ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

STUDY OF POLYMER SUPPORTED CATALYSIS OF SOME TRANSITION METALS ON THE CONVERSION OF CYCLOHEXANOL AND CYCLOHEXENE

AHMED HUSSEN

JUNE 1997

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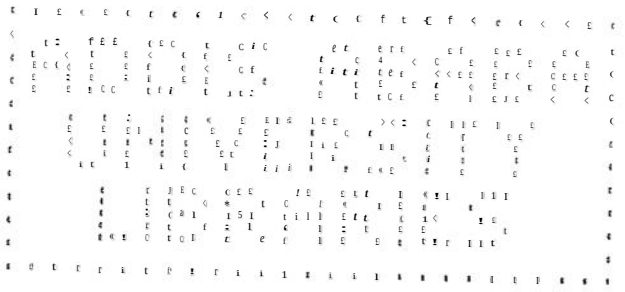

DEDICATED TO THE MEMORY OF

- SAYYID QUTB (Author of " *IN THE SHADE OF QURAN")*
- MY FATHER , HUSSEN DEKEBO
- MY MOTHER , AMANE WARE

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ABSTRACT

STUDY OF POLYMER SUPPORTED CATALYSIS OF SOME TRANSITION METALS ON THE CONVERSION OF CYCLOHEXANOL AND CYCLOHEXENE

BY

AHMED HUSSEN

ADVISOR: Dr. NEGUSSIE RETTA

The synthesis of titanium molybdophosphate (TMP), lead vanadophosphate (LVP) and lead selenophosphate (LSP) are reported. The chemical composition, IR spectrum, hydrogen ion liberation capacity and pH titration curve for each exchanger have been studied.

As the investigation of the catalytic nature of synthetic inorganic polymers were the core objective of this project, catalytic application of TMP and LVP as a support have been studied after loading Fe^{+3} on each, in dehydration of cyclohexanol and hydration of cyclohexene .From GC analysis both Fe^{+3}/TMP and Fe^{+3}/LVP was found to be efficient in dehydrating cyclohexanol but not the opposite reaction. 81 % and 38 % conversion have been achieved for each catalyst Respectively with in four hour refluxing. Using retention time coincidence test and peak enhancement technique the only reaction product was identified to be cyclohexene.

1. INTRODUCTION

Catalysis is a dominant feature in various biological and chemical reactions. It is a key to the efficiency of chemical conversion. Most of the products in the chemical industry are manufactured through catalysis, and problem of energy, natural resources and pollution (concern for the environment) are problems which are amenable to solution by catalysis. Catalysis plays an important role in pollution problems, not only in the removal of pollutants, but also in improving the selectivity of manufacturing processes so that undesirable by-products are not produced. In general it is vitally important in our daily life, since a large proportion of the products that make everyday life depend to some extent on catalysis[1,2].

"A catalyst is by definition a substance that increases the rate of approach to equilibrium of a chemical reaction without being substantially consumed in the reaction" [2].

The catalytic effect is attained due to intermediate chemical interaction of the reagents with the catalysts and the participation of the latter in the formation of activated complexes in a series of elementary steps, opening up a new reaction pathway, which requires minimum activation energy in comparison to the non catalysed reaction. What makes activation energy to be decreased in the presence of a catalyst ?. This could be accounted by the incomplete rupture of the initial bonds in the activated complex, which requires lower activation energy than the energy required to break the bond in the absence of the catalyst [3, 4].

A possible point of view suggests that the symmetry of the molecular orbitals is important in catalytic effects. The electronic structure of the reagents can be unfavourable because of the incompatible symmetry of the interacting orbitals. Forbidding a reaction on symmetry grounds causes a high activation energy. In the presence of a catalyst, new reaction pathway is opened due to the intermediate interaction of the reagents with the

catalysts in a path in which orbital symmetry is favourable. In other words, the catalysts can eliminate symmetry forbidden routes leading to a lower activation energy [3].

Catalysts may be best characterized by the following features [3,4,5].

1. Unchangeableness of the catalyst

A catalyst which is added in a reaction mixture remains unchanged at the end of the reaction as regards to quantity and chemical composition. It is likely that a catalyst may under go some physical change.

2. Selectivity of the catalyst

If thermodynamics permit several reaction routes, a catalyst may accelerate preferentially some or even specific to only one of them.

3. Equilibrium point is un-affected

In reversible reactions, it is observed that the catalyst accelerates the reverse reaction to the same extent as the forward reaction so that the ratio of their velocity, the equilibrium constant, remains unaffected.

4. Speed up a reaction

A reaction which are possible thermodynamically but which can not otherwise proceed at all because of kinetic difficulties, die accelerated to take place at reasonable time.

5. Regenerability

A catalyst could be regenerated, repeatedly used. Thus there is a possibility of conversion of high amounts of substrate using small quantities of catalyst.

These features of catalysts caused wide usage of catalytic reactions in industry. It has become the most effective and economical method of governing chemical processes.

1.1. CLASSIFICATION AND BACK GROUND FOR THE PRESENT INTEREST IN SUPPORTED CATALYSTS.

Cataiysts are usually classified according to the phase relationship between the catalyst and reactants as homogeneous and heterogeneous catalysts [4]. In heterogeneous catalysis, the catalyst and the substance to be catalysed are in two different phases. The catalyst is introduced to the reaction mixture as a solid to facilitate a reaction through adsorption of some or all of the reactant on its surface. Hence the rate of reaction is directly proportional to the exposed surface area of the catalyst. Heterogeneous catalysts may be thought of as the first generation of catalysts.

In homogeneous catalysis (second-generation catalysts) there is no phase bounda17 between the reactant and the catalyst, both being uniformly distributed in the reaction mixture.Such catalysts normally operate in solution and the catalyst is dissolved in the reaction mixture. Therefore, in homogeneous systems, the rate of catalytic reaction is directly proportional to the concentration of the catalyst [4,6].

Even though in general both homogeneous and heterogenous catalysts accelerate the rate of reaction by minimizing the activation energy, there is a significant difference between the two, owing to the different environment they encounter. Each liaS its own advantage arid disadvantage [6,7].

1. Recovery of the catalyst: The major disadvantage of homogeneous catalysts is the problem of separating the very expensive catalyst from the products at the end of the reaction. With heterogeneous catalysts this can be achieved by some kind of coarse filtration whereas with homogeneous catalysts a very efficient distillation or ion-exchange process is usually required.

2. Efficiency: In heterogeneous systems, the catalytic reaction must necessarily take place through adsorption of the reactants on the surface of the catalyst so that all atoms and

molecules of the catalyst not present at the surface remain unused. In contrast all molecules of the homogeneous catalysts are theoretically available as catalytic centres so that these catalysts are potentially more efficient in terms of the amount of catalyst needed to catalyse a given amount of reaction.

3. Reproducibility: Homogeneous, catalysts have the advantage over heterogeneous catalysts of being totally reproducible because they have a definite stoichiometry and structure. But the structure of the surface of a heterogeneous catalyst is heavily dependent on both method of preparation and its history subsequent to preparation.

4. Specificity: A given homogeneous catalyst will generally have only one type of active site and, therefore, will often be more specific than a heterogeneous catalyst where several types of active site may be present in the form of different surface defects. These defects are extremely difficult to control. The specificity of a homogeneous catalyst can often be selectively modified by altering the other ligands present in such a way as to alter either the electronic nature or the steric requirements of the site.

5. Thci'inal stability: Tho thermal stability of hotorogonoou3 cntnly3t3, such as pure metals and metal oxides, is often much higher than that of homogeneous catalysis. Since the rate of most reactions increases Willi temperature, a high operating temperature may be an advantage.

6. Solvent: There is no restriction in solvent selection for heterogeneous catalysts whereas the range of appropriate solvent for a homogeneous catalyst is often limited by the solubility characteristic of the catalyst.

7. Controllability: Since homogeneous catalysts have definite structure its properties can be controlled in a systematic manner by varying the ligand group attached to the transition metal.

When we examine the advantages and disadvantages of these two categories of catalysts from the point of view of most desired qualities of a catalyst such as high activity, chemical selectivity and easy recovery, it might appear that the balance would lie with homogeneous catalysts. However, this is not so. Recovery of homogeneous catalyst is a major problem in a large scale industrial production. It has a number of practical problems like corrosion, deposition of the catalyst on the walls of the reactor, which would render the process un-economic and contamination of the reaction products which would be unacceptable in the case food stuff production. Owing to this major problem most industry has not been so far very greatly interested to adopt homogeneous catalysis in chemical process (apart from one or two rather notable exception namely Wacker process for the oxidation of ethylene to acetaldehyde (boiling point 20.8nC) and Monsanto process for the carbonylation of methanol to yield acetic acid (boiling point 117.9°C), which depend in part for their success on the relatively low boiling points of the products) inspite of their obvious advantages, over heterogeneous catalysts [6,7].

Recently, considerable research effort has been expended in developing catalysts that combine as many as possible of the advantages of each of the two extreme types. To this end one ot'the major approach is to build the catalyst mainly transition metal cations and transition metal complex, on an insoluble support thus combining the advantages of homogeneous and heterogeneous catalysts. This remark, the beginning of supported catalysis which may be thought as the third generation of a catalyst [6-8]. This is also not unusual in the biological systems where enzymes in most cases are supported with membrane [2].

The original objective in supported catalysis was undoubtedly to get over the solubility problems of homogeneous catalysts which made their separation after reaction

such a problem. However, there have been other advantages. In particular the selectivity of the supported catalysts is often greater than their homogeneous counterparts because, in addition to the electronic and steric selectivity present in the free complex, further selectivity in both molecular size and relative polarity is introduced by the groups in the polymer around the active site. These groups, which are a consequence of the three-dimensional nature of the polymer, have no counterpart in homogeneous catalysts. Moreover these groups may prevent, or at least reduce, the ability of poisons to destroy the catalytic activity [6]. There are a number of examples coming to light where the supported catalysts have much greater activities than their homogeneous counterparts because the support is able to prevent harmful side reaction such as dimerization of the active species [2,6,9,10]. Supported catalysts have the advantage over homogeneous catalysts that they can be used in the presence of any solvent, i.e the solvent can be freely optimized without any restraints imposed by the catalyst [6,9].

However, the solvent may have a profound effect on the polymeric support in causing swelling and resulting in large changes in the size of the pores and available surface area. This can affect both the reaction rates and the selectivity of the active centre towards differently sized substrates. This limitation can be overcome by the use of inorganic oxides, such as silica, as the support to which liganding groups may be attached [7]. Supported catalysts could also be applied in purification of contamination of water supplies which is an ever increasing problem [11].

In general polymer supported catalysts are best fitting to the most desired properties of a catalyst, combining the advantages of both extreme types. Thus, they are inevitably going to be very essential. We may expect in the future to see supported complex catalysts used in reactions where high selectivity is important such as in the pharmaceutical and dye stuffs industries [6]

1.2. SUPPORT MATERIALS

A number of materials both inorganic (silica, zeolites, glass clay, metal oxides such as alumina) and organic (polystyrene, polyamines, polyvinyls, etc.) have been used as a basic support [6].

The support is usually expected to be inert to the reaction mixture, possess large surface area, be porous and withstand the required reaction condition. Since the catalytic activity of a metal catalyst is restricted to the surface, the maximum catalytic activity is attained by highly dispersing the metal on the support, thereby enhancing the specific metal's surface area. Porosity is also important for it provides voids in which most of the metal in a supported catalyst is deposited; besides it serves as a site of transport for reactants and products during catalysis [9,12,13].

Supports for metallic catalysts are not necessarily inert, apart from the way in which the support may control the morphology of the supported metal, it may play a direct role in the catalytic reaction itself, thus acting as bi-functional. The best known examples are catalysts such as platinum/alumina or platinum/zeolite in which the acidic support function as the seat of carbonium ion in isomerization activity, while the platinum provides a hydrogenation/dehydrogenation function. Because of these sort of possibilities one should always treat the support as an integral part of a supported metal catalyst [13,14].

Inorganic support materials have attracted more attention than organic polymers which are mostly linear; they mainly have a tridimensional crystalline structure and are mostly heterochain polymers [15]. This rigid structure of inorganic polymer support is an important advantage over the organic polymers which posses enough flexibility. Polymer flexibility can lead to deactivation through intermolecular condensation reactions. Groups bonded to relatively rigid polymers may be efficiently held apart from each other and accessible to reactants, whereas groups in more flexible (more solution like) polymer gels

maybe inefficient catalysts because they accommodate reactants poorly. Thus anchoring a catalyst to a support can sometimes make possible a catalytic reaction that otherwise could scarcely even take place. This point illustrates that the physical properties of the polymer support are critical [2].

Another advantage lies in greater control of diffusional factors. Organic polymer swelling under variable temperature and solution conditions makes practical control of diffusional variables difficult. Inorganic polymers are preferred for stable diffusional characteristics because of their rigidity [9].

Lack of stability of the organic polymer at temperatures greater than 130°C restricted their application, whereas inorganic support materials are used as catalysts under condition much more severe than the organic polymers can withstand [2]. Organic polymer supported transition metal complex catalysts also lose activity by leaching of catalytic groups. For instance the deactivation of a hydroformylation catalyst consisting of rhodium complexes attached to phosphine groups in cross-linked polystyrene resulted from this metal loss [2,16]. Such critical problems could be managed by making use of inorganic support material owing to their structural rigidity.

The field of supported catalyst, is rapidly expanding and they clearly have an important future. The physical and chemical properties of support materials used have a significant role in regulating the catalytic properties of the attached groups.

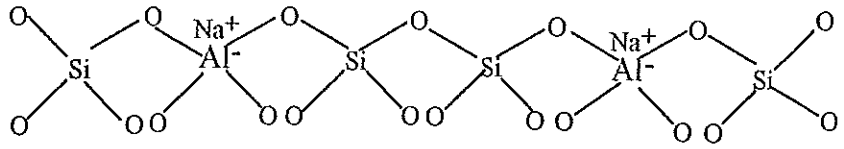
As it is discussed above from the industrial application point of view, inorganic support materials are far more useful than organic polymer materials. Virtually any solid can in principle be used as a catalyst support for dispersed metal. However, in practice the range of materials in reasonably common use is restricted and there are a few such as zeolites, silica, clay, glass, carbon, and some metal oxides like alumina which over-shadow the rest [13]. Some of the main features of these materials are highlighted in subsequent

section devoted to some of them as follows.

Zeolites:

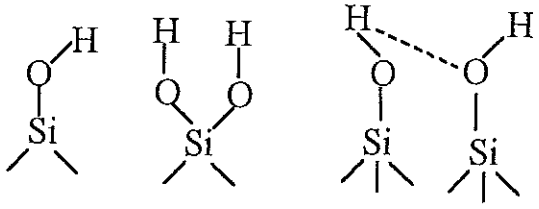
Zeolites are crystalline alumino silicates which are composed of order arrangements of SiO_4 and AlO_4 tetrahedral, linked by corner sharing of oxygen. The zeolites are structurally unique in having cavities or pores with molecular dimension as a part of their crystalline structures. The alumino silicate structure is ionic, incorporating Si^{4+}, Al^{3+} and O^{2-}, when some of the Si^{4+} ions in the SiO_4 tetrahedra in this framework are replaced by Al^{3+} ions, an excessive negative charge is generated. A compensating source of positive charge must be added, namely, cations in addition to the frame work Si^{4+}. These non-framework cations play a central role in determining the catalytic nature of zeolites. Zeolites are ion exchangers. Bringing an aqueous salt solution in contact with the zeolite leads to incorporation of cations from the salt into the zeolite, replacing some of the non-framework cations initially present. This characteristic nature provides an opportunity for modifying the properties of a zeolite [2,13].

A segment of a zeolite in the sodium form is represented as follows.

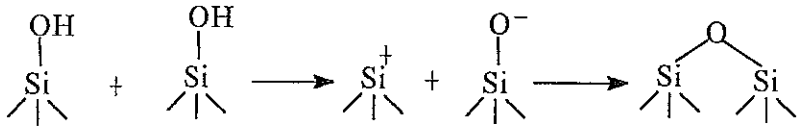


Silica:

Silica is an amorphous solid, being relatively simple and unreactive, can be thought of as a "peg board". The hydrogel is all aggregate of primary particles made up of a network of interconnected covalently bonded SiO_4 tetrahedra. The functional groups that terminate silica include -OH groups.



When the surface is heated, water is driven off, if the temperature is raised to ~ 450°C. Stable and relatively unreactive "siloxane bonds" are formed.



Taking advantage of the reactivity of these groups, which are weakly acidic, one can attach many kind of catalytic groups to the surface and expect that a reaction will be catalysed by the anchored groups with the support playing a negligible role [2,13]

Clay:

Sheet silicates (often called clays) are among many inorganic solids with a regular structures that incorporate spaces having molecular dimensions. Cationic metal complex catalysts can be intercalated between the negatively charged sheets of swelling. They have cation exchange property like zeolites. The space between the layers are accessible even to a large molecules.

Recent work has revived interest in these materials as catalysts, as large cation pillars have been used to hold the layers apart and allow entry of large molecules found in the heaviest fraction of petroleum. These molecules are too large to enter zeolite pore and the clays are an intriguing alternative [2,13,17].

Porous glass:

Porous glass consists of polymeric chains of silicon dioxide with a fringe consisting of a variable amount of alkali metal ions. It has many silanol-type hydroxy groups effective for the sorption of metal ion via an ion-exchange method. These characteristics indicated that the porous glass can be a good catalyst support having an arbitrary microspore size distribution and a high extent of dispersion of metal [12,15].

Alumina:

Al_2O_3 has complex structure with an intermediate bonding between ionic (MgO) and covalent (SiO_2).

The primary particles of a transition alumina are crystallites terminated by layers of oxygen anions and for charge neutrality, the surface must incorporate cations, which are typically H^+ present in -OH groups. Dehydroxylation of the surface leads to the formation of coordinatively unsaturated O^{2-} ions and Al^{3+} ion which is a Lewis basic and Lewis acidic site respectively [2,13].

Carbon :

The use of carbon as a catalyst support offers several advantages. It is cheap and is relatively inert material. After an activation process, a porous network is developed which gives very high surface areas. Furthermore, expensive supported precious metals can be easily recovered by burning of the carbonaceous support. It is also able to reduce the metal precursor introduced during catalyst preparation [2,18]. In general surface hydroxylation is an important charcterstics of these support materials because the OH groups are involved when the support is impregnated with a metal complex [19].

These features are equally important for a given substance to be used as a support material in catalysis. Inspite of all these similarity, almost all of the studies that have been made on synthetic inorganic polymers is devoted to the study of their ion exchange property and column chromatographic application for separation of different metal-cations [22-25]. Except one report [26] where zirconium phosphate loaded with several transition metal ions is mentioned as a potential catalyst.

This analogy with those widely used support materials (silica, zeolite, clay, sand, etc.) together with their simplicity in preparation [22,27] stirred our interest to study the catalytic application of lead vanadophosphate and titanium molybdophosphate as a support material to transition metal cations. To our knowledge this is the first attempt to study the catalytic role of such materials and their synthesis is also reported for the first time.

1.3. Objective of the present work

1. To synthesze and characterize new synthetic inorganic polymers such as titanium molybdophosphate (TMP) lead vanadophosphate (LVP) and lead selenophosphate (LSP).
2. To explore their catalytic application as a support.

2. LITERATURE REVIEW

2.1. GENERAL

Transition metal ions are among the most important catalytic species owing to the availability of partly filled d-orbitals that makes possible the coordinative bonding of suitable neutral molecules to the central metal ion [13,28].

Supported metal catalyst plays a central role in heterogeneous catalysis. The study of heterogeneous catalysis dates back to the early 1800s. Faraday was one of the first scientist to examine the ability of platinum to facilitate oxidation reactions. The catalytic processing of crude oil to fuels and other petrochemical products continued to impact society and life styles during the 1900s. As we approach the 21st century, we would have difficulty imagining our world without the fruits of heterogeneous catalysis [29].

Catalytic species bonded to organic polymers may be nearly uniform in character and function catalytically just as their molecular analogues do in solution. Hence organic polymer supported catalysts are structurally simple. Whereas most inorganic support materials (except a few like zeolite and clays that have well-defined crystalline structure) are structurally non-uniform and because of this supported metal particles are non-uniform in size and shape and too small to be characterized precisely [2,30].

Recently, the only means to characterize surface catalysis is using ultra high vacuum surface techniques like X-ray photoelectron spectroscopy which could define surfaces at the atomic level [2,31]. Organic polymer supported catalysts provide a transition from well-understood soluble catalysts to the more complex surface catalysts, which rests on a weak structural foundation. Surface catalysis is only poorly understood in comparison with solution catalysis [2]. Preparation and catalysis by inorganic materials supported catalysis is the subject of this review.

2.1.1. Preparation

Catalytic materials exist in various forms and their preparation involves different procedures with a multitude of possible preparation schemes.

Generally there are only two main routes for the preparation of almost all catalysts. These can be divided into two categories: methods in which the catalytically active phase is generated as a new solid phase by either precipitation or a decomposition reaction, and methods in which the active phase is introduced and fixed onto a prexisting solid by a process which is intrinsically dependent on the surface of the support [32].

Recently, the latter method (impregnation technique) is a widely adopted procedure for the preparation of supported catalysis in the patent literature [33-38].

The mounting of dissolved aqueous precursors on oxide support (where surface hydroxyl acts as a proton donor/proton acceptor sites) is generally accomplished by the so-called impregnation method. This term denotes a procedure where by a certain volume of solution containing the precursor of the active element of the catalyst is contracted with the solid support [13,31,32].

If the volume of solution either equals or is less than the pore volume of the support, the technique is referred to as incipient wetness [32]. When the interaction strength of the active precursor in solution with the support is weak, the method of incipient wetness impregnation followed by drying may be used to apply high loading of precursors. The maximum loading is limited by the solubility of the precursor in the pore filling solution [32].

Sesar and co-workers [39] used incipient wetness technique for the preparation of nickel-supported catalysts.Similarly Gandi and Montes [18] used this method for the preparation of nickel and cobalt activated charcoal supported catalysts from aqueous solution of $Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$, respectively.

In the wet impregnation technique (also called soaking or dipping) an excess of solution is used. After a certain time, the solid is separated from solution, and the excess solvent is removed by drying [32]. The amount of the active precursor mounted onto the porous carrier, its concentration profile with in the carrier grains and its chemical environment on the support surface depend significantly on the conditions during these first two steps (impregnation and calcination (drying)) in catalyst preparation [32].

In general the variation of the amount of catalytically active species mounted on to support surface is reported to be attributed to the most important impregnation parameters such as pH, concentration of the impregnating solution and impregnation time [32,40,41].

As it is mentioned above, catalyst drying is the second major step in the preparation procedure. Besides drying at about (~120°C) to drive off water, a catalyst is heated to a higher temperature (~ 500°C), a processe known as calcination, after which it is chemically treated (reduction) to produce active catalysts [31].

However catalyst preparation could also be possible directly without subsequent calcination [13,34]. Catalysts prepared by Cornelis and co-workers (carbon and alumina-supported Ge, Mo, Fe-Mo, and Co-Mo sulfide catalysts) were only dried at 383 K for 16 h without further heat treatment or calcination procedure. This is because it was reported before that by other workers, drying at 383 K caused, considerable active phase sintering and consequently a lower catalytic activity [36].

Bifunctional catalysts could also be prepared by simultaneous impregnation of the aqueous solution containing the metal of interest [34,36,42].

Ion exchanger is the other method for introducing catalytically active species onto a support.

Catalyst systems, which require charge compensating ions have received the most attention as versatile materials suitable for ion exchange,this includes zeolites and cationic

clays. These are ideal ionexchangers because the crystalline lattice bears electric charges. Compensation of electric charges is a prerequisite for stability of the crystalline structure. As a consequence, the lattice charge is compensated by oppositely charged ions bound electrostatically in extra lattice positions. These ions are readily exchanged by ions bearing an equivalent charge from aqueous solutions [32]. Different catalytically active cations could be introduced (supported) onto such inorganic polymers by the virtue of their being ion exchangers.

Two pioneering catalyst preparation methods were also reported in the same year 1978. One is the paper in which Brunelle demonstrated the importance and versatility of electrostatic adsorption in catalyst preparation; the other is the publication in which Summers and Ausen demonstrated the occurrence of an alternate mechanism for precursor bonding during catalyst impregnation, namely adsorption by ligand substitution. The latter authors studied the reaction of amine complexes of Pt, Pd, Rh, Ir, Au and Ru with alumina and suggested that there are two reaction pathways during equilibrium adsorption. One of these involves displacement of ligands from the coordination sphere of the adsorbate complex, this was the case with complexes containing halogenides as ligands [13,32]. The other pathway which does not involve ligand substitution was observed for complexes of the type $[M(NH_3)_4]^{2+}$ and $[M(NH_3)_5Cl]^{2+}$, which are adsorbed electrostatically. Since then, other examples, of adsorption of complex ions through partial substitution of their ligands by surface hydroxyl have been reported [32].

Adsorption of amine complexes of Cu^{2+} and Ni^{2+} on silica by Olivier *et al.* [32] reaction of rhodium allyl complexes and OH groups terminating the surface of silica [43], catalysts reported by Yermakov and co-workers [43] and immobilization of transition metal carbonyls on inorganic support [41] are among catalysts prepared by this method.

into the zeolite. Since some complexes are too large to pass through the narrow opening. A relatively well understood example is methanol carbonylation catalyzed by Rh(I) complexes in faujasites.

Oligomerization and hydroformylation of olefins,oxidation of hydrocarbons are also among the reactions catalyzed by transition metal ions in zeolites [2]. Iwamoto *et al.* [44] have shown copper ions (Cu^{+} and Cu^{+2}) in ZSM-5 to be active in a redox cycle for the catalytic decomposition of NO to give N_2 and O_2.

Naphtha reforming is one of the most important of the catalytic processes, and its development provided much of the stimulus for advances in the understanding and further applications of supported metal catalysts.

Platinum is the metal with the most suitable properties for meeting the goals of naphtha reforming that is to maximize the production of high-octane-number compounds so that naphtha would be an optimum motor fuel that prevents engine knock. However by itself it is lacking some of the desirable characteristics of strong acid catalysts.

Haensel and co-workers discovered Pt-supported on less-thoroughly washed Al_2O_3 made from aluminum chloride, to be active for the desired reforming reactions than on SiO_2 or on Al_2O_3 made from aluminum nitrate. This observation led to the application of Pt/Al_2O_3 catalysts in which the acidity of the transition alumina was increased by incorporation of chloride [2].

Transition-metal oxides and salts, supported on inorganic gels such as alumina and alumina-silica oligomerize ethylene to α-olefin , $C_{6\text{-}10}$. On the surface of these catalysts Bronsted acid and coordinative centers exist, which together are responsible for the olefine oligomerization [45].

It is well known that several members of the sheet silicate family can form interlammellaer complexes (intercalates) with a wider range of organic molecules. Adams

product. However for longer chain alkenes isomeric products were obtained as in the case of the reaction of hex-1-ene with acetic acid in the presence of Cr^{+3}-exchanged montmorillonite in which the products were 70% of 2-hexylacetate and 30% of 3-hexyl acetate [50]. The same research group reported the elimination of ammonia from amines in the presence of (Al^{+3}, Cr^{+3} or Cu^{+2})-exchanged montmorillonites [50].

The hydrogenation of benzene and methyl-benzenes (mono-di, and trimethyl benzenes) was studied by Takeshige *et al.* [12], over a nickel catalyst supported via an ion-exchange method on porous glass prepared from borosilicate glass (PVG) with an alumina content ranging from 3 to 5%. They found that the micropore distribution shifts to a fine pore size and becomes sharper (fine and more uniform micropores develop) with increasing alumina content.

Although the reaction rates for benzene and toluene do not significantly change with the alumina content in the borosilicate glass, the rate of 1,3,5-trimethylbenzene (mesitylene), which is the bulkiest molecule among the hydrocarbons tested, decreased as the content of the alumina in the support increased. This result indicates that a catalyst support with molecular shape selectivity can be prepared form borosilicate glass by controlling its alumina content.

Furthermore the performance of Ni-PVGs was compared with reference catalysts supported on a silica gel (JRC-53-30 Ni and JRC-53-50Ni) provided by catalysis society of Japan, which were prepared by an impregnation method.

It was found that nickel dispersion of Ni-PVGs is from 3.5 to 7 times greater than that of JRC-53-50Ni. The hydrogenation rates over Ni PVGs were approximately the same as that over JRC-53-50Ni even though the nickel loading of the Ni-PVGs (5.58, 4.78. 3.65 wt %) was lower than that of the reference catalyst (33.95 wt %). The hydrogenation rate on Ni-PVG-5 was about 16 times greater that on JRC-53-30 Ni.

Supported metal sulfides are catalytically active for a wide range of hydroprocessing reactions, that are also catalyzed by metals. The most active metal sulfides are typically several orders of magnitudes less active than the most active metals. But in contrast to the metals, they are not poisoned by sulphur compounds. Therefore they are the catalysts of choice with feed stocks that contain sulphur [2].

Cornelis *et al.* [36] made a comparative study of alumina and carbon-supported catalysts for hydrogenolysis and hydrogenation of model compounds and coal-derived liquids. Liquids derived from coal need to be purified in order to reduce their content of heteroatoms (such as sulphur, nitrogen and oxygen). It is a well-established fact that these constituents cause a substantial environment pollution. They are also known to have harmful effect on the efficiency of the installations to which they are applied.

They have concluded that all of the hydrotreating reactions studied (hydrodesulfurizaton (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrogenation) i.e, sulphur, oxygen, and nitrogen removal and hydrogenation are catalyzed by both alumina -and carbon-supported Fe, Mo, Fe-Mo, and Co-Mo sulfide catalysts. The application of carbon supported catalyst is particularly advantageous at relatively low hydrogen pressures, while alumina-supported catalysts generally are the more active at high pressures. These activity differences were ascribed to differences in active phase-support interaction. Due to their being relatively inert, carbon substrates do not interact strongly with the active material. The alumina surface, However, possesses high concentrations of surface hydroxyl groups, which can serve as relatively strong chemisorption sites for the metal components during the preparation procedure. The metal ions, which are, especially after calcination of the catalyst precursor (like in commercial alumina-supported catalyst), strongly bonded to the alumina surface, may be less readily reduced than when supported on carbon. Carbon-supported sulfide catalysts may thus be economically attractive

compared to the conventional alumina-supported ones for application on coal, liquefaction process at relatively low hydrogen pressure. Obviously, the same applies to heavy oil and bitumen upgrading.

The influence of phosphorus on structure and hydrodesulfurization activity of sulfided Co and Co-Mo catalysts supported on carbon and alumina were studied by Bouwens *et al.* [51]. The results indicated that phosphorus decreased the thiophene HDS activity of the carbon-supported catalysts considerably but did not affect the activity of the alumina-supported catalysts. Whereas for the oxidic catalyst precursor it was indicated that irrespective of the support, phosphate improves the dispersion of the metals in the oxidic phase, due to a close contact between the metal oxide phase and the phosphate. In the sulfided catalyst, the interaction between the phosphate and the metal sulfide phase depends on the support material. In the alumina-supported catalysts phosphate doesn't influence the structure of the metal sulfide phase, while in the carbon-supported catalysts, a M(II)-phosphate phase is formed which is responsible for the decrease in HDS activity.

The conventional wisdom in heterogeneous catalysis is that catalysis requires the presence of a transition metal surface. The metal surface supposedly activates hydrogen and hydrocarbon C-H bonds and brings the reactive intermediates together in such a way that the reaction can occur [52]. But Maier's research indicates that inert silica becomes catalytically active in the presence of a transition metal underlayer [52,53].

Although the catalytic activity of such a silica (SiO_2) surface is lower than that of an exposed transition metal surface, the reaction catalyzed on both appears almost identical. From these result they strongly suggested that the primary action of transition metals in heterogeneous C-H activation catalysis is solely to activate hydrogen. Thus ,they postulated that the activated H_2 (dissociated hydrogen) represents the active site on these catalysts and the exposed transition metal is not required. According to Maier a number of lines of

evidence suggest that the observed catalytic activity is due to defects in the amorphous silica that probably mediate the transport of molecular and dissociated hydrogen through the inert silica overlayer. A note-worthy selectivity difference between the catalysis on the silica surface under the exposed metal surface was also observed with the hydrogenation of 1,2-dimethyl cyclohexene and 2-hexyne.

In general these findings open up the possibility for new catalysts based on metal underlayers with a variety of overlayer materials that could provide unique selectivity, activity and stability against poisoning [52,53].

Vanadia-based catalysts are also well-known for catalyzing a great variety of industrial reactions. Recent studies have shown that V_2O_5 supported on a metal oxide support such as Al_2O_3, SiO_2 and TiO_2 is a superior catalyst to the unsupported crystalline V_2O_5 for the selective oxidation and ammoxidation of many hydrocarbons. Thus, the support metal oxide plays a major role in determining the dispersion and activity of the V_2O_5 when supported [37].

Many of the contaminants of water supplies are organic chemicals, arising as inevitable byproducts from industrial processes, agricultural treatment of crops and accidental spills or leaks from container. Some of these contaminants can be removed from the water by adsorption onto solids or purged to the atmosphere by pressurized air. The transfer of the contaminant from the water to another phase is not an ideal remedy, destructive oxidation treatment provides more permanent solution. For this purpose, TiO_2 supported on sand was reported to be used in photo-oxidative degradation of coloured organic contaminants like methylene blue, Rhodamine B and methyl orange [11].

The ability of rhodium catalysts to produce ethanol as well as a variety of other substances such as methanol, hydrocarbons, higher alcohols, acetaldehyde, and acetic acid in carbon monoxide hydrogenation has been known since 1987. The activity and selectivity

of rhodium catalysts are influenced greatly by many parameters, such as the support used, the precursors and the preparation techniques, and to a lesser extent by the reaction experimental condition. Thus, on Rh/SiO_2 catalysts, methane and higher hydrocarbons are the main products and little or no ethanol is observed; while on Rh/CeO_2 catalysts ethanol is the main product with up to 80% selectivity [54].

Gandia and Monles [18] studied the effect of thermal treatments on the properties of nickel and cobalt activated-charcoal-supported catalysts.

They found a remarkable high activity and selectivity for acetone hydrogenation to 2-propanol under unusual and severe experimental conditions (473 K). Activated charcoal has been found to be a very reactive support towards dispersed nickel and cobalt particles. Thus during the catalyst preparation and activation treatments several processes like metallic precursor reduction by the support and metal surface contamination can occur.

Ganapati and Pranav [55] used heteropolyacid (dodecaetungstophosphoric acid (DTPA)) supported on silica and carbon as well as some solid acidic catalysts for esterification. These catalysts are found to be effective for the preparation of phenethyl acetate and cyclohexyl acetate which are two of the basic esters having wide application in perfumery and flavour industries. Even though DTPA/silica and DTPA/carbon is less in the order of catalytic activity (based on unity weight) relative to other catalysts included in their study it is very superior from the view point of activity, selectivity, reusability and non corrosiveness in comparison with the homogeneous catalysts.

Capka and Hetflesjs [56] have prepared a series of Rh, Pd and Pt complexes whose tet-phosphine, tet-amine, cyano or pyridine ligands are bonded directly or through alkylene chain to inorganic supports. Various methods were employed to introduce these functional groups, each utilizing the reactivity of surface hydroxyl groups of inorganic oxide support.The catalysts were tested for hydrosilylation of several alkenes and 1,3-butadiene

by trichloro-, triethyl-, and triethoxysilane and it was found to be more selective and effective in comparison to the soluble catalysts.

Michael and co-workers [57] reported that silica-supported zirconium hydrides are highly efficient olefin isomerization catalysts that possess modest olefin hydrogenation activity. Rhodium hydrate supported on silica was also reported to be effective for olefin hydrogenation and active even toward hindered olefines.

3. EXPERIMENTAL

3.1. General

3.1.1. Apparatus

IR spectra in the region of 4000 - 500 cm^{-1} were recorded on Perkin-Elmer spectronic 1000-SPIR IR-spectrophotometer as KBr disc.

Analyses of the composition of the samples were made by Varian specter AA20 atomic absorption spectrometer and Varian DM80 UV-visible spectrophotometer. pH measurements were made using Beckman Chem-mate pH-meter. Gerhardt and Gallenkamp flask shakers were used for shaking different samples. The reaction products of catalysis were followed up using Varian Model 3700 gas chromatograph. Griffin oven was used for the determination of moisture content of the samples.

3.1.2. Reagents

Sodium molybdate (Riedel-deHaen), potassium phosphate diabasic (BDH), titanium(IV) chloride (Riedel-deHaen), ortho phosphoric acid (Riedel-deHaen), sodium dihydrogen phosphate (BDH), lead nitrate (Analar), ammonium metavanadate (BDH) and sodium selenite (Sigma) were used for the synthesis of the three ion exchangers. Hydrochloric acid (Riedel-deHaen) was used to convert the exchangers into H^+- form.

Ion exchange property was studied using sodium chloride (E. Merck), sodium hydroxide standard solution (BDH-CVS) and potassium hydroxide (BDH).

Ferric chloride anhydrous (BDH) and copper nitrate (Riedal-deHaen) were used as a catalyst precursor. Catalytic study was made using cyclohexene (Riedal-deHean), cyclohexanol (BDH) and n-hexene (BDH).

3.2. Synthesis of support materials

3.2.1. Titanium Molybdophosphate (TMP)

1 M aqueous solutions of sodium molybdate (20 mmol) ($Na_2MoO_4.2H_2O$) and potassium hydrogen phosphate (20 mmol) (K_2HPO_4) were prepared. Solution of titanium tetrachloride, 1M, was prepared by diluting 10 mL of commercially produced $TiCl_4$ (20 mmol) using 4 M HCl as a solvent. TMP where the mole ratio of titanium (IV): molybdate: phosphate is 1:1:1 was obtained first by mixing $Na_2MoO_4.2H_2O$ (20 mL) and K_2HPO_4 (20 mL) dropwise with constant stirring at room temperature. A clear colourless solution having a pH of 11 was obtained. To this mixture 20 mL of $TiCl_4$ was added dropwise from a burette under the same condition.

A very light white yellowish precipitate was formed and the pH goes quickly below zero. Orthophosphoric acid (10 mL) was added finally to ensure complete precipitation [27]. The solution was heated for 1/2 h at about 40°C with continuous stirring. The precipitate so obtained was kept for 12 h , washed with distilled water and centrifuged, dried at 40°C for two and half days. In this procedure actual yield of 11.66 g was obtained. The sample was ground and sieved. The grain size which passes through 170 mesh , 8.9 g was taken and soaked in 200 mL of 0.1 M HCl for 24 h to convert it to H^+ form. The sample was filtered out and washed until it becomes free from Cl^- ions and dried again at 40°C for 16 h.

3.2.2. Lead Vanado Phosphate (LVP)

50 mL of 1 M aqueous solution (50 mmol) of sodium dihydrogen phosphate ($NaH_2PO_4.2H_2O$) and lead nitrate $Pb(NO_3)_2$ were prepared.

500 mL of 0.1 M (50 mmol) NH_4VO_3 (in which 1.05 g remains undissolved after it was shaken for 24 h) were prepared in distilled water. Lead vanadophosphate where the mole ratio of vanadate : phosphate : Pb(II) is theoretically 1:1:1 was obtained first by adding a

clear colourless solution of 1 M $NaH_2PO_4.2H_2O$ (50 mL) dropwise to a beaker containing 500 mL of NH_4VO_3 solution with constant stirring at room temperature. A red yellow solution having a pH of 6 was formed. This mixture was added from a burette dropwise to a beaker containing 50 mL 1 M $Pb(NO_3)_2$ with constant stirring at room temperature. A yellow precipitate was obtained at a pH of 1.7. The solution was heated for 1/2 h at 40°C with constant stirring. The precipitate so obtained was kept for 2 days, washed, filtered and dried at 40°C for two days. Actual yield of 16.25 g was obtained. The filtrate was also reserved for further use. The sample was ground and sieved. A grain size which passes through 170 mesh, 10.9 g was soaked in 200 mL of 0.1 M HCl for 24 h to convert it to H^+ form.The sample was filtered out and washed until it becomes free from Cl^- ions and dried again at 40°C for 16 h.

3.2.3. Lead selenophosphate (LSP)

Aqueous solution of sodium selenite (20 mmol) (Na_2SeO_3), sodium dihdrogen phosphate (20 mmol) ($NaH_2PO_4.2H_2O$), and lead nitrate (40 mmol) ($Pb(NO_3)_2$), 1 M concentration of each was prepared.

Lead selenophosphate where the mole ratio of selenite: phosphate: Pb(II) is 1:1:2 was obtained first by mixing Na_2SeO_3 (20 mL) and $Na\,H_2\,PO_4.2H_2O$ (20 mL) dropwise with constant stirring at room temperature. A clear colourless solution having a pH of 7.4 was obtained. This mixture was added from a burette to a beaker containing 40 mL $Pb(NO_3)_2$ with constant stirring at room temperature. A very large amount of white precipitate which exactly looks like milk cheese was obtained at a pH of 1.1. The solution was heated for 1/2 h at 40°C with constant stirring. The precipitate so obtained was kept for a short period of time, washed with distilled water and centrifuged, and dried at 40°C for two days. Actual yield of 13.09 g was obtained. The sample was ground and sieved. A grain size which passes through 170 mesh,10.08 g was taken and soaked in 200 mL of 0.1 HCl for 24 h to

convert it to H^+ form. The sample was filtered out and washed until it becomes free from Cl^- ions and dried again at 40°C for 16 h.

3.2.4. Composition Analysis

Lead content of the samples was determined by AAS while the titanium and phosphorus contents were determined by spectrophotometry. Molybdnium and vanadium were analyzed qualitatively using AAS.

A. Determination of lead

1.4×10^{-3} g of LVP and 4.6×10^{-3} g LSP were taken separately and dissolved in 5 mL HNO_3 and then subjected to AAS under the following conditions. Air - C_2H_2 flame, wavelength 217 nm, slit width 1 nm, hallow cathode lamp, current 5 A and integration time 4 s. Calibration curve was made using three standard solutions of lead nitrate in acidic medium (HNO_3) having 50, 100 and 200 ppm of lead.

B. Determination of phosphorus and titanium

1 g of lithium metaborate, 0.5 g lithium tetraborate and 0.2 g of sample were fused together in platinum crucible at 950°C. Fused melt was cooled and dissolved in water and then diluted to 500 mL using distilled water. 5 mL of the stock solution was taken for phosphorous determination as P_2O_5 by measuring absorbance at 830 nm, with slit width 4 cm using phosphomolybdic method [58]. Similarly for titanium as TiO_2 the absorbance was measured at 380 nm, slit width 3 cm using 4,4,diantipyryl methane as a reagent [58].

3.3. Hydrogen Ion Exchange Capacity

Hydrogen ion liberation capacities of the three exchangers were determined by batch operation as follows [59].

A 50 mL volume of 0.01, 0.1, 0.2, 0.5, 1, 2, 3 and 4 M sodium chloride solutions were shaken with 0.1 g of each exchanger (TMP, LVP, LSP) using Gerhardt flask shaker

continuously for 12 h at speed of 120 cycles / min. After equilibration 10 mL portions of aliquot were taken and titrated with standard solution of 0.01 M NaOH for LVP and TMP, with 0.001 M NaOH for LSP using phenolphthalein as indicator in each case.

The effect of the concentration of neutral salt solution on the exchange capacity is shown in Figs. 1, 2 and 3. The results obtained from titration of the protons liberated by different concentration of salt with standard sodium hydroxide solution are reported in Table 1.

3.4. pH Titration Curves

pH titration measurement was done in a series of experiments as follows.

0.1 g of each exchanger (LVP, TMP and LSP) in H^+ form was firstly shaken with 50 mL of distilled water for 2 h , after which pH of the three samples were recorded using pH meter. Lateron at each interval of adding 1 mL of 0.1 M KOH, the solution was stirred for 2 h . After equilibrium has been attained the corresponding pH was recorded. pH titration curves as a function of titrant for each exchanger are given in Fig. 4, 5, and 6.

3.5. Moisture Content Determination

0.5 g of each of LVP, TMP and LSP was taken in a crucible. The samples were heated to a temperature of 105°C for 1.5 h. This was repeatedly performed until the change in weight (Δw) becomes constant. For each sample seven trails were made.

3.6. Supported Catalyst Preparation

3.6.1. Identification of a transition metal ion to be loaded

A preliminary test was conducted with two transition metal cations i.e. Cu^{+2} from $Cu(NO_3)_2$ and Fe^{+3} from $FeCl_3$ so as to identify the metal to be loaded.

0.1 g of each exchanger selected for catalytic study (LVP and TMP) where mixed

with 20 mL of 10^{-3} M $FeCl_3$ (prepared by diluting 10^{-2} M $FeCl_3$ which was prepared by dissolving 0.1622 g/100mL) and 10^{-3} M $Cu(NO_3)_2$ (prepared by diluting 10^{-2} M $Cu(NO3)_2$ which was prepared by dissolving 0.188 g/100mL). The four samples were shaken using gallenkamp flask shaker for 20 minutes intermittently at an interval of 15 minutes for a total of 2 h. The supernatant of each sample was subjected to atomic absorption spectrometer to determine the concentration of iron and copper. The results are given in Table 2.

3.6.1.1. Experimental condition of atomic absorption spectrometer

For both iron and copper determination air-C_2H_2 flame system and hallow cathode lamps were used, under the following specific condition for each.

Iron: Wavelength 248.3 nm, slit width 0.2 nm, integration time 4 s, current 5 A. Calibration curve was made using three standard solution of ferric chloride in acidic medium (0.1 M HCl) having 27.92, 55.85 and 111.7 ppm of iron.

Copper: Wave length 324.8 nm, slit width 0.5 nm, integration time 4 s, current 5 A. Calibration curve was made using three standard solution of copper nitrate in acidic medium (0.01 M HNO_3) having 31.77, 63.54 and 127.08 ppm of copper.

3.6.2. Preparation of Fe^{+3}/LVP and Fe^{+3}/TMP

2.5 g of each exchanger (LVP and TMP) was mixed with 250 mL of 0.033 M $FeCl_3$ in two erlenmeyer flasks. The mixtures of the two samples were shaken for 20 minutes for a total of 2 h , then kept to equilibrate for 48 h. The precipitate was centrifuged, washed with double distilled water until a negative test for chloride was observed.

The precipitate was dried in a temperature controlled oven at 75°C for 4 h and cooled in a desiccator, finally ground until all the particles could pass via 170 mesh size. A 25 times diluted solution of the catalyst precursor (0.033 M $FeCl_3$) and the supernatant of each sample were subjected to atomic absorption spectrometer for determining the amount of

iron loaded on each support (LVP and TMP). The results are given in Table 3.

3.7. Catalytic Study of Fe^{+3} Supported on to LVP and TMP

3.7.1. Refluxing cyclohexanol with Fe^{+3}/LVP and Fe^{+3}/TMP

0.2 g of Fe^{+3}/LVP and Fe^{+3}/TMP was taken in different 250 mL twonecked round bottom flask. To each 2 mL of distilled cyclohexanol was added. After putting on the magnetic stirrer, the flask was closed with stopper and the mixture was stirred for 1 h. The flask was then fitted to a condenser and thermometer and then the mixture was refluxed on heating mantle at a temperature range of 120°C - 168°C for 4 h. The supernatant was isolated from the black residue by centrifuge. Cyclohexanol was also refluxed without adding a catalyst to see the effect of heating under the same condition.

All samples refluxed with Fe^{+3}/TMP were subjected to GC analysis under the following conditions :

Column: capillary DB-5 non-polar stationary phase (30 m x 0.25 mm: i.d. x 1.5 m film thick). Temperature: Oven 40 - 220°C, injector 200°C, FID 250°C, program rate - 8°C/min. Flow rate: H_2-30 mL/min, air-300 mL/min. and carrier gas N_2-1.5 mL/min. Sample size : 0.02 μL.

For a sample refluxed with Fe^{+3}/LVP, prepacked 15% FFAP column was used instead of capillary column without changing the remaining parameters above. The results of GC analysis are given in Table 4.

3.7.2. Refluxing cyclohexene with Fe^{+3}/LVP and Fe^{+3}/TMP

0.2 g of Fe^{+3}/LVP and Fe^{+3}/TMP was taken separetly in 250 mL twonecked round bottom flask. To each 2 mL of distilled cyclohexene and n-hexene as a solvent were added.

After putting on the magnetic stirrer, the flask was closed with stopper and the mixture was stirred for 1 h. The flask was then fitted to a condenser and thermometer and then the mixture was refluxed on heating mantle at a temperature of 66-69°C for 4 h. The yellow mixture was changed into green . The mixture was separated by centrifugation. To compare the effect of the catalyst, a mixture of distilled cyclohexene and n-hexene was also refluxed as a control without the addition of the catalyst under the same condition. The supernatant liquid isolated as well as the control sample were all subjected to a gas chromatographic analysis under the same conditions as in 3.7.1. The results of the relative retention times and percentages of the starting material and the refluxed samples are given in Table 5.

4. RESULT AND DISCUSSION

4.1. IR Spectra and Composition

Different studies [59,60] indicated that the properties of inorganic ion exchangers are dependent on the method of preparation. Method of preparation has a considerable effect on the degree of hydration and composition of the sample, which in turn are responsible for the shape, size of cavities inside the exchanger and chemical stability. Because of this in the processes of synthesis, we prepared a number of samples (not less than 10) for each exchanger under different reaction conditions by varying parameters such as temperature, time, sequence of mixing the reactant, to identify the optimum procedure that gives a good yield.

4.1.1. Titanium molybdophosphate (TMP)

Titanium and phosphorous content of this exchanger was quantitatively determined using UV-visible spectrophotometer. The results indicate 12.65% titanium and 5.95% phosphorous. Molybdate presence was also confirmed qualitatively. It's moisture content was found to be 18%.

The infrared spectrum of TMP in H^+ form exhibits four major absorption bands in the regions 3500-3000, 1647, 1017 and 629 - 743 cm^{-1}. The strong broad peak at 3500 - 3000 cm^{-1} is characteristic of interstitial (free) water molecule and hydroxyl group.Sharp and strong peak at around 1647 cm^{-1} is due to bending mode of interstitial water molecule [61]. Very strong peak at 1017 cm^{-1} is due to the phosphate group particularly P - O stretching. A peak from 600 - 500 cm^{-1} is O - P - O bending mode [61]. In the region below 700 cm^{-1} Ti - O stretching frequencies are also expected [62]. Therefore a broad peak in the region 760 - 600 cm^{-1} may probably be an overlap from O - P - O bending and Ti - O stretching frequencies. Mo-O stretching is also expected at further lower frequency.

4.1.2. Lead vanadophosphate (LVP)

From stoichiometric point of view a mole ratio of 1:1:1 is expected in the synthesis of LVP. However, this could not be exactly achieved in the main synthesis due to low solubility of ammonium metavanadate. Both $NaH_2PO_4.2H_2O$ and NH_4VO_3 separately reacts with $Pb(NO_3)_2$ to give $Pb(H_2PO_4)_2$ (white ppt) and $Pb(VO_3)_2$ (yellow ppt). On treating this two products with 2 M HNO_3 the former remains undissolved while the latter completely dissolves. To verify the non-existence of $Pb(H_2PO_4)_2$ in the final product, a small portion of the final product (LVP) was treated with 2 M HNO_3 and it was found to dissolve completely, this indicate the absence of $Pb(H_2PO_4)_2$ as a contaminant.

Elemental analysis by AAS and UV-visible spectrophotometry indicates that LVP contains 57.58% lead, 6.15% phosphorous and presence of vanadate was also assured qualitatively. The moisture content of LVP was found to be less than 1/4 of TMP that is only 4%.

Infrared spectrum of LVP in H^+ form revealed ,broad peak in the region 3500 - 3400 cm^{-1} maybe due to the presence of free water molecules and hydroxyl groups. The peak in the region 1648 - 1629 cm^{-1} may also be attributed to bending mode of free water molecule (O-H bending). The two peaks at 1384 and 1348 cm^{-1} have similarity to the ir spectrum of one of the starting compound NH_4VO_3 thus it can be ascribed to vanadate group. Very strong peak at 1005 cm^{-1} is attributed to P-O stretching of phosphate group. A peak between 541 -670 cm^{-1} may be ascribed to O - P -O bending frequencies and a metal oxygen streching could also be associated to this frequency.

4.1.3. Lead selenophosphate (LSP)

Elemental analysis indicates 65.5% lead and 2.39% phosphorus and moisture content is found to be 0.08% which is very small compared to the other exchangers.

Infrared spectrum of LSP showed major peaks in the region 1384, 977 - 1030 and 831 - 461 cm^{-1}.

In general it shows many strong and sharp peaks in the frequency region below 1500cm^{-1}. A peak at 1384 cm^{-1} may be ascribed to selenite group since IR spectrum of Na_2SeO_3 (one of the starting material) showed a strong peak at about 1314 cm^{-1}.The shift may be due to interaction with the phosphate group and the metal . Strong peak at 977 - 1030 cm^{-1} is due to the phosphate group P - O stretching [61]. Strong and sharp peaks in the region 831- 461cm^{-1} may be due to selenite frequencies (800 -650 cm^{-1}) [25] and phosphate group (O - P - O bending are also in the region 700 - 460 cm^{-1}) [25]. Hence we are unable to assign the specific peaks in the region.

In general the IR spectrum of these three exchangers indicates strong peak in the frequency region 980 -1140 cm^{-1} characteristic to the presence of ionic phosphate group which is the major ingradient in the synthesis of each case.

Characteristic peaks to the presence of lattice water i.e., a peak in the frequency region 3500 - 3200 cm^{-1} and at 1630 - 1600 cm^{-1} [61] are clearly seen in TMP and LVP of course with a greater intensity for the former than the latter. But these peaks are very weak in the case of LSP and even it could not be distinguished.

4.2. Ion-Exchange Property

The term ion-exchange is generally understood to mean the exchange of ion of like sign between a solution and a solid highly insoluble in contact with it [63]. An ion-exchanger is a porous, insoluble polymer containing immobile, electrically charged groups

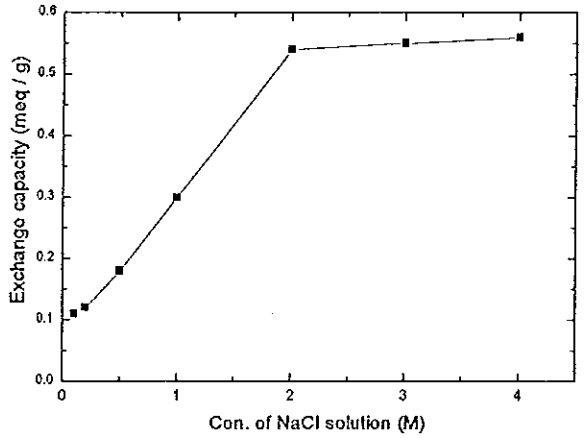


Fig. 1. Ion-exchange capacity of LVP as a function of the concentration of Na^+.

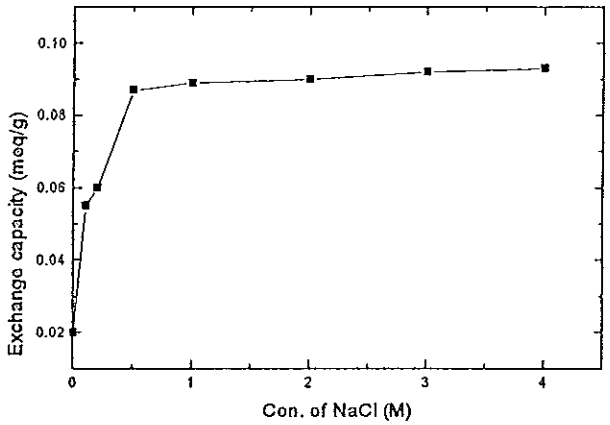


Fig. 2. Ion- exchange capacity of TMP as a function of the concentration of Na^+.

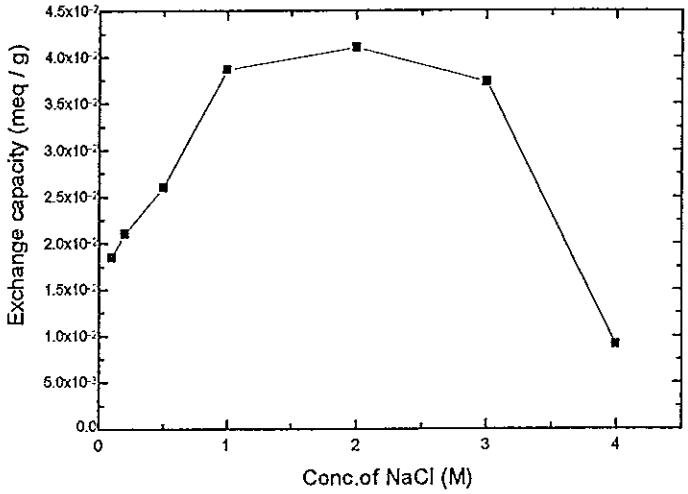


Fig. 3. Ion- exchange capacity of LSP as a function of the concentration of Na^+.

4.2.2. pH titration curves

pH titration curves give information about the nature (acidity or basicity) of the exchangeable groups present in the polymeric structure [59]. The curves obtained by plotting the volume of titrant as a function of pH are given in Fig. 4, 5, and 6.

LVP shows two inflection points at pH of 4.5 and 9.2 indicating the presence of two exchange sites of different acidity. Thus LVP is a diabasic cation exchanger. Moreover the pH value at which the 1st inflection occurs (4.5) reveals that LVP is a rather strongly acidic cation exchanger.

LSP is a monobasic weakly acidic cation exchanger since it has one inflection at pH 6.9. Similarly niobium selenite and zirconium vanadophosphate were reported by other workers [23,69] to be monofunctional cation exchangers from their respective pH titration curves. The breaks in the titration curve of TMP is not clearly seen relative to that of LVP and LSP. From the existing curve one may not say, it is a monobasic cation exchanger

because it may probably show some more inflection points if a small volume of titrant is added. Thus it is more likely to say TMP is a polybasic and a moderately acidic cation exchanger than monobasic. This is not unusual as similar conclusion was drawn for stannic selenolphosphate by other workers [24].

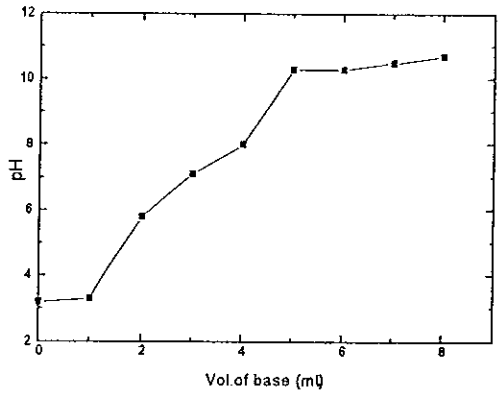


Fig. 4. pH titration curve for LVP.

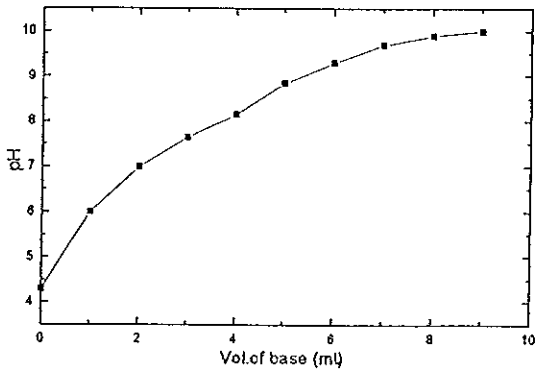


Fig. 5. pH titration curve for TMP.

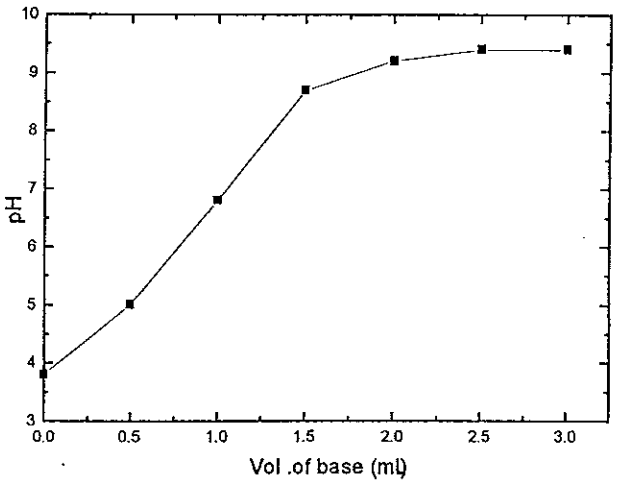


Fig. 6. pH titration curve for LSP.

4.3. Supported Catalyst Preparation

Based on characterization results such as exchange capacity and moisture content LVP and TMP have been selected for catalytic study. A result from preliminary test (Table 2) indicates that a supernatant of LVP shaken with Cu^{+2} aqueous solution reads 62.4 ppm, which is almost the same to the concentration of the original aqueous solution of Cu^{+2} (63.4 ppm). Thus, Cu^{+2} remains in the aqueous phase rather than to be exchanged on the polymer (LVP), whereas one third of Cu^{+2} has been exchanged with TMP.

LVP is found to have high selectivity for Fe^{+3}. Since the supernatant of LVP shaken with Fe^{+3} solution reads only 0.7 ppm out of the original aqueous solution which was 56.5 ppm. TMP has also a good selectivity for Fe^{+3} (since supernatant of TMP shaken with Fe^{+3} reads 23.5 ppm out of 56.5 ppm in the stock solution) than Cu^{+2} (in which the supernatant of TMP shaken with Cu^{+2} reads 45.5 ppm out of 63.4 ppm in the stock solution). Generally since both exchanger have a good selectivity for Fe^{+3} but a bad for Cu^{+2} cation, Fe^{+3} is selected to be loaded on to the support in all subsequent catalytic studies of our work. The preparation procedure for the two supported catalysts (Fe^{+3}/ LVP and Fe^{+3}/ TMP) was adopted from the preliminary test except equilibration for 48 h which is equivalent to impregnation technique. Result from atomic absorption analysis in Table 3, indicates that 21.7% and 0.92% Fe^{+3} has been loaded on LVP and TMP, respectively.

Table 2. AAS determination of Fe and Cu incorporated on the polymer.

Sample	Concentration (PPM)
Cu^{+2} aqueous original solution	63.4
Supernatant of (Cu^{+2},LVP)	62.4
Supernatant of (Cu^{+2}, TMP)	45.4
Fe^{+3} aqueous original solution	56.5
Supernatant of (Fe^{+3}, LVP)	0.7
Supernatant of (Fe^{+3},TMP)	23.5

Table 3. AAS dtermination of Fe incorporated on LVP and TMP.

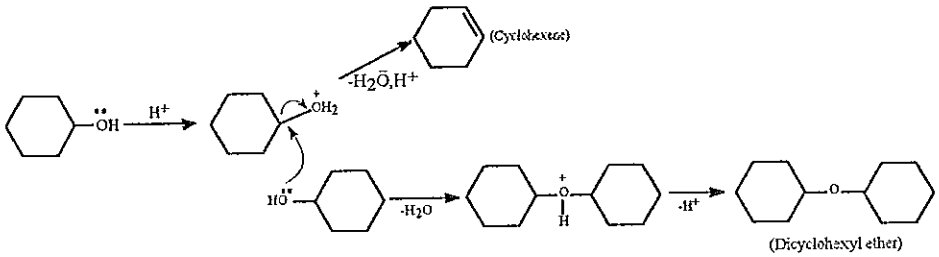
Sample	Concentration (ppm)
Original Fe^{+3} aqueous solution	76.0
Filtrate of Fe^{+3} / LVP	59.5
Filtrate of Fe^{+3} / TMP	75.3

4.4. Catalytic study of Fe^{+3} supported onto LVP and TMP

Addition of water to alkenes and elimination of water from alcohols are some of the reactions attempted in this study. Mostly these reactions were carried out under reflux conditions at different temperature using transition metal cations exchanged inorganic support materials (clay, silica, alumina, etc.) as a catalyst [61].

4.4.1. GC analysis of cyclohexanol refluxed with Fe^{+3} / TMP and Fe^{+3} / LVP

From catalytic reaction mechanism of cation-exchange clay catalysis of alcohols, the major expected products are alkenes and ethers [49], thus the expected products of refluxing cyclohexanol are cyclohexene and dicyclohexyl ether. The mechanism leading to these products is given by the following reaction scheme.



Scheme 1

As it is shown in the Table, the catalytic action of Fe^{+3} / TMP and Fe^{+3} / LVP is observed in the decrease in the percentage of the starting material and the appearance of a new peak which was originally absent in the pure cyclohexanol chromatogram.

Table 4.Relative retention times (RT in minutes) and percentage (%) of major peaks in the starting cyclohexanol and after refluxed with Fe^{+3} / TMP and Fe^{+3}/LVP

Fe^{+3}/TMP *				Fe^{+3}/LVP **			
Pure cyclohexanol		cyclohexanol refluxed with Fe^{+3}/TMP		pure cyclohexanol		cyclohexanol refluxed with Fe^{+3}/LVP	
RT	%	RT	%	RT	%	RT	%
9.22	96.32	9.24	13.33	13.67	96.6	13.73	36.83
-	-	5.11	81.22	-	-	1.19	38.01

* using capillary DB-5 column

** using prepacked 15% FFAP column

Cyclohexanol refluxed with Fe^{+3} / TMP shows two major peaks at retention time of 9.24 and 5.11 minutes. The first peak (at 9.24 minutes) has a retention time almost identical with pure cyclohexanol having RT of 9.22 minutes with percentage purity of 96.32% . The only difference is that there is a significant decrease in the percentage composition of the starting material after it is refluxed with Fe^{+3}/TMP. Correspondingly a new peak appears at retention time of 5.11 minutes with a percentage composition of 81.22% as a second major peak, which is not in the chromatogram of the unrefluxed cyclohexanol. This clearly indicates that a radical change has occurred to the starting material.

Similarly the GC analysis of cyclohexanol refluxed with Fe^{+3} / LVP indicates two major peaks at retention time of 13.73 and 1.19 minutes with percentage composition of 36.83 and 38.01, respectively. The first peak has almost the same retention time with the major peak (at 13.67 minutes) observed on the original chromatogram of unrefluxed pure cyclohexanol. The only difference is that the percentage composition of major peak (at 13.67 minutes) which was initially 96.6% is decreased into 36.83% after refluxing. Besides a new peak at retention time of 1.19 minute with percentage composition of 38.01% which

Fe^{+3} / TMP is found to be very much effective in dehydrating cyclohexanol (81% conversion) than that of Fe^{+3} / LVP which has 38% conversion.

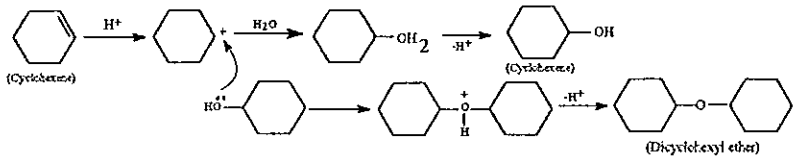
The result we have obtained using Fe^{+3} / TMP is very much comparable to the result of other workers [49] in which they reported that dehydration of cyclohexanol using Al^{+3}-exchanged montmorillonite at a temperature of 200°C (which is even greater than that we used) for the same reaction time (4 h) to yield exclusively 88% cyclohexene. Moreover Fe^{+3} /TMP has an activity of three fold greater in the efficiency of dehydrating cyclohexanol as compared to the result obtained using Fe^{+3}-exchanged local clay (25.04%) [70] a work done two years ago in the same department, almost under the same reaction conditions.

Fe^{+3} / TMP and Fe^{+3} /LVP have different efficiency in their catalytic activity. Generally to account activity differences among such solid catalysts one has to consider structural aspects, the nature of active sites and how they are involved in surface catalysis [26]. It is also necessary to characterize in terms of composition, dehydration behaviour, porosity, structural modifications induced by chemical treatment and the possible structure types taken up by the transition metal ions [2,26].

All of these points one way or the other, are related to the surface phenomena which is poorly understood [2] in comparison to homogeneous catalysis. Thus structural aspects are not considered in our empirical studies because of many limiting factors.

4.4.2. GC analysis of cyclohexene refluxed with Fe^{+3} / TMP and Fe^{+3} / LVP

From the point of view of the expected reaction products of refluxing alkenes with cation exchange clays [50] the mechanism of refluxing cyclohexene could be schemed as follows:



Scheme 2

In the mechanism cyclohexene is first protonated and the electrophilic carbocation formed will react with interlameller water to produce cyclohexanol. In the presence of excess cyclohexene, the produced cyclohexanol may react with the protonated cyclohexene and produce cyclohexyl ether.

Table 5.Relative retention times (RT in minutes) and percentage (%) of major peaks in the starting cyclohexene, n-hexene mixture and after refluxed with Fe^{+3} / LVP and Fe^{+3} / TMP

Cyclohexene, n-hexene mixture (So)		So with Fe^{+3}/LVP		So with Fe^{+3} / TMP		So refluxed with out a catalyst	
RT	%	RT	%	RT	%	RT	%
5.18	56.48	5.10	68.29	5.06	64.92	5.12	69.56
3.89	42.98	3.77	31.35	3.72	34.73	3.80	30.1

When we compare the chromatogram of cyclohexene and n-hexene mixture abbreviated as (So) with that of So refluxed with the two catalyst as well as without a catalyst as a control, we hardly find any difference among these chromatograms. All have two major peaks at retention time around 5.1 minute and 3.8 minutes (Table 5)

corresponding to cyclohexene and n-hexene respectively. There is no appearance of new peaks in the refluxed samples. This indicates that Fe^{+3}/ LVP and Fe^{+3}/ TMP catalysts are not active in hydrating cyclohexene as they are in dehydration of cyclohexanol.

As to why these catalysts are unable to hydrate cyclohexene, many factors may be involved as it is mentioned above in relation to the activity difference between the two catalysts. However, from the point of mechanisms cited above one can see that protonation is the first step in both hydration and dehydration reactions. The support materials used are acidic cation exchangers. Thus there catalysts have exchangeable surface proton that could protonate the electron rich site and of course we have seen the efficiency of these catalyst in doing so in the case of dehydration reaction. Therefore probably what matters is the availability of water molecule that could attack the electrophilic carbocation, formed in the first step.

LVP and TMP may have low moisture content relative to other inorganic support materials like clay. Even the available amount might have been removed from the drying conditions and storing in a desiccator over calcium chloride. Besides it is evidentially indicated by other workers that the water molecules are all bound to the transition-metal ions [26]. Thus in light of this the triply charged ferric cation introduced on to LVP and TMP, will act as a Lewis acid and will strongly be coordinated to the lone pair of the water molecules. Therefore, the scarcity of the water molecule and the affinity of the Fe^{+3} for water molecules may be some of the responsible factors for facilitating dehydration of cyclohexanol to cyclohexene and inability of Fe^{+3} / LVP and Fe^{+3} / TMP to hydrate cyclohexene to cyclohexanol.

5. CONCLUSION

IR spectrum, composition analysis and other analytical data are consistent with the proposed synthetic inorganic polymers. In general LVP, TMP and LSP are found to be acidic cation exchangers showing diabasic, monobasic, and polybasic titration curves and LVP is found to have highest exchange capacity (0.55 meq/g) for Na^{+} ion relative to TMP (0.09 meq/g).

By loading ferric cation onto TMP and LVP, efficient conversion (81 and 38% respectively) of cyclohexanol into cyclohexene has been achieved. However, the reverse process has not occurred under this particular reaction condition. This probably can be attributed to the scarcity of the water molecule in the support material (TMP and LVP) and the affinity of the Fe^{+3} for the water molecules.

Therefore Fe^{+3}/TMP and Fe^{+3}/LVP acts as dehydrating catalysts by converting cyclohexanol predominantly into cyclohexene.

This result demonstrates the promising feature of synthetic inorganic polymers as a support in catalysis.

REFERENCES

1. Tamaru K., *Dynamic Heterogeneous Catalysis*, Accadamic press, London, 1978, p. 2.
2. Bruce C. G., *Catalytic Chemistry*, John wiley, New York, 1992.
3. Golodets G. I., *Heterogeneous Catalytic Reactions Involving Molecular Oxygen*, Elsevier, Amsterdam, 1983, p. 6.
4. Subhash-Satish, *Catalysis and Adsorption*, Pragati prakashan, Meerut, 1973, p. 3.
5. Warren T. F. , Rama Chandran and Hayrettin Turk, *Pure Appl. Chem.* **60** (1988) 395.
6. Hartley F. R. and Verzey P. N., *Advances in Organometallic Chemistry*, Acadamic Press, New York, 1977, p. 190.
7. Allum K. G., Hanock R. D., Howell I. V, Pitkethly R. C and Robinson P. J, *Journal of Organomet. Chem.* **87** (1975) 189.
8. George W.P. and Rechard E. P. , *J. Chem. Edu.* **63** (1986) 188.
9. David C. B and Stanley H. L. , *Chem. Rev.* **81** (2) (1981) 110.
10. Grubbs R. H., Gibbons C. Koll L.C Bonds W.D Brubaker C.H, *J. Am. Chem. Soc.* **95** (1973) 2373
11. Ralph W. M., *Wat. Res* .**25** (10) (1991) 1169 .
12. Takeshig E., Kojii Y., Takamilei and Issel Fujiyoshi, *Can. J. Chem. Eng.* **64** (1986) 1008.
13. Anderson J. R., *Structure of Metallic Catalysts*, Acadamic Press , London, 1975, p. 28.
14. Stevenson S. A., Dumesia J. A., Baker R. T. K and Elia Ruckens Toin, *Metal-*

32. James A. Schwarz, *Chem. Rev.* **95** (1995) 477.

33. Linares-Solano, Reinoso F. rodriguez and Martinez de Lecea C. Salinas, *Carbon* **20** (1982) 177.

34. Peterson G. R and Scarrah W. P, *JAOCS,* **61** (1984) 1593.

35. Vazquez M. I, Escardino A., Aucejo A. and Corma A; *Can. J. Chem. Eng.* **46** (1986) 272.

36. Cornelis K. Groot, Vincentius H. J de Beer and Roel Prins, *Ind, Eng. Chem. Prod. Res. Dev.* **25** (1986) 522.

37. Narisimha K. B, Maphipal Reddy B. and Rao P. Kanta, *J. Phys. Chem.* **94** (1990) 7336.

38. Yasuaki Okamoto, Kozo Negata, Toshinori Adachi, Toshinobu Imanaka, Kazuhiro Inamura and Toshiyuki Takyu, *J. Phys. Chem.* **95** (1991) 310.

39. Cesar Ovalles, Vladimir Leon, Shella Reyes and Francisco rosa, *J. Catal.* **126** (1991) 368.

40. Goula M. A, Kordulis CH., Lycourghiotis A. and Fierro J. L. G., *J. Catal.* **137** (1992) 285.

41. David C. Bailey and Stanely H. Langer, *Chem. Rev.* **81** (1981) 13146.

42. Hugo Celio and Michael Trenary, *J. Phys. Chem.* **99** (1995) 6024.

43. Foley H. C, Decanio S. J, Tav KD. Chao Kj.Onuferko JH, C. Dywosky and Gates B.C. , *J. Am, Chem. Soc.* **105** (1983) 3047.

44. Iwamoto, yokoo M. Sakai S.K and Kagawa S. *J. Chem. Soc. Faraday Trans. I,* **77** (1881) 1629

45. Jadwiga Skupinska, *Chem. Rev.* **91** (1991) 613.

46. John M. Adams, Ballantine J. A, Graham S. H Laub R. J, Purnell J. H. Reid P. I, Wafa Y. M Shama and John M. Thomas, *J. Catal.* **58** (1979) 238.

47. Adams J. M; Dacies S. T; Graham S. H, Thomas J. M, *J. Catal.* **78** (1982) 197.

48. Muthukumaru S. P and Ravindranthan M. *J. Chem. Soc. Chem. Commun* (1994)1813.

49. Ballantine J. A, Mary Davies, Haward Purnell, Mongko Raycnakorn John M. T. and Kevin J. W., *J. Chem. Soc. Chem. Commun.* (1981) 427.

50. Ballantine J. A, Mary D., Howard P., Mongkon R., John. M. T. and Kevin J. W., *J. Chem. Soc. Chem. Commun.* (1981) 8.

51. Bounwens S. M A. M, van der Kraen A. M, J De beer V. H. and Prins R. *J. Catal.* **128** (1991) 559.

52. Rudy Baum, *Science*, Oct 12, (1987) C and EN 17

53. Alan B. Mctwen, Wilhelm F. Maier, Ronald H. Fleming and Scott M. Baumann, *Nature*, **329** (1987) 531.

54. Martinengo S. and Zanderighi L., *J. Catal.* **146** (1994) 422.

55. Ganapati D. Y and Pranav H. M., *Ind. Eng. Chem. Res.* (1994) 2198.

56. Capka M. and Heflejs J. *J. Coll. Czech. Chem. Commun.* **39** (1974) 154

57. Michael D. Ward, Thomas V. Harris and Jeffrey Schwartz, *J. Chem. Soc. Chem. Commun.* (1980) 357.

58. Watkins, P. S., *Analyst*, **104** (1979) 1124.

59. De A. K. and Chowdhurry K., *J. Chromatogr.* **101** (1974) 73.

60. Harvel S. S and Nancollas G. H, *J. Inorg. Nucl. Chem.* **32** (1970) 3023.

61. Nakamoto N., *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, (1962) p. 166.

62. Bailar, Emeleus J. L, Nyholm H. J R and Dickenson A. F "*Comprehensive Inorganic Chemistry*" Vol 3 1st ed. Pergamon Press, Oxford, (1975) p 377 .

63. Knupadhyaya, *A text Book of Inorganic Chemistry,* Acadamic Press, New York, 1990 p. 890.

64. Mikes O., *Laboratory Hand Book of Chromatographic and Allied methods,* Ellis Horwood, Chichester, 1979 p. 241.

65. Yasachi I. *J. Inorg. Nucl. Chem.* **26** (1964) 2241.

66. Donaldson J. O. Fuiler M. J price J. M, *J. Inorg. Nucl. Chem.* **30** (1964) 2841.

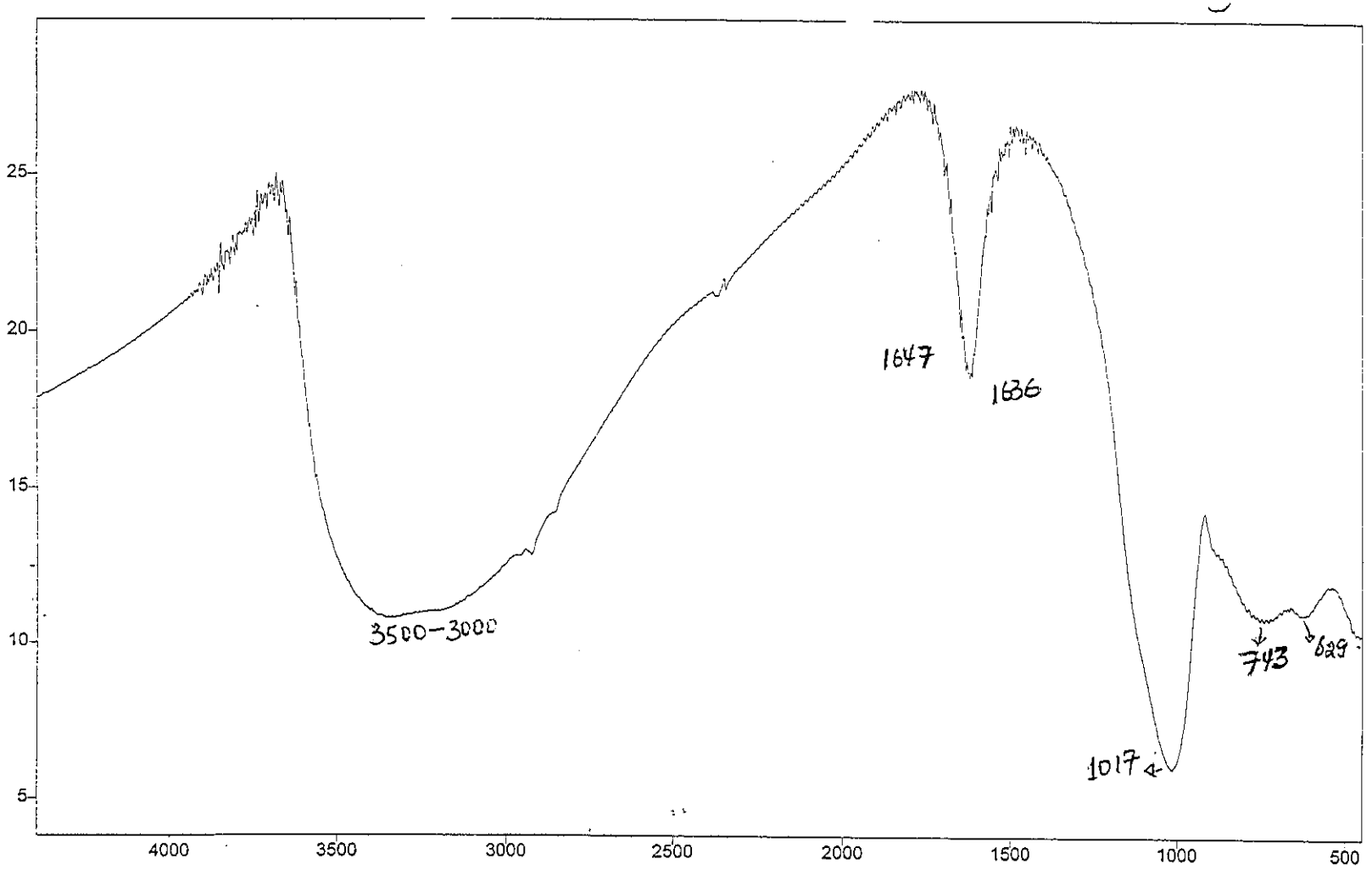
67. Sisay T. *M. Sc. Thesis,* Addis Ababa University (1989).

68. Kinfe K. *M. Sc. Thesis,* Addis Ababa University (1993).

69. Rawat J. P. and Rafat A.K, *Indian J. Chem.* **20A** (1981) 756.

70. Belina T. *M. Sc. Thesis,* Addis Ababa University (1995).

APPENDIX



IR-Spectrum of titanium molybdophosphate (TMP)

Transmittance / Wavenumber (cm-1) ...r of Scans= 10 Apodization=

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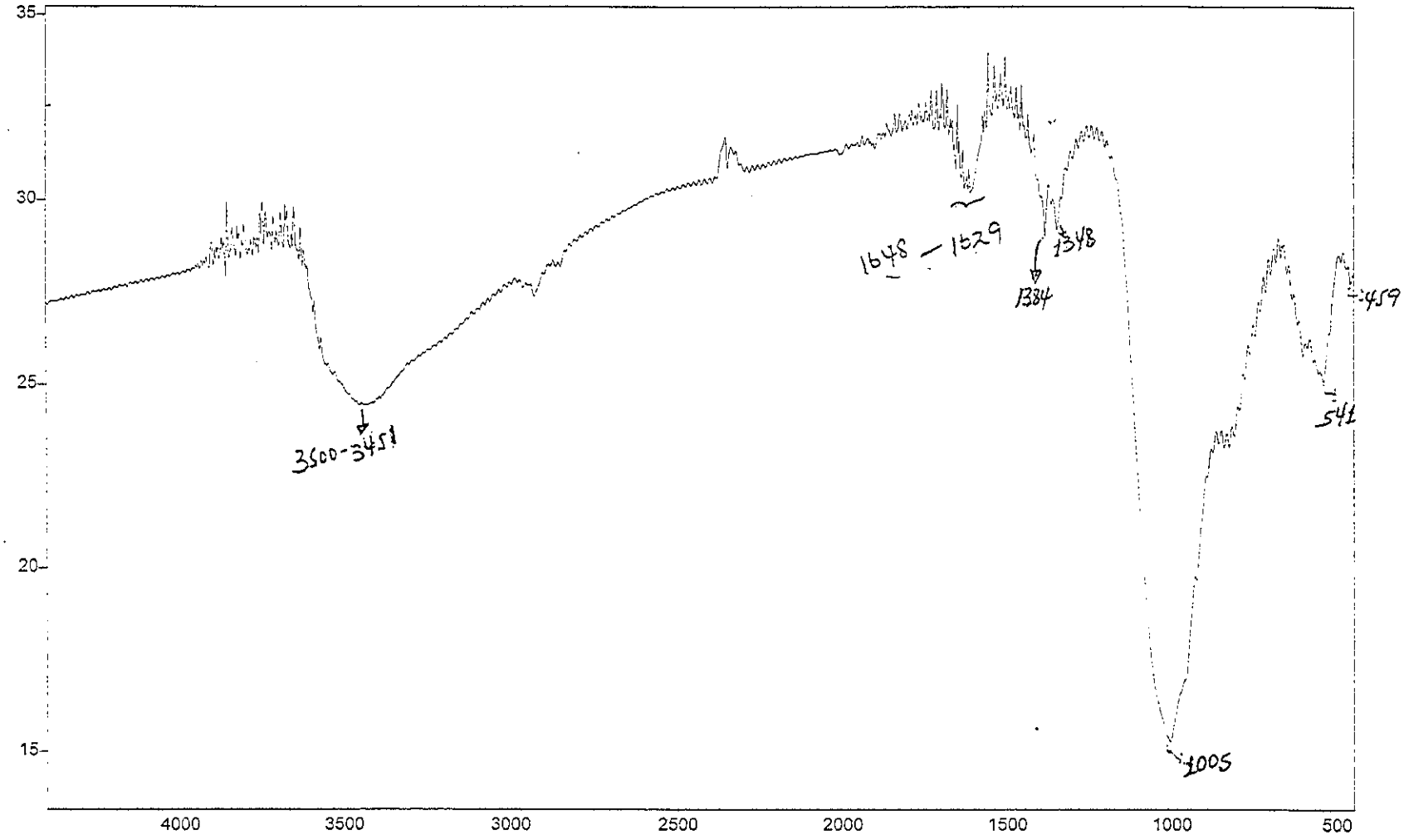
TITANIUM MOLYBDATE PHOSPHATE



IR- Spectrum of lead vanadophosphate (LVP)

Transmittance / Wavenumber (cm-1)

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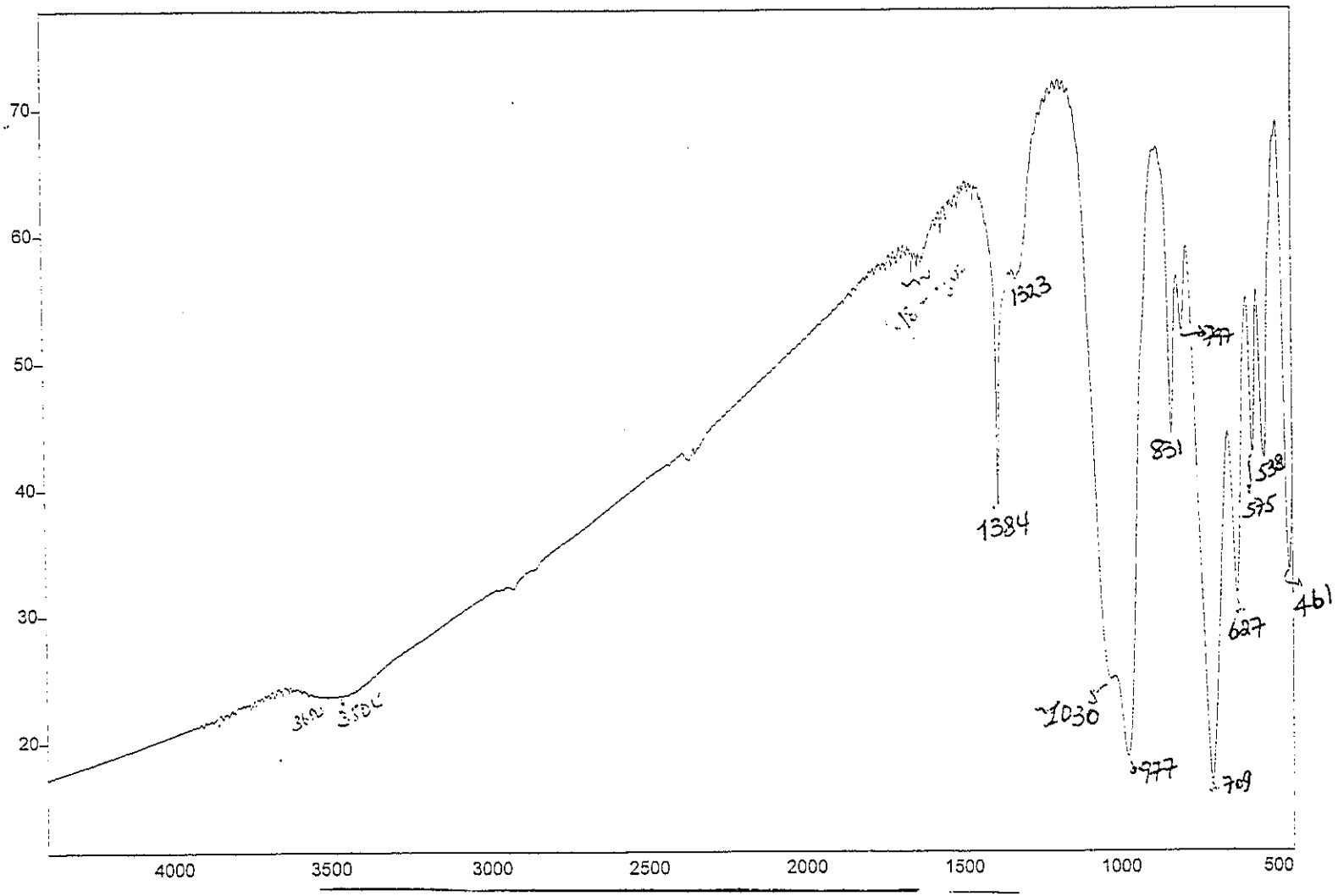
Lead Vanado Phosphate

60



IR-Spectrum of lead selnophosphate (LSP)

Transmittance / Wavenumber (cm-1)

mber of Scans= 10 Apodization=

File # 2 : LSP

1/13/97 9:56 AM Res=4 cm-1

Chromatogram of pure cyclohexanol

Chromatogram of pure cyclohexanol refluxed with Fe^{+3}/ TMP
CHANNEL A INJECT 05/15/97 14:42:32
2.70
3.56
4.01
4.25
4.61
4.80
4.93
5.11
5.25
8.21
9.47
9.56
10.22
12.25
13.68
17.89
128

Chromatogram of pure cyclohexanol refluxed without a catalyst

Chromatogram of pure cyclohexanol using 15% FFAP column

Chromatogram of pure cyclohexanol refluxed with Fe^{+3}/LVP using 15% FFAP column

Chromatogram of pure cyclohexanol.refluxed without a catalyst (15% FFAP)

Peak enhancement on cyclohexanol refluxed with Fe^{+3}/LVP

Chromatogram of S_0 refluxed with Fe^{+3}/LVP

Chromatogram of S_0 refluxed with Fe^{+3}/TMP