  Bull. Chem. Soc. Jpn., 61, 2181—2184 (1988)

Ion-Exchange Properties of Niobium(V) Materials. II. Synthesis and Characterization of Crystalline Niobium(V) Phosphate

Mohsin QURESHI,* Jai Prakash GUPTA,†† Hina KHAN, and Anees AHMAD†
Chemistry Section, Z. H. College of Engg. and Technology, Aligarh Muslim University, Aligarh 202002, India
†Analytical Laboratory, Chemistry Department, A.M.U. Aligarh 202002, India
(Received February 9, 1987)

An attempt has been made to synthesize and characterize the crystalline niobium(V) phosphate. The characterization was done on the basis of pH titration, X-ray, XPS, TGA, DSC, and IR studies. It is an ion exchange material which shows about 20% higher chemical stability over the amorphous niobium(V) phosphate. It was found to have a pseudocubical unit cell structure with a_0(H)=10.244 Å and a stiff three dimensional zeolytic structure. The empirical formula of the compound was obtained as $Nb_2O_5 \cdot 1.5\ P_2O_5 \cdot 7.5\ H_2O$. The proposed chemical formula is $(NbO)_2(HPO_4)_3 \cdot 6H_2O$ (d_{110}=7.23 Å). The exchanger is monofunctional in nature having the maximum exchange capacity of 4.6 meq g^{-1} for potassium ion at pH 8.5

During the last few years some niobium and tantalum based inorganic ion exchangers have been systhesized and their ion-exchange properties and analytical applications have been explored.[1-8] The exchangers were mostly amorphous or poorly crystalline. These studies suffer from the fact that the gels used were poorly characterized and/or the correct exchange capacity was not determined. In order to obtain thermodynamically meaningful results, the gel has to be well characterized.[9] Qureshi et al.[3] showed for the first time that when niobium antimonate is refluxed with mother liquor, its ion exchange behavior becomes more reproducible. Clearfield et al.[9] refluxed a precipitated gel of zirconium phosphate for 48 h in 0.5 M (M=mol dm^{-3}) phosphoric acid. These refluxed gels were more resistent to hydrolysis and their behavior was more reproducible than that of unrefluxed gels.

It is worthwhile to study the crystalline materials in detail as these materials show a more reproducible behavior and hence they can be used for the mechanistic studies. It is rather difficult to locate the exact exchange sites in amorphous materials and very little information exists regarding the structural aspects of amorphous inorganic ion exchangers. Further the amorphous materials show a greater tendency towards hydrolysis than the corresponding crystalline materials.

In this paper the results on the preparation and characterization of the crystalline niobium(V) phosphate are presented. Its structural properties have been elucidated on the basis of TGA, DSC, IR, XPS, and X-ray diffraction studies. An attempt has also been made to investigate the mechanism of ion exchange of alkali metal ions on this material and to locate the possible exchange sites.

Experimental

Reagents and Synthesis. Diniobium pentaoxide was obtained from BDH (Poole, England). All other reagents of analytical reagent grade were used.

Niobium solution (0.1M)[12] was prepared by dissolving calculated amount of Nb_2O_5 in concd H_2SO_4 in presence of sufficient amount of $(NH_4)_2SO_4$. The crystalline niobium(V) phosphate has been synthesized by mixing niobium solution (0.1M) and phosphoric acid (0.5M) in the volume ratio of 1:4. The pH of this mixture was adjusted to 1 with concentrated ammonia solution. The precipitate so obtained was left with mother liquor for 24 h. Then it was filtered and washed with dimineralized water until the filtrate was neutral to litmus and free from SO_4^{2-} ions. The gel was dried at 45 °C in an oven and then refluxed with 1M H_3PO_4 for 10 h. The exchanger was again washed and dried and stored over saturated solution of $BaCl_2$. It is partially in H^+-form and hence designated as C-NbPx. For ion-exchange studies, C-NbPx was converted completely into H^+-form by the batch method of Townsend[23] using 1M HNO_3. The sample will hereafter be referred to as C-NbP-H^+ in the H^+-form and C-NbP-M^+ (M^+=Li^+, Na^+, K^+ etc.) in the metal form.

Ion-Exchange Capacity. The breakthrough capacity measurements for Li^+, Na^+, Rb^+, and Cs^+ were done by the column elution method[13] using a column of 0.5 cm (i.d.). The feed (0.5 M) was passed until its pH became equal to that of the effluent collected. The hydrogen ions so eluted were titrated against standarized 0.1 M NaOH.

Composition and Chemical Stability. The exchanger was analyzed for the presence of niobium and phosphorus gravimetrically while its chemical stability in different solvents was checked spectrophotometrically using Bausch and Lomb Spectronic-710 spectrophotometer by the methods described earlier.[12]

Thermal Analysis. The TGA was performed by using 0.1 g sample. The heating was done in the atmosphere of air at the rate of 10 °C min^{-1}. The DSC was recorded in the atmosphere of helium at a flow rate of 200 ml min^{-1} and a heating rate of 10 °C min^{-1}. The results are given in Figs. 2(a) and 2(b). DuPont Thermal Analysers Model 950 and 900 were used for TGA and DSC studies respectively.

Water Absorption. The sample in H^+-form (0.5 g) was heated at 120 °C for 24 h in a covered silica crucible. It was then stored in a desiccator over a saturated solution of ammonium nitrate. The weight of the sample along with the crucible was recorded at different intervals.

pH Titration. The pH titrations were carried out by Topp and Pepper method.[10] Each sample of dry C-NbP-H^+ (200 mg) was equilibrated with 20 ml portions of

†† Present address: FOSROC Technology Ltd., Bourne Road, Aston, Birmingham, England.

0.1 M (MCl-MOH) solutions at 25±0.5 °C (M^+=Li^+, Na^+, K^+, and Cs^+). The molar ratio of MCl/MOH was varied to maintain a constant ionic strength (μ=0.1) of the equilibrating mixture. After 24 h the pH of the supernatant solutions were recorded and plotted against the milli equivalents of OH^- added per gram of dry exchanger (Fig. 1). Orion Research Microprocessor Ionalyzer/901 having combination glass electrode was used for the pH measurements.

X-Ray Diffraction and XPS Studies. Powder X-ray diffractograms of the exchanger in H^+, Li^+, Na^+, and K^+-forms were taken using nickel filtered Cu $K\alpha$ radiations. On the other hand only two samples of the exchanger, namely, C-NbPx and C-NbP-K^+ were used for XPS (or ESCA) studies (see Table 1).

IR Studies. The infrared spectra of niobium phosphate in H^+, Li^+, Na^+, and K^+-forms along with that of niobium hydroxide, synthesized in the laboratory, were taken using the KBr disc technique and recorded on a Perkin Elmer Spectrophotometer-621. The results are shown in Fig. 3.

Results and Discussion

The crystalline phase of niobium(V) phosphate, C-NbP, shows reproducibility in its ion-exchange capacity, composition and other characteristics. The chemical dissolution data of C-NbP-H^+ (Table 2) show an overall ca. 20% higher chemical stability over the amorphous niobium(V) phosphate[12] probably due to its crystalline nature. The trend of its stability, in different media, is similar to that of the amorphous material, i.e., HNO_3>HCl>CH_3COOH≫tartaric acid>H_2SO_4>NH_4OH>KOH. The same trend of stability of the two materials may be due to their similar chemical nature. They are less stable in sulfuric and tartaric acids due to the formation of sulfate and tartarate of niobium. On the other hand they are more soluble in ammonium and potassium hydroxides because of high pH.

The breakthrough capacities (meq g^{-1}) of C-NbP for the alkali metal ions decreas in the order K^+ (1.37)>Na^+(1.06) >Rb^+(0.86) >Cs^+(0.84) >Li^+ (0.70) showing a preferential uptake for potassium ions and the least uptake for lithium ions. The pH titration curves (Fig. 1) shows a similar trend. Furthermore, this order of uptake is only possible when the exchanger has an inelastic matrix. If the matrix were elastic, it would have resulted in a different order of exchange, probably parallel to the Hofmeister's lyotropic series i.e., Li^+<Na^+<$K^+$$Rb^+$<$Cs^+$. This adsorption sequence has been observed in zirconium phosphate and organic cation-exchange resins, which possess the elastic structure.[8] As we do not find this order of uptake in the crystalline niobium(V) phosphate, we can say that it may have a stiff three dimensional structure having a fixed pore size.

The results of X-ray diffraction (XRD) studies of C-NbP-H^+ show a large number of d-values of which the important $d(I/I_0)_{hkl}$ are 7.23 $(85)_{110}$, 4.55 $(41)_{210}$, 3.23 $(100)_{310}$, 2.28 $(43)_{420}$, and 1.42 $(29)_{551,711}$. The XRD of the different cationic forms (H^+, Li^+, Na^+, and K^+-forms) of the exchanger show that their d values are very close to each other and hence one can say that the exchanger possesses an appreciably stiff structure. The analysis of the X-ray data reveals its pseudocubical unit cell structure with $a_0(H^+)$=10.224 Å.

Since the exchanger is precipitated in presence of large amounts of SO_4^{2-} and NH_4^+ ions with the help of concentrated ammonia solution, it is reasonable to assume the possible contamination of the exchanger with these ions. XPS (or ESCA) studies were conducted to check this possibility. It is worth noting from Table 1 that only initially some NH_4^+ ions are present (as shown by a peak of nitrogen) in the exchanger which are later replaced by the potassium ions when the exchanger is converted into K^+-form. The XPS studies show no sign for the presence of sulfur and this rules out the possibility of sulfate contami-

Table 1. Binding Energies and Percent Atomic Compositions of Niobium(V) Phosphate Obtained by XPS

Element	BE	C-NbPx	C-NbP(K^+-form)
	eV	At. comp./%	At. comp./%
Phosphorus	150	13.6	14.4
Niobium	230	8.8	10.1
Potassium	320	—	2.1
Nitrogen	416	2.9	—
Oxygen	545	49.3	52.8
Carbon	300	25.4	20.6

Table 2. Solubility of Crystalline Niobium(V) Phosphate in Different Solvents

Solvent	C-NbP		NbP3	
	Nb/mg L^{-1}	P/mg L^{-1}	Nb/mg L^{-1}	P/mg L^{-1}
4M Sulfuric acid	841.5	20.9	1051.5	26.2
4M Nitric acid	0.0	0.9	0.0	1.2
4M Hydrochloric acid	0.0	1.4	0.0	1.8
1M Tartaric acid	292.1	1.4	343.7	1.8
1M Acetic acid	0.0	53.3	0.0	65.0
4M Ammonia	145.8	71.2	180.0	91.7
0.1M Potassium hydroxide	1651.0	553.0	2000.0	675.0
1M Sodium chloride	0.0	23.1	0.0	62.5
1M Ammonium nitrate	0.0	18.7	0.0	43.7
Demineralized water	0.0	5.2	0.0	10.4

NbP3 = Amorphous niobium phosphate [12]

nation of the exchanger. Hence we can say that initially the exchanger (C-NbPx) contains some ammonium ions in exchanged form only and not due to entrapped ammonia/ammonium salt. The binding energies also confirm the presence of Nb and P in their pentavalent state. The ESCA of the sample shows surface contamination of niobium(V) phosphate due to carbon (Table 1). This contamination may be due to (i) rotary pump oil vapours adsorbed on the surface of the pellet during the pressing, (ii) the presence of niobium carbide as an impurity in Nb_2O_5, (iii) the adsorption of atmospheric CO_2 by the exchanger leading to the formation of carbonate on the surface of the material. Similar results were obtained by Alberti in the ESCA spectra of $ZrPO_4$.[10,11] The percent atomic composition of the surface obtained by XPS shows the Nb/P mole ratio between 1.42—1.54 (Table 1) which is very close to the 1.5 obtained by chemical analysis of the sample. This shows that the surface and the bulk composition is the same. On the basis of these findings one can assign the following formula to the H^+-form of C-NbP.

$$(NbO)_2(HPO_4)_3 \cdot nH_2O \quad (1)$$

The infrared spectra of C-NbP-H^+ (Fig. 3,b) shows a band between 3600—3100 cm^{-1} having two strong maxima at 3150 and 3450 cm^{-1}. They are characteristic of stretching vibrations of coordinated water molecules and this implies that hydrogen bonding exists between OH groups and water molecules surrounding them.[18] A sharp peak at 1630 cm^{-1} corresponds to the deformation vibration of interstitial water molecules and the hydroxyl group [$\delta(H_2O)$ and (OH)]. The sharp peak at 1400 cm^{-1} and a broad and strong peak at 1010 cm^{-1} may be assigned to the deformation vibration of P-OH groups [δ_2(P-OH)]. The peak at 690 cm^{-1} corresponds to the P-O stretching while those at 510 and 380 cm^{-1} may correspond to M-O interatomic vibrations [ν_1(Nb-O, P-O)]. The small peaks appearing between 260—200 cm^{-1} are due to the lattice vibrations.

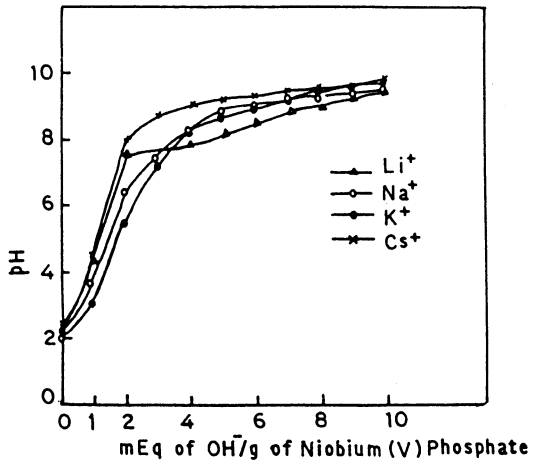

Fig. 1. pH-titration curves of Li^+, Na^+, K^+, and Cs^+, ions on the crystalline niobium(V) phosphate.

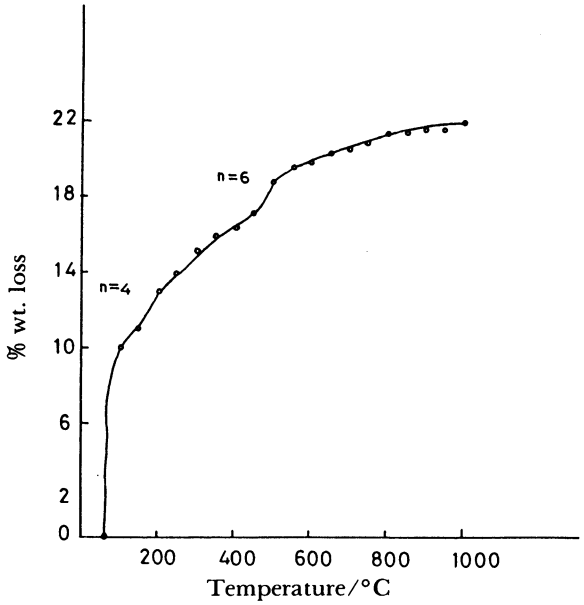

Fig. 2(a). TGA curve of crystalline niobium(V) phosphate(C-NbP-H^+).

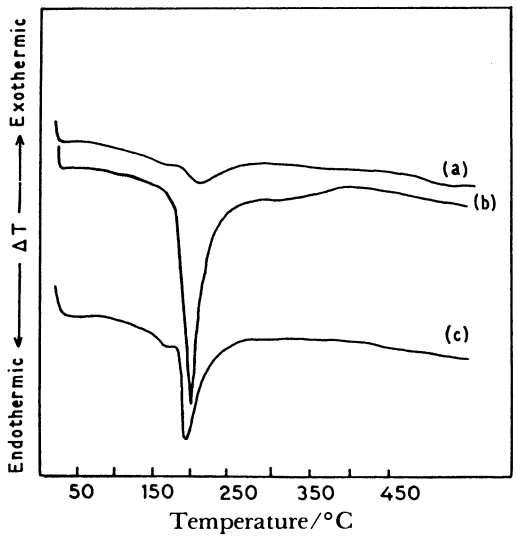

Fig. 2(b). DSC curves of crystalline niobium(V) phosphate; a=C-NbP-H^+, b=C-NbP-Na^+, c= C-NbP-K^+.

On comparing the IR spectroscopic behavior of niobium phosphate in the H^+-form with those in the Na^+ and K^+-forms (Fig. 3), it is found that all the three have a similar type of lattice structure. In the spectra of these three samples, bands relating to acidic HPO_4^{2-} groups (3150, 2320, 1400, and 510 cm^{-1}) are found.[18] If the alkali metal content approaches the total capacity value, these frequencies virtually disappear and only bands relating to water of crystallization are visible. Such a change suggests that the material was composed of strongly hydrogen bonded three dimensional aggregate,[19,20] having HPO_4^{2-} groups as the cation exchange sites. Here the proton of HPO_4^{2-} group is exchanged by M^+.

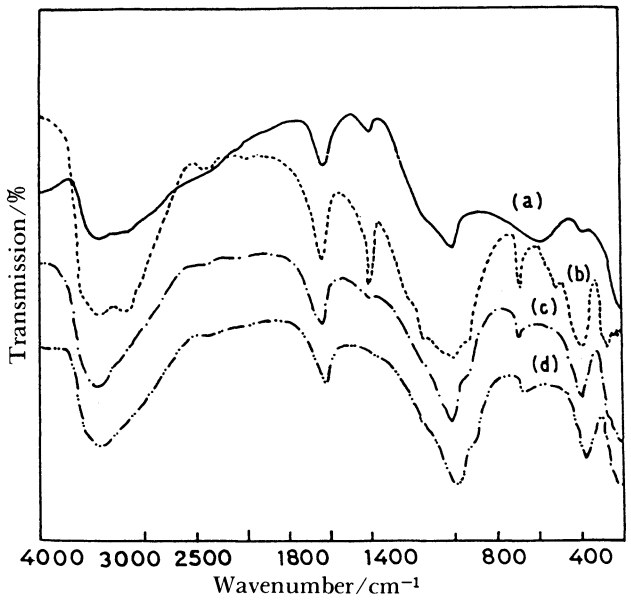

Fig. 3. IR spectra of niobium hydroxide and crystalline niobium(V) phosphate;
a=Nb-OH, b=C-NbP-H^+, c=C-NbP-Na^+, d=C-NbP-K^+.

$$HPO_4^{2-} + M^+ \rightleftarrows MPO_4^{2-} + H^+$$

Further the thermoanalytical investigations of C-NbP-H^+ indicate a weight loss of 22% up to 1000 °C (Fig. 2a). Assuming that at this temperature the composition of the sample is $Nb_2O_5 \cdot 1.5\ P_2O_5$, the number of moles of water lost per formula weight of the exchanger was calculated as 7.5.[21] It is the total number of moles of water present, a part of these are present as water of crystallization (6 mol) and the rest as water of constitution (1.5 mol). The later split up to form the OH species of the anionic part (HPO_4^{2-}) of which H^+ seems to give hydrogen exchange capacity in the H^+-form of the exchanger.[22] The DTA curves of the sample in H^+, Na^+, and K^+-forms are shown in Fig. 2b. It is evident that most of the water of crystallization is removed up to 200 °C after which there is a continuous energy consumption and loss in weight. It may be due to the removal of the remaining water of crystallization which are probably coordinated to niobium.

The weight loss at a higher temperature in C-NbP-H^+ may be owing to the condensation of HPO_4^{2-} species to $P_2O_7^{4-}$. This process of dehydration is an irreversible process above 200 °C and the water lost is not regained even after immersing the treated sample in water. But at 150 °C, 3.32 moles of water per formula weight are reversibly lost by the exchanger. The exchanger reabsorbs the lost water when left in atmosphere and results in the cracking of the former.

Further there is only one inflection point in the pH titration of C-NbP-H^+ corresponding to the monofunctional behavior of this material (see Fig. 1). Its ion-exchange capacity as determined by the titration curve, is 4.6 meq g^{-1} for K^+ at pH 8.5.

On the basis of these findings we can write the empirical formula as follows

$$(NbO)_2(HPO_4)_3 \cdot 6H_2O \quad (d_{110} = 7.231\ \text{Å}) \qquad (2)$$
[Theoretical Exchange Capacity = 4.88 meq g^{-1}]

This formula agrees well with the experimental findings. The uptake of K^+ ions (46 meq g^{-1}) is very close to the theoretical exchange capacity of the proposed formula.

The CSIR (INDIA) is thanked for financial assistance.

References

1) M. Qureshi, J. P. Rawat, and A. P. Gupta, *J. Chromatog.*, **118**, 167 (1976).
2) M. Qureshi, J. P. Rawat, and A. P. Gupta, *J. Chromatographia*, **11**, 202 (1978).
3) M. Qureshi, J. P. Gupta, A. P. Gupta, and T. Gupta, *J. Chromatog.*, **144**, 231 (1977).
4) M. Qureshi, A. P. Gupta, D. V. Nowell, and J. P. Gupta, *J. Inorg. Nucl. Chem.*, **40**, 545, (1978).
5) M. Qureshi, A. P. Gupta, I. S. Thakur, and V. P. Singh, *Sep. Sci. Tech.*, **15**, 1255 (1980).
6) J. P. Rawat and S. Q. Mujtaba, *Can. J. Chem.*, **53**, 5286 (1975).
7) J. P. Rawat and P. S. Thind, *J. Phys. Chem.*, **80**, 1387 (1976).
8) M. Qureshi, J. P. Gupta, and V. Sharma, *Anal. Chem.*, **45**, 1901 (1973).
9) A. Clearfield, "Inorg. Ion Exch. Mater. I. CRC: Boca Raton," Florida, U.S.A. (1982), Chap. I, p. 16.
10) G. Alberti, U. Constantino, G. Marletta, O. Puglisi, and S. Pignataro, *J. Inorg. Nucl. Chem.*, **43**, 3329 (1981).
11) G. Marletta, O. Puglisi, S. Pignataro, G. Alberti, and U. Constantino, *Polyhedron*, **2**(3), 157 (1983).
12) M. Qureshi, A. Ahmad, N. A. Shakeel, and A. P. Gupta, *Bull. Chem. Soc. Jpn.*, **59**, 3247 (1986).
13) O. Samuelson, "Ion Exchange Separations in Analytical Chemistry," Stockholm (1944).
14) G. E. F. Lundell and J. I. Hoffman, "Outlines of Methods of Chemical Analysis," Wiley, New York (1958), p. 117.
15) N. H. Furman, "Standard Methods of Chemical Analysis," Van Nostrand, New York (1971), 6th ed., p. 812.
16) D. Alan Westland and Jerome Bezaire, *Anal. Chim. Acta*, **66**, 187 (1973).
17) APHA-AWWA-WPCF, Standard Methods for the examination of water and waste water, 14th ed., 1975, p. 479.
18) J. A. Marinsky and Y. Marcus, "Ion Exchange and Solvent Extraction Series," Marcel Dekker, Inc., New York (1973), Vol. 5, p. 19.
19) W. Feitknecht, R. Giovanoli, W. Michaelis, and M. Muller, *Z. Anorg. Allgen, Chem.*, **417**, 114 (1975).
20) J. Burgess, "Metal Ions in Solution," Ellis Hawood, London (1978), Chap. 10.
21) G. Alberti, U. Costantino, and L. Zsinka, *J. Inorg. Nucl. Chem.*, **36**, 3549 (1972).
22) J. S. Gill and S. N. Tandan, *J. Radioanal. Chem.*, **36**, 345 (1977).
23) R. M. Bairer, R. R. Townsend, *J. Chem. Soc., Faraday Trans., 1*, **72**, 661 (1976).