

**SYNTHESIS AND STRUCTURE
OF
ORGANICALLY TEMPLATED VANADIUM OXIDES**

by

SANJEEV SHARMA

Department of Chemistry

Submitted

In fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

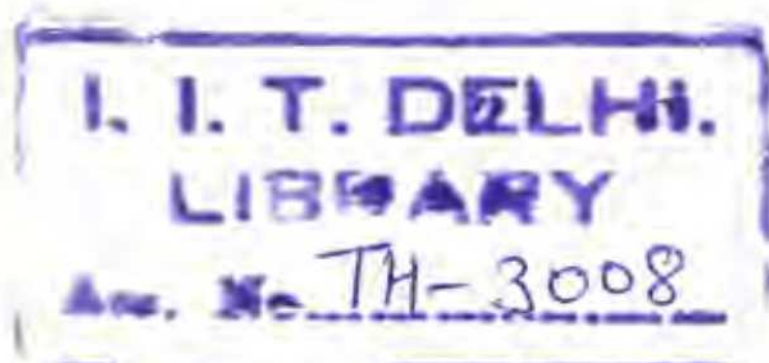
to the



INDIAN INSTITUTE OF TECHNOLOGY, DELHI

March, 2004

oxides
SMA-5



TH
54-31:54.07
SMA-5



CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and Structure of Organically Templated Vanadium Oxides**" being submitted by **Mr. Sanjeev Sharma** to the Indian Institute of Technology, New Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. Sanjeev Sharma has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which, to my knowledge has reached the requisite standard.

The results contained in the dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.



(A. Ramanan)

(Associate Professor)
Department of Chemistry
Indian Institute of Technology
New Delhi 110016

March, 2004

Dedicated to my Parents

ACKNOWLEDGEMENTS

I take pleasure in recording my sincere thanks to Dr. A. Ramanan, Associate Professor, Department of Chemistry, Indian Institute of Technology, New Delhi, for his inspiring guidance and constant encouragement throughout the course of this investigation.

My sincere thanks are due to Prof. H. M. Chawla, Head of chemistry Department, for providing me necessary facilities in the department. Thanks are also due to all the faculty members and supporting staff of the department for their kind help and cooperation.

My grateful thanks are due to Prof. M. S. Whittingham and Peter Zavalij, SUNY at Binghamton, USA for providing single crystal structures, Dr. J. J. Vittal, National University of Singapore, Singapore, for single crystal data collection, Prof. Martin Jansen, MPI FKF, Stuttgart, Germany, for help with and EDAX, TGA, SEM, TEM analysis and for providing me financial aid during my visit.

I am really thankful to IIT-Delhi for the research fellowships.

I am grateful to all the members of my family for their constant encouragement throughout my academic career, which undoubtedly, has added much to my will and vigour to pursue my research work.

I thank my colleagues Duraisamy, Ayyappan, Minakshi, Purnendu, Shailesh, Pavani, Sudarshan, Sameer, Jency and Aria for the support both in the laboratory and outside.

Finally, I also wish to express my appreciation and warm feelings of gratitude to all my friends Rajiv, Mukesh, Vishal, Rakesh, Anubhav, Kranti, Sundeep, Manish, Shobhit, Anoop, Pabak, Nihar (MPI, Mainz, Germany), Sonal, including Kailash, Nachi (MPI FKF, Stuttgart, Germany), Dr. M. Panthofer (MPI FKF, Stuttgart, Germany), T. C. Deviraj (NSU, Singapore) and Tarun (Harvard University).

Sanjeev Sharma

[SANJEEV SHARMA]

ABSTRACT

One of the great challenges of modern chemistry is to create multifunctional structures, which have well defined cavities and surfaces with sites or areas of different reactivity by linking preorganised robust building blocks. Given the significance of transition metal oxide surfaces and proven roles of polyoxovanadates and their derivatives in catalysis and materials science, it is conceivably valuable to attempt to design and prepare transition metal oxide based materials with desired and controllable properties by assembling well defined building blocks. In the past decade, the family of vanadium oxides incorporating structure directing organic cations has been exploited extensively. The contemporary research focuses on the association of an organic component acting as structure directing moiety with the inorganic framework of the solid to provide novel organic inorganic hybrid materials. The control of inorganic structure by an organic component opens up a new route for the synthesis of novel organic inorganic hybrid solids. Understanding the driving force behind the formation of such solids still remains a formidable challenge and is an area of current interest. As yet there is no systematic treatment of the formation and topology of the variety of structures. The present study is an attempt to form new polyoxovanadates and investigate their crystal structure.

This thesis is mainly devoted to the synthesis and structural characterisation of vanadium oxides templated by organic molecules. We have employed several organic templates like amines, quarternary salts, long chain amines and surfactants to emphasize the role of organic templates in the formation of new solids based on vanadium oxides. The organic template employed in this study are tetraphenylphosphonium bromide, tetraphenylarsonium chloride, tetrabutylphosphonium bromide, tetraethylammonium

bromide, tetramethylammonium bromide, morpholine, ethylenediamine, diazabicyclooctane, 1,3 diaminopropane, octadecylamine, hexadecylamine, dodecylamine, dodecylpyridinium bromide and cetylpyridinium bromide. With a view to demonstrate the effect of subtle changes in the reaction conditions leading to novel products, we have employed both solution evaporation as well as hydrothermal and ion exchange methods. The thesis is divided into four chapters and describes synthesis, characterisation and ion exchange behavior of organically templated vanadates. An appendix included at the end, describes the synthesis and characterisation of a few hexagonal vanadium molybdenum oxides.

Chapter I describes a brief survey on the importance of metal oxides with a major focus on vanadium oxides. A brief summary of the synthesis and structure Major focus is placed on polyoxovanadates clusters that are formed in presence of templating organic molecules in aqueous medium. An overview on the extended vanadium oxides formed in presence of organic salts is also discussed. The effect of reaction parameters such as pH, temperature, molar ratio of the reactants, nature of the templating organic bases, *etc.* are also discussed in terms of the structure of final solid formed. In addition, we have also described vanadium oxides templated with large size amine molecules and surfactant that exhibits interesting nanostructures and porosity.

Chapter II describes the formation of polyoxovanadates from aqueous solution in the presence of organic templates such as tetraphenylphosphonium bromide, tetraphenylarsonium chloride and morpholine, *etc.* The effect of reaction parameters such as pH, reactant concentration, temperature and structure directing organic molecules in

formation of supramolecular clusters is highlighted. New oxo-vanadium clusters along with morpholine intercalated layered phosphovanadate are reported in this chapter. A zero-dimensional, mixed-valent phosphovanadate cluster $[\text{Morp}]_6[\text{P}^{\text{V}}\text{O}_4\text{C}^{\text{IV}}_3\text{V}^{\text{V}}_{11}\text{O}_{32}(\text{OH})_6]\cdot 2\text{H}_2\text{O}$ is obtained under self assembly conditions while a two-dimensional layered solid $[\text{Morp}]_{0.23}[\text{V}^{\text{VI},\text{V}}\text{OPO}_4]\cdot 1.1\text{H}_2\text{O}$ is obtained under reducing conditions. Use of spherically symmetrical organic cations resulted in the formation of organic-inorganic hybrid salts. A novel one-dimensional cyclic tetrameric metavanadate $[\text{PPh}_4]_2\text{V}_4\text{O}_{11}$ is reported for the first time in polyoxovanadates chemistry using tetraphenylphosphonium as counter cation. The size and shape of tetraphenyl phosphonium seems to play an important role in linking of discrete cyclic tetramer $\text{V}_4\text{O}_{12}^{4-}$ units. Under analogous conditions tetraphenylarsonium resulted in the formation of $[\text{AsPh}_4]_2(\text{morph})_4\text{V}_{10}\text{O}_{28}\cdot 2\text{H}_2\text{O}$. Crystal structure revealed the presence of discrete decavanadate clusters along with morpholinium and tetraphenylarsonium counter cations.

Chapter III describes the isolation and structural characterization of organic cation incorporated vanadium oxides by mild hydrothermal reactions. The chapter is divided into two parts, part A deals with the use of relatively smaller cations as host or templates whereas part B describes use of long chain amines and surfactant molecules for the formation of nanostructures and mesophases.

In chapter IIIA we have discussed synthesis of new organically templated vanadium oxides under mild hydrothermal conditions. A fressonite type phase $(\text{NH}_4)_2\text{V}_3\text{O}_8$ and $(\text{DABCO})_2\text{V}_4\text{O}_{10}$ were prepared by employing dicaynamide and DABCO as structure

directing agents. V_4O_{10} is one of few example of topotactic intercalation of organic cations in vanadium oxide layers. Use of ethylenediamine and 1,3 diaminopropane in presence of copper ions resulted in the formation of Muller type cluster based solids: a zero dimensional cluster $[Cu(en)_2]_3[V_{15}O_{36}(Cl)]$ and a three dimensional network solid $[Cu(pn)_2]_4[V_{18}O_{42}(OH_2)].4H_2O$. Several new layered vanadium oxide bronzes are reported in this chapter employing alkyl salts as host species viz $[(C_6H_5)_4As]_{0.19}V_2O_5$, $[(C_6H_5)_4P]_{0.20}V_2O_5$, $[(C_4H_9)_4P]_{0.19}V_2O_5$ and $[(C_2H_5)_4N]_{0.58}V_2O_5$. X-ray powder diffraction patterns are dominated by intense (00l) reflections with layered distances varying with the size of organic cation. All synthesised vanadates exhibits structural similarity with Oka's bi layer model with organic molecules occupying inter lamellar region.

In chapter IIIB we have presented our results on the synthesis and structure of nano and mesoporous vanadium oxides. Use of long chain amines under hydrothermal conditions resulted in the formation of vanadium oxide nanotubes. We have employed a mixture of reduced vanadium oxide along with vanadium pentaoxide as an alternative starting material, which resulted in an efficient and convenient method for the synthesis of vanadium oxide nanotubes. Unlike previous reports this method does not involve either sol gel treatment or room temperature hydrolysis prior to hydrothermal reaction. A new mesostructured vanadium oxide has been synthesised by using dodecylpyridinium surfactant as structure directing agent.

Chapter IV describes ion exchange reactivity of layered vanadates using various metal ions viz. Na^+ , K^+ , Ag^+ . Amorphous phases were obtained with alkali metal ions whereas in case of silver, formation of stable β - $AgVO_3$ phase took place. In comparison to vanadium oxide xerogels these precursors form silver vanadates quite readily under room

temperature conditions and offers a new synthetic route for the synthesis of other silver vanadates phases.

An appendix included at the end of these chapters, describes the synthesis of metal ion incorporated vanadates. New oxides with stoichiometry $M_xVMO_5O_{18}.yH_2O$ ($M = Li^+$, Na^+ , K^+ , Cs^+ , Rb^+ and NH_4^+) has been made by direct hydrothermal synthesis using mixture of molybdenum and vanadium oxide in presence of alkali metal salts. Unlike previous studies, our work suggests that hexagonal molybdates could be stabilized in the presence of monovalent cations with varying ionic size under hydrothermal condition. The phases were characterised using chemical analysis, powder X-ray diffraction, scanning electron microscopy and EDAX.

TABLE OF CONTENTS

CERTIFICATE	(i)
ACKNOWLEDGEMENTS	(ii)
ABSTRACT	(iii)
LIST OF FIGURES	(viii)
LIST OF TABLES	(xiii)
ABBREVIATIONS	(xv)

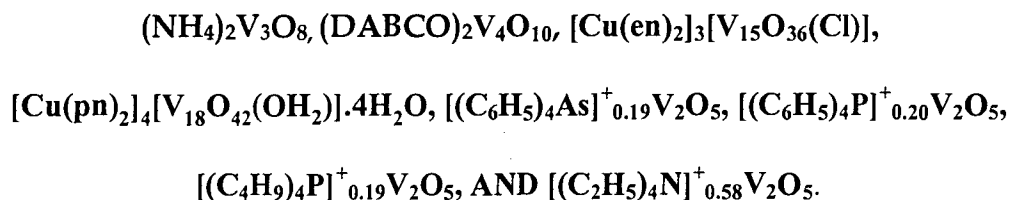
CHAPTER 1: SYNTHESIS AND STRUCTURAL ASPECTS OF ORGANICALLY TEMPLATED VANADIUM OXIDES

I.1	Introduction	2
I.2	Various Factors Influencing Formation of Vanadium Oxide Based Solids	4
I.3	A Brief Survey of Organically Templated Vanadium Oxides	7
I.3.1	Oxovanadium Clusters	8
I.3.1.1	Metavanadate and related structures	9
I.3.1.2	$\{V_8O_{23}\}$ cluster	12
I.3.1.3	decavanadate clusters $\{V_{10}\}$	13
I.3.1.4	$\{V_{12}\}$ clusters	15
I.3.1.5	$\{V_{13}\}$ and $\{V_{14}\}$ clusters	18
I.3.1.6	$\{V_{15}\}$, $\{V_{18}\}$ or $\{V_{19}\}$ clusters	19
I.3.1.7	$\{V_{22}\}$ clusters and $\{V_{34}\}$ clusters	23
I.3.2	Extended vanadium oxide structures	24
I.3.3	Vanadium oxide nanotubes	33
I.3.4	Vanadium oxide mesophases	37
I.4	Motivation for the present work	42
I.5	References	44

**CHAPTER II: FORMATION OF NOVEL POLYOXOVANADATE
CLUSTERS IN THE PRESENCE OF ORGANIC BASES : ISOLATION AND
STRUCTURES OF $[\text{Morp}]_6[\text{P}^{\text{V}}\text{O}_4\text{C}\text{V}^{\text{IV}}_3\text{V}^{\text{V}}_{11}\text{O}_{32}(\text{OH})_6] \cdot 2\text{H}_2\text{O}$,
 $[\text{Morp}]_{0.23}[\text{V}^{\text{IV},\text{V}}\text{OPO}_4]1.1\text{H}_2\text{O}$, $[\text{PPh}_4]_2\text{V}_4\text{O}_{11}$ AND
 $[\text{AsPh}_4]_2(\text{morph})_4\text{V}_{10}\text{O}_{28} \cdot 2\text{H}_2\text{O}$**

II.1	Introduction	57
II.2	Experimental	58
II.2.1	Experimental methods	58
II.2.2	Synthesis and characterization	60
II.3	Results and discussion	65
II.3.1	Single crystal X-ray structure of PV_{14}	65
II.3.1.1	Structural description of PV_{14}	68
II.3.2	Structural description of VPO	75
II.3.3	Single crystal X-ray structure of V_4O_{11}	79
II.3.3.1	Structural description of V_4O_{11}	79
II.3.4	Single crystal X-ray structure of V_{10}	87
II.3.4.1	Structural description of V_{10}	89
II.3.5	Formation of polyoxovanadates by slow evaporation method	97
II.4	Conclusions	102
II.5	References	103

CHAPETR IIIA: ORGANICALLY INTERCALATED LAYERED VANADIUM OXIDE BRONZES: ISOLATION AND CRYSTAL STRUCTURES OF



IIIA.1	Introduction	106
IIIA.2	Experimental	107
IIIA.2.1	Experimental methods	107
IIIA.2.2	Synthesis and characterization	110
IIIA.3	Results and discussion	122
IIIA.3.1	Single crystal X-ray structure of V_3	122
IIIA.3.1.1	Structural description of V_3	127
IIIA.3.2	Single crystal X-ray structure of V_4	130
IIIA.3.2.1	Structural description of V_4	130
IIIA.3.3	Single crystal x-ray structure of V_{15}	138
IIIA.3.3.1	Structural description of V_{15}	138
IIIA.3.4	Single crystal X-ray structure of V_{18}	151
IIIA.3.4.1	Structural description of V_{18}	151
IIIA.3.5	Structure of layered vanadium oxide bronzes	157
IIIA.3.6	Synthesis of vanadium oxides under hydrothermal conditions	162
IIIA.4	Conclusions	165
IIIA. 5	References	166

CHAPTER IIIB: HYDROTHERMAL SYNTHESIS OF VANADIUM OXIDE

NANOTUBES AND MESOPHASES

IIIB.1	Introduction	169
IIIB.2	Experimental	170
IIIB.2.1	Experimental methods	170
IIIB.2.2	Synthesis and characterization	172
IIIB.3	Results and discussion	180
IIIB.3. 1	Formation of vanadium oxide nanotubes	180
IIIB.3. 2	Transmission electron microscopy of VO _x NTs	180
IIIB.3.3	Formation of mesostructured vanadium oxide	185
IIIB.3.4	Mechanism of formation of mesophases	192
IIIB.4	Conclusions	193
IIIB. 5	References	194

CHAPTER IV: ION EXCHANGE REACTIVITY OF LAYERED

VANADIUM OXIDE BRONZES

IV.1	Introduction	196
IV.2	Experimental	198
IV.2.1	Synthesis and characterization	198
IV.3	Results and discussion	199
IV.3.1	Structural Features of AgVO ₃	202
IV.3.2	Electron microscopic analysis of AgVO ₃	202
IV.4	Conclusions	208
IV. 5	References	209

**APPENDIX: HYDROTHERMAL SYNTHESIS OF HEXAGONAL
VANADIUM MOLYBDENUM OXIDES, $MVMO_5O_{18}$**

A.1	Introduction	212
A.2	Experimental	215
A.2.1	Experimental methods	217
A. 2. 2	Synthesis and characterisation	217
A. 3	Results and Discussion	218
A.3.1	Structural analysis of M_xVMO_5 phases	230
A. 4	Conclusions	234
A.5	References	235
BIODATA OF THE AUTHOR		237

List of Figures

S. No	Title	Page No
Fig. I.1	Existence of various vanadate species as a function of pH and concentration	6
Fig. I.2	Examples of metavanadates (a) 1D VO_3 chain $\{\text{VO}_3\}$ (b) cyclic trimer $\{\text{V}_3\text{O}_9\}$ (c) cyclic tetramer $\{\text{V}_4\text{O}_{12}\}$ and (d) 2D layered $\{\text{V}_2\text{O}_6\}$	11
Fig. I.3	Structure of (a) $\{\text{V}_{10}\text{O}_{28}\}$, (b) $\{\text{V}_{12}\text{O}_{32}\}$, and (c) bi capped Keggin type $\{\text{V}_{15}\text{O}_{36}\}$	16
Fig. I.4	Examples of high nuclearity clusters (a) Muller Type $\{\text{V}_{15}\text{O}_{36}\}$ (b) $\{\text{V}_{18}\text{O}_{42}\}$ and (c) $\{\text{V}_{22}\text{O}_{54}\}$	22
Fig. I.5	Vanadium oxide layer structure in V_4O_{10} (a) $(\text{TMA})\text{V}_4\text{O}_{10}$ and (b) $(\text{enH}_2)\text{V}_4\text{O}_{10}$	27
Fig. I.6	Vanadium oxide layer structure in (a) $(\text{TMA})\text{V}_3\text{O}_7$ and (b) $(\text{DABCO})\text{V}_6\text{O}_{14}$	29
Fig. I.7	A view of $\{\text{V}_8\text{O}_{20}\}$	31
Fig. I.8	Intergrowth structure of $\{\text{V}_{18}\text{O}_{46}\}$	31
Fig. I.9	Some examples of nanostructures (a) zirconia nanoparticle, (b) α - MoO_3 nanorods, (c) single walled carbon nanotube (d) multiwalled vanadium oxide nanotube, and (e) cross section image of vanadium oxide nanotubes	35
Fig. I.10	Members of microporous zeolites family	39
Fig. I.11	TEM images of (a) mesoporous silica and (b) mesoporous vanadium oxide	39
Fig. II.1	Synthetic scheme for the formation of PV_{14} and VPO	59
Fig. II.2	Synthetic scheme for the formation of V_4O_{11} and V_{10}	59
Fig. II.3	TGA plots for (a) PV_{14} and (b) VPO	62
Fig. II.4	FTIR spectra of (a) PV_{14} and (b) VPO	62
Fig. II.5	Scanning electron micrographs of (a) PV_{14} and (b) VPO	64
Fig. II.6	TGA plots of (a) V_4O_{11} and (b) V_{10}	64

Fig. II.7	FTIR of (a) V_4O_{11} and (b) V_{10}	66
Fig. II.8	SEM pictures of (a) V_4O_{11} and (b) V_{10}	67
Fig. II.9	Unit cell packing diagram of PV_{14}	74
Fig. II.10	ORTEP view of the cluster anion in PV_{14}	74
Fig. II.11	H bonding pattern in PV_{14}	76
Fig. II.12	Powder X ray pattern of VPO	78
Fig. II.13	Structure model of VPO intercalated with morpholinium cation	78
Fig. II.14	A perspective view of 1D chain running along (101) plane	82
Fig. II.15	Unit cell view of V_4O_{11} down the a axis (H atoms are omitted for the clarity)	82
Fig. II.16	Unit cell packing diagram for decavanadate	90
Fig. II.17	A view of the decavanadate clusters connected through H-bonding	90
Fig. II.18	Pictorial view of various oxygen sites in decavanadate cluster anion	91
Fig. IIIA.1	Schematic diagram of reaction scheme 1	108
Fig. IIIA.2	Schematic diagram of reaction scheme 2	108
Fig. IIIA.3	TGA curves for (a) V_3 and (b) V_4	112
Fig. IIIA.4	DTA curves for (a) V_3 and (b) V_4	112
Fig. IIIA.5	FTIR plots for (a) V_3 and (b) V_4	113
Fig. IIIA.6	TGA curves for (a) V_{15} and (b) V_{18}	113
Fig. IIIA.7	DTA curves for (a) V_{15} and (b) V_{18}	115
Fig. IIIA.8	FTIR spectras for (a) V_{15} and (b) V_{18}	115
Fig. IIIA.9	TG curves of intercalated vanadium oxide bronzes: (a) TPAVO (b) TPPVO (c) TBPVO and (d) TEAVO	117
Fig. IIIA.10	DTA curves of intercalated vanadium oxide bronzes: (a) TPAVO (b) TPPVO (c) TBPVO and (d) TEAVO	117
Fig. IIIA.11	FTIR curves of intercalated vanadium oxide bronzes: (a) TPAVO (b) TPPVO (c) TBPVO and (d) TEAVO	118

Fig. IIIA.12	^{13}C NMR of intercalated vanadium oxide bronzes (a) TPAVO (b) TPPVO (c) TBPVO and (d) TEAVO	121
Fig. IIIA.13	SEM images of intercalated vanadium oxide bronzes: (a) TPAVO (b) TPPVO (c) TBPVO and (d) TEAVO	124
Fig. IIIA.14	TEM images of (a) TPAVO and (b) TPPVO	125
Fig. IIIA.15	A view of V_3 along the z axis with ammonium ions occupying inter lamellar region	128
Fig. IIIA.16	View of V_4 along z axis	132
Fig. IIIA.17	A view along a showing intercalated DABCO cations between vanadium oxide layers	133
Fig. IIIA.18	Disorder in DABCO cations	133
Fig. IIIA.19	ORTEP view of cluster anion V_{15}	140
Fig. IIIA.20	Polyhedral view of V_{15}	140
Fig. IIIA.21	Tricosahedral oxygen coordination of chloride anion $\{\text{ClO}_{21}\}$	141
Fig. IIIA.22	Packing arrangement of V_{15} along the x -axis	141
Fig. IIIA.23	ORTEP view of cluster anion V_{18}	153
Fig. IIIA.24	Polyhedral view of V_{18}	153
Fig. IIIA.25	Rhombicuboctahedron oxygen coordination of chloride anion $\{\text{O}_w\text{O}_{24}\}$	154
Fig. IIIA.26	Packing arrangement of V_{18} along the y -axis	154
Fig. IIIA.27	Powder X-Ray pattern of intercalated vanadium oxide bronzes: (a) TPAVO (b) TPPVO (c) TBPVO and (d) TEAVO	158
Fig. IIIA.28	Patterson's function plots along c axis for various phases.	160
Fig. IIIA.29	(a) Electron density plots exhibiting doublet and (b) proposed model for intercalated vanadates.	161
Fig. IIIB.1	Schematic diagram of synthetic scheme	171
Fig. IIIB.2	TGA curves of synthesized nanotubes (a) ODAVO (b) HDAVO and (c) DDAVO	174
Fig. IIIB.3	DTA curves of nanotubes (a) ODAVO (b) HDAVO and (c) DDAVO	174

Fig. IIIB.4	FTIR spectra of VOxNTs (a) ODAVO (b) HDAVO and (c) DDAVO	175
Fig. IIIB.5	SEM photograph of VOxNTs exhibiting tubular shaped morphology	177
Fig. IIIB.6	TGA curves of synthesized mesophases (a) CTPVO and (b) DDPVO	178
Fig. IIIB.7	DTA curves of synthesized mesophases (a) CTPVO and (b) DDPVO	178
Fig. IIIB.8	FTIR spectra of mesophases (a) CTPVO and (b) DDPVO	179
Fig. IIIB.9	Powder X ray diffraction pattern of VOxNTs (a) ODAVO (b) HDAVO and (c) DDAVO	181
Fig. IIIB.10	TEM image of VOxNTs	183
Fig. IIIB.11	TEM images of VOxNTs after reaction period (a) one day and (b) two days	184
Fig. IIIB.12	Powder X-ray pattern of (a) CTPVO (b) DDPVO mesophases	186
Fig. IIIB.13	Powder X-ray pattern of DDPVO mesophase at temperatures (a) without heating (b) 150 (c) 250 (d) 350 and (e) 450°C	187
Fig. IIIB.14	TEM image of vanadium oxide mesophases DDPVO	189
Fig. IIIB.15	N ₂ adsorption- desorption isotherm of mesophase DDPVO	190
Fig. IIIB.16	Pore size distribution of mesophase DDPVO	190
Fig. IIIB.17	N ₂ adsorption- desorption isotherm of CTPVO	191
Fig. IIIB.18	Pore size distribution of mesophases CTPVO	191
Fig. IV.1	Powder X ray pattern of (a) TPPVO (b) Na ⁺ ion exchanged and (c) K ⁺ ion exchanged solids	200
Fig. IV.2	DTA curve for ion exchanged product	200
Fig. IV.3	DSC curve for ion exchanged product	201
Fig. IV.4	Evolution of AgVO ₃ as a function of time (a) 0 hrs (b) 16hrs (c) 36 hrs (d) 48 hrs	201

Fig. IV.5	Indexed Powder X ray pattern of AgVO_3	203
Fig. IV.6	Scanning electron micrographs (a) TPPVO (b) & (c) AgVO_3	205
Fig. IV.7	TEM pictures of layered vanadium oxide precursors (a) TPAVO (b) TPPVO	206
Fig. IV.8	TEM pictures of AgVO_3 nanorods with nano silver sticking on the surface	207
Fig. A.1	A perspective view of $\alpha\text{-MoO}_3$	213
Fig. A.2	A view of $\beta\text{-MoO}_3$	213
Fig. A.3	Polyhedral view of h-MoO_3	216
Fig. A.4	Schematic diagram of reaction scheme employed	216
Fig. A.5	Powder X-ray diffraction pattern of synthesized hexagonal phases	219
Fig. A.6	Representative FTIR spectra of KVMO	220
Fig. A.7	SEM photograph of (a) LiVMO (b) NaVMO (c) KVMO (d) RbVMO (e) CsVMO and (f) $(\text{NH}_4)\text{VMO}$	223
Fig. A.8	^7Li solid state NMR of LiVMO	225
Fig. A.9	^{51}V solid state NMR of (a) LiVMO (b) NaVMO (c) KVMO (d) RbVMO (e) CsVMO and (f) $(\text{NH}_4)\text{VMO}$	225
Fig. A.10	TGA curves of (a) NaVMO (b) KVMO (c) RbVMO and (d) CsVMO	226
Fig. A.11	DTA plots of (a) LiVMO (b) NaVMO (c) KVMO (d) RbVMO (e) CsVMO and (f) $(\text{NH}_4)\text{VMO}$	227
Fig. A.12	Powder X-ray diffraction patterns of LiVMO as a function of temperature	228
Fig. A.13	Powder X-ray diffraction of KVMO as a function of temperature	229
Fig. A.14	Reitveld refinement profile of (a) LiVMO (b) KVMO and (c) CsVMO	232

List of Tables

Table I.1	Some examples of applications of inorganic oxides	3
Table I.2	Surface areas, pore sizes and structures of some porous transition metal oxides	40
Table II.1	Crystal and experimental data of PV ₁₄	69
Table II.2	Atomic coordinates($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of PV ₁₄	72
Table II.3	Selected bond distances ($\text{\AA}$) for PV ₁₄	73
Table II.4	Selected bond angles ($^\circ$) for PV ₁₄	77
Table II.5	BVS calculations for PV ₁₄	77
Table II.6	Non-bonding interactions [distances($\text{\AA}$)] in PV ₁₄	77
Table II.7	Crystal and experimental data for V ₄ O ₁₁	80
Table II.8	Atomic Coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for V ₄ O ₁₁	83
Table II.9	Selected bond distances ($\text{\AA}$) and bond angles ($^\circ$) of V ₄ O ₁₁	86
Table II.10	Crystal and experimental data for V ₁₀	88
Table II.11	Atomic Coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for V ₁₀	92
Table II.12	Selected bond distances ($\text{\AA}$) for V ₁₀	94
Table II.13	Selected bond angles ($^\circ$) for V ₁₀	95
Table II.14	H-bonding interactions [distances ($\text{\AA}$)] in V ₁₀	96

Table IIIA.10	Selected bond distances (Å) and bond angles (°) of V_{18}	156
Table IIIA.14	Bond Valence sum value for V_{18}	156
Table IIIB. 1	Chemical composition and layer spacing of VOxNTs and vanadium oxide mesophases	175
Table A.1	Refined cell parameters for hexagonal phases	220
Table A.2	Composition of hexagonal vanadium molybdates	226
Table A.3	Refined atomic positions of hexagonal phases	233

ABBREVIATIONS

2,2'-biphenanthroline	2,2'-biphen
2,2'-bipyridyl	bipy
diethylenetriamine	dien
Cetyltrimethylammonium	CTA
Diazabicyclooctane	DABCO
1,3 Diaminopropane	pn
Dodecylamine	DDA
Dodecylpyridinium	DDP
Ethylenediamine	en
Hexadecylamine	HDA
Morpholine	morph
3N-Morpholinepropane Sulfonic Acid	MOPS
Octadecylamine	ODA
1,10-phenanthroline	1,10-phen
Phenylphosphonic acid	PPA
Tetraphenylarsonium	TPA
Tetraphenylphosphonium	TPP
Tetrabutylphosphonium	TBP
Tetraethylammonium	TEA
Tetramethylammonium	TMA
Vanadium Oxide Nanotubes	VO _x NTs