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# Studies on a New Phosphatic Derivative of Th(IV)-Titriplex IV-interacted 13X Zeolite

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A new phosphatic derivative of mixed phases including crystalline $AlPO_4$ has been prepared from amorphous siliceous Th(IV)-Titriplex IV-interacted 13X zeolite. Interaction of orthophosphoric acid at elevated temperature resulted in the decomposition of the complexone and a new derivative. This has been characterized by XRD, thermal and FTIR studies and can have catalytic and environmental significance due to the presence of $AlPO_4$ and fixed Th(IV) species.

## INTRODUCTION

A great deal of attention has been paid to novel molecular sieves containing aluminophosphates with defined microporous structure and adsorption properties.[1] A series of silico-aluminophosphate molecular sieves with nomenclature SAPO has been prepared and studied.[2] $AlPO_4$ crystals comprise alternating $AlO_4$ and $PO_4$ tetrahedra which produce an electroneutral framework.[3] While $AlPO_4$ can be commercially useful for its catalytic properties,[4–6] siliceous and mixed Th(IV) species can be useful for fixation of the metal used in nuclear technology. In the present work a Th(IV)-complexone interacted 13X zeolite sample has been used to prepare a phosphatic derivative which is more crystalline and contains $AlPO_4$ in a mixed phase of siliceous Th(IV) as indicated by XRD, thermal and FTIR studies.

## EXPERIMENTAL

Preparation and characterization of the Th(IV)-Titriplex IV-interacted 13X zeolite derivative have been reported earlier.[7] A part of the sample was kept immersed in excess orthophosphoric acid (BDH) for 20 days and then heated over an electric heater continuously to boil off excess acid. Initially decomposition of the complexone resulted in a black crust floating on the surface of the evaporating fluid. Most of the carbon layer was removed with a nickel spatula and a dry ash-grey residue was finally obtained. Its FTIR spectrum was recorded on a Perkin-Elmer 983 model spectrophotometer in KBr pellets between 4000 and 450 $cm^{-1}$. Thermal data (TG, DTG, DSC) were recorded using a Mettler TA3000 thermal analyzer in static air at 20 K $min^{-1}$ heating rate and X-ray diffractograms before and after TG analysis upto 700°C were obtained using Phillips 1700

automated powder diffraction system with $Cu_{K\alpha}$ radiations. Relevant data are presented in Tables 1 and 2 respectively.

TABLE-1
THERMAL DATA (TG, DTG AND DSC)

| Total wt. loss (%) | Wt. loss (%) with temp. range (°C) | DTG peaks (°C) | DSC peaks (°C) with temp. range | ΔH Endo (mJ) | ΔH (J/ G) |
|---|---|---|---|---|---|
| 2.2869 | 1.8689; 30.0–393.3 | 43.3 | 66.2; 30.0–150.0 | 922.920 | 43.6780 |
| | 0.1002; 393.3–446.7 | 408.3 | 213.3; 150.0–260.0 | 66.539 | 3.1491 |
| | 0.0587; 446.7–478.3 | 446.7 | 315.4; 300.0–340.0 | 30.327 | 1.4353 |
| | 0.1209; 510.0–585.0 | 533.3 | | | |

TABLE-2
X-RAY DATA

| Sample | No. of peaks | Major peaks | |
|---|---|---|---|
| | | d-spacing (Å) | $I/I_{max}$ (%) |
| 13X zeolite before TG analysis up to 700°C | 41 | 14.4183 | 100.00 |
| | | 3.8138 | 47.98 |
| | | 3.3422 | 48.62 |
| | | 2.8884 | 54.54 |
| New derivative before TG analysis up to 700°C | 24 | 5.9182 | 70.06 |
| | | 3.8456 | 100.00 |
| | | 3.3484 | 48.48 |
| | | 3.0002 | 62.82 |
| | | 2.9555 | 45.44 |
| | | 2.8562 | 44.44 |
| | | 2.8310 | 58.21 |
| 13X zeolite before TG analysis up to 700°C | 39 | 14.7737 | 100.00 |
| | | 3.8394 | 54.39 |
| | | 3.3611 | 50.77 |
| | | 2.9042 | 49.88 |
| | | 2.8968 | 43.89 |
| New derivative after TG analysis up to 700°C | 26 | 6.5308 | 41.07 |
| | | 5.9103 | 76.25 |
| | | 3.8398 | 100.00 |
| | | 2.9589 | 41.98 |
| | | 2.8299 | 47.63 |

## RESULTS AND DISCUSSION

Th(IV)-Titriplex IV-interacted 13X zeolite, dealuminated and ammoniated, contained *ca.* 12% thorium and 0.05 mol of the complexone 1,2-diamino-

cyclohexane NNN'N'-tetraacetic acid. The complexone as an amino derivative could behave like an organic template in the preparation of phosphatic constituent like $AlPO_4$. In some previous procedures for preparation of SAPO molecular sieves amines like di-*n*-propylamine[8] and tripropylamine[9] have been used as organic template. Recently $AlPO_4$ has been synthesised by microwave heating in the presence of triethylamine.[10] On heating the mixture of Th(IV)-titriplex IV-interacted zeolite sample with orthophosphoric acid the complexone decomposed to form the black crust of carbon. Even after removal of the layer by mechanical means some carbon still remained to avoid any preferential oxidation of the elements like Th(IV), Al(III) and Si(IV). Thus the new sample obtained after evaporating off the excess fluid can only be a phosphatic mixture as reported in earlier studies.[11,12]

The FTIR spectrum of the new derivative exhibits strong absorption bands at 1383 $cm^{-1}$, 1172 $cm^{-1}$, 1146 $cm^{-1}$ and 1130 $cm^{-1}$ for $\nu(P{=}O)$ and $\nu(P{-}O)$ vibrations. In the mid-IR region a very weak band is observed for traces of water at 1626 $cm^{-1}$. Other bands are seen at 1054 $cm^{-1}$ (strong) for asymmetric T—O stretching, at 690 $cm^{-1}$ (medium) for symmetric T—O stretching, at 495 $cm^{-1}$ (strong) for double ring and at 416 $cm^{-1}$ (medium) for T—O bending besides two weak bands at 669 $cm^{-1}$ and 609 $cm^{-1}$ for $\delta$(O—P—O) vibration. Other weak bands are also seen at 3795 $cm^{-1}$, 3777 $cm^{-1}$ and 3375 $cm^{-1}$ respectively for high frequency OH groups, P—OH groups and low frequency OH groups.

Compared to 41 and 39 peaks found in the X-ray diffractogram of original 13X zeolite before and after thermal analysis upto 700°C, the new interacted derivative has 24 and 26 peaks in its X-ray diffractograms before and after TG analysis upto 700°C. However, the derivative Th(IV)-Titriplex IV-interacted 13X showed no crystalline characteristics. Therefore, the new derivative shows loss of crystallinity with respect to 13X zeolite but recrystallisation after phosphoric acid treatment at elevated temperature of the Th(IV)-Titriplex IV derivative. The principal peaks shown in Table 2 indicate maximum peak intensity at d-spacing of 3.84° of the new derivative before and after TG analysis and at least four common peaks at 5.92°, 2.96° and 2.83° besides 3.84° among the major ones recorded in the diffractograms. The crystal structure definitely shows the presence of $AlPO_4$, besides other species of Th(IV) and Si(IV) in a mixed phase. It is quite likely that Th(IV) and Si(IV) may also be present in the form of $Th_3(PO_4)_4$ and $Si_2P_2O_7$. Slight changes in the X-ray diffractogram obtained after TG analysis may be due to the loss of last traces of water and phase transformation of $AlPO_4$ which is polymorphic.

Like $AlPO_4$ the TG analysis shows only minor weight loss of about 2.3% up to 700°C. Only one step is prominent up to 393.3°C recording about 1.87% weight loss. DSC studies also confirm the thermal events to occur within 393.3°C (Table-1). Other weight loss steps and DTG and DSC peak temperatures do not contribute any special significance in the thermal behaviour of the new derivative.

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