HYDROTHERMAL SYNTHESIS AND CHARACTERISATION OF CRYSTALLINE

SODIUM   ZIRCONIUM PHOSPHATES

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ABSTRACT

Sodium zirconium phosphates have been synthesised hydrothermally in the presence of triethylamine, aiming at the formation of zeolite type porous crystalline sodium zirconium phosphates. The materials have been characterised by X-ray and electron diffraction, electron microscopy, thermal analysis, framework IR and ^{31}P MASNMR spectroscopies and adsorption techniques. The compounds are monoclinic, with lattice parameters, a = 15.29 Å, b = 8.80 Å, c =18.26 Å, and β = 123°. ^{31}P MASNMR spectra of this compound exhibited three distinct resonances at d= −8.4, −20.1 and −24.5 ppm respectively corresponding to three crystallographically nonequivalent positions for the phosphorus atoms . The materials were microporous and adsorbed significant amounts of water, n-hexane, benzene, m-xylene, cumene, tetrabutylamine and 1,3,5 trimethyl benzene.

MATERIALS INDEX : zirconium, sodium, phosphates, microporous material

INTRODUCTION

The synthesis of crystalline zirconium phosphates was first reported in 1964 by Clearfield and Stynes(1), who determined the formula as $Zr(HPO_4).H_2O$ (α-ZrP) based on chemical composition, dehydration and ion-exchange behaviour. Since then, many other crystalline phosphates of zirconium such as $Zr(HPO_4)_2$ (β -ZrP), $Zr(HPO_4).2H_2O$ (γ-ZrP) etc. have been prepared.(2-3)

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These crystalline phosphates have a layer structure . Each layer
consists of an infinite sheet of zirconium atoms sandwiched
between two sheets of hydrogen phosphate groups.(2) In addition
to the above group, a family of sodium zirconium phosphates
(NZP) known as Nasicon ceramics have also been synthesised at 473
K under hydrothermal conditions.(4)   The structure of
$NaZr_2(PO_4)_3$, a typical member of this family, consists of a
three-dimensional network made up of PO_4 tetrahedra sharing
corners with ZrO_6 octahedra and a three-dimensionally linked
interstitial space where sodium atoms may occupy four available
positions.(5)
    All the above crystalline materials have negligible
adsorption capacity for hydrocarbons. In the present paper, we
report the hydrothermal synthesis, in presence of organic bases,
of a crystalline microporous zirconium phosphate with significant
adsorption capacity similar to zeolites. While there are many
intriguing aspects to the structure of this material, this may be
the first example of a crystalline porous zirconium phosphate.

EXPERIMENTAL.

Synthesis of crystalline zirconium phosphate

    2 moles of $ZrOCl_2$. $8H_2O$ and one mole of NaCl were dissolved
in 100 ml of deionised water. Three moles of H_3PO_4 were added
dropwise under constant stirring. The resulting slurry was dried
on water bath and the material was further heated at 383 K to
remove the hydrochloric acid formed during the reaction. The
dried product was rehydrated by adding 50 ml. of deionised water.
Triethylamine, $(C_2H_5)_3N$, (in an amount equal to the moles of
NaCl) was added dropwise to the above slurry under constant
stirring. The resulting mixture (pH=4.1) was stirred for two
hours and then heated in an autoclave at 473 K for various
intervals of time. The pH of the reaction mixture decreased from
4.1 to 1.5 during the crystallisation.   The product was then
filtered, washed with deionised water, dried at 383 K in air, and
finally calcined in air at 873 K for ten hours to remove the
organics.

Characterization

    The material was analysed by wet chemical methods and by
inductively coupled plasma spectroscopy (JOBIN YVON). The degree
of crystallinity was evaluated by X-ray diffraction (Philips PW
1730, Ni filtered Cu-K$\propto$). The infrared framework vibration
spectra of the samples (Nujol mull technique) were recorded with
a Pye Unichem SP-300 spectrophotometer. Thermal analysis (TG,
DTG,DTA.) in flowing air was carried out with 50 mg. samples at a
heating rate of 10 K min^{-1} (NETZCH STA 409). Sorption
measurements were carried out using a McBain balance at 293 K.
Prior to adsorption, the samples were outgassed in vacuum (10^{-6})
at 673 K for several hours. Sorption of water, n-hexane,
cyclohexane and other sorbates was carried out at a relative
pressure of P/P_o=0.5. For transmission electron microscopy (TEM)
samples were crushed to a fine powder and ultrasonically
dispersed in isopropyl alcohol. A drop of this suspension was

then placed on a carbon film supported over a TEM specimen grid.
The samples, thus prepared, were then examined with an electron
microscope (JEOL MODEL 1200 EX operating at 120 KV). The lattice
parameter calibration with gold film showed the accuracy of the
measurement to be better than + 0.1%. Porosity measurements were
carried out using an Autoscan 60 mercury porosimeter. Solid state
^{31}P magic angle spinning NMR spectra were recorded at 121.442 MHz
on a Bruker MSL 300 FT-NMR spectrometer. A home built probe
employing Andrew-Beams type rotor design (6) was used for
recording ^{31}P spectra. The magic angle was precisely set by
monitoring rotational echoes (7) of the ^{89}Br satellite
transitions in powdered potassium bromide (8). π/2 pulse was
typicallly 4 us. Chemical shifts were referenced to external 85%
H_3PO_4.

RESULTS AND DISCUSSION

1) Chemical composition

The as-synthesised zirconium phosphate on calcination in air at
873 K underwent a weight loss of 7.3%. There was no further
weight loss on calcination up to 1273 K. Evolved gases included
both water and organic material. The results of the thermal
analysis are disussed in detail later. The sample calcined at 873
K had a chemical composition (wt%) Na = 2,   Zr = 43.34,   P =
17.16 and   O=37.5. Thus the anhydrous composition of the sample
may be formulated as $NaZr_5(PO_4)_7$. The chemical composition (wt%)
calculated on the basis of this formula is   Na = 2.0, Zr = 39.8,
P = 18.9 and O = 39.1.

X-ray / electron diffraction and transmission electron microscopy
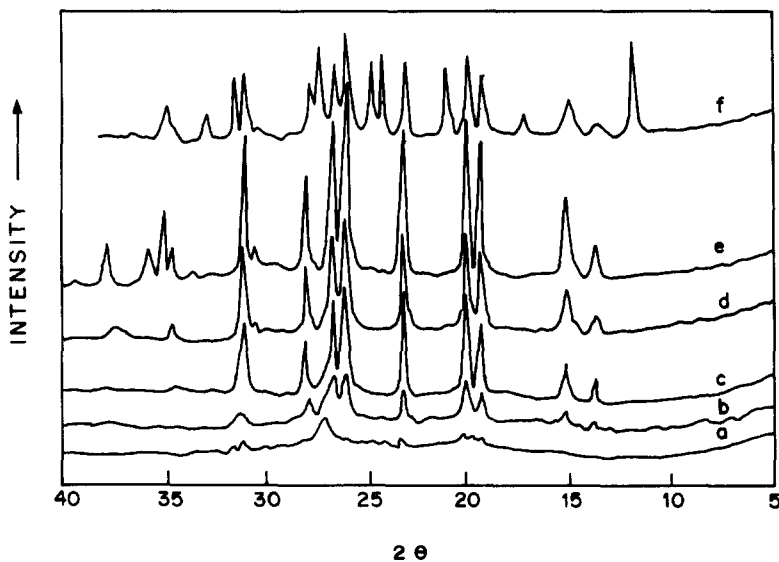
2 θ

FIG.1

X-ray diffraction patterns of as-synthesised sodium zirconium
phosphate. Curves : a) 4 days, b) 6 days, c) 8 days, d) 12 days,
e) 16 days, f) 20 days.

Fig.1 illustrates the evolution of the XRD pattern of the as-synthesised material over a period of 20 days. The sample remain amorphous after 4 days of crystallisation (Fig. 1 curve a). Crystallization starts after 6 days and increases progressively thereafter. The sample obtained on the 16th day is fully crystalline (Fig. 1, curve e). This XRD pattern remains unchanged even after calcination in air at 873 K (Fig. 1, curve e). No amorphous matter could be seen by transmission electron microscopy (Fig.2 a). When hydrothermal synthesis is continued beyond 16 days, there is a change in the XRD pattern of the material obtained (Fig. 1 curve f). A new material $Zr_3(PO_4)_4$, identified by its reported XRD pattern (9) starts forming. The material obtained on the 16th day (Fig.1, curve e) is the subject of this investigation. The " d " values for this sample are given in Table 1. It may be remarked that all the XRD lines for this material starts appearing right from the initiation of crystallization and grow progressively, suggesting that they belong to only one phase. The TEM photograph (Fig.2a) further confirms that the material responsible for the XRD pattern (in Fig.1, curve e) consists of only one phase. The selected area electron diffraction pattern of the sample (Fig.2b) also shows the absence of two phases.
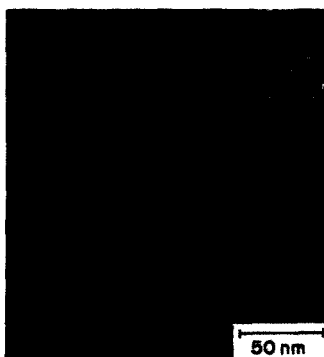

FIG.2a
Transmission Electron
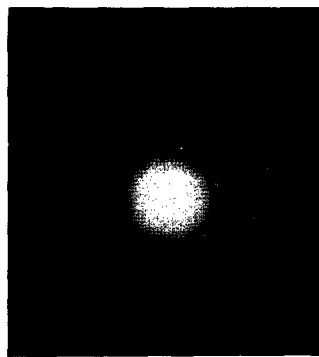Micrograph of sodium
zirconium phosphate.
$(NaZr_5(PO_4)_7)$

FIG.2b
Selected Area Electron
diffraction pattern
of sodium zirconium
phosphate.$NaZr_5(Po_4)_7$

The pattern remained unchanged irrespective of the area of the sample selected for diffraction studies. The observed "d" values are compared with those of some known zirconium phosphates like $NaZr_2(PO_4)_3$, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), $Zr(HPO_4)_2$ (β-ZrP), and $Zr(HPO_4)_2 \cdot 2H_2O$ (γ-ZrP) in Table 1. It is apparent that the XRD spectrum and "d" values do not match with those published earlier (2,9). The above mentioned zirconium phosphates have layer structures and behave as ion exchangers (10). Adjacent layers are arranged in such a way as to produce cavities between the layers. However, the passageways leading into these cavities are rather restricted thereby causing low adsorption capacity.

TABLE 1
" d "values (Å) of Zirconium phosphates

present study	$NaZr_2(PO_4)_3$	α-ZrP	β-ZrP	γ-ZrP	$(NH_4)_x ZrH_{1-x}(PO_4)_2$
6.3 (19)	6.31(s)	10.0(100)	9.40(90)	12.2(90)	6.46(ms)
5.86(39)	4.55(vs)	4.50(50)	5.40(100)	5.81(100)	5.64(w)
4.52(63)	4.39(vs)	4.19(vs)	4.65(50)	4.62(35)	4.74(ms)
4.31(73)	3.80(vs)	3.86(30)	3.83(20)	4.35(35)	4.35(ms)
3.76(18)	3.17(vs)	3.66(30)	3.56(85)	3.74(45)	3.83(w)
3.34(100)	2.87(vs)	3.45(50)	3.30(90)	3.31(90)	3.31(s)
3.27(65)	2.67(s)	3.15(15)	3.12(40)	3.20(35)	3.21(vs)

TABLE 2
Analysis of X-ray diffraction pattern of $NaZr_5(PO_4)_7$
a(m) = 15.24,   b(m) = 8.80,   c(m) = 18.26 Å .   B = 123°

Intensity (relative)	d (Å) (observed)	d (Å) (calculated)	hkl
mw	6.25	6.30	200
ms	5.86	5.88	111
s	4.48	4.42	020
vs	4.31	4.35	021
vs	3.76	3.80	310
s	3.34	3.32	311
ms	3.27	3.30	302
ms	3.16	3.16	203
vs	2.85	2.80	132
w	2.56	2.59	223
ms	2.51	2.54	332

s = strong,   w = weak,   m = medium,   v = very.

For example in β-ZrP, the free space of the passageways is just sufficient to allow an unhydrated K^+ to diffuse unobstructed (11). In view of the significant adsorption capacity for large hydrocarbon molecules exhibited by the material of the present study (see later) it is unlikely to be identical to the layered phosphates reported earlier.

The well known $NaZr_2(PO_4)_3$ with the Nasicon structure was also obtained by us when the initial pH of the mixture was changed to 6.2 (instead of 4.1).

Thermal Analysis
The weight loss of 7.3% is associated mainly with the two exotherms in DTA (at 593 and 863 K respectively) and may be ascribed to the loss of the occluded organic matter. All organics are removed below 873 K and there is no weight loss or heat changes upto 1273 K showing the thermal stability of the material.
    The calcined product was exchanged with ammonium acetate (5% aqueous solution.) and it was observed that 40% of the sodium was exchanged for NH_4^+.
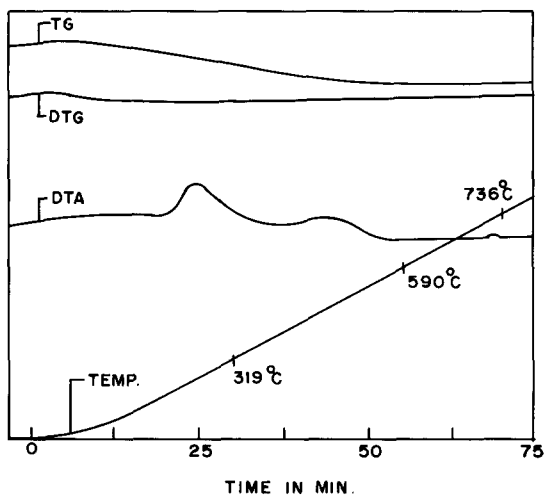
FIG.3
DTA, TG, and DTG curves of $NaZr_5(Po_4)_7$

Infrared spectroscopy

The framework infrared spectrum of the as-synthesised material
is given in the Fig. 4. (curve A).

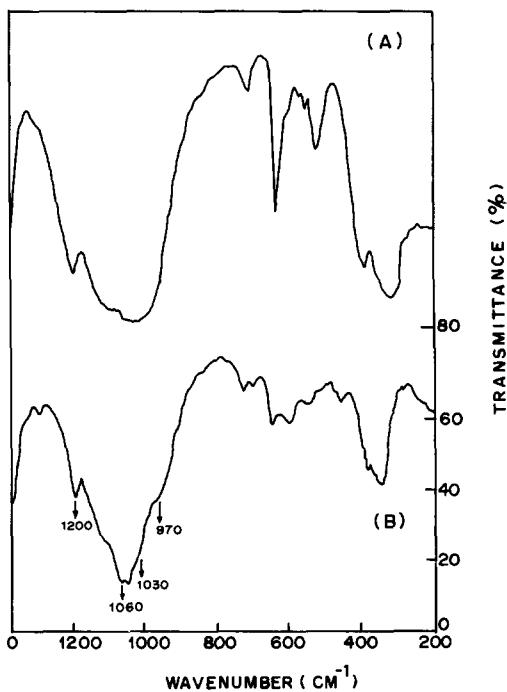**FIG.4**
IR spectra of, A - $NaZr_5(Po_4)_7$, B - $NaZr_2(Po_4)_3$

The IR spectrum of the known sodium zirconium phosphate $NaZr_2(PO_4)_3$ (Nasicon) is also included in Fig.4. (curve B).

Four bands observed at 970, 1030, 1060 and 1200 cm^{-1} are internal modes of the PO_4^{-3} tetrahedra. The other bands in the region of 800-200 cm^{-1} do not match with any of the reported phases in the sodium zirconium phosphate system.

Transmission Electron Microscopy

Transmission electron micrograph of the as-synthesised compound is shown in Fig. 2a. It is observed that crystallites are thin transparent sheets in rectangular shape. The electron diffraction pattern of the compound is shown in Fig.2b and it remains invariant at various places observed in TEM, confirming the presence of single phase crystalline material. The d values calculated from this electron diffraction matche well with the d values obtained from XRD pattern as shown table 1.

The X-ray diffraction pattern can be indexed assuming a monoclinic cell. The lattic parameter calculated on the assumption of a monoclinic cell are, a = 15.24 Å, b = 8.80 Å, c = 18.26A°, and β = 123°. The observed and the calculated d values (table 2) match well, confirming the monoclinic symmetry of the compound.

^{31}P MASNMR

Fig. 5.(curve A) shows the ^{31}P MASNMR of the $NaZr_2(PO_4)_3$ compound having the Nasicon structure. The peak at d= -24.7 ppm, is in excellent agreement with the reported value of d= -24.7 ppm for the same material but synthesized by a different method. (12) The ^{31}P MASNMR spectrum of the porous phase $NaZr_5(PO_4)_7$ is shown in Fig. 5 (curve B). Due to the multiplicity of ^{31}P peaks it was necessary to record the NMR spectrum at two different spinning speeds. This technique enabled us to locate three distinct ^{31}P resonances at d= -8.4, d= -20.1 and d= -24.5 ppm respectively. For the monoclinic type Nasicon structure with the space group Cc the phosphorous atoms occupy three crystallographically non – equivalent sites giving rise to the three ^{31}P signals observed in the NMR spectrum (Fig.5, curve B).

Comparison with $LiZr_2(PO_4)_3$ shows that while the three line ^{31}P pattern is reproduced in our system also (13), the exact signal positions do not match. In view of the different XRD pattern, lattice parameter values and composition of our compound, the ^{31}P NMR spectra is not expected to be identical to the Nasicon material.

Sorption Study

Adsorption capacities measured on a McBain adsorption unit are given in Table 3. It is observed that water and other sorbates are adsorbed reversibly showing the porous nature of the material. The material adsorbed sorbates like 1,3,5,trimethyl benzene, but did not adsorb tri-isopropyl benzene showing the pore size of the calcined product to be around 0.8 nm.
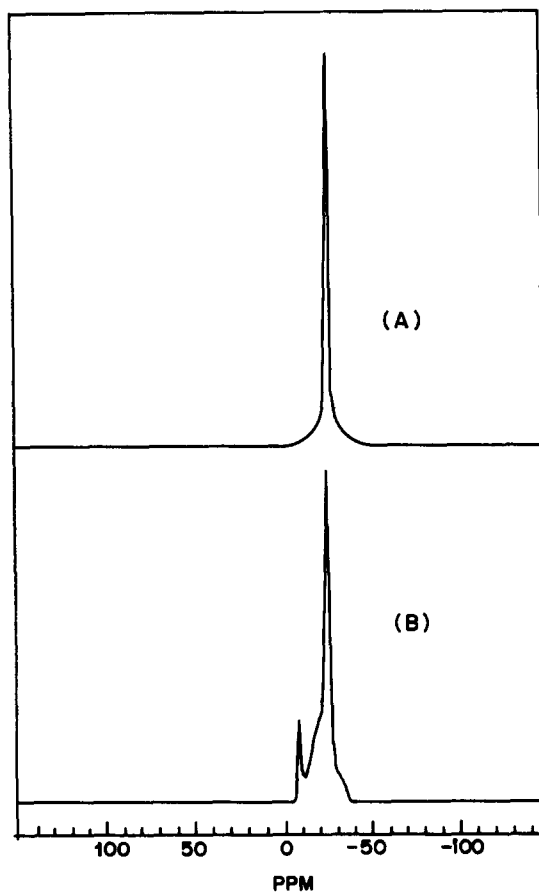
<u>FIG.5</u>
^{31}P MASNMR spectra of A : $NaZr_2(Po_4)_3$,   B : $NaZr_5(Po_4)_7$

TABLE 3
Adsorption results of the calcined $NaZr_5(Po_4)_7$

Sorbate	wt%	vol% (ml/gm)	moles/gm(10^2)
1) water	13	0.13	0.722
2) n-hexane	5.83	0.088	0.0575
3) Benzene	5.2	0.0591	0.0666
4) m-xylene	6.86	0.0789	0.0646
5) Cumene	7.59	0.0878	0.0631
6) 1,3,5 Trimethyl benzene	7.2	0.0833	0.06
7) Tributyl amine	8.6	0.0867	0.0463
8) 1,3,5, tri-isopropyl benzene	nil	--	--

CONCLUSION

A monoclinic Sodium zirconium phosphate with the $NaZr_5(Po4)_7$ composition is formed when synthesised hydrothermally in presence of triethylamine at lower pH. The material was analysed using chemical analysis, XRD, TEM, Thermal analysis, ^{31}P MASNMR and identified as a new phase. The material is microporous and showed adsorption properties similar to zeolites. Using hydrothermal synthesis and by using various structure directing templates, it may be possible to prepare porous Zirconium Phosphates with different structures and properties which may lead to a new class of Zeolites.

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