ADSORPTION AND CATALYTIC PROPERTIES OF ACTIVATED CARBON, INERT OXIDES
AND INORGANIC ION EXCHANGERS

A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF PHILOSOPHY

IN

CHEMISTRY

HINA

ALIGARH MUSLIM UNIVERSITY
ALIGARH
1987
This is to certify that the work embodied in this dissertation is the original work of the candidate and is suitable for submission for the award of M.Phil. degree in Chemistry of the Aligarh Muslim University Aligarh.

R. Qureshi
(Mohsin Qureshi)
Supervisor
ACKNOWLEDGEMENTS

I wish to express my sincere and earnest thanks to Prof. Mohsin Qureshi, Emeritus Scientist, who spared his precious time to guide and inspire me at each and every step throughout the course of this work.

My cordial thanks are due to Prof. A. U. Malik, Chairman, Chemistry Section, Z.H. College of Engg. and Tech., AMU for providing necessary research facilities. I am grateful to Dr. Safia Mehdi, R.R.L. Hyderabad for the X-ray analysis.

I owe many thanks to my lab. colleagues and friends especially to Dr. Anees Ahmad, Shahreer Ahmad and Nishat Manzar for their unfailing cooperation. I am no less grateful to my parents for their constant encouragement. Financial support by the C.S.I.R., New Delhi is gratefully acknowledged.

( HINA )
# CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER I</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER II</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>32</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>35</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>39</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>56</td>
</tr>
</tbody>
</table>
## LIST OF TABLE AND FIGURES

<table>
<thead>
<tr>
<th>Table/Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Comparison of X-ray Data of NbOPO$_4$ (ASTM No.19–366) and Heated Niobium Phosphate</td>
<td>48</td>
</tr>
<tr>
<td>Fig. 2.1</td>
<td>IR Spectra of Refluxed Niobium (V) Phosphate</td>
<td>40</td>
</tr>
<tr>
<td>Fig. 2.2</td>
<td>IR Spectra of Heated Niobium (V) Phosphate</td>
<td>44</td>
</tr>
<tr>
<td>Fig. 2.3</td>
<td>IR Spectra of Niobium (V) Phosphate prepared from N$_2$O$_5$ (NPO)</td>
<td>41</td>
</tr>
<tr>
<td>Fig. 2.4</td>
<td>IR Spectra of Niobium (V) Phosphate prepared from NbCl$_5$ (NPC)</td>
<td>42</td>
</tr>
<tr>
<td>Fig. 2.5</td>
<td>X-ray Diffractograms of Refluxed Niobium (V) Phosphate (NPR)</td>
<td>46</td>
</tr>
<tr>
<td>Fig. 2.6</td>
<td>X-ray Diffractograms of Heated Niobium (V) Phosphate (NPT)</td>
<td>49</td>
</tr>
<tr>
<td>Fig. 2.7</td>
<td>X-ray Diffractogram of Niobium (V) Phosphate by HF Method</td>
<td>52</td>
</tr>
<tr>
<td>Fig. 2.8</td>
<td>X-ray Diffractogram of Niobium (V) Phosphate prepared from NbCl$_5$ (NPC)</td>
<td>53</td>
</tr>
<tr>
<td>Fig. 2.9</td>
<td>X-ray Diffractograms of Niobium (V) Phosphate prepared from Nb$_2$O$_5$ (NPO)</td>
<td>54</td>
</tr>
</tbody>
</table>
INTRODUCTION

The adsorption and catalytic properties of a material form one of the most fascinating areas of surface chemistry. Since the molecules on the surface have a different environment from those in the bulk of the material, the surface has a different free energy from the bulk of the material [1]. When the molecules of a gas or liquid are concentrated on the surface of a solid, the molecules are said to be adsorbed on the solid surface. This is a surface process which is different from the penetration of one component through the body of another which is called absorption.

The surface enters into reactions as a catalyst. This type of catalysis called heterogeneous catalysis is understandable only on the basis of some of the information deduced in adsorption studies. Similarly the conclusions that are drawn from the chemical reactions on a surface help to answer some of the problems unsolved by direct adsorption studies.

The goal of modern physicochemical studies of surface phenomena is the understanding of these phenomena by means of a molecular model. The photoelectron (ESCA) method can be applied to reveal some of the bonding properties of adsorbed species. Infrared absorption spectra, which
reveal the characteristic vibrations of the adsorbed species, can also be obtained by using infrared transparent materials and a technique that involves total internal reflection.

Heterogeneous catalysis is a procedure of great importance in industrial chemistry. This fact and the challenge of the many unexplained phenomena makes the study of the adsorbed state one of the most exciting areas of modern physicochemical research.

Adsorption is sometimes classified as physical and chemical. The chemical adsorption is more commonly called as chemisorption. If the molecules are adsorbed to a solid surface by essentially physical forces it is called physical adsorption. On the other hand if the molecules form chemical bonds with the solid surface the phenomena is called as chemisorption. Most interest in adsorption and in the closely related field of heterogeneous catalysis, is in chemisorption.

A very important but little understood process is the adsorption of a solute of a solution onto a solid adsorbent. This procedure is followed, for example, in the decolorizing of solutions using, ordinarily, activated charcoal. The separation technique of chromatography also makes use of
the relative adsorption tendencies of the solutes of a solution.

A fairly satisfactory empirical isotherm, which can be applied to adsorption of gases has been principally used for adsorption from solution. This is known as the Freundlich isotherm. If \( Y \) is the weight of solute adsorbed per gram of adsorbent and \( c \) is the concentration of the solute in solution, the empirical relation is \( Y = Kc^{1/n} \), where \( K \) and \( n \) are empirical constants.

Many chemical processes occur in the presence of certain surfaces that do not proceed at all in the absence of such surfaces or do so very slowly. Such reactions are said to be exhibiting heterogeneous catalysis. The effect of the surface is often so profound that it may be difficult to remember that this effect is that of hastening the approach to an equilibrium state.

The most dramatic surface catalytic effects must be attributed to reactions of chemisorbed species. Physical adsorption is effective in raising the local concentration of the reagents and in supplying a reservoir of thermal energy to these reagents. Chemisorption on the other hand may result in a rather drastic disruption of the bonding in an adsorbed molecule.
It is therefore clear that heterogeneous catalysis can be understood in detail only when the nature of the adsorbed species is so understood. At present only some features of the heterogeneous catalysis can be given a molecular description. It is true, however, that one of the most fruitful approaches to an understanding of the adsorbed state is through studies of a reaction that the molecules of this state undergo.

The adsorbents which have been commonly studied are alumina, silica, carbon and cellulose [2]. In addition to these some adsorption studies have been reported on tin oxide, titanium oxide, thorium oxide and zirconium oxide [3].

A new branch of catalysts has been developed during the last ten years. They are solid acids such as zirconium phosphate and metals supported on zirconium phosphate.

In order to study in a systematic manner it is worthwhile to choose only a few adsorbents. As activated carbon is one of the less studied adsorbents it was chosen for a detailed study. Another novel adsorbent is niobium phosphate. Niobium phosphate is similar to zirconium phosphate but it has not been studied to any detailed extent and its metallic forms are expected to show interesting catalytic properties.

Any detailed study of an adsorbent must begin with
the consultation of literature on this material. Once the literature has been consulted, the second important step is the characterisation of the adsorbent.

Many forms of the so called amorphous carbon such as charcoals, soot, and lampblack are actually microcrystalline forms of graphite \[4\]. In some soots the microcrystals are so small that they contain only a few unit cells of the graphite structure. The physical properties of such materials are mainly determined by the magnitude of their surface areas. The finely divided forms, which present relatively vast surfaces with only partially saturated attractive forces, readily adsorb large amounts of gases and solutes from solutions \[5,6\]. Active carbons impregnated with salts of palladium, platinum or other metals are widely used as catalysts. Thus the adsorption studies on activated carbon are of theoretical as well as of practical interest.

In what follows some recent studies on activated carbon and niobium phosphate are summarized. The characterisation of niobium phosphate based on infrared studies, X-ray diffraction studies and thermal behaviour is the subject matter of the second chapter.
Some Recent Studies on the Adsorption Properties of Activated Carbon

The numerous studies on the adsorption of different types of organic and inorganic substances on activated carbon are summarised below:

Adsorption of hydrocarbons

Koval'skaya et al. studied the adsorption of aromatic hydrocarbons on activated carbon (AC) and measured the adsorption capacity on the dry and damp sorbents [7]. They showed that the capacity decreases with increase in moisture content. The adsorption capacity for paraffins and cycloparaffins on steam-activated carbon at high temperature was studied using a micro-chromatographic method by Selim et al. [8]. Pirbazari et al. studied the selective removal of benzene from water with the help of activated carbon in the presence of other organic substances such as humic acid [9]. A mini dynamic adsorption technique was developed by Bilello et al. for determining carbon adsorption capacities [10]. Kitagawa measured the breakthrough curves for hexane and benzene solutions and ethane [11, 12]. He found a linear relationship between breakthrough time and bed volume [11]. In case of ethane, surface diffusion is the predominant intraparticle transport
process at lower temperatures [12]. Andreev found a correlation between adsorption coefficients of potassium salts of nitroalkanes and their degrees of hydration and polarizabilities. Adsorption increases in order of $\text{KCH}_2\text{NO}_3 < \text{KCH} (\text{NO}_3)_2 < \text{KC} (\text{NO}_2)_3$ which parallels the order of decreasing free energy of hydration [13].

The thermodynamic behaviour of various hydrocarbons and some other organic compounds with respect to adsorption on AC have been studied and their mechanisms were explored in terms of free energy changes by Ikuo et al. [14]. The free energy change for the adsorption process was compared with the free energy change for the precipitation process from solution into the pure liquid solute.

**Adsorption of alcohols**

The use of AC for the adsorption of aliphatic alcohols and aromatic alcohols has been studied by many researchers. Rozadowski determined the sorption and desorption mechanisms with the help of thermodynamic measurements [15]. Adsorption isotherm of alcohols have been reported on activated, granular and fibrous carbons [16, 17, 18]. A modified Langmuir equation is given to describe the adsorption of dissolved solids by AC where the theory and the experimental results show a good agreement [19]. Gorchakova et al. proposed the
effect of temperature on the molecular rearrangement of adsorbed alcohols on BAU carbon [18]. The breakthrough curves and its dependence on bed length has also been reported.

**Adsorption of Phenols**

Adsorption of phenols from dilute aqueous solutions on porous and nonporous carbon and activated carbon have been reported. Mahajan et al. studied the effect of temperature on the nature of carbon surface and the adsorption of phenols [20]. Yasushi et al. studied the effect of concentration on the adsorption behaviour of phenols and found a typical breakthrough curve [21]. The thermoanalytical studies on AC for adsorption and desorption of phenols was conducted by Vincenzo et al. [22]. Massaki measured the adsorption rates of p-nitrophenol, benzophenol and p-chlorophenol from dilute solutions [23] whereas Sheindrof did the same for p-bromophenol and other phenols during wastewater treatment by AC, where Freundlich adsorption isotherms are applicable [24]. Russel et al. conducted the equilibrium studies for different phenols and found a fast attainment of equilibrium with powdered AC as compared to granular one [25].
Adsorption of organic acids

Chubarova et al. studied the sorption capacity of AC for adipic acid from aqueous solution under cyclic operation conditions [26]. Jain et al. reported the adsorption of fumaric and maleic acids on sugar charcoal to be a discontinuous process [27]. The fate of fulvic acid during water treatment was studied by Breeman et al. [28], while its identification by adsorption on AC was studied by Stanislaw et al. [29].

Adsorption of dyes on AC

Nowadays the dyes are also being removed from dying effluents by adsorption on AC from coal. The temperature, the nature of the dye and AC and the presence of some electrolytes have marked effect on their adsorption behaviour. Increase in temperature and the addition of NaCl increases the adsorption rate and lengthens the breakthrough time of the dyes [30]. Gordon proposed a 3 step adsorption model for the adsorption of dyes on AC [31-33]. The various kinetic studies were also conducted on the adsorption of different dyes namely, victoria blue, disperse blue 7 etc. [34, 35].

Adsorption of pesticides and pollutants

The adsorption of various pollutants and pesticides
have been studied on AC. Yoshitaka et al. studied the effective surface diffusivities of an aqueous solution of chlorinated organics in water on AC using different concentrations [36]. Il’Yasov et al. proposed the mechanism of adsorptions using an isothermic model of adsorption [37]. The adsorption of p-nitroaniline from aqueous solutions by a thick layer of active carbon of varying porous structure and its mechanism were reported by Mamchenko et al. [38].

Lagana et al. studied the behaviour of fifty one compounds on graphitised carbon and the sorption capacities and the extent of recoveries for the chlorinated pesticides were determined [39]. The irreversible adsorption of lower aliphatic amines on pure AC surface was studied by Roman et al. [40]. The effect of pH on adsorption of dissolved organic acids, bases, anionic and cationic surface active agents, nonionic organic compounds and polymers from industrial effluents were studied by Wang and Martin [41, 42]. The pH effect becomes more significant as the acidity and basicity of the adsorbate in solution increases [42].

The adsorption of aflatoxin B₁, the lung and gastrointestinal toxicant was studied by Deeker et al. and effective conditions were determined [43]. Kaplin observed that AC is capable of adsorbing staphylococial toxin at a rate of 7.7 unit toxin/g of carbon [44]. The adsorbing capacity of AC
increased $\geq 3$ fold when the carbon is coated with antistaphylococcal $\gamma$-globulin fraction or human hyper immune plasma. Luzinokov studied the bare plasma coated AC for the adsorption studies of barbital and barbiturate and made a comparison of the two adsorbents [45].

Whitaker et al. has used the isothermal and continuous flow column systems for the adsorption studies of selected pesticides by AC [46]. Lovett and Peltorak reviewed the use of AC for the control of odourous air pollutants [47]. The AC impregnated with quinilidine has been used for removing the alkylhalides contaminants from gas stream by Covach et al. [48]. The use of AC for the treatment of municipal, industrial, and waste waters have been review in detail with hundreds of references in literature [49-51]. Numerous predictive models have been developed to explain the surface and bulk adsorption of organics and inorganics on AC [38, 52, 53-58]. The behaviour of adsorbate and adsorbents, the sites of adsorption, single and multicomponent adsorption and desorption systems were studied and their mechanisms have been proposed and tested accordingly [59-70].

Many research papers, purely theoretical in nature, have appeared describing the kinetics and thermodynamic
behaviour of different adsorbates on AC [71-79]. Seigfried has reviewed in a synopsis of 35 pages, the method of calculation of breakthrough curves for the adsorption kinetics of organic pollutants in air on AC [75]. The Polanyi potential adsorption theory and its application to adsorption from water solution on AC has been reviewed by Milton Manes [80, 81]. A significant use of this theory and that of solvophobic theory have recently been reported by some workers [82, 83].

Adsorption of inorganics on AC

Different types of studies have been conducted to determine the adsorbability of inorganics on AC surface. The potentiometric studies on AC and carbon black immersed in aqueous solution of electrolytes were conducted by Helena et al. [84]. The samples studied were subjected to various modified treatments: demineralisation, oxidation in liquid and gaseous phases, saturation with hydrogen and degassing etc. The contact time, the amount of anions in the solution and change in pH have marked effect on the potential of carbon. The adsorption of strontium on AC indicates that it increases with equilibrium time and at pH 1.5-3 [85]. Gerard made the magnetic susceptibility measurements on sorbate sorbent system to detect sorption mechanism [86]. Vilinskaya proposed a qualitative model of electrolyte
adsorption in porous materials \[87\]. Attempts have also been made to predict the microporosity and adsorption characteristics of AC, which are reviewed by Katsumi and Dubinin \[88, 89\].

Kraus et al. performed the adsorption experiments of acids from concentrated electrolytes by AC \[90\]. The studies included removal of HNO\(_3\) from LiNO\(_3\) solutions, HCl from NaCl and LiCl solutions and HClO\(_4\) from NaClO\(_4\) solutions. The H\(_2\)O in the carbon pores was related to a H\(_2\)O-organic solution model. Huang removed Cr\(^{+6}\) from electroplating and metal finishing waste waters effectively with the help of AC \[91\]. He also reviewed the chemical interactions between inorganics and AC \[92\]. Ryszard and Witold used AC as anode for electrode position of Ni, Cu, and Zn \[93\].

The sorption of Cl\(^-\), Br\(^-\) and I\(^-\) from aqueous methanol solution on AC pretreated with HF and NaCl was reported by Jankawska et al. \[94\]. Yankovska et al explained the adsorption of these ions through ion exchange mechanism with the formation of charge transfer surface complexes with acceptor characteristics of the carbon surface \[95\]. The adsorption isotherms of I\(_2\) solution in different organic solvents, organic solvent mixtures were reported by Światkowski and coworkers \[96\]. The characteristics and mechanism of iodine sorption from aqueous, H\(_2\)O-organic and
organic media were studied and discussed in terms of charge transfer complex with carbon as well as with the solvents [97].

The AC has also been utilised in the purification of air from the inorganic gases and vapors. The vapors of ammonia and acids were removed as air impurities by Krokov [98]. The adsorption and desorption isotherms of \( H_2S \) in micropores of AC show a hysteresis phenomena [99]. The adsorption isotherm of \( NO_2 \), \( CS_2 \) and \( H_2S \) were determined by Hoppe et al. on AC [100]. Andriew et al. determined the rate parameters for adsorption of \( CO_2 \) in beds of carbon particles and extract these results from pulse response method [101].

**Activated carbon filled with inorganic materials**

Inorganic materials have long been utilised in the removal of impurities from water and waste waters, where the surface and/or bulk adsorption takes place. The ion exchange mechanism has been found to play a significant role in these processes.

Kraus et al. in 1974 reported that AC can be used as a carrier for inorganic adsorbents which by themselves are difficult to prepare in forms suitable for column operations [102]. The 'filled AC' combines the hydraulic properties of the granular AC with the specific adsorptive properties of the 'filler'.
Activated carbons as carriers for finely divided inorganic adsorbents seem attractive. They are low cost materials widely available in a variety of mesh sizes. They are highly porous and can hold large amounts of filler. Kraus et al. made a greater contribution in this direction and prepared for the first time iron oxide (hydrous \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \)) filled AC. With \( \text{Fe}_3\text{O}_4 \) the object was to prepare an activated carbon which would exhibit magnetic properties without impairment of 'conventional' adsorption. With \( \text{Fe}_2\text{O}_3 \) they showed that adsorptive capacity for strontium, e.g., was greatly increased reflecting the properties of the hydrous oxide.

The ACs filled with ZnS and CdS were also prepared by them [103]. ZnS-AC has been reported as an excellent adsorbent for Ag. In this paper of ZnS-AC, some comments have been made on the kinetics of adsorption on filled AC. It has been proposed that three different types of diffusion reactions control such type of adsorption. Kraus et al. extended their studies with the preparation of \( \text{SnO}_2 \) filled AC [104]. This material was found to have an unusually high selectivity for lithium permitting its separation from the other alkali metals. They have also prepared AgCl-filled AC, which is selective for \( I^- \) [105].
Ohashi et al. prepared Mo(VI) and Fe(III)-filled AC and conducted the studies for the adsorption of orthophosphate on these materials [106].
(B) Some Recent Studies on Niobium Phosphate

Among the salts of niobium, phosphates are the most extensively studied materials. Sukharev et al. prepared ion-exchanging niobium phosphate by the treatment of Na$_2$HPO$_4$ solution with the alkaline potassium niobate in the presence of HCl [107-111]. A hydrated niobium phosphate was also prepared by them with or without the presence of trivalent cations such as Ce$^{3+}$, Fe$^{3+}$ or Cr$^{3+}$ during synthesis. Phosphorus to niobium mole ratio was found higher for the phase prepared in the presence of these ions. On the basis of the distribution studies it has been calculated that the presence of trivalent cation during the synthesis of niobium phosphate does not affect the sorption of divalent ions but a remarkable effect was observed for trivalent cations. The improved kinetic parameters were observed in this case. The ionic diffusion coefficients were also calculated. They further studied the kinetics of formation of the sorption phases of amorphous niobium phosphate with the variation of pH and the concentrations of Fe$^{3+}$ and Ce$^{3+}$ ions. The preferential uptake of $H_2[Fe(PO_4)_2]^{-}$ and $H_5[Fe(PO_4)_3]^{-}$ was also reported.

Shtin et al. reported the reaction of aqueous KOH solution with (NbO)$_2$HPO$_4$ and subsequently formation of $K_4Nb_{12}O_{37}27H_2O$ [112, 113]. They further studied the
complexing of Nb(V) with phosphoric acid and found the composition: \( \text{Nb(OH)}_{z}H_{4+z}(\text{PO}_4)_3 \) where \( z = 2-5 \).

Chernokov et al. prepared crystalline niobium phosphate of the composition: \( \text{NbOPo}_4 \cdot 2\text{H}_3\text{PO}_4 \cdot 5\text{H}_2\text{O} \) with the treatment of Nb(V) solution in HF with \( \text{H}_3\text{PO}_4 \) [114]. The phase was characterized through IR spectra, TGA and X-ray diffractogram. X-ray shows d-spacing value of 3.38, 6.47 and 11.2 Å. Thermal analysis revealed that the phase transition occurs at 1250°C.

Posplov et al. synthesized granular niobium phosphate in HNO₃ solution having \( \text{H}_3\text{PO}_4 \) and potassium niobate [115, 116]. The sorbent properties of the phosphate varies in relation to the niobium content and the sorption capacity was found greater with the use of alkaline solution of potassium niobate.
REFERENCES

1. Barrow G.M.,

2. Heftman E.,

3. Clearfield A.,

4. Cotton A. and Wilkinson G.,

5. Smisek M., Cerny S.,
'Active Carbon', Elsevier 1970.


7. Koval'skaya A.P., Subbotin A.I.,

8. Selim M.M., Nabarawy, El. T.A.,

10. Bilello L.J., Beaudet B.A.,

11. Kitagawa, H.,

12. Kitagawa H.,
Carbon 18(6), 448, (1980).

13. Andreev V.N., Tselsinskii I.V., Selivanov V.F.,
Bulgakov QV., Pul’tsina T.S.,

14. Ikuo A., Hayashi K., Kitagawa M., Urahala T.,

15. Rozadowski M.,

16. Kohei, U., Yoshinobu, K., and Yasushi, N.,

17. Recht H., Astaklov V.A., Gromyko T.A., Lukin V.D.,

18. Gorchakova N.K., Khabalov V.V., Glutsenko, V.,
Deposited Doc. SPSTL 198 Khp-D 808 (1980).

19. Eckhard W.,
Z. Chem. 23(7), 264, (1983).
20. Mahajan O.P., Moreno-Castilla C., Walker P.L.,

21. Yasushi T., Tomohiro W., Shunji S.,

22. Vincenzo A., Giuseppe B., Vito B., Lorenzo L.,

23. Massaki M., Yoshinori I., Toyohiko H.,

24. Sheindrof C., Rebhuna M., Sheintuch M.,

25. Russell P.C., Andrew B.,

26. Chubarova T.F., Belotserkovsku G.M., Dashkovsku I.D.,
    Yakolev. V.I., Emel'Yanova N.A., Proskuryakov V.A.

27. Jain K.D., and Jha J.B.
    J. Indian Chem. Soc. 18, 321 (1941).

28. Breeman V.A.N., Nieuwstad T.J., Vander M.O.G.C.,

29. Stanislaw J., Sander K.A.
30. Hiroshi K.,


32. Gordon M.,

33. Gordon M.,

34. Gordon M., Michael Q.S., Sweeny A.G.,

35. Gordon M.,

36. Yoshitaka S., Junichi T., Tomoji S., Motoyuki S.,

37. Il’yasov Kh. T., Bataev V.V., Tarasova G.S.,
Deposited Doc. SPSTL., 491, Khp D-82, 8 pp (1982).


39. Lagana A.,
anal. Chem. 52(13), 2033 (1980).
40. Roman W., Rozadowski M.,

41. Lawrence W.K.P., Richard L.P., Denis G.W., Wang M.S.,
    569, (1972).

42. Martin R.J., Iwugo K.O.,

43. Walter D.J., Corby D.G.,

44. Kaplin N.N., Serkov, V.F., Alekseeva V.N., Bitygov A.Y.,
    Sorina L.I.,

45. Luzhmikov E.A. Goldin M.M., Strakhova N.M.,

46. Whittaker K.,
    Int., Order No. 8113773, From Diss. Abstr. Int. B.

47. Lovett W.D., Peltorak, R.L.,
48. Julius K., Lauis E.P.,

49. Cavagnaro D.M.,

50. Cavagnaro D.M.,

51. Ford D.L.,

52. Martich V.E., Mamchenko A.V., Yakimova T.V., Koganovsku A.M.
Nauki 2, 36, (1982).

53. Siddiqi, K.S., Thomas W.J.,

Woodfield K.L.
Report 61983, EPA 600/2-83-047, Order No PB 83-222778,
(US) 83(19), 4667, (1983).

55. Sircar S.,
56. Gu T., Manes M.,

57. Stoeeki H.F.,

58. Stanton M.,

59. Eckard W.,

60. Merk W., Fritz W., Schluender E.U.

61. Fritz W., Schlender E.U.,

62. Chan H.J., Madey R.,

63. Worc E.,

64. Frick B., Sontheimertleinrich R.,

65. Madey R., Photinos P.J.
66. Fritz W., Merk W., Schluender E.U.

67. Larinov O.G., Popov E.A., Chimtov K.V.

68. Kuznetsova T.A., Begum L.B., Koval's Kaya A.J.,
Tolmachev A.M., Kisarov, V.M.,

69. Jankowaska H., Swiatowski A., Oscik J., Kusak R.,

70. Madey R., Photinous P.J.,
61, 333, (1980).

71. Peel R.G., Benedek A.,

72. Bell B.A., Molof A.H.,

73. Yenkie N., Venkatachalam K.A.,

74. Jonas L.A., Sansone E.B.,

75. Siegfried R., Roff, G.,
76. Wilson D.J.,

77. Onofrio M., Gozzelino G.,
    ICP, 10 (12), 41, (1982).

78. Sircar S.,

79. Rudzinski W., Narkiewicz M.J., Schollner R., Herben H.,
    Elnicka W.D.,

80. Greenbank M., Manes M.,

81. Manes M.,

82. Altshuler G., Belfort G.,

83. Arbuckle W.B.,

84. Helena J., Slawomir N., Andrzej S.,
85. Rivera-Utrilla J., Ferro-Gauia M.A., Mata A.A.,

86. Gerard R.,

87. Vilinskaya V.S., Korobanov A.A.,
Burshtein R.Kh., Gerasimova A.V.,

88. Katsumi H.,
Kagaku to Kogyo (Osaka) **57**(7), 254, (1983).

89. Dubinin M.M.

90. Kraus K.A., Fredrick N.,

91. Huang C.P., Bowers A.R.,

92. Huang C.P.

93. Ryszard S., Witold T.,
Powloki Ochr. **10**(8), 2, (1982).

94. Jankowska H., Sterlko V.V., Swiatkowski A., Brzhezitski E.,
95. Yankovska G., Swiatkowski A., Brzhezitski E., Sterlko V.V.,

96. Swiatkowski A., Gruehalski, S., Wisniewska E.,

97. Swiatkowski A.,

98. Krokov, V.V.,
USSR SU 865353 (Cl B01 D 53/02), 23 Sep. 1981, Appl.

99. Boki K., Tanada S., Kita T., Sakaguehi K.,
Experimentia, 37(8), 815 (1981).

100. Hoppe H., Winkler F., Huschenbelt R., Boessel M.,

101. Andrew J., Smith J.M.,
AIChEJ 26(6), 944, (1980).

102. Kraus K.A., Nelson F., Phillips H.O.,

103. Kraus K.A., Nelson F., Gilbert J.S.,

104. Ho P.C., Nelson F., Kraus K.A.,
J. Chromatog. 147, 263 (1978).
105. Kraus K.A., Ho P.C.,

106. Ohashi K., Saito J., Sai A., Matojima K., Yamamoto K.,

107. Sukharev, Yu. I., Egorov, Yu. V. and Pustovalov, N.N.
Otkryliva, Izobret. Promobraztsy Tovarnyl. Znaki,
1969, **46**(3), 22.

108. Sukharev, Yu. I., Egorov, Yu. V. and Pustovalov, N.N.

109. Sukharev, Yu. I., Dranitsina, N.V., Egorov, Yu. V.,
Kalugina, N.N., Pustolov, N.I.N. and Fominykh, V.E.


111. Sukharev, Yu. I., Egorov, Yu. V. and Belkina, R.M.

112. Shtin, A.P. and Chernyavskaya, E.I.

113. Shtin, A.P. and Gorelov, A.M.
Inst. Khim. Sverdlovsk. USSR Deposited Publication
114. Chernokov, N.G., Egorov, M.P. and Kutsepim, V.F. 

115. Posplov, A.A., Krylov, V.N., Deulin, G.I., Slobodchikova 
L.M., and Dushin R.B.,

116. Posplov, A.A., Deulin, G.I., Egorov, N.V., Drylov, N.N., 
Pitalev, V.G. and Slobodchikova, L.M. 
Zh. Prikl. Khim. (Leningrad) 1981, 54(6), 1226-31, 
(Russian).
CHAPTER II

X-RAY AND INFRARED STUDIES ON THE THERMAL BEHAVIOUR

OF CRYSTALLINE NIOBIUM PHOSPHATE
INTRODUCTION

The most characteristic property of inorganic ion exchangers is their stability towards heat and radiations. The study of their catalytic behaviour for the manufacture and synthesis of organic compounds is, therefore, of current interest. No doubt they also show sufficient chemical stability. The capability of these insoluble solid materials for exchanging the counter ions and providing the sufficient surface area for the catalysts are the main reasons of their catalytic activity.

Platinum black, Raney nickel and transition metal complexes such as palladium complexes are widely used as catalysts in many organic reactions. In recent years some new inorganic compounds have been used as catalysts which are found to be better than palladium and nickel. One such catalyst is Sr-doped LaCoO$_3$, which at high temperatures operates better than platinum black for the reduction of oxygen by hydrogen in fuel cells [1]. The reactions occur at the surface. Thus the larger the surface area the higher the catalytic activity. The ion exchangers serve this purpose. Both the exterior and interior of the particles of these compounds can be used. Furthermore, the surface area can be increased by introducing larger groups between the layers of exchangers as in the case of
zirconium phosphate [2,3]. On the other hand the exchangers can also be used as molecular sieves (e.g. zeolites) owing to their rigid structure with constant pore size [4].

Watanabe, Y., [5] developed a single step synthesis (instead of a three step process) of methyl isobutyl ketone, an important industrial solvent using Pd-doped catalysts. The cation substituted zirconium phosphate is also reported to catalyse decomposition, dehydration, hydrolysis, oxidative dehydrogenation, hydrogenation, condensation, polymerisation and oxidation reactions [6-10] by many researchers.

It is therefore, worthwhile to study systematically the catalytic activities of the inorganic ion exchangers. Qureshi, M. and Ahmad, A. [11] have recently reported that niobium phosphate is an important and highly stable inorganic ion exchanger. The crystalline form of this exchanger is of special interest due to its zeolitic type structure [12].

The literature survey reveals that very few catalytic studies have been reported on the inorganic ion exchangers and none on niobium phosphate. In order to get some meaningful results the exchanger has to be well characterised and its preparative method standarized. Hence an attempt has been made and reported to synthesise and characterise the
crystalline niobium phosphate by different methods. It will be helpful to obtain the crystal structure surface properties and other catalytic parameters pertaining to the catalytic activity of this exchanger. The catalysis of important organic reactions will be studied in detail in future to explore the technological importance of these materials.
(a) **Reflux Method**

To prepare 0.1 M niobium solution 13.291 g \(\text{Nb}_2\text{O}_5\) was heated with 400 ml of concentrated \(\text{H}_2\text{SO}_4\) containing 135 g ammonium sulphate until a clear solution was obtained. After cooling the clear solution, 200 ml concentrated \(\text{H}_2\text{SO}_4\) was added to it and the whole mass diluted to 1 litre with deionized water.

The crystalline phase of niobium phosphate has been synthesised by mixing 0.1 M niobium sulphate solution with 0.5 M phosphoric acid in the ratio of 1:4. The pH of this mixture was then adjusted to 1 with concentrated ammonia solution. The precipitate so obtained was left with the mother liquor for 24 hr. Then it was filtered and washed with deionized water until free from sulphate ions. The precipitate was then refluxed in 5 M \(\text{H}_3\text{PO}_4\) for different periods. The precipitate was washed and dried at 40°C and then it was converted into \(\text{H}^+\) form with 1M \(\text{HNO}_3\). The precipitate was again washed until free from acid. Finally it was dried at 40°C and stored in the dessicator over saturated solution of \(\text{BaCl}_2\). The samples prepared by this method are designated as NPR.

(b) **HF Method**

Here the crystalline niobium phosphate was synthesised
by the method of Alberti [13]. In this method a solution of 0.5 M in Nb(V) and 3 M in HF was prepared. It was shaken well until a clear solution was obtained. In three plastic beakers 90, 80 and 50 ml of the above Nb(V) solution was mixed with 10, 20 and 50 ml of concentrated phosphoric acid respectively, in order to have three different [Nb]/[H₃PO₄] mole ratio. The HF was allowed to evaporate for some days at 60°C. The volume of the solution was maintained constant by adding distilled water. The precipitates so obtained were washed with distilled water to pH 3.5-3.8 and stored over a saturated BaCl₂ solution.

The 0.5 M Nb(V) solution was prepared by two methods:

(i) 33.77 gm of NbCl₅ is mixed with 37.5 ml of (40 % W/V) HF. It was shaken well until a clear solution was obtained. The whole volume was diluted to 250 ml with demineralized water. The three samples prepared by using above Nb(V) solution and phosphoric acid in 9:1, 8:2 and 1:1 mole ratio and are designated as NPH-1, NPH-2 and NPH-3 respectively. The NPH-3 sample was also converted into H⁺, Li⁺ and Cs⁺ forms and are represented as NPC-H, NPC-Li and NPC-Cs respectively.

(ii) 16.61 gm of Nb₂O₅ was mixed with 37.5 ml of (40 % W/V) HF and was shaken until a clear solution was obtained.
The total volume was maintained to 250 ml by adding demineralized water. Niobium phosphate synthesised by using above solution was converted in H⁺, Li⁺ and Cs⁺ forms and are designated as NPO-H, NPO-Li and NPO-Cs respectively.

**Heat Treatment**

Crystalline niobium phosphate in H⁺ form was heated at different temperatures for four hours in automatic temperature controlled muffel furnace. The infrared spectra and X-ray diffractograms of these heated samples were then taken, which are shown in Figures 2.2 and 2.6.

**Infrared Studies**

The infrared spectra of the crystalline niobium phosphate prepared by different methods were recorded with the standard KBr disc technique. (Figures 2.1-2.4). The spectra of the exchanger heated at different temperatures were also recorded.

**X-ray Diffractogram**

Powder X-ray diffractogram of the different forms of crystalline niobium phosphate synthesised by different methods were taken using nickel filtered Cu-Kα radiations (λ = 1.5404 Å). The X-ray pattern of the exchanger in H⁺, Li⁺ and Cs⁺ forms were also recorded. The results are shown in Figures 2.6-2.9.
RESULTS AND DISCUSSION

Infrared Studies

(i) Effects of Method of Preparation

The crystalline niobium phosphate has been prepared by three different methods. The infrared spectra of niobium phosphate in H\(^+\) form (Fig. 2.3, 2.4) reveals the fact that all the samples have a similar structure. Each spectrum shows a band between 3600 and 2900 cm\(^{-1}\). The samples synthesised by reflux method has two maxima at 3400 and 3100 cm\(^{-1}\) (Fig. 2.1) while samples by HF method have some sharp peaks at 3640, 3480, 3400 and 2920 cm\(^{-1}\) (Fig. 2.3, 2.4). They are characteristic of stretching vibrations \([\nu_1 (H_2O \text{ or } OH)]\) of coordinated H\(_2\)O molecules and this implies that strong H-bonding exists between hydroxyl groups and water molecules surrounding them. Therefore this bond may be attributed to long hydrogen bond P-O-H .... O-H and P-O-H ... O-H [14]

The peak at 2920 cm\(^{-1}\) may also be assigned to the deformation vibration of water of crystallisation \([\delta_1 (H_2O)]\).

The samples prepared by the reflux method (Fig. 2.1) show sharp and broad peaks at 1630, 1400, and 690 cm\(^{-1}\) and a broad band at 1000 cm\(^{-1}\). On the other hand the remaining two samples which were prepared by the HF-method [Fig. 2.3, 2.4] show sharp peaks at 1600 and 695 cm\(^{-1}\), a weak peak at 1380 cm\(^{-1}\) and sharp, broad triplet at 1000 cm\(^{-1}\). The peaks
Fig. 2.1 I.R. Spectra of Niobium (V) Phosphate Refluxed (NPH) for (a) 5, (b) 20, (c) 50, and (d) 100 hrs.
Fig. 2.3 I.R. Spectra of Niobium (V) Phosphate Prepared from NbCl₅ (NPC) in (a) H⁺, (b) Li⁺ and (c) Cs⁺ Forms
Fig. 2.4 I.R. Spectra of Niobium (V) Phosphate prepared from Nb$_2$O$_5$(NPO) in (a) H$^+$, (b) Li$^+$ and (c) Cs$^+$ forms
at 1630 and 1600 cm$^{-1}$ corresponds to the deformation vibration of interstitial water molecules and the hydroxyl group [$\delta_1$(H$_2$O) and (OH)]. The peaks at 1400 cm$^{-1}$ and 1380 cm$^{-1}$ and band at 1000 cm$^{-1}$ may be assigned to the deformation vibration of P-OH groups [$\delta_2$(P-OH)]. The peaks at 690 and 695 cm$^{-1}$ correspond to the M-O stretching vibrations [$\nu_2$(Nb-O), (P-O)] [15,16].

(ii) Effect of heating

The infrared spectra of niobium (V) phosphate heated at various temperatures are given in Fig. 2.2. All the spectra refer to the niobium phosphate in H$^+$ form. Only NPT-Na refers to that of Na$^+$ form dried at 40°C. A comparison of NPT-I and NPT-Na is very interesting. When the H$^+$ ion of POH group is replaced by Na$^+$, the hydrogen bonding is diminished and the bands become narrower. It provides a clue that probably H$^+$ of P-OH is responsible for the ion exchange and can provide the catalytic site.

On heating from 40 to 300°C, probably the absorbed water molecules are lost which makes the peak and the band more narrower. However at 400°C the P-OH groups of phosphate molecules begin to condense and the condensation is completed at 800°C. Therefore on heating at 800°C (NPT-8) the peaks and the band completely disappear. The effect of
Fig. 2.2 I.R. Spectra of Niobium (V) Phosphate Heated (NPT) at (a) 40°, (b) 300°, (c) 500°, (d) 600°, (e) 800°, (f) 1000°C in H+ form and (g) 40° in Na+ form.
heating on the band between 940 and 1130 cm\(^{-1}\) is quite different. Since this band is due to P-O vibrations [14], it remains unaffected up to 300°C with the loss of water molecule. Above 300°C the band becomes narrower due to condensation of P-OH groups to P-O-P groups. At 300°C all the P-OH groups condense and a very sharp peak is obtained at 1030 cm\(^{-1}\) owing to the presence of P-O-P groups. In this way we can say that NPT-8 is completely a new phase having no hydroxyl groups or water or free ionic sites responsible for ion exchange.

**X-Ray Diffraction:**

**Crystallisation by the reflux method**

The precipitated niobium phosphate gel was refluxed for different periods in 5M H\(_3\)PO\(_4\) with the hope of getting a more stable and reproducible material as suggested by Clearfield [17]. The X-ray diffractogram of these samples were taken in hydrogen form and it was observed that the refluxing has a marked effect on the crystallinity of the compound [Fig. 2.5].

The maximum refluxing time used in this study was 100 hrs. The X-ray diffractogram of the niobium phosphate sample refluxed for 100 hrs which we will describe as NPR-100 showed 28 peaks. When the sample was refluxed for 50 hrs
Fig. 2.5  X-ray Diffractograms of Niobium(V) Phosphate Refluxed (HPR) for (a) 5, (b) 20, (c) 50 and (d) 100 hrs
(NPR-50) it showed only 25 peaks. Similarly sample refluxed for 20 hrs and for 5 hrs (NPR-20, NPR-5) showed 24 and 14 crystalline peaks respectively. It is clear from this that the maximum increase in the number of peaks takes place when the refluxing time is increased from 5 to 20 hrs. Any further increase in the refluxing time has a small effect on the number of peaks, but the intensity of the peaks increases showing thereby that the crystalline character slowly gets stabilized after 100 hrs of refluxing.

(ii) Effect of Heating

Heating also has a marked effect on the crystallinity of niobium phosphate but here the changes occurring are different from those obtained by refluxing. Heating causes the dehydration of niobium phosphate by (i) the removal of adsorbed water molecule (ii) the removal of coordinated water molecule (water of crystallisation) (iii) the condensation of phosphate to pyrophosphate groups.

It is evident from figure 2.6 that the number of peaks and their intensities have increased considerably on heating up to 1000°C. A comparison of the d values of the samples heated up to 800°C and 1000°C with that of JCPDs. Data file shows that it is probably niobium oxyphosphate, NbO(PO₄), [ASTM card no. 19-886]. Table 2.1 shows the hkl planes and the d-values of NbO(PO₄) and sample heated
Table 2.1: Comparison of X-ray Data of NbOPO₄ (ASTM No. 19-866) and Heated Niobium Phosphate.

<table>
<thead>
<tr>
<th>NIOBIUM OXY-PHOSPHATE^a</th>
<th>NIOBIUM-PHOSPHATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NbOPO₄, 19-866)</td>
<td>800°C</td>
</tr>
<tr>
<td>hkl</td>
<td>d(I/I₀)</td>
</tr>
<tr>
<td>110</td>
<td>4.51(50)</td>
</tr>
<tr>
<td>101</td>
<td>3.45(80)</td>
</tr>
<tr>
<td>200</td>
<td>3.19(100)</td>
</tr>
<tr>
<td>111</td>
<td>3.04(60)</td>
</tr>
<tr>
<td>211</td>
<td>2.35(50)</td>
</tr>
<tr>
<td>220</td>
<td>2.25(60)</td>
</tr>
<tr>
<td>002</td>
<td>2.05(50)</td>
</tr>
<tr>
<td>310</td>
<td>2.02(70)</td>
</tr>
<tr>
<td>301</td>
<td>1.88(70)</td>
</tr>
<tr>
<td>112</td>
<td>1.86(50)</td>
</tr>
<tr>
<td>311</td>
<td>1.81(50)</td>
</tr>
<tr>
<td>202</td>
<td>1.72(50)</td>
</tr>
<tr>
<td>212</td>
<td>1.66(40)</td>
</tr>
<tr>
<td>321</td>
<td>1.62(70)</td>
</tr>
<tr>
<td>400</td>
<td>1.59(80)</td>
</tr>
<tr>
<td>222</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Geometry: Tetragonal (a = 6.387 Å, c = 4.104 Å)
Symmetry: P₄/n (85)

^a = Lango and Kierkegaard
Acta Chimica Scan. 20, 1, 72-78 (1976)
Fig. 2.6 X-ray Diffractograms of Niobium (V) Phosphate Heated (NPT) at (a) 40°, (b) 300°, (c) 500°, (d) 600°, (e) 800°, (f) 1000°C in H⁺ form
at 800°C and 1000°C. Hence we can say that our sample when
heated above 800°C attains a tetragonal geometry with a = 6.387
c = 4.104 Å and P₄/n (85) symmetry. On comparing the X-ray
data of the unheated sample with that of NbO(PO₄), it appears
that the sample have some contamination of ammonium meta
niobate NH₄NbO₃ [ASTM card no. (7-590)] which disappears after
heating. Hence care must be taken in washing and in the
conversion of the sample to some cationic form. So we propose
that Townsand method [18] be used for the complete conversion
of the sample into the cationic form. This method will be
helpful in the removal of the NH₄⁺ contamination caused by
the use of large amount of (NH₄)₂SO₄ during synthesis.

Since heating destroys the ion exchange sites (as
described earlier) due to the condensation of P-OH to
P-O-P groups, therefore, the H⁺ form of exchanger cannot
be converted into crystalline ion exchanger by heating. It
seems better if Na⁺ form of niobium phosphate be heated upto
1000°C to obtain a crystalline ion exchanging niobium phos­
phate. In this way ion exchange sites will remain preserved
and the substance will become more crystalline.

(iii) Effect of Nb/H₂PO₄ Mole Ratio in HF Media

In the HF method, where crystalline niobium phosphate
was obtained by the slow decomposition of niobium flouro
complex in the presence of phosphoric acid. The Nb/H₃PO₄ mole ratio was changed in order to find out the optimum conditions of precipitation of crystalline niobium phosphate. X-ray diffractograms of the sample in H⁺ form (Fig. 2.7) indicates that when these two solutions are mixed in equal volumes, a better form of crystalline niobium phosphate (NPH-3) is obtained. It has maximum number of peaks with sufficient intensities. The compound has a d_max value of 15.49 Å having 24% relative intensity, while the d value of 100% relative intensity is 7.36 Å. It is also worthy to note that the latter d-value is minimum amongst this set for the NPH-3 sample. Further the results for this sample are more reproducible than the remaining two.

No doubt some minor changes are seen in the X-ray pattern, when the exchanger is converted into Li⁺ and Cs⁺ form [Figure 2.8, 2.9] but the trend is irregular which is inexplicable at present. Sample NPC (Fig. 2.8) shows a slight expansion of lattice where d (100%) changes from 7.36 Å (in H⁺ form) to 7.68 Å in Li⁺ and Cs⁺ forms. NPC and NPO have almost similar X-ray pattern in H⁺, Li⁺ and Cs⁺ form, but d (100%) of NPO-H is 7.75 Å as compared to that of NPC-H which is 7.36 Å. In the Li⁺ and Cs⁺ forms both the samples have a d (100%) of 7.68 Å.

Finally we can say that the HF method provides
Fig. 2.7 X-ray Diffractograms of Niobium (V) Phosphate Synthesised by HF Method, where [Nb]/[H₃PO₄] Mole Ratios are (a) 9:1, (b) 8.2 and (c) 1:1.
Fig. 2.9 X-ray Diffractograms of Niobium (V) Phosphate Prepared from Nb₂O₅(NPO) in (a) H⁺, (b) Li⁺ and (c) Cs⁺ forms.
better crystalline form of niobium phosphate (exchanger) when niobium and phosphoric acid solutions are mixed in equal volumes (NPH-3). Further the use of niobium pentachloride gives the compound with smaller d-value while that of niobium pentaoxide gives the compound with higher d-values (see NPC-H and NPO-H of Fig. 2.8 and 2.9). The crystallattice of NPC compounds expands while that of NPO shrinks when they are converted into Li⁺ and Cs⁺ forms, giving thereby a lattice with almost equal interlayer spacings. This hints out the possibility that the two phases (i.e. NPC and NPO) are interconvertable passing through this intermediate shown by Li⁺ and Cs⁺ form

\[ \text{NPC} \leftrightarrow \text{Li}^+ \text{ or Cs}^+ \text{ form of intermediate} \leftrightarrow \text{NPO} \]

But at this juncture it is purely a theoretical speculation and requires detailed experimental studies.
References

1. Howe A.T.,

2. Alberti A., Constantino U., Kornyei J., Glovagnotti M.L.,

3. Dines M.B., Digiacomo P.M., Challahan K.P.,
   Griffith P.C., Lane R.H., Cooksey R.E.,
   Chap. 13, (1982).

4. Ginestra A.L., Ferragina C., Massuci M.A., Patrono P.,
   Rocco R.D., Tomlinson A.A.G.,

5. Watanabe Y., Matsumura Y., Izumi Y., Mizutane Y.,

6. Cheng S., Peng G.Z., Clearfield A.,

7. Frianeza T.N., Clearfield A.,

8. Clearfield A., Thakur D.S., Cheung H.,

9. Hattori T., Hanai H., Murakami Y.,
10. Clearfield A.,  

11. Ahmad A.,  
Synthetic Inorganic ion exchangers, Ph.D. Thesis,  
Department of Chemistry, A.M.U. Aligarh.

12. Qureshi M. and Ahmad A.,  

13. Alberti G., Constantino U., and Giovagnotti M.L.L.,  

14. Gill G.S., and Tandon S.N.,  

15. Marinsky J. and Marcus Y.,  
'Ion Exchange and Solvent Extraction Series',  

16. Qureshi M., Ahmad A., Gupta J.P. and Khan H.,  

17. Clearfield A.,  
Inorganic Ion Exchange Material, I.CRC : Boca Raton,  
Flourida, USA Ch.I, pp. 16 (1982).

18. Barrer R.M., and Townsend R.R.,  