STUDY OF TITANIUM MOLYBDOPHOSPHATE (TMP), LEAD VANADOPHOSPHATE (LVP) AND ZIRCONIUM VANADOPHOSPHATE (ZrVP) SUPPORTED CATALYSIS BY SOME TRANSITION METAL IONS IN THE CONVERSION OF CYCLOHEXANOL AND CYCLOHEXENE.

A THESIS
PRESENTED TO
THE SCHOOL OF GRADUATE STUDIES
ADDIS ABABA UNIVERSITY

IN PARTIAL FULFILMENT OF
THE REQUIREMENT FOR THE DEGREE
OF MASTER OF SCIENCE IN CHEMISTRY

BY
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JUNE 1998

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DEDICATION

To my Mother W/o Megenagna Mulaw and my Family

Who never lost Faith

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my research advisor, Dr. Negussie Retta, for his generous advice and encouragement at all stages of this research work. And also my appreciation goes to Dr. M. Shakir, for his advice and for his reading of the proofs in the preparation of the thesis.

I would like to thank the chemistry department of the AAU for providing the necessary materials for this work. I am also greatly indebted to Dr. V. Marx, Dr. B. S. Chandravanishi and Dr. Raju for making numerous helpful suggestions during the course of the project.

This work would have not come to reality without the help and welcoming cooperation of Ato Sisay Gebeyehu, Ato Belachew and Ato Yasin Yimer of the Institute of Geological Survey for running AAS and UV-Visible; Dr. Taddele Worku and Ato Fikremariam of Essential Oil Research Centre for running GC; Dr. Ermias Dagne , Ato Daniel Bisrat, Ato Aman Dekebo and W/t Tsegereda Tafesse for running IR and GC. I am also grateful to Ato Ahmed Mustefa for his helpful behaviour in providing computer service; W/t Woinishet Gebeyehu and W/t Senait Dagne for allowing me to use their lab. facilities.

With this regard I would like to express my deepest gratitude and appreciation to Dr. Wondimagegn Mammo (Head Department of Chemistry) for his positive attitude and opening his office whenever sought. At this moment I would also like to extend my thanks to my colleagues and friends.

Finally I wish to thank the Southern Nations Nationalities People (SNNP) Educational Bureau for granting me the sponsorship to join the school of graduate studies in AAU.

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ABSTRACT

TMP, LVP and ZrVP as an inorganic material support for transition metal catalysts are used in this project. The basic parameters such as: elemental analysis, IR spectrum, hydrogen ion exchange capacity, pH titration and moisture contents for each exchanger have been studied.

Catalytic applications of ZrVP, LVP and TMP as a support by loading Cr^{3+} on each , and Cu^{2+} and Fe^{3+} on ZrVP, have been studied in dehydration of cyclohexanol and in the hydration of cyclohexene. From the GC analyses the supported catalysts were found to be efficient in dehydrating cyclohexanol but not for the hydration of cyclohexene. The major product identified by retention time coincidence test and peak enhancement technique was cyclohexene. In this work the most efficient being ZrVP and the percentage composition of the product obtained are 48% for ZrVP/Fe^{3+}, 35% for ZrVP/Cr^{3+} and 29% for ZrVP/Cu^{2+}.

1. INTRODUCTION

1.1 Catalysts

In an energy conscious world it is perhaps fitting to start any discussion of catalysis by emphasizing that chemists have long been interested in ways of minimizing the energy requirements of chemical reactions and to this end have diligently sought out suitable catalysts [1].

The flame of catalysis was lit in the most literal sense of this word in Jena on July 23, 1823, when J.W. Doebereiner exposed platinum sponge at room temperature to a flow of hydrogen and air. To his astonishment he saw that the metal got so hot that within minutes a flame appeared. He reported his finding first to his boss, the Duke's minster, J.W. Von Goethe, then to the scientific community. J. Berzelius, the unofficial leader of the scientific world of that day, expressed his fascination and invented a new word for the new phenomenon calling it catalysis [1, 2].

"By definition, a catalyst is a substance which changes the kinetics of a chemical process without changing its thermodynamics" [2].

A catalyst usually works by forming chemical bonds to one or more reactants, in homogeneous or heterogeneous phases, and thereby facilitating their conversion. But it does not significantly affect the reaction equilibrium [3].

Catalysis is very essential for many chemical reactions, from enzymatic process in living organisms to industrial production of commodity chemicals. In general term, most desired properties of catalysts are high activity and chemical selectivity, but often those goals must be tempered by practical considerations of cost and ease of use [4].

Catalysts may control chemical reactions either by increasing the reactivity between molecules brought together into play in the reaction or by facilitating the interaction between the reacting molecules by loosening certain linkage or bonds within them [5].

One suggestion regarding the mechanism of catalysis is the symmetry of molecular orbital. The electronic structure of the reagents could be unfavourable because of the incompatible symmetry of the interacting orbital. Forbidding a reaction on symmetry grounds causes a high activation energy. In the presence of a catalyst, a 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 catalyst can eliminate symmetry forbidden routes leading to a lower activation energy [6].

In general catalysts may be best characterized by defining their properties [7, 8]. Catalysts do not contribute energy to a reaction or change the equilibrium point of reversible reactions. They do not initiate reactions, but have an accelerating effect which when combined with selectivity, may result in the ability to direct reactions. And also, catalysts may have the ability of entering into a reaction over and over again by self-regeneration so that the catalyst is unchanged on completion of the reaction, small amounts of the catalyst thus being able to transform large quantities of the reacting substances.

Catalysis in these days has become the keystone of the chemical structure of large sections of industries which together produce billions of dollars worth products annually. Thus, it has become the most effective and economical method of governing chemical processes. Basically, catalysts are categorized according to the phase relationship between the catalysts and the substrates as homogeneous or heterogeneous [4, 8, 9]. Catalysts may have simple chemical structures as base or acid, or intricate structures as a certain metal complexes or may occur in nature as enzymes.

Heterogeneous catalysis, that are also called first generation catalysts, are operated at an interface between two phases. Since they are mostly solids, they promotes the reactions by adsorbing the substrates on their pores. Thus, the rate of a reaction is directly proportional to the exposed surface area of the catalyst. On the contrary, homogeneous systems are operated in a single phase. Since, the catalysts are mostly in the solution form, the rate of the reaction may be proportional to the amount of the catalyst. They are termed as second generation of catalysis.

Although, the above two types of catalysts enhance the reaction by minimizing the activation energy through creating a new pathway, they may have significant differences due to the different environment they encounter. Thus, it is worth looking for their advantages and disadvantages [10,11].

1. Separation of the catalyst

The major problem of homogeneous catalysts is the separation of the catalyst at the end of the reaction from the reaction mixture. With heterogeneous catalysts this can be achieved easily by coarse filtration, whereas with homogeneous systems a very efficient distillation or ion-exchange process is usually required.

2. Efficiency

In heterogeneous catalysis, the reaction must take place on the surface of the catalyst and only the catalyst which is present at the surface will involve in the reaction; while in the homogeneous system the catalyst is available as the 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 systems have the advantages of being totally reproducible due to their definite stoichiometry and structure. But the structure of the surface of heterogeneous catalysts is mainly dependent on both its method and its history subsequent to preparation.

4. Specificity

Homogeneous catalysts have only one type of active site and, therefore, will often be more specific than heterogeneous catalysts where several types of different surface defects are present.

5. Controllability

It is closely related to specificity. Since a homogeneous catalyst has a definite structure, it can be much more easily modified in order to control a reaction.

6. Thermal Stability

Thermal stability of most heterogeneous catalysts are often much higher than that of homogeneous catalysts. Since the rate of most reactions increase with temperature, a higher operating temperature may be an advantage.

7. Solvent

Homogeneous system is often limited by the solubility characteristics of the catalyst whereas there is no range of solvents for heterogeneous catalysts.

At first sight it might appear that the balance of advantages lie with homogeneous catalysts. But the problem of catalyst separation is so important that, apart from one or two rather notable exceptions, chemical processes based on homogeneous catalysts are very rare. This may be attributed to the fact that the use of homogeneous catalysts on an industrial scale could lead to a number of practical problems including corrosion, deposition on the wall of the reactors and recovery of the catalyst from the reaction products [11, 12].

Recently, considerable research effort has been expanded to develop catalysts that combine as many as possible of the advantages each of the two extreme types. In this regard attaching of the transition metal complexes on the surface of a solid support are promising and will be the subject of the present review. And, therefore, we are in the era of third generation of catalysis [12, 13].

Even though the supported catalysis developed recently, the principle dated back to late 18th century. In 1783 J. Priestley reported that the spirit of wine after passing through the heated stem of a ceramic tobacco pipe was converted to "that kind of air which burns with a lambed white flame" ie., the catalytic dehydration of ethanol to ethylene over a solid acid was discovered [2].

Industrial practice emphasizes the significance of carriers as supports for catalysts in certain types of catalytic processes. The term catalyst carrier as used here in refers to a major catalyst constituent that serves as a base, support, carrier, or binder for the active constituent but which by itself has little, if any, catalytic activity for the reaction in question [5, 14].

In general, some of the advantages of the supported metal catalysis are as follows [12-15].

i. Overcome solubility problems of homogeneous catalysts thereby enhance separation.

ii. The selectivity is much better. This is due to the fact that, in addition to the electronic and steric factors present in the free complex which enhance selectivity, the molecular size and relative polarity which is introduced by the groups in the polymer around the active sites also plays a major role in selectivity.

iii. They prevent, or at least reduce, the ability of poisons to destroy the catalytic activity.

iv. They can be used in the presence of any solvent ie., the solvent can be freely optimized without any restrains imposed by the catalyst.

v. They increase catalyst stability by keeping fine crystals of the active constituent too far apart for sintering to occur. Also increase activity by increasing the accessibility of the active surface by the substrate.

vi. Helps to dissipate heat and prevent local overheating which would cause sintering with resultant loss in active surface. High heat conductivity supports are favoured for such purposes. For example, in the catalytic oxidation of ethylene, metallic silver supports are commonly used.

vii. They may also be used in a continuous flow reactor.

Even though, supported catalysts have advantages of selectivity with respect to substrate and ease of separation of the catalyst after reaction, as compared to homogeneous catalysts, most industrialists still tend to ask about the relative activities of the two types of catalysts. At present the supported catalyst are generally less active than the homogeneous, although they can approach 80% activity. The lower activity of the supported catalysts reflects the fact that some of the metal centres are bound in substrate- inaccessible sites within the pores of the catalyst; accordingly, the less of these sites there are, as in silica, the greater is the activity [16].

In general, polymer supported catalysts used in such a reaction with high selectivity and quality are needed as in the pharmaceutical and food stuff industries. Thus, we may see in the near future wide applications of supported complex catalysts in many chemical industries.

1.2. Objective of the Present Work

I. Preparation and characterization of inorganic support materials LVP, TMP and ZrVP and identification of transition metals which will bind to the support materials.

II. Studying of the metals catalytic prospect in the conversion of cyclohexanol and cyclohexene.

2. LITERATURE REVIEW

2.1. The Support Materials

The price some nations paid for growing industrialization is growing pollution of air and water, but again the world turns to catalysis for the salvage of a healthy environment. Now a days, an explosive growing of catalytic technology mainly directed towards peaceful applications is expanding. In this regard, supported complex catalysts are reliable and promising. Thus, the field of supported catalysts is a 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 [2].

There are very wide conditions under which supported transitional metallic catalysts are used and as a consequence there are wide range of possible support materials. Many of these are particulate or granular, although fibrous materials are also used; monolithic porous ceramic has recently become important ie., depending on the nature of the material, the specific surface area (SA per unit mass) and the pore structure can vary enormously [13].

In this regard, it is worth looking at the classification and varieties of the support materials which are used to bind the metal complexes. They may in general be classified into inorganic salts and oxides and organic polymers. The inorganic support materials may include: clays, glasses, zeolites, metal oxides such as chromia, alumina, titania, etc, and organic support polymers that include agarose, urethanes, poly amino acids, etc, have been used as a basic support or carrier in many patent literatures [13, 21, 22].

In general, the support materials as mentioned in the introductory part must fulfil characteristics of good mechanical properties, adequate thermal stability, readily accessible sites for anchoring potential active centres, and limited solubility in the reaction medium. But, there are some basic differences between the organic and inorganic support materials and to have a knowledge, let us have a look at each of them separately [17].

The primary requirement for a useful organic polymer support is incorporation of functional groups which are potent ligands. The groups bound to them may be nearly uniform in character and function catalytically just as their molecular analogues do in solution. Moreover, the polymer catalysts are structurally rather simple [18]. Some of the disadvantages of organic supports may include the following. They are not resistant to attrition and abrasion, ie., they are used in fixed-bed and not stirred reactors. They are subject to deactivation by soluble cations (such as tramp iron) in feed systems, as a result of ion exchange. Organic polymers constantly slough off low-molecular weight fragments that contaminate and discolour products of catalytic reactions. Also, the lack of stability of the polymers at high temperatures restricts the applications [19].

On the other hand, inorganic supports may have rigid structure which prevent such deactivation relative to organic polymers. In addition, organic polymer swelling under variable temperature and solution conditions make practical control of diffusional variables difficult. Inorganic substrates can be preselected for stable diffusional characteristics at most reaction conditions. But, the major disadvantage of inorganic supports is the surface of the solids are so complex [17, 20].

Thus, as a concluding remark, inorganic support materials have attracted more attention than organic polymers, and the catalysts, which are now coordination complexes supported on inorganic solids, are extremely efficient.

2.2. Catalyst Preparation

The preparation of catalysts by immobilizing active transition metal complexes on solid supports such as organic polymers, inorganic oxides, and related materials has recently attracted widespread attention. They have the attractive features of being reproducible and allowing control and knowledge of the nature of the incipient species immobilized on the support. There is further promise, yet unfulfilled, of identifying important catalyst features through synthesis and experiment. In addition, immobilized metal carbonyl can be decomposed to produce highly dispersed supported metal oxide particles [17].

It is long known that, the chemical and physical properties of a catalyst are determined by the total history of its preparation. To obtain active catalysts it is important to use established procedures and experimental techniques. Some of the guiding principles and techniques used in the laboratory preparation of solid catalysts will be discussed here [23].

Metal is introduced to the support, usually from aqueous solution or suspension by processes such as impregnation, adsorption or ion exchange, co-precipitation or deposition, followed by drying and hydrogen reduction. There is a vast range of empirical variations to preparative recipes, and an extensive catalogue is given by Innes. Metal deposition by decomposition of volatile metal compounds has also been described in many patent literatures [24].

Incorporation of metal ions into support materials may apply the principle of cation exchange phenomenon. Ion exchange is a diffusion process and its rate depends upon the mobility of the ions. The replaceability of cations depends upon such factors like experimental conditions, cations involved and the kind of support materials, therefor, there is no single universal replaceability order. However, cation exchange capacity is influenced by some important parameters such as effect of concentration, nature of ions, and population of the exchange position [24]. Thus, out of several catalyst preparation methods, we will focus on the most common one, ie., impregnation technique.

The technique of impregnating an active component (or components) on an inactive support is frequently the simplest possible method of producing a catalyst. However, as already stated, a number of complicating factors arise even in such a simple method of preparation [14].

Impregnation of a support normally involves the use of a soluble compound of the desired constituent dissolved in a liquid, which is usually water. It is also possible to perform a vapour phase impregnation of the support if one confined a volatile compound of the desired constituent. Impregnation by a solution may be carried out on either dried porous supports or undried precipitates or gels. In the case of dried supports one may use either a powdered or granular material. A granular support is usually preferred since it eliminates pelleting or extrusion of the finished catalyst [14].

In its simple form impregnation method of catalyst preparation may involve the following steps: (1) evacuating the support, (2) contacting the support with the impregnating solution, (3) removing the excess solution, (4) drying and (5) calcination and activation. Frequently it is necessary to add a precipitation and washing step either before or after drying. In addition, it is generally desirable to obtain preliminary information regarding the equilibrium distribution of the solution. Such information is necessary to establish the quantity and concentration of the active component and the desired concentration of the active component on the support [27, 28].

Evacuating of the support prior to contacting it with the impregnating solution gives more uniform distribution of the active component Frequently, trapped air in the pores of the support prevents complete penetration of the solution. In many cases, this step is unnecessary, provided sufficient time of contact between the support and impregnating solution is allowed. An excess of impregnation solution is usually used. Removal of this excess solution can be accomplished by either filtration or decantation. Centrifuging is an effective method of removing liquid between the solid particles [29]. Now, let us see some examples regarding the preparation of catalysis.

Reaction of acetaldehyde on CeO_2-supported catalysis were prepared by impregnation technique. For example, Pd/ CeO_2 (3%) was prepared by impregnating CeO_2 with a solution of 1 M HCl containing palladium ions (eg. $PdCl_2$) the catalyst was then dried for 5 h at 400 K and calcined again for 5 h at 673 K. Co/CeO_2 (3%) was prepared by the same procedure as for Pd/CeO_2.

Pd-Co/CeO_2 was also be prepared co-impregnating a solution of $Co(NO_3)_2$ and $PdCl_2$ (1 M HCl) with CeO_2 followed by drying and calcination as the above condition [30].

Sibeijn and co workers prepared the boria-modified alumina by multi step pore-volume impregnation of γ-Al_2O_3 with an aqueous solution of H_3BO_3.The solid was dried at 383 K for at least 2 h and calcined at a temperature of 688 K. The Rh_2O_7 catalysts were also prepared by the same procedure [31]. But, before these work, Anderson prepared Rh/γ-Al_2O_3 by the standard impregnation technique using $RhCl_3$ solution [24].

In the separate work, Hugo and co-workers prepared catalysts Pt/Al_2O_3 and Rh/Al_2O_3 by impregnation method using H_2PtCl_6 and $RhCl_3.H_2O$ on alumina respectively. After drying at 100 °C the solids were calcined at 400° C by reduction in flowing 5% H_2/N_2 at 500° C. They also prepared bimetallic non alloy PtRh/Al_2O_3 catalyst first by impregnating the support with H_2PtCl_6(aq). The solid was then dried, calcined and reduced. Finally the solid again impregnated with $RhCl_3.H_2O$(aq) [32].

In order to achieve a homogeneous dispersion on an oxide such as SiO_2 with such a low isoelectric point, experimental conditions envisage the use of high pH and active metal cationic complexes. Folgado et al prepared a series of pH aerosil catalyst with different amount of metal

(0.1-2.0 wt%) following a method of adsorption from solution, using a tetra amine platinum(II) chloride as departure salt and 9.74 pH [29]. Narsimha and co-workers prepared SnO_2-supported with 0.5-5.5 wt% V_2O_5 by the standard wet impregnation technique and is characterized by spectrophotometric methods [21].

Catalytic preparation could also be possible directly without subsequent calcination [13, 33]. Carbon and alumina supported Fe, Mo, Fe-Mo catalysts were prepared by Cornelis and co-workers without calcination. Samples containing two different metals were prepared by a two step impregnation with ammonium heptamolybdate or cobalt nitrate solutions, the samples were dried at 383 K for 16 h. Samples impregnated with iron nitrate solution were dried at 293 K for 16 h in flowing air (100 cm^3/min), since it was reported before that drying at 383 K caused considerable active phase sintering and consequently a lower catalytic activity. None of the catalysts was subjected to any further heat treatment or calcination procedure [33].

In several cases, the use of excess impregnating solution is undesirable. In these instances enough solution is added to completely wet the support. This can be done by spraying the solution on the support while it is tumbled in a rotating bottle. This method is known as incipient wetness [14]. Gandi and Montes [35] used incipient wetness technique for the preparation of nickel and cobalt activated charcoal supported catalysts from aqueous solutions of $Ni(NO_3)_2.6H_2O$ and $Co(NO_3).6H_2O$ respectively. Similarly Cesar and co-workers [36] used this method for the preparation of Ni/SiO_2 and Ni/Al_2O_3 catalysts.

The simplest method which is used to quantify the amount of catalyst incorporated into the support material is Atomic Absorption Spectroscopy, AAS. But to have the detailed knowledge of supported catalysts, the concept of surface science is vital. Surface science thrives on high quality interdisciplinary research that has also enriched physical chemistry over the past decades. Our ability to investigate surface on a molecular level and to utilize well-characterized single crystal surfaces for these studies provided us with definite and detailed physical pictures of surface structure, the surface chemical bond, and dynamic phenomenon including adsorption, desorption, and catalysis. In this regard, the most frequently used spectral techniques are Auger Electron Spectroscopy, (AES), Low-Energy Electron diffraction, (LEED), etc. [37, 38].

2.3. Catalytic Applications

Despite some drawback arised due to the nature and properties of organic support polymers, extensive catalytical work have been done. For instance, strong acid polymers are used as catalysts in a number of industrial processes, including esterification, phenol alkylation, propylene hydration, and methyl t-butyl ether synthesis [9].

Recent developments involving polymer supported metal complexes as catalysts in oxidation reaction, using dioxygen, hydrogen peroxide, alkyl hydro peroxides, hypochlorite anion and iodoso benzene as oxidants are reported [39]. Rollman produced a bi-functional polymeric catalyst which contained both Co(II) tetraphenyl porphyrin and a base to act as a proton acceptor [40]. This system readily catalyzed the oxidation of thiol by molecular oxygen. Separate work on phthalocynaine tetra sodium sulphonate has been bound by ionic forces to polyvinyl amine and used for epoxidation of cyclohexene using dioxygen as the oxidant is shown [41].

In polymer supported oxidation reactions of organic compounds there are a number of closely related studies involving the attachment of oxo-metal complexes to ion exchange resins. Linden and Farona supported oxo-vanadium(IV) species on a sulphonic acid type cation exchange resin and successfully epoxidized both cyclic and acyclic alkenes using t-butyl hydro peroxide [42].More recently Nolte and his co-workers have been trying to model mono oxygenase enzymes using polymer supported manganese(II) tetra phenyl porphyrins [44]. Cyctochrome models have been reported that epoxide alkenes under relatively mild conditions [46]. They utilize the synthetic metallo(III) porphyrin and an oxygen source such as hypochlorite or iodosyl benzene, or alternatively a combination of molecular oxygen and a reducing agent.

Polymer supported palladium(II) catalysts also form the basis of many hydrocarbon oxidation reactions. In deed $PdCl_2$ has been supported on a styrene divinyl benzene copolymer resin containing $CH_2N(CH_3)_2$ groups. The catalyst is reported to yield vinyl acetate along with acetaldehyde and ethylene oxide from a feed of ethylene, dioxygen and acetic acid [39]. An organic quinone polymer containing sulphonic acid groups has been used to support Pd(II), yielding a catalyst effective for the conversion of ethylene to acetaldehyde [46].

In the earlier stage, most inorganic support materials, used as a potential for separation of inorganic ions or as ion exchangers. They used as an important practical applications in nuclear technology [47]. The discovery that large cations can be taken up by ionic forms with large inter layer distance has opened new development. Analytical separation or concentration of the cations can be performed [48]. Also amorphous zirconium phosphate has been utilized in kidney machines for the removal of ammonium ions from blood [49]. Owing to the discontinuous phase transition during exchange, insoluble acid salt forms could be used to maintain constant ionic fraction of a pair of cations, such as Na^+, K^+, in solution [48].

Supported catalysts beyond their catalytic applications in industries may used to keep safe environment. We know that contamination of water supplies is an ever increasing problem. Many of the contaminants are organic compounds and may decomposed in the presence of TiO_2 powder coated on sand illuminated with near-UV light and there is interest in this process as a means of purifying water. These and other chlorinated organic compounds have been shown to be completely mineralized to carbon dioxide and water [50, 51].

Cerium has proven to be a powerful modifying agent of catalysts for important industrial or environmental reactions such as the cracking of heavy oil on zeolites or the automotive exhaust gas conversion. Thus, cerium based catalysis, in the presence of a transition metal, have revealed interesting properties for numerous reaction, most of them including redox steps: catalysis for exhaust gas depollution for an automobiles (TM/Ce/Al_2O_3; TM/CeO_2 or TM-Ce/C; TM= Ni, Co, Pd, Rh); water reduction at low temperatures (TM/CeO_2; TM=Pt, Pd); water gas shift (Pt/CeO_2); wet oxidation of ammonia (TM-Ce/oxides; TM= Co, Ni, Mn); hydrocarbon conversion (TM/CeO_2, TM-Ce/Al_2O_3 or SiO_2; TM= Pt, Pd, Ni); thio resistance to sulphurised hydrocarbons charges (Ni/CeO_2) [52, 53].

Idriss et al [30] investigate the reactions of acetaldehyde on the surface of CeO_2, 3 wt% Co/CeO_2 by temperature programmed desorption (TPD) and infrared spectroscopy (FT-IR). In the study several reactions of acetaldehyde were observed; they can be classified as oxidation, reduction, or carbon-carbon bond formation reactions. Oxidation to acetal and reduction to ethanol were observed on all catalysts. In the process four C-C bond formation reactions were observed: (1) β-aldolization to crotonaldehyde and crotyl alcohol (most prominent on CeO_2 alone), (2) acetate ketonization to acetone and CO_2 on CeO_2 and Co/CeO_2, (3) acetyl reaction with methyl species to give acetone on Pd/CeO_2, Co/CeO_2 and Pd-Co/CeO_2 this acetone desorption was coincident with propane desorption on Pd/CeO_2 and Co/CeO_2), (4) reductive coupling two molecules of acetaldehyde to butene and butadiene (on Ce and Co/CeO_2). Thus, Pd-Co/CeO_2 adsorption four times more CO than did Pd/CeO_2 or Co/CeO_2 and was the most active for acetaldehyde conversion.

The catalytic hydro-cracking of hydrocarbons is an important process in the petroleum refining industry. It is mainly used for production of gasoline with high octane number, middle distillates, lubricants and for the upgrading of petrochemical feedstock. In this regard, the ability of Rh catalysts to produce ethanol as well as a variety of other substances such as methane, hydrocarbons, higher alcohols, acetaldehyde and acetic acid in CO hydrogenation has been known. The activity and selectivity of Rh catalysts are influenced greatly by many parameters, including the support and/ or promoters used, the precursors of the preparation techniques, and to a lesser extent, by the reaction experimental conditions. 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 ethanol is the main product with up to 80% selectivity [54, 55].

On the other hand, when Rh/SiO_2 catalyst used in the conversion of synthesis gas at atmospheric pressure and temperature of around 470 K, the major products are in fact hydrocarbons. But, when Rh/ZrO_2 is used the major selectivity on a carbon bases are 42% for ethanol, 32% for methane and 12% for methanol. When zinc oxide is the support, the synthesis is directed overwhelmingly towards methanol (99%) [56].

Cesar and co-workers studied the homologation of propene with methane using alumina- and silica supported nickel catalysts. The catalysts were activated under a methane flow previous to the reaction . Experiments were carried out in a propene/mixture at 350 °C showed that the Ni/SiO_2 system was more active for the homologation reaction (81.4%) selectivity to butane than its alumina analog (6.2% selectivity to C_4 compounds). The concentration in the silica catalyst was higher than in its alumina analog, suggesting that, most probably, these species were involved as intermediates in the propene homologation reaction. The silica based catalyst showed higher metal dispersion than that found in its alumina counter part. This can be attributed to the formation of $NiAlO_4$ on the catalyst surface, which can also explain the lower activity observed for butane production [36].

In particular Schleyer and co-workers [57] reported that methane reacted with benzene, cyclo pentane, and propene to produce small amounts of toluene, methyl cyclo pentane, and butane, respectively, using silica-supported nickel catalysts. Sodesawa et al [58] reported oxidative methylation of propene with methane to butane in the presence of oxygen using a 3% Na_2O/La_2O_3 catalyst. A maximum 10.1% yield of C_4 compounds was obtained . And also Osada et al [59] reported the oxidative methylation of toluene with methane over alkali- promoted Y_2O_3-CaO catalysts to give ethyl benzene and styrene. The order of selectivity to higher hydrocarbons is Li > Na > K.

Isomerization of n-paraffins is an industrially important octane upgrading process. Various bi-functional catalysts containing noble metals like Pt and Pd over various supports such as silica-alumina, chlorinated alumina, crystalline aluminosilicate (zeolites) have been widely studied and proven to possess high isomerization selectivity. Shil and Bhatia [58, 60] studied the isomerization of n-hexane in the presence of excess hydrogen at 643 K in a flow reactor over NiCa-Y (nickel calcium Y type faujasite) and NiH-M (nickel hydrogen mordenite) catalysts. Thus, NiCa-Y containing 1.86 wt%. Ni exhibited maximum isomerization activity and selectivity.

Cu^{2+} and Cu^{+} in ZSM-5 (zeolite) have been shown to be active in a redox cycle for the catalytic decomposition of NO to N_2 and O_2. Michael and co-workers [61] have reported that silica supported zirconium hydrides are highly efficient olefin isomerization catalysts. On the other hand, Adam et al [62] have shown that by refluxing hex-1-ene, hept-1-ene or oct-1-ene in hexane solution with cation exchanged montmorillonite, the alkenes are converted to the corresponding bis-sec-alkyl ethers. A number of cations may facilitate the conversion, the most efficient being Cu^{2+}, Cr^{3+}, Al^{3+}, Fe^{2+}, and Fe^{3+}.

To date, only a few applications of the catalytic activity of synthetic inorganic support materials are known. Kalman et al [63] have successfully employed the copper form of the zirconium phosphate for the oxidation of CO to CO_2 and this has found wide application in the control of automobile pollution. Recently, zirconium phosphate has been loaded with several transition metal ions, and these materials were found promising as catalysts support [64, 65]. Zirconium phosphate has also been employed as a support for gas solid chromatography [65].

3. EXPERIMENTAL

3.1. *Chemicals and Apparatus*

All reagents: sodium molybdate (Riedel-de Haen), potassium phosphate diabasic (BDH), titanium(IV) chloride (Riedel-de Haen), orthophosphoric acid (Riedel-de Haen), ammonium meta vanadate (BDH), zirconyl nitrate hydrate (Aldrich), ferric chloride anhydrous (BDH), copper chloride hydrate (Riedel-de Haen), chromium chloride hydrate (Riedel-de Haen), cyclohexene (Riedel-de Haen), and cyclohexanol (BDH) were used as obtained.

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

IR spectra in the region of 4000-500 cm^{-1} were recorded on perkin Elmer Spectronic 1000-SPIR Spectrophotometer using KBr disc. pH measurements were made using Beckman chem-mate pH metre. Gerhardt and Gallen kamp flask shakers were used for shaking different samples. The reaction products of catalysis were followed up using Variant model 3700 gas chromatography using capillary DB-5 non-polar stationary phase at oven temperature of 40-220 °C , FID 250 °C and program rate 4 °C\min and also using the GC HP 6890 on HP 5 column. The support catalysts were calcined using Naber oven. Analysis of the composition of the samples were done using Varian spectra AA20 atomic absorption and Varian DU80 UV-Visible spectrophotometer.

The AAS analysis were done under the following conditions.

A Hallow cathode lamp with lamp current: 5 mA (Fe),4 mA (Cu), and 5 mA (Cr).

Wave length: 324.8 nm (Cu), 248.3 nm (Fe) and 281.1 nm (Cr).

Photomultiplier volt: 234.2 (Cu), 396.9 (Fe) and 281.1 (Cr). Oxidant: air-acetylene.

The GC analysis were done under the following conditions.

Column capillary: DB-5 non polar stationary phase (30 m x 0.25 mm: id 1.5 m film thick).

temperature: oven 40-220 °C, injector 200 °C, FID-250 °C, program rate 4 °C/min.

Flow rate: H_2-30 mL/min, Air-300 mL/min and carrier gas N_2-30 mL/min. Sample size: 0.02 μL. For samples refluxed with calcined catalysts, the GC analysis was done on HP 6890 using HP 5 column.

3.2. *Preparation of Inorganic Support Materials*

3.2.1. *Titanium molybdophosphate (TMP)*

One molar aqueous solution 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 1 M was prepared by diluting 10 mL of commercially produced 9.12 M $TiCl_4$ solution 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) drop- wise with constant stirring at room temperature. A clear colourless solution having a pH of 11 was obtained. To this mixture 20 mL $TiCl_4$ was added drop wise from a burette under the same condition. A very light white yellowish precipitate was formed and the pH drops below zero.

Orthophosphoric acid (10 mL) was added finally to ensure a complete precipitation. The solution was heated for 30 min at about 40 °C with continuous stirring. The precipitate so obtained was kept for 12 h, washed with distilled water, centrifuged, dried at 40 °C for 2.5 days to give 12.00 g product. The product was grounded and sieved to pass through 170 mesh. Finally, the product obtained was soaked in 200 mL of 0.1 M HCl for 24 h to convert it to H^+ form. The solid was filtered and washed until free from Cl^- and dried again at 40 °C for 16 h [66].

3.2.2. *Lead vanadophosphate (LVP)* .

One molar aqueous solution of sodium dihydrogen phosphate (50 mmol, $NaH_2PO_4.2H_2O$) and lead nitrate (50 mmol, $Pb(NO_3)_2$) were prepared. 500 mL of 0.1 M (50 mmol, NH_4VO_3) was also prepared in aqueous solution.

LVP where the mole ratio of vanadate : phosphate : lead(II) is 1 : 1 : 1 was obtained first by adding a clear solution of 1 M $Na_2HPO_4.2H_2O$ (50 mL) drop-wise 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 drop wise to a beaker containing 1 M $Pb(NO_3)_2$ with constant stirring at room temperature to give a yellow precipitate at pH 1.7.

The solution was heated for 30 min at 40 °C , allowed to stand for 2 days, the precipitate was filtered, washed and dried at 40 °C for 2 days (yield 16.0 g). A grain size which passes through 170 mesh and was soaked in 200 mL of 0.1 M HCl for 24 h to convert it to H^+ form. The solid was filtered and washed until free from Cl^- and dried again at 40 °C for 16 h [66].

3.2.3. *Zirconium vanadophosphate (ZrVP)*

One molar aqueous solution of sodium dihydrogen phosphate (50 mmol, $NaH_2PO_4.2H_2O$) and zirconyl nitrate (50 mmol, $ZrO(NO_3)_2$) were prepared. 500 mL of 0.1 M (50 mmol, NH_4VO_3) was also prepared in aqueous solution.

ZrVP was obtained first by adding a clear solution of 1 M $NaH_2PO_4.2H_2O$ (50 mL) drop -wise to a beaker containing 500 mL of 0.1 M NH_4VO_3 solution with constant stirring at room temperature. A red yellow solution having a pH of 6 was obtained. 150 mL of this mixture was added from a burette drop wise to a beaker containing 50 mL of 1 M $ZrO(NO_3)_2$ with constant stirring at room temperature to give a greenish yellow precipitate at pH 2.4.

The mixture was well stirred for 30 min and allowed to settle for 2 days, the precipitate was filtered and dried at 40 °C for 2 days,. The product obtained was kept in the mother liquor and refluxed at 50-60 °C for 60 h, then filtered, washed and dried at 40 °C for 2 days (yield 9.8 g). A grain size which passes through 170 mesh product was soaked in 200 mL of 0.1 M HCl for 24 h to convert it to H^+ form. The solid was filtered and washed until free from Cl^- and dried at 40 °C for 16 h [67].

3.3. *Hydrogen Ion Exchange Capacity*

Hydrogen ion liberation capacities were determined by batch operation as follows [68]

A 50 mL volume of 0.1, 0.2, 0.5, 1.0, 2.0, 3.0 and 4.0 M sodium chloride solutions were prepared and shaken with 0.1 g of each exchanger (TMP, LVP, ZrVP in H^+) using Gerhardt flask shaker continuously for 12 h at a speed of 120 cycles/min. After equilibration 10 mL portions of supernatant were taken and titrated with standard solution of 0.01 M NaOH using phenolpthalien solution as indicator.

The results obtained from titration of the proton liberated with standard sodium hydroxide solution using phenolphathalien solution as indicator are given in Tables 2, and in figs. 1, 2, and 3.

3.4. *pH Titration Curves*

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

0.1 g of TMP, LVP and ZrVP in H^+ form were first shaken with 50 mL distilled water for

2 h, and after equilibrium was achieved, the pH was measured. Then 1 mL of 0.1 M KOH was added, stirred for 2 h and after equilibrating the solution the corresponding pH were recorded. The experiment was repeated until the change in pH became constant. The pH titration curves as a function of titrant for each exchanger is given in figs. 4, 5, and 6.

3.5. *Moisture Content Determination*

0.5 g of TMP, LVP and ZrVP were taken in three different crucibles and heated to a temperature of 150 °C for 90 min. This was repeatedly done until the change in weight (Δ w) becomes constant.

3.6. *Preparation of Cr^{3+}/TMP, Cr^{3+}/LVP, Cr^{3+}/ZrVP, Fe^{3+}/ZrVP, and Cu^{2+}/ZrVP*

A preliminary test was conducted with seven transition metal salt solutions by soaking with the three exchangers (Cr^{3+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}). Based on the results from AAS, some of the metals were loaded on the support materials.

3.0 g of each exchanger (LVP, TMP and ZrVP in the H^+ form) was mixed with aqueous solution of 300 mL of 0.033 M $CrCl_3.6H_2O$ in different flasks, 3.0 g of ZrVP/H^+ was mixed with 300 mL of 0.033 M $FeCl_3$ using 0.1 M HCl as a solvent and 3.0 g of ZrVP/H^+ was again mixed with 300 mL of 0.033 M $CuCl_2.2H_2O$ aqueous solution in an earliminary flasks. The samples were shaken for 20 min intermittently in an interval of 15 min for a total of 2 h, and allowed to settle for 48 h (which is equivalent to impregnating technique). Then the precipitates was filtered and washed until free from Cl^- and dried.

1.5 g of each dried sample was heated at 348 K for 4 h and the rest 1.5 g of each sample was calcined in a furnace at 700 K for 4 h, then cooled and grounded to pass 170 mesh. The amount of transition metal cations loaded on the exchangers are given in table 3. The amount of metal cations incorporated into the support materials were determined using AAS.

3.7. *Catalytic Study of Transition Metals Supported on TMP, LVP and ZrVP*

0.3 g of each supported catalyst was taken in a different 250 mL two necked round bottom flasks. To each 3 mL of distilled cyclohexanol was added. After putting the magnetic bar, the flask were fitted with condenser and ground thermometer and were refluxed on heating mantle at a temperature range of (161-110 °C) for 4 h and 7 h. The experiments were done using the supported catalysts at 348 K and 700 K. The supernatant was isolated by centrifuge and the GC analyses were conducted.

In the case of cyclohexene, in each flask was added 3 mL cyclohexene, 2 mL distilled water and 0.3 g of each of the supported catalysts. Otherwise we followed the same procedure like that of the above procedure except the refluxing temperature was 66-69 °C. All the samples refluxed with supported catalysts were subjected to the GC analyses. The results are given in table 4.

4. RESULTS AND DISCUSSION

4.1. General

Different studies [68, 69] indicate that the properties of inorganic ion exchangers or support materials are dependent on the conditions of preparation. The method of preparation has considerable effect on the composition of the exchange material. This factor is responsible for the shape and size of cavities inside the exchanger and the chemical stability. Therefore, before discussing the experimental results, it is worth looking for the basic parameters of the support materials.

Table 1. Measurement of the basic parameters

	TMP	LVP	ZrVP
Solubility	Almost insoluble in most solvents and 1 M mineral acids	Almost insoluble in most solvents and 1 M mineral acids	Almost insoluble in most solvents and 1 M mineral acids
Exchange capacity (meq/g)	0.098	0.58	0.75
Basicity	monobasic and moderately acidic	diabasic and strongly acidic	monobasic and moderately acidic
Moisture content (%)	21.7	8.1	32.4
Particle size of materials	170 mesh	170 mesh	170 mesh
Elemental analysis	20.22% (Ti), 8.2% (Mo), 6.31% (P), 18% (H_2O)	49.8% (Pb), 7% V, 5.92% (P), 9.2% (H_2O)	19% (Zr), 9.8% (V), 8.72% (P), 24.8% (H_2O)

Measurements of the basic parameters (table 1) indicates that LVP, TMP and ZrVP can function as a support for the transition metal cations and enhance their catalysis role. The ion exchange capacity determined for ZrVP (0.75), LVP (0.58) and TMP (0.098). The highest value is attributed for ZrVP which may be due to the increased number of binding sites such as O^- of the matrix.

4.2. Composition of the Support Materials

The elemental analyses for ZrVP, TMP and LVP were quantitatively determined using the atomic absorption and UV-Visible spectrophotometers. The water of hydration was determined using Naber Oven. The data obtained for the elemental analysis of ZrVP from table 1 account for 62.33% of the constituents. The remainder can be attributed to the oxygen which is covalently bonded with Zr, V and P to form ZrO, V_2O_5 and P_2O_5 [67]. A similar arguments can be made to the LVP (71.92%) and TMP (62.32%).

4.3. Infrared Studies

The ir spectrum of ZrVP in H^+ forms exhibits some major bands. The strong and broad band in the region of (3400-3000 cm^{-1}) particularly at 3145 cm^{-1} is symmetric and anti symmetric stretching for interstitial (or free) water and hydroxyl groups [70].The strong peak at 1630 cm^{-1} may indicate for bending mode of interstitial water (H-O-H), which shifts to the lower frequencies when bound to different metal cations [67]. This may indicate that the O^- is the only group in the matrix of the exchanger responsible for the adsorption of the different cations [67]. In addition a sharp and strong peak at 1402 cm^{-1} may represent for vanadate group, since it has similar spectrum to that of the starting NH_4VO_3. There is a strong and broad peak in the spectrum at 1040 cm^{-1} due to the stretching frequency of (P-O) [69]. There are also peaks in the region of 738 and 525 cm^{-1} representing Zr-O stretching and O-P-O bending respectively.

The ir spectrum of TMP in H^+ forms exhibits four major absorption bands in the regions 3500-2900, 1624, 1021, and 750-600 cm^{-1}. The strong and broad peak at 3500-2900 cm is characteristic of interstitial (free) water molecule and hydroxyl group. Sharp strong peak at around 1624 cm^{-1} is due to the bending mode of interstitial water molecule. A very strong peak at 1021 cm^{-1} is due to the phosphate group particularly P-O stretching. In the region below 750 cm^{-1} Ti-O stretching frequencies are also expected [71]. Thus, a broad peak in the region 750-600 cm^{-1} may probably be due to both O-P-O bending and Ti-O stretching frequencies. Mo-O interaction is also expected at further lower frequency.

The ir spectrum of LVP in H^+ form revealed, a broad peak in the region 3670-3500 cm^{-1} which may be due to the presence of symmetric and anti symmetric stretching frequencies of free water molecules and hydroxyl groups. The other peak in the region 1615 cm^{-1} may also be attributed to the bending mode of free water. The two peaks at 1383 and 1350 cm^{-1} have similarity to the ir spectrum of the starting compound NH_4VO_3, thus it can be ascribed to the vanadate group. Very strong peak at 1003 cm^{-1} is attributed to (P-O stretching) of phosphate group. A peak between 670-540 cm^{-1} may be ascribed to O-P-O bending frequencies and a metal oxygen interaction could also be associated to this frequency.

4.4. Hydrogen Ion Exchange Capacity

The capacity of ion-exchanger is the number of available ionic sites per gram of dry exchanger and is expressed as milli equivalents per gram (meq/g). The exchange capacity is generally taken as a measure of the hydrogen ion liberated by a neutral salt such as sodium chloride. It is found to depend upon both the concentration and volume of salt solution [67, 68, 72]. As it can be seen from table 2 (A, B, and C) and Figs. 1, 2, 3. The exchange capacity for LVP, TMP, and ZrVP get saturation for sodium chloride solution of concentration at 2 M, 0.5 M and 2 M respectively. From the tables we can see that ZrVP has the highest exchange capacity to the proton for Na^+ ion (0.75 meq/g) relative to TMP which is only 0.098 meq/g. On the other hand, LVP has the exchange capacity of 0.58 meq/g which is moderate relative to the above exchangers.

The difference in exchange abilities may be due to several reasons. Possibly due to the differences in composition, the structure, nature of the support materials, etc. To comment on these, the knowledge of the spectrophotometric techniques is mandatory. Thus, our explanation is based on ir and other basic parameters mentioned on table 1. The exchange with ZrVP in H^+ highest may be due to the increased number of binding sites such as O^- of the matrix in ZrVP.

Table 2. Ion-exchange capacities of the exchangers as a function of Na^+ ion.

A. Lead vanadophosphate (LVP)

Conc. of NaCl solution (M)	NaOH (0.01 M) per supernatant solution (mL)	Exchange capacity (meq/g).
50 mL 0.1	1.2	0.12
50 mL 0.2	1.4	0.14
50 mL 0.5	2.0	0.20
50 mL 1.0	2.8	0.28
50 mL 2.0	5.6	0.56
50 mL 3.0	5.7	0.57
50 mL 4.0	5.8	0.58

B. Titanium molybdophosphate (TMP)

Conc. of NaCl solution (M)	NaOH (0.01 M) per supernatant solution (mL)	Exchange capacity (meq/g).
50 mL 0.1	0.55	0.055
50 mL 0.2	0.58	0.058
50 mL 0.5	0.90	0.090
50 mL 1.0	0.94	0.094
50 mL 2.0	0.96	0.096
50 mL 3.0	0.96	0.096
50 mL 4.0	0.98	0.098

C. Zirconium vanadophosphate (ZrVP)

Conc. of NaCl solution (M)	NaOH (0.01 M) per supernatant solution (mL)	Exchange capacity (meq/g).
50 mL 0.1	1.7	0.17
50 mL 0.2	2.2	0.22
50 mL 0.5	407	0.47
50 mL 1.0	6.2	0.62
50 mL 2.0	7.1	0.71
50 mL 3.0	7.3	0.73
50 mL 4.0	7.5	0.75

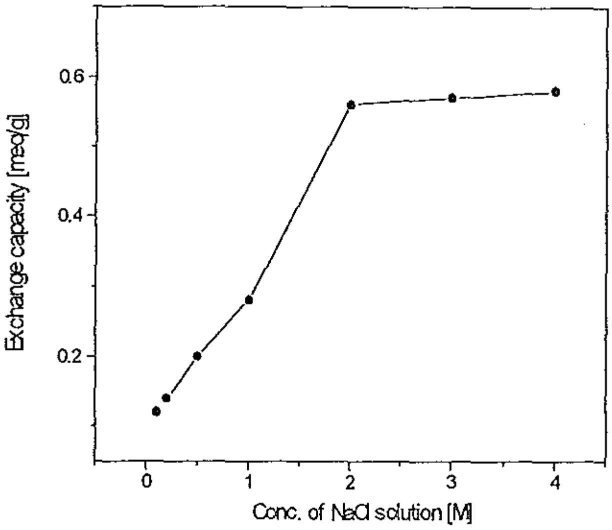


Fig. 1. Ion Exchange Capacity of LVP as a function of Conc. for Na^+ ion

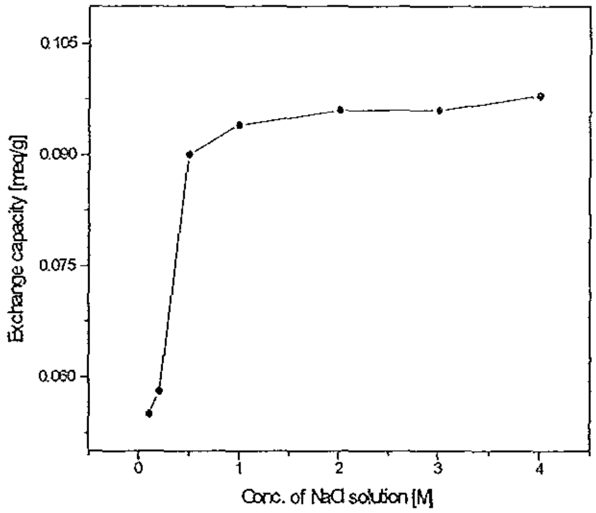


Fig. 2. Ion Exchange Capacity of TMP as a function of Conc. for Na^+ ion

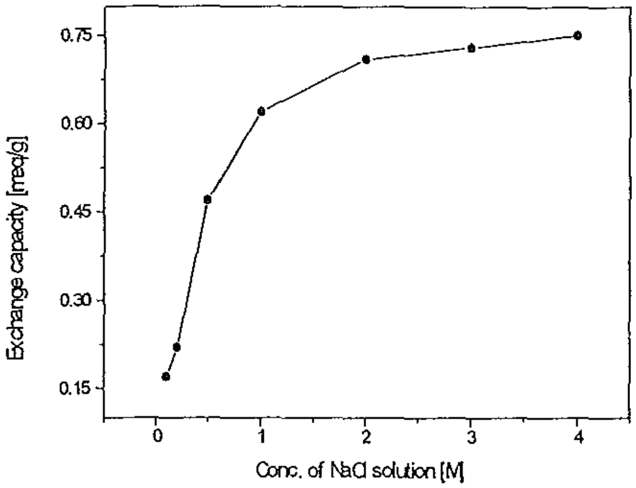


Fig. 3. Ion Exchange Capacity of ZrVP as a function of Conc. for Na^+ ion

4.5. pH Titration Curves

pH titration curves may give information about the nature (acidity or basicity) of the exchangeable groups present in the polymeric structure [68]. The curves which were obtained as pH versus volume of titrant were shown in Figs. 4, 5 and 6.

The titration curve of LVP shows two inflection points at pH 4.5 and 8.6 indicating the present of two exchangeable sites (diabasic). Moreover, the pH value at 4.5 reveals that LVP is rather strongly acidic cation exchanger. In the case of TMP the pH titration curve has one inflection point at pH 6.8 and may has an exchangeable site and is thus monobasic. Moreover, the pH value at 6.8 reveals that TMP is moderately acidic cation exchanger. Finally, for ZrVP the titration curve shows one inflection point at pH of 6.5 and may indicate one exchangeable site and is thus monobasic. In addition, the pH value of 6.5 may reveal that ZrVP is also moderately acidic cation exchanger.

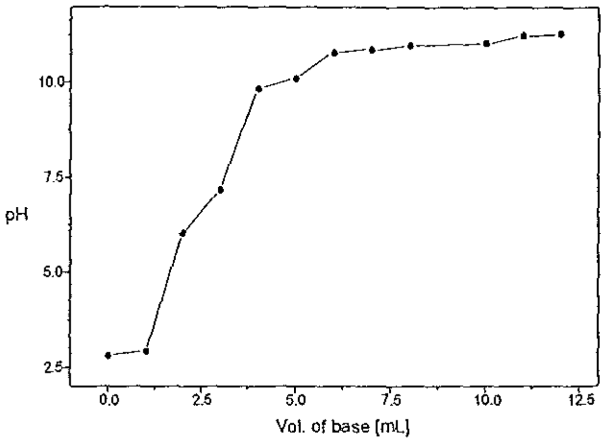


Fig. 4. pH Titration Curve of LVP

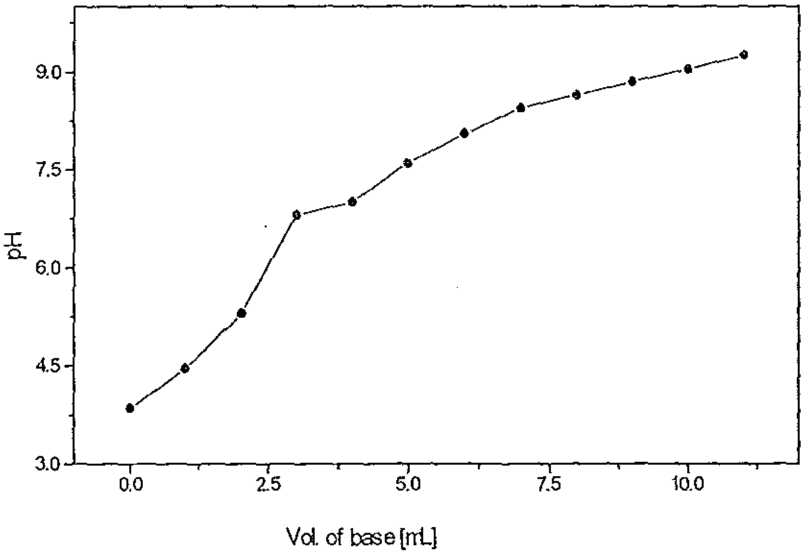


Fig. 5. pH Titration Curve of TMP

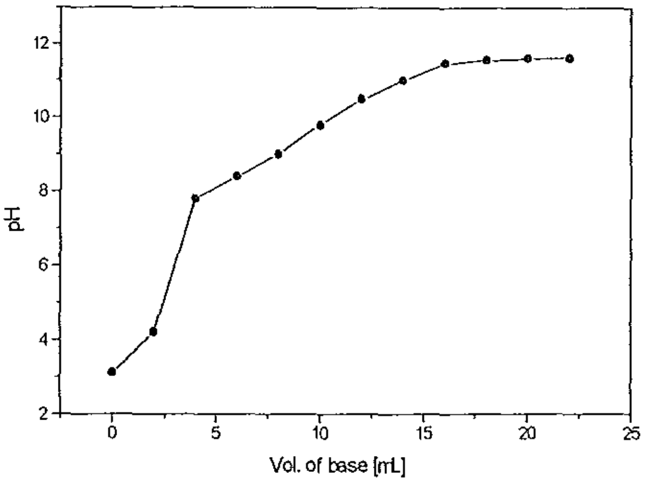


Fig.6. pH Titration Curve of ZrVP

4.6. Supported Metal Catalysts Preparation

Based on the basic parameters on table 1, we have seen that TMP, LVP and ZrVP are good ion exchangers and used as a support for the transition metal cations. Thus, having these in mind, we have conducted a preliminary test with several transition metal salts and finally we have managed to load Cr^{3+},Fe^{3+},and Cu^{2+} on ZrVP and Cr^{3+} on both LVP and TMP.

The quantitative determination of the amount of metal cations loaded on the support materials were determined by AAS. From the results in table 3, we have 17.65% Cr^{3+}, 35.13% Fe^{3+} and 15.15% Cu^{2+} in ZrVP and 3.92% Cr^{3+} in LVP and 11.76% Cr^{3+} in TMP.

As it could be seen from the composition of the exchangers, the increasing order of the water of hydration is: LVP (9.2%) < TMP (18%) < ZrVP (24.8%). Water of hydration is one of those anionic species that are expected to form the matrix. Thus the smaller amount of anionic matrix in the exchanger may not be strong enough to withstand the effect of highly concentrated salt solution. As a result the exchanger may probably start leaching. The significant effect of anionic groups on exchange capacities is also demonstrated by other workers [73, 74] and they have indicated that the sorption capacity decreases as the amount of anionic groups decreases. Thus, the sorption of ZrVP/ H^+ highest may be due to the increased number of binding sites such as O^- of the matrix.

Table 3. Determination of metals incorporated on the support materials.

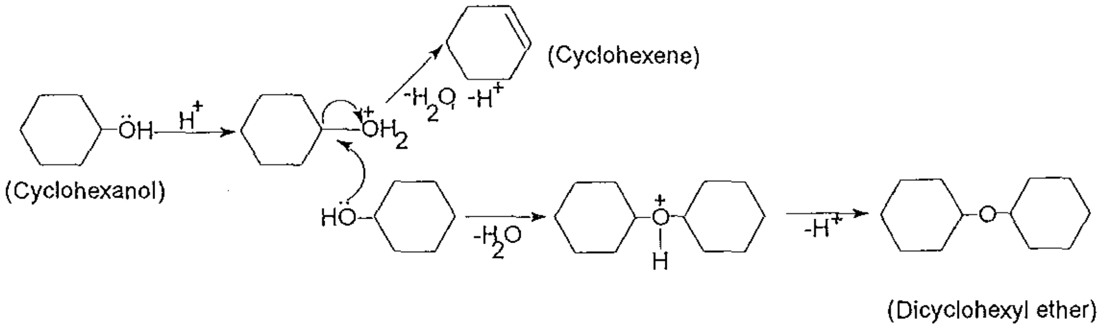
Samples	concentration in (ppm)
Cr^{3+} aqueous original solution	51
Filtrate of (Cr^{3+}/LVP)	49
Filtrate of (Cr^{3+}/TMP)	45
Filtrate of (Cr^{3+}/ZrVP)	42
Fe^{3+} (in 0.1 HCl) original	74
Filtrate of (Fe^{3+}/ZrVP)	48
Cu^{2+} aqueous original solution	90
Filtrate of (Cu^{2+}/ZrVP)	76

4.7. Catalytic Study of Transition Metal Cations Supported onto TMP, LVP and ZrVP and their GC Analysis

Elimination of water from alcohols and addition of water to alkenes 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 supported in inorganic support materials (alumina, silica, clay, etc.) as a catalyst.

We know that cyclohexanol undergoes general reactions scheme as that of secondary alcohols [75], and in acidic media dehydration and formation of ether takes place. From catalytic reactions of cations-exchange clay catalysis of alcohols, the major expected products are alkanes and ethers [76]. Thus, by refluxing cyclohexanol with different supported catalysts, we may expect the dehydration product which is cyclohexene together with the formation of dicyclohexyl ether.

The mechanism leading to these products is given by the following reaction scheme.



Scheme I

Table 4. Relative retention time (RT in minutes) and percentage of major peak in the starting cyclohexanol and after refluxed (for 7 h) with five supported catalysts calcined at 700 K.

Pure cyclohexanol		Cu^{2+}/ZrVP		Fe^{3+}/ZrVP		Cr^{3+}/ZrVP		Cr^{3+}/LVP		Cr^{3+}/TMP	
RT	%	RT	%	RT	%	RT	%	RT	%	RT	%
-	-	1.99	11.8	2.02	11.7	-	-	-	-	-	-
-	-	2.04	29.1	2.04	47.9	2.04	34.9	2.04	6.9	2.03	6.2
-	-	2.07	7.94	2.07	8.32	-	-	-	-	-	-
4.79	94.9	4.72	44.7	4.78	26.5	4.79	58.4	4.8	87.4	4.77	87.1
4.92	5.1	4.91	6.57	4.95	6.05	4.95	6.68	4.95	5.71	4.92	5.86

The catalytic action of Cu^{2+}, Fe^{3+} and Cr^{3+} on ZrVP and Cr^{3+} on both LVP and TMP samples are estimated on the basis of decrease in the percentage of the starting material and in the percentage appearance of new peaks which were originally absent in the pure cyclohexanol chromatogram. The two new major peaks appeared in all the samples have identical retention time (2.037 and 4.715 min for ZrVP/Cu^{2+}, 2.044 and 4.778 min for ZrVP/Fe^{3+}, 2.041 and 4.791 min for ZrVP/Cr^{3+}, 2.043 and 4.799 min for LVP/Cr^{3+} and, 2.031 and 4.769 min for TMP/Cr^{3+}). And also additional minor peaks appeared in the catalytic reactions of Cu^{2+} and Fe^{3+} supported catalysts, which were absent in the original chromatogram, having RT of 1.994 and at 2.071 min for Cu^{2+}/ZrVP and 2.015 and 2.071 min for Fe^{3+}/ZrVP. These probably shows that the catalysts have produced the same reaction products, but with different efficiency.

With Cu^{2+}/ZrVP, the major peak (at 4.715 min) has a RT almost identical with the pure cyclohexanol (RT 4.793 min) with the percentage purity of 94.902. The only difference is that there is a significant decrease in the percentage composition of the starting material after it is refluxed with Cu^{2+}/ZrVP. Correspondingly a new peak appeared at RT of 2.037 min with the composition of 29.058% as a second major peak, which is not in the chromatogram of the un refluxed cyclohexanol. In addition, there are peaks at RT of 1.994 min with 11.775% composition and at RT 2.071 min with the percentage composition of 7.936 which are again not present in the original chromatogram of cyclohexanol alone. This clearly indicates that a radical change has occurred to the starting material due to the effect of catalysis.

Similarly, the GC analysis of cyclohexanol with Fe^{3+}/ZrVP gave two major peaks at RT of 4.778 and 2.044 min with percentage composition 26.484 and 47.887 respectively. The first peak has almost identical RT with the pure cyclohexanol peak (4.793 min), the only difference is that the % composition of the cyclohexanol decreased dramatically from 94.902 to 26.484%. The additional two minor peaks appeared are exactly identical to that of the Cu^{2+} reaction products, but with the slight composition changes. Also, for Cr^{3+}/ZrVP the pure cyclohexanol chromatogram shows a decrease in the composition (at RT 4.791 min) from 94.902 to 58.43% and exhibits a new peak at 2.041 min with the composition of 34.892% , but no other additional peaks appeared unlike that of Cu^{2+} and Fe^{3+} supported catalysts do. On the other hand, Cr^{3+}/LVP and Cr^{3+}/TMP shows very slight difference in the original chromatogram. Cr^{3+}/LVP shows peaks at RT 4.799 min with composition of 87.397% and at RT of 2.043 min with 6.890% composition; Cr^{3+}/TMP exhibits peaks at RT of 4.769 min with composition of 87.08% and at RT of 2.031 min with the percentage composition of 6.204.

In order to get primary information about the new peaks of the catalysis reactions of cyclohexanol, retention time coincidence was applied by running the pure cyclohexene under the same chromatographic conditions as that of the catalysis reaction samples. The major peak obtained for distilled cyclohexene with RT of 2.046 min was just identical to the RT of the new major peaks appeared for the refluxed cyclohexanol with the five supported catalysts ie., the retention times are 2.037 min for Cu^{2+}/ZrVP, 2.044 min for Fe^{3+}/ZrVP, 2.041 min for Cr^{3+}/ZrVP, 2.043 min for Cr^{3+}/LVP and 2.031 min for Cr^{3+}/TMP. Therefore, from this analysis we may say that the new peaks appeared around the RT of cyclohexene in each case may correspond to the cyclohexene produced as a result of the catalytic action of the support materials. Furthermore, to confirm for the RT, we have mixed the distilled cyclohexene and cyclohexanol and the GC analysis was conducted. The result again demonstrates that the RT agrees with the above results given.

Thus, from the retention time coincident test as well as peak enhancement, it is possible to conclude that the major peaks appeared in the chromatogram of the catalytically refluxed samples is dehydration product, cyclohexene.

Therefore, the supported metal catalysts have demonstrated to be dehydrating agent of cyclohexanol and the catalytic activities could be a result of Lewis or Bronsted acid sites. The order of decreasing of the dehydrating ability is Fe^{3+}/ZrVP (48%) > Cr^{3+} /ZrVP (35%) > Cu^{2+}/ZrVP (29%) > Cr^{3+} /LVP (7%) > Cr^{3+} /TMP (6%). In all of the cases ZrVP supported catalysts have greater efficiency than that of LVP and TMP. Generally, to account for the activity differences among such solid supported catalysts one has to consider structural aspects, the nature of active sites, surface defects and how they are involved in the surface catalysis [64]. 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 [38, 64]. All of these ideas in one or the other way, are related to the surface phenomena which is poorly understood [38, 77] in comparison to homogeneous catalysis.

The reverse process, reflux of cyclohexene with five supported catalysts, was not possible even in the presence of water. Many factors may be involved, why these catalysts are unable to hydrate cyclohexene, as it is mentioned above in relation to the activity difference between the supported catalysts. Although, from the reactions mechanism of hydration and dehydration process, protonation is the first step, the former process, which is hydration of cyclohexene did not under go. One possible explanation may be, since, we have used the triply charged Fe(III), Cr(III) cations and a doubly charged Cu(II) ion, have strong affinity Lewis acid sites to wards water molecules bound the water molecules. Thus, the hydration reactions may be hampered by this phenomenon.

On the other hand, the inaccessibility of spectroscopic instruments like GC-MS, did not enable us to get further analyses of the chromatogram.

Confirmatory tests were carried out in order to examine the presence of the cations. Qualitative tests were done using KSCN, to confirm for the presence of a trace amounts of Fe(III) ion. The thiocyanate solution may exhibit a deep red colour in the presence of Fe^{3+} due to the formation of $Fe(SCN)_3$. But, the test with Fe^{3+}/ZrVP refluxed sample shows no sign of such element. Like wise for Cu^{2+}/ZrVP refluxed we have used NaOH solution, and no sign of pale blue precipitate observed which is an indication of Cu^{2+} ion. Furthermore, quantitative tests were done for the five catalytically refluxed samples using AAS. But, the result obtained confirms the absence of such elements. Therefore, we conclude that all the reactions undergo and the products obtained are from the supported catalysis.

5. *CONCLUSION*

The supported metal catalysts have demonstrated to be dehydrating agents of cyclohexanol and in this work ZrVP supported catalysts shows a promising dehydrating ability. The catalytic activities could be the result of Lewis or Bronsted acid sites. Similar results by other workers have been reported using montmorillonite in the Al^{3+} form at temperatures 200 °C [76]. The reverse process was not possible even by refluxing the cyclohexene in the presence of water.

From the studies of fundamental properties, the results demonstrate the feature of synthetic inorganic materials as a support in catalysis is promising .

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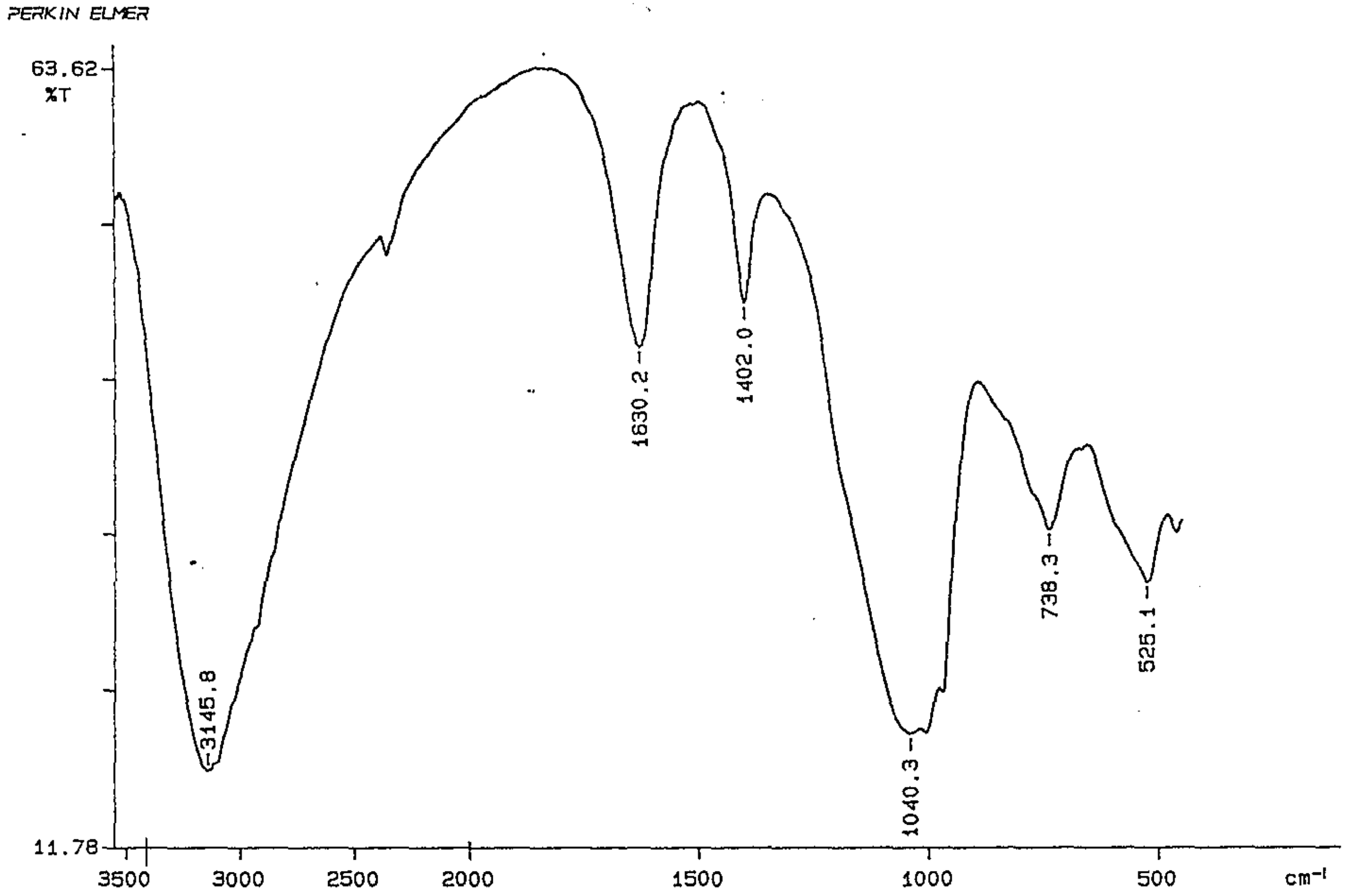

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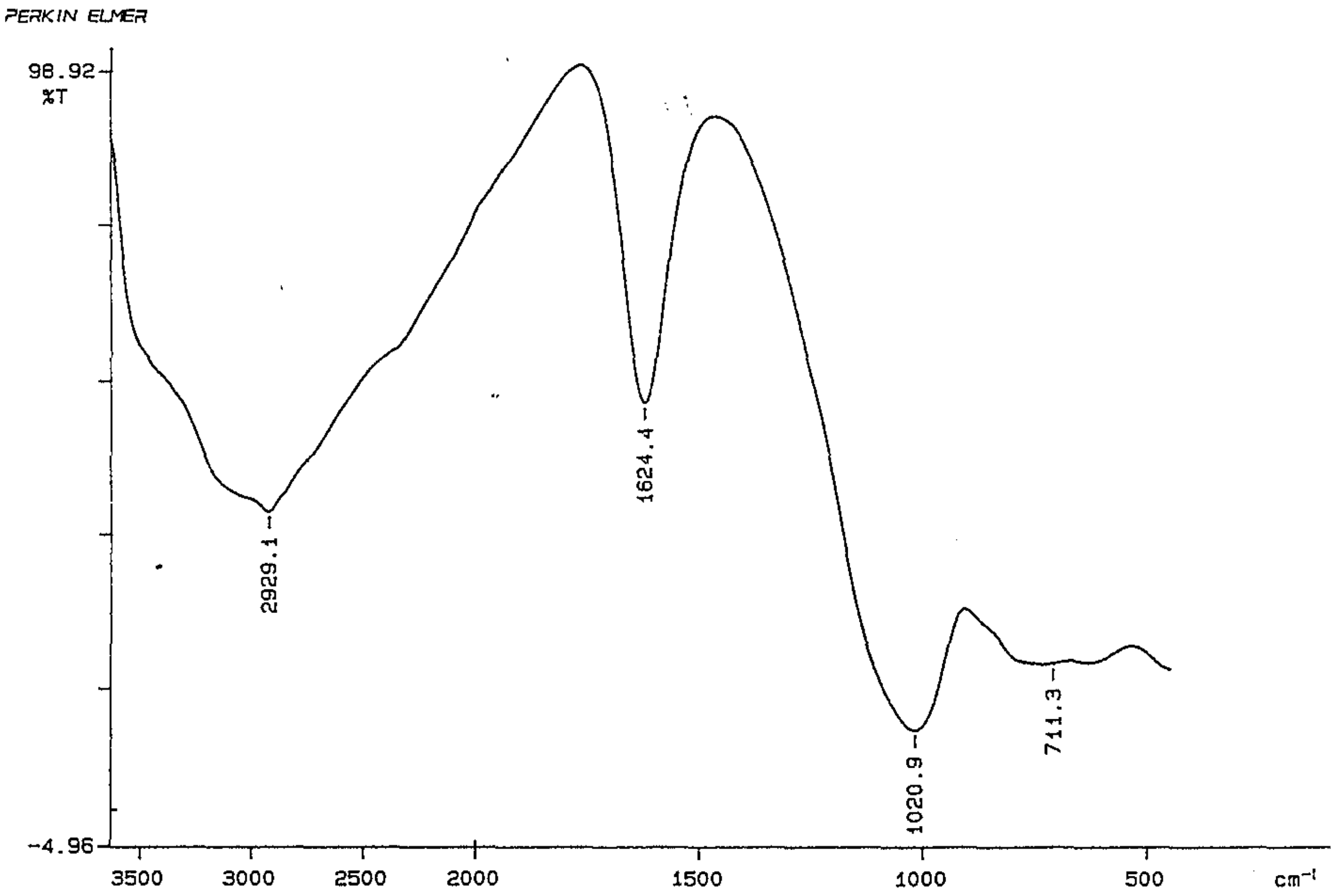

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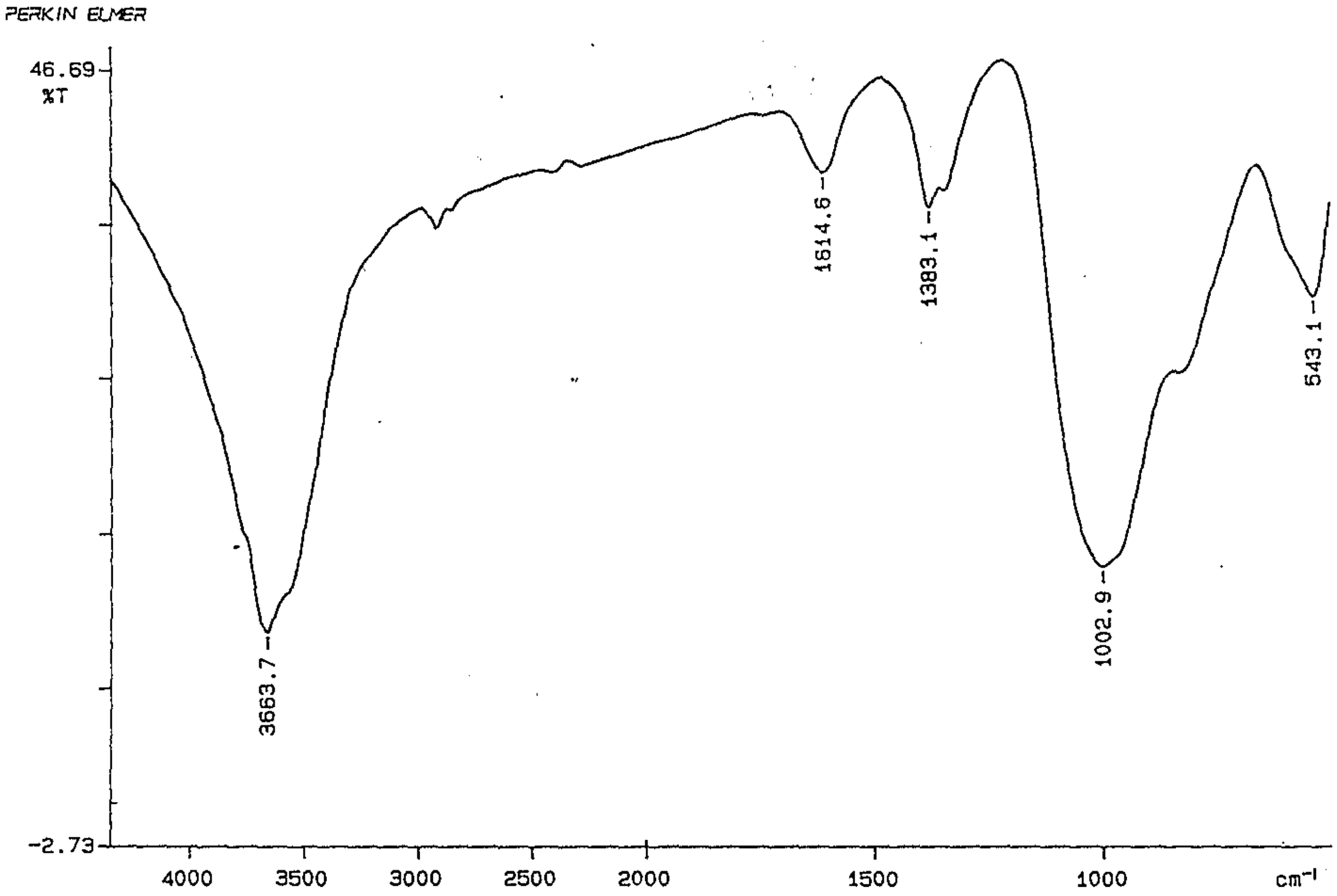
YohannT1 .TMP/H KBr



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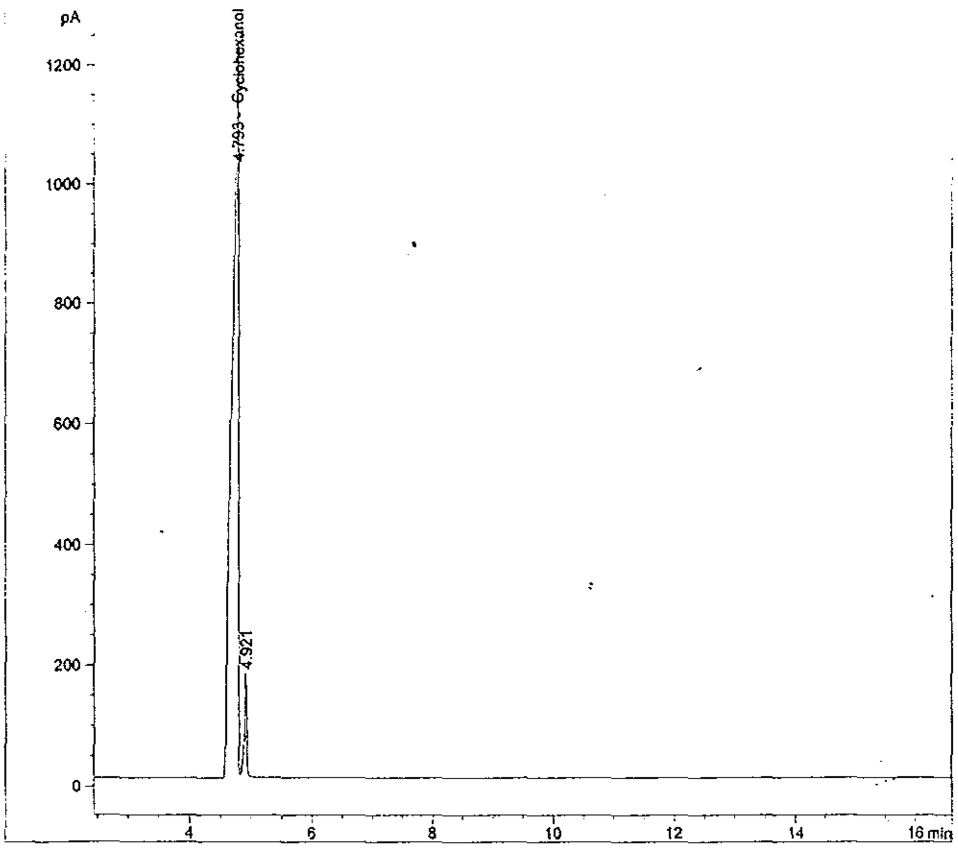
Current Chromatogram(s)



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-----------------------------------------------------------------
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      2                  0.000 475.620   5.098   0.000    4.921
-----------------------------------------------------------------
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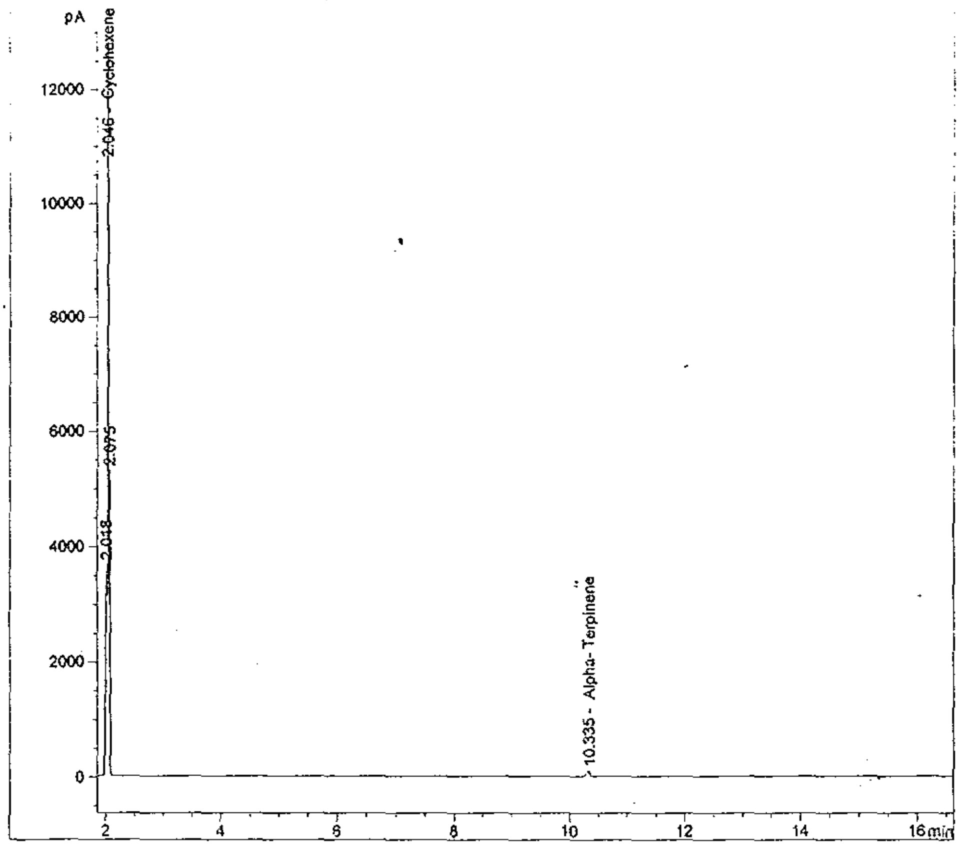
Pure cyclohexanol

Print of window 38: Current Chromatogram(s)

Current Chromatogram(s)



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------------------------------------------------------------------
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          2               0.000 1.520e4  54.880   0.000    2.046
          3               0.000 6.237e3  22.514   0.000    2.075
          4               0.000 423.345   1.528   0.000   10.335
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Totals:                   0.000
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distilled cyclohexene

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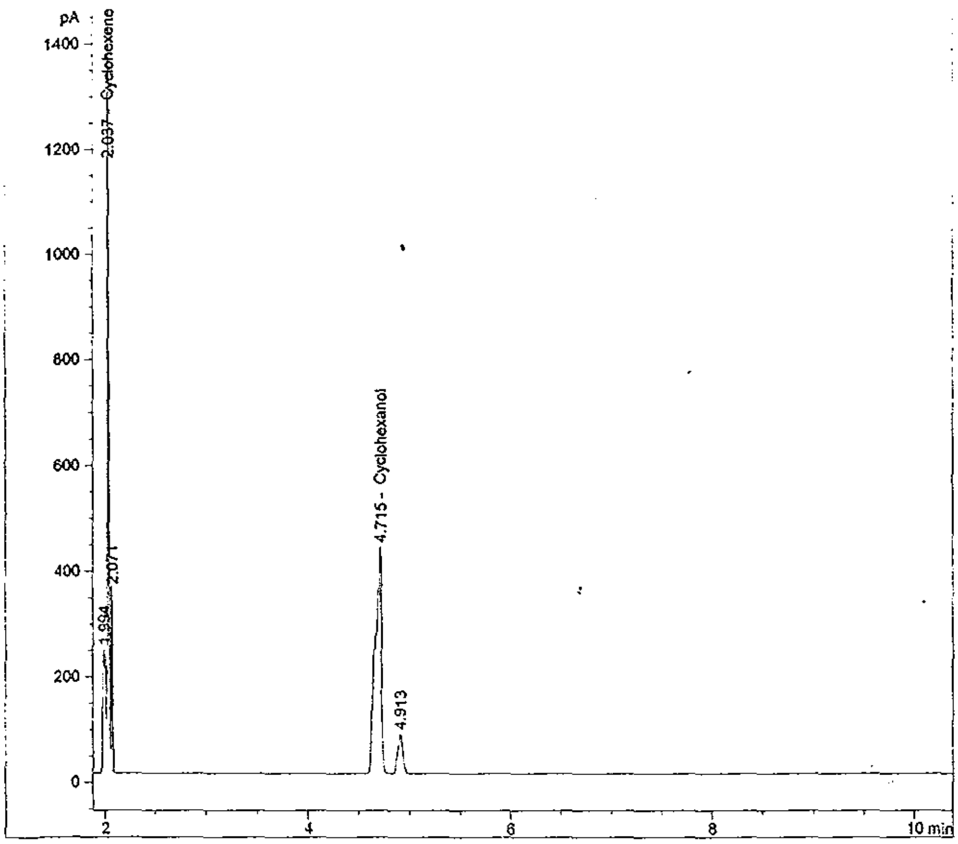
Current Chromatogram(s)



```
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----------------------------------------------------------------
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  2                     0.000 1.207e3  29.058   0.000    2.037
  3                     0.000 329.518   7.936   0.000    2.071
  4                     0.000 1.854e3  44.661   0.000    4.715
  5                     0.000 272.784   6.569   0.000    4.913
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Cu^{2+}/ZrVP

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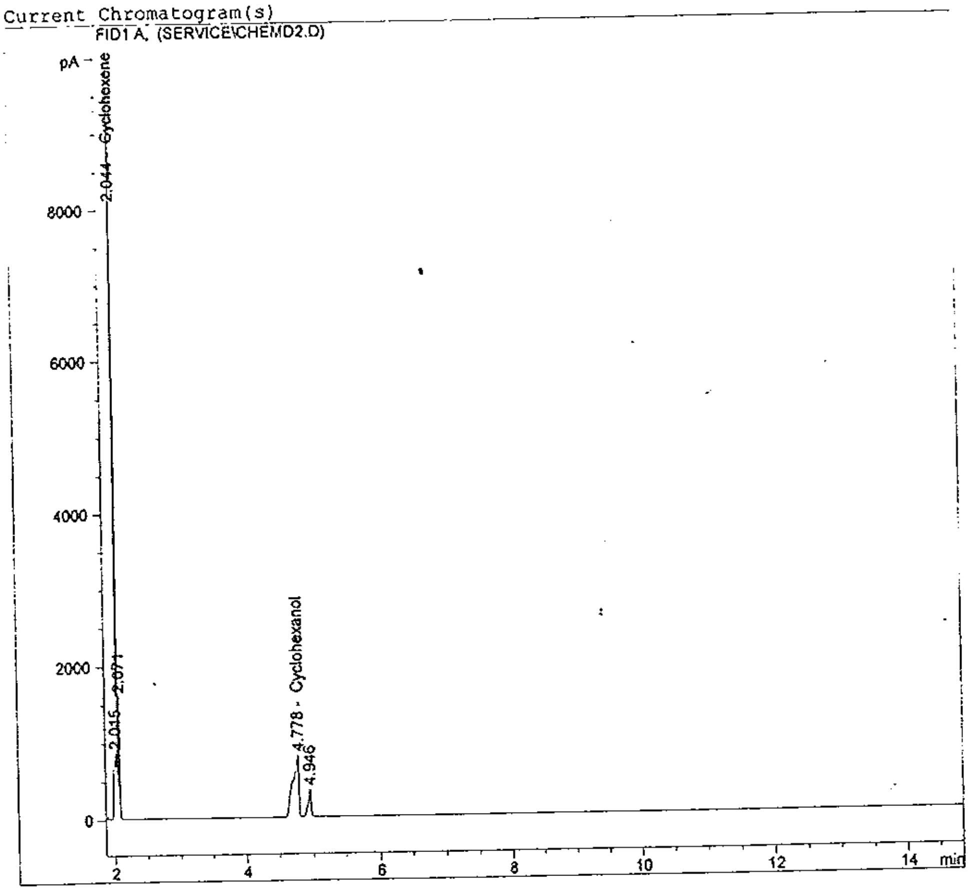

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      3                0.000 1.498e3   8.316   0.000    2.071
      4                0.000 4.772e3  26.484   0.000    4.778
      5                0.000 1.089e3   6.046   0.000    4.946
---------------------------------------------------------------
Totals:                0.000
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Instrument 1 5/8/98 4:52:29 PM Tsegereda

Fe^{3+}/ZrVP

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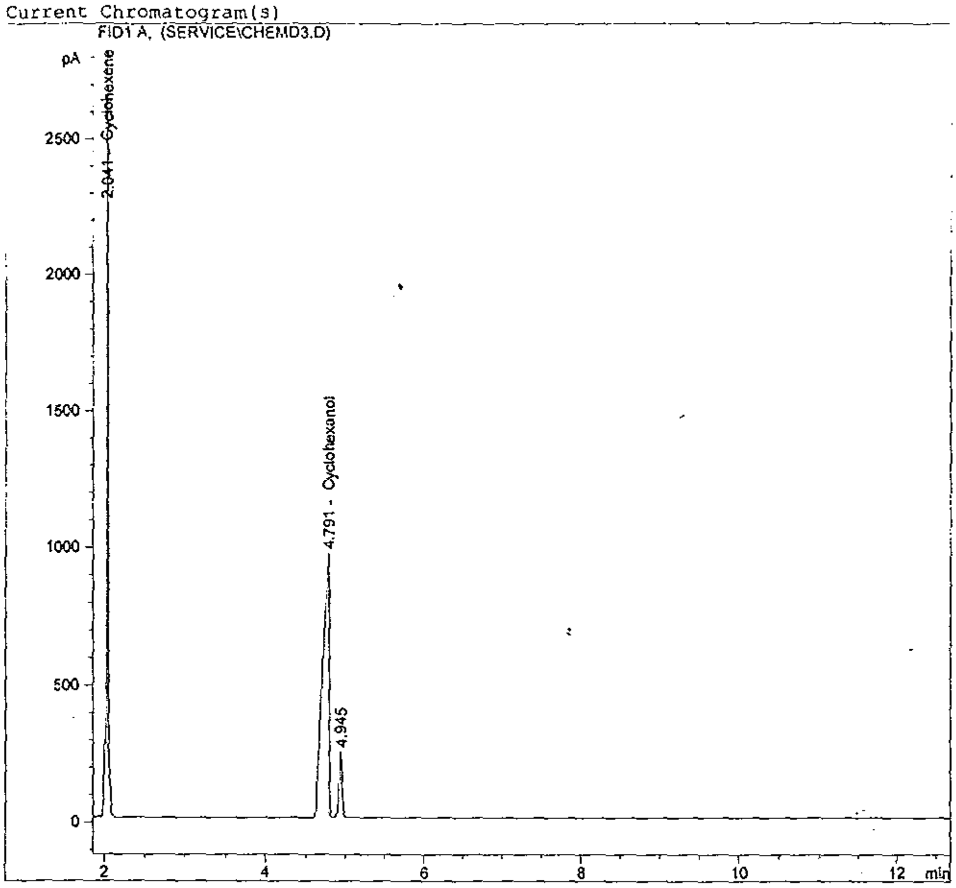

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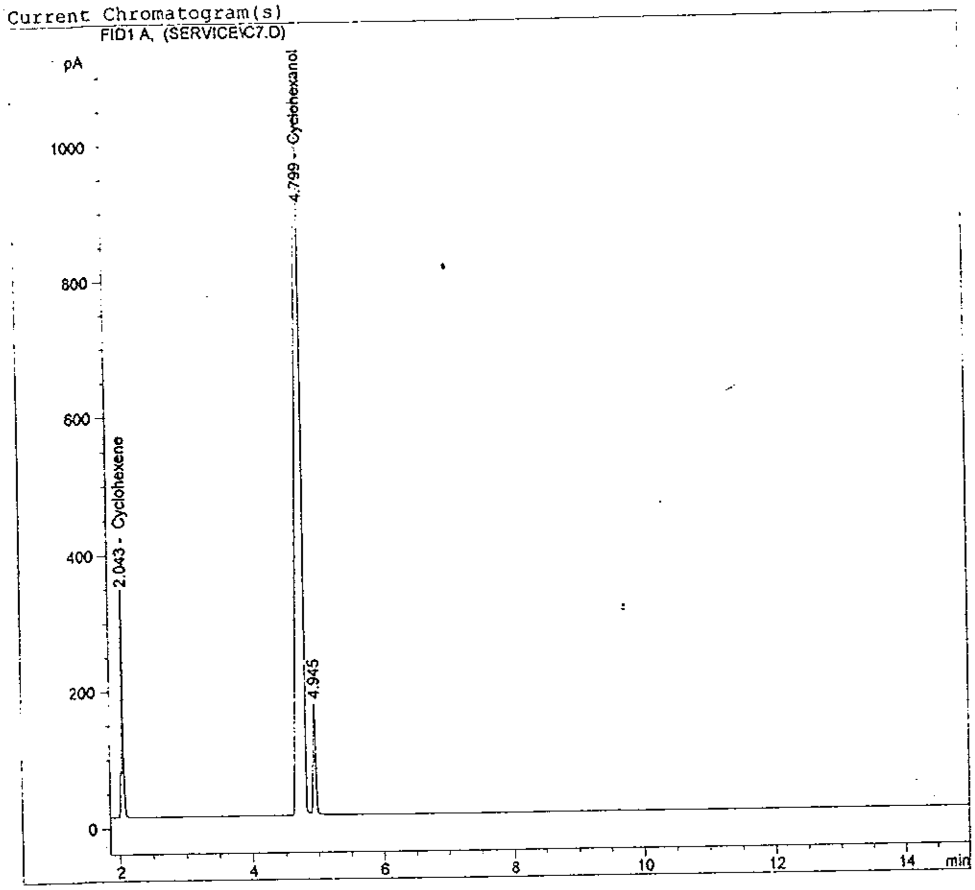
 #     Compound Name  Amount    Resp.   Resp.%  Exp.RT  Meas.RT
----------------------------------------------------------------
 1                    0.000  3.358e3   34.892   0.000    2.041
 2                    0.000  5.623e3   58.430   0.000    4.791
 3                    0.000  642.725    6.678   0.000    4.945
----------------------------------------------------------------
Totals:               0.000
```

Cr^{3+}/ZrVP

Print of window 38: Current Chromatogram(s)



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#     Compound Name  Amount    Resp.   Resp.%  Exp.RT  Meas.RT
--------------------------------------------------------------
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2                     0.000 6.594e3   87.397   0.000    4.799
3                     0.000 431.110    5.714   0.000    4.945
--------------------------------------------------------------
Totals:               0.000
```

Instrument 1 5/11/98 2:31:18 PM Tsegereda

Cr^{3+}/LVP

```
Print of window 38: Current Chromatogram(s)
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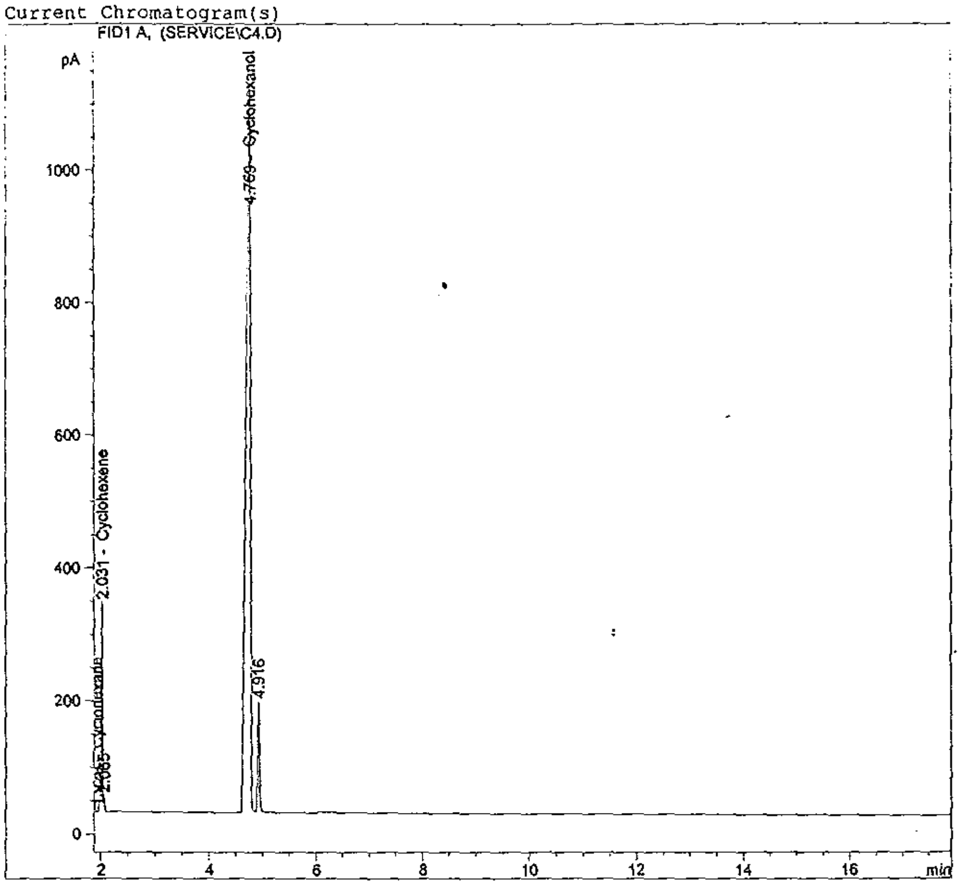

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------------------------------------------------------------------
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     2                   0.000    1.504    0.021    0.000    1.929
     3                   0.000  443.453    6.204    0.000    2.031
     4                   0.000   23.717    0.332    0.000    2.065
     5                   0.000  6.225e3   87.081    0.000    4.769
     6                   0.000  418.857    5.860    0.000    4.916
                         0.000   35.900    0.502    0.000   21.071
------------------------------------------------------------------
:otals:                  0.000
```

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Instrument 1 5/11/98 2:15:15 PM Tsegereda
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Cr^{3+}/TMP

የአዲስ አበባ ዩኒቨርሲቲ
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ADDIS ABABA UNIVERSITY
Addis Ababa,ETHIOPIA

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Date June 19/1998
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Ref.No. CD/92/3-12a/98

To: **Prof Theodros Solomon**
Dean, SGS

From: **Wendimagegn Mammo** Wendimagegn Mammo
Chairman, Department of Chemistry

Subject: **<u>MSc Theses</u>**

The following MSc Candidates in Chemistry have successfully defended their MSc theses between June 8 and 12, 1998.

1. Tesfaye Refera
2. Abi Tadesse
3. Derib Shewangizaw
4. Yohannes Ali
5. Kahsay G/Medhn
6. Kasim Ahmed

The research supervisors of all have testified that they have incorporated all comments made by the examining panel in their final versions of their theses.

Thank You

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