2659	8.1	
41.105	2.1942	2.1996	6.7	
41.895	2.1546	2.1599	16.1	
42.605	2.1203	2.1255	10.6	
43.715	2.0690	2.0741	7.3	
44.235	2.0459	2.0509	10.6	
45.270	2.0015	2.0064	3.6	
45.750	1.9816	1.9865	8.1	
46.330	1.9582	1.9630	9.9	
47.030	1.9306	1.9354	9.1	
48.340	1.8813	1.8860	7.5	
48.975	1.8584	1.8630	7.9	
13.395	6.6048	6.6210	58.5	Sample 4 (calcined Sample 2)
16.605	5.3345	5.3476	43.4	
21.875	4.0598	4.0698	97.7	
26.170	3.4024	3.4108	93.1	
31.130	2.8707	2.8778	46.6	
33.350	2.6845	2.6911	38.9	
35.430	2.5315	2.5378	75.8	
41.025	2.1983	2.2037	100.0	
42.770	2.1125	2.1177	22.1	

$$\alpha_1 = 1.54060\text{Å}, \alpha_2 = 1.54439\text{Å}$$

Table 2—Thermal data [Temp. range = 25-700°C; heating rate = 10°C min ⁻¹]						
Sample	Sample wt. (mg)	Wt. loss (%) (temp. range)	Total wt. loss (%)	Rate of wt. loss (% min ⁻¹ × 10 ⁻¹)	Peak temp. (°C)	Colour change
Sample 1	16.586	7.20(26.7-325.0)	17.88	2.42	34.2	brown to grey and yellow
		1.53(325.0-435.8)		1.38	360.8	
		2.70(435.8-587.8)		1.78	552.5	
		6.45(587.8-697.5)		5.86	696.7	
Sample 2	13.404	5.21(27.5-80.0)	25.03	9.94	52.5	white to off-white
		13.75(80.0-298.5)		6.29	106.0	
		6.07(300.0-500.0)		3.04	363.5	

Sample	Sample wt. (mg)	Temp. range (°C)	ΔH (mJ)		ΔH (J/H)	Peak temp. (°C)
			Endo	Exo		
Sample 1	16.597	25-190	2485.7		149.77	69.3
		190-240	125.92		7.587	208.7
		280-440	588.51		35.459	323.6
		440-520	119.28		7.187	478.4
				27.691	1.669	562.4
Sample 2	6.134	25-240	2706.9		441.29	68.4
		25-540	11115.0		1812.1	119.5

Thermal data as obtained from TG, DTG and DSC studies are presented in Table 2. Sample 1 exhibits weight loss in four steps, the first and the fourth being more prominent, the latter showing maximum rate loss between 587.5 and 697.5°C with peak temperature at 697.7°C. Sample 2 on the other hand exhibits three steps of weight losses upto 500°C, the step between 80.0 and 298.5°C being the most prominent. Sample 2 is much less thermally stable than sample 1 with the highest peak temperature at 363.5°C. It is not possible from the TG and DTG results to actually pinpoint the nature of thermal events. Zeolites show weight loss for dehydration and dehydroxylation and zeolite X conforms to this total loss of 26.35% which is quite close to the expected loss of its water content. Samples 1 and 2 with different interacted species like Tl(I), oovanadium(IV) and the organic reagent do not conform to known behaviour of the starting materials such as TiNO_3 , VOSO_4 or the organic reagent⁴.

But the nature of residue for sample 1 clearly suggests that it contains similar products as that reported in the solid state interaction of Kalignost and Tl(I)-exchanged zeolite A⁵. Thus the successive thermal events in sample 1 are dehydration, dehydroxylation, oxidation and decomposition of the complexone resulting in a blackish product mixed with yellow granules. The oxidation to Ti_2O_3 and reduction to Ti_2O can occur first at 435.8-587.5°C and then at 587.5-697.5°C. The last step weight loss of ~6.5% at the fastest rate of weight loss for sample 1 agrees well with the expected loss of ~7.3% for the reaction $\text{Ti}_2\text{O}_3 + 4\text{H} = \text{Ti}_2\text{O} + 2\text{H}_2\text{O}$. Alternatively,

the reported volatilisation of thallos chloride above 425.0°C with the weight loss of 2.23% at 475.0°C may also occur at 435.8-587.5°C as the weight loss of 2.70% recorded over this temperature range suggests this possibility⁶. The exothermal reaction at 520-580°C ($\Delta H = 27.691$ mJ) with peak temperature at 562.4°C found for sample 1 by DSC can be attributed to such behaviour. The carbon content of 0.4805% corresponds to 0.0104 mol of Titriplex IV in sample 1. Sample 2 contains only 0.439% carbon (=0.0095 mol complexone), but 3.25% nitrogen (=4.09% NH_4^+). This indicates the possibility of the presence of NH_4^+ as cation or adsorbed ammonia in the acid form of dealuminated zeolite support. This would explain the three step weight loss as deammoniation, dehydration and decomposition of complexone for sample 2. The peak temperatures of 52.5, 106.0 and 363.5°C confirm these steps. The residue of sample 2, dirty white in colour, indicates presence of traces of carbon as a result of the decomposition of the complexone.

²⁷Al MAS NMR spectra

Sample 1 has the ratio of 4-coordinate Al (at 56 ppm) to 6-coordinate Al (at 6.8 ppm) of ca. 1:1. In sample 3, obtained after heating sample 1, only 4-coordinate Al is observed. (Fig. 1). Because of the presence of a quadrupole power pattern, it is difficult to say how many Al peaks are there although there should be atleast two. The spectrum shows that the environment of Al is not very symmetric. Sample 2 has the ratio of 4-coordinate Al (at 56.6 ppm) to 6-coordinate Al (at 2.6 ppm) of ca. 15:1. Sample 4

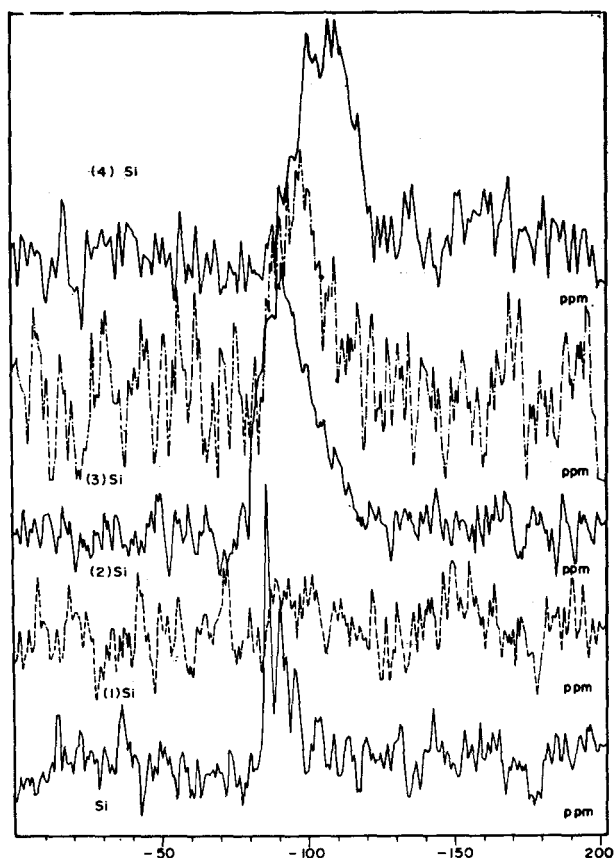


Fig. 2— ^1H - ^{29}Si CP/MAS NMR spectra for 13X, (1) & (3) for sample 1 & 3; (2) & (4) for sample 2 & 4

contains both 4 and 6-coordinate Al at *ca.* 56.6 ppm and *ca.* 0736 ppm respectively. The environment of 4-coordinate Al is much more asymmetric in sample 4 than in sample 2.

^{29}Si MAS NMR and ^1H - ^{29}Si CP/MAS NMR spectra

In sample 1, no signal could be found for ^{29}Si , even using 12 min recycle delay. As there was no signal from the cross-polarization experiment, it meant that relaxing time in the rotating frame, $T_{1\rho}$, of ^1H is very long. This is an indication that sample 1 has a dense phase. In zeolites, each Si atom is accessible to the paramagnetic O_2 molecule from air which provides relaxation for ^{29}Si . In dense phase, this is not the case. Sample 3, however, shows the presence of at least six different kinds of 4-coordinate Si. In sample 2, these are indistinguishable kinds of 4-coordinate Si which are all different. But sample 2 after calcination shows at least six different kinds of 4-coordinate Si (Fig. 2).

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