SYNTHESIS AND STRUCTURE OF ORGANICALLY Ttemplated 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

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, dodecyl amine, 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 $[Morp]_6[P^VO_4 \subset V^{IV}_3V^V_{11}O_{32}(OH)_6].2H_2O$ is obtained under self assembly conditions while a two-dimensional layered solid $[Morp]_{0.23}[V^{VI,V}OPO_4]1.1H_2O$ 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 $[PPh_4]_2V_4O_{11}$ 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 $V_4O_{12}^{4-}$ units. Under analogues conditions tetraphenylarsonium resulted in the formation of $[AsPh_4]_2(morph)_4V_{10}O_{28}.2H_2O$. Crystal structure revealed the presence of discrete decavanadte 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 $(NH_4)_2V_3O_8$ and $(DABCO)_2V_4O_{10}$ 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

CHAPTER II: FORMATION OF NOVEL POLYOXOVANADATE CLUSTERS IN THE PRESENCE OFORGANIC BASES : ISOLATION AND STRUCTURES OF $[Morp]_6[P^VO_4 \subset V^{IV}_3V^V_{11}O_{32}(OH)_6].\ 2H_2O$, $[Morp]_{0.23}[V^{IV,V}OPO_4]1.1H_2O$, $[PPh_4]_2V_4O_{11}$ AND $[AsPh_4]_2(morph)_4V_{10}O_{28}.2H_2O$

CHAPETR IIIA: ORGANICALLY INTERCALATED LAYERED VANADIUM OXIDE BRONZES: ISOLATION AND CRYSTAL STRUCTURES OF $(NH_4)_2V_3O_8$, $(DABCO)_2V_4O_{10}$, $[Cu(en)_2]_3[V_{15}O_{36}(Cl)]$, $[Cu(pn)_2]_4[V_{18}O_{42}(OH_2)].4H_2O$, $[(C_6H_5)_4As]^+_{0.19}V_2O_5$, $[(C_6H_5)_4P]^+_{0.20}V_2O_5$, $[(C_4H_9)_4P]^+_{0.19}V_2O_5$, AND $[(C_2H_5)_4N]^+_{0.58}V_2O_5$.

CHAPTER IIIB: HYDROTHERMAL SYNTHESIS OF VANADIUM OXIDE NANOTUBES AND MESOPHASES

CHAPTER IV: ION EXCHANGE REACTIVITY OF LAYERED VANADIUM OXIDE BRONZES

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

List of Figures

List of Tables

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	VOxNTs