

NOTE

Preparation and Characterization of New Phosphatic Derivatives of Synthetic Zeolite-4A provided by Indian Petrochemicals, Baroda

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Thermal behaviour of tri-cresyl phosphate (TCP) interacted Th(IV)-4A and TCP/4A have been investigated by TG-DTA up to 900°C. The IR spectral studies confirm the interaction of TCP; crystalline nature of these derivatives has been investigated by XRD.

Phosphatic derivatives of zeolite molecular sieves with nomenclature SAPO are used as the catalyst in many commercially important processes.¹⁻⁴ A great deal of attention has now been paid to prepare new SAPO derivatives with defined microporous structure and their use as catalysts.^{5,6} A series of SAPO molecular sieves has been prepared and studied.⁷ In the present case an organic phosphate tri-cresyl phosphate (TCP) has been used to prepare new silico-alumino-phosphate derivatives of 4A zeolite. The phosphate derivatives of 4A have been characterized by TG, DTA, IR and XRD methods.

Synthetic zeolite-4A in powder form obtained from Indian Petro-Chemicals Ltd. Baroda was first cation-exchanged with Th(IV) ion by interacting 4A zeolite with saturated aqueous solution of thorium nitrate and the reactants were heated from time to time over a water bath (373 K). During the interaction much swelling occurred and a thick white gelatinous mass was obtained. After drying in an oven at 110°C zeolite-4A and its cation-exchanged derivative were kept in contact with excess of TCP $[(\text{CH}_3\text{-C}_6\text{H}_4)_3\text{PO}_4]$, b.p. 537 K for several days. After filtering off the excess liquid the zeolite samples were kept on a filter-paper dried in air. FT-IR spectra were recorded on a Perkin-Elmer spectrometer in KBr pellets between 4,000 cm^{-1} and 400 cm^{-1} . Thermal data (TGA and DTA) were recorded using a SETARAM thermal analyzer in dynamic air at 10°C/minute heating rate and XRD data were obtained using Rigaku X-ray diffractometer

IR spectral analysis: 4A zeolite exhibits characteristic infrared bands of the hydrated aluminosilicate in the FT-IR plot. The peaks observed can be attributed to $\nu(\text{OH})$ (3418 cm^{-1}), $\delta(\text{HOH})$ (1651 cm^{-1}), asymmetric stretch of Si-O (1002 cm^{-1}) and symmetric stretch of T-O (667 cm^{-1}) (sample-1).

The Th(IV) exchanged-4A derivative exhibits similar IR band features with appearance of new intense bands at 1514 cm^{-1} and 1384 cm^{-1} due to formation of non-framework aluminium atoms during dealumination process (sample-2).

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Presence of the adsorbed species of phosphorous compounds in TCP adsorbed-4A (sample-3) and TCP adsorbed Th(IV)-4A (sample-4) is confirmed by IR absorption band around $1500\text{--}1200\text{ cm}^{-1}$, $1200\text{--}900\text{ cm}^{-1}$ and $650\text{--}300\text{ cm}^{-1}$ due to $\nu(\text{P—O})$, $\nu(\text{P=O})$ and $\delta(\text{O—P—O})$ respectively, and shows usual framework infrared bands.

Thermal analysis (TG and DTA): 4A zeolite shows a fast weight loss of 14.76% up to 280°C and is attributed to loss of physically adsorbed water and a further slow weight loss of 1.04% up to 450°C is considered due to dehydroxylation process. DTA pattern for 4A shows endothermic peaks at 170°C , 350°C and 400°C due to dehydration and dehydroxylation process.

The Th(IV)-4A (sample-2), 4A-TCP (sample-3) and 4A-Th(IV)/TCP (sample-4) showed weight losses of 24.94%, 53.08% and 28.54% respectively. The thermochemical processes associated with the weight losses in these samples are dehydration and desorption of adsorbate TCP. Desorption processes occur at lower temperature and decomposition process at elevated temperature. The decomposition of phosphorus compounds like phosphites and phosphates of various composition have been found to occur over varying temperature limits.⁸ In sample-2, DTA endothermic peaks at 170°C and 290°C due to dehydration process and an exothermic peak at 870°C may indicate phase transition occurring in Th(IV)-4A derivative.

Sample-3 shows DTA peaks (endothermic) at 300°C and 390°C corresponding to the desorption of adsorbate TCP.

DTA peaks (endothermic) in DTA pattern of sample 4 at 170°C and 310°C are due to dehydration and desorption of adsorbate TCP.

X-ray analysis: Sample-1 shows 9 prominent peaks in the XRD pattern which contains its cubic structure. Sample-2 shows a decrease in the crystallizing character of 4A zeolite due to introduction of Th(IV) in place of Na(I) ions, which is an evidence of less intense XRD peaks. Sample-3 retained its crystalline character after interacting TCP with 4A. Seven crystalline peaks are identified in the X-ray diffractogram obtained between 2θ angles of 5° to 70° . The intensities of these peaks are comparable to those of 4A zeolite.

Crystalline character of sample-4 (Th(IV)-4A/TCP) is further reduced.

Sample	IR bands (cm^{-1})	
1.	3445, 1651, 1002, 667, 555 and 465	
2.	3415, 1631, 1384, 1514, 913, 851 and 568	
3.	3445, 1651, 1505, 1488, 1312, 1298, 1143, 1164, 972, 822, 781, 687, 552 and 464	
4.	3418, 1633, 1504, 1384, 850, 745 and 566	
S. No.	Weight loss (%) at different temperature	Thermochemical processes
1.	15.8 % wt. loss up to 440°C	dehydration, dehydroxylation
2.	24.94% up to 550°C	dehydration, dehydroxylation
3.	53.08% up to 360°C	dehydration, desorption
4.	28.54% up to 640°C	dehydration, desorption

X-RAY DATA BETWEEN 2 θ ANGLES 5° TO 70°, TARGET—Co

2 θ -Angle	d (Å)	hkl
<i>Sample-1</i>		
11.629	8.836	(110)
14.263	7.210	(111)
18.572	5.547	(210)
23.537	4.389	(220)
25.019	4.132	(221)(300)
27.734	3.735	(311)
31.400	3.308	(321)
34.730	2.998	(410)
<i>Sample-2</i>		
35.712	2.635	(332)
23.593	4.390	(220)
23.779	4.349	(221)
26.754	3.869	(230)
28.403	3.649	(222)
30.367	3.418	(321)
<i>Sample-3</i>		
11.820	8.693	(110)
25.250	4.095	(300)
27.991	3.701	(222)
31.594	3.288	(321)
34.897	2.985	(410)
36.711	2.842	(420)
39.873	2.625	(422)
<i>Sample-4</i>		
28.196	3.675	(222)
40.382	2.593	(422)
41.089	2.557	(500)

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