Oxidation of Organic Entities Using Heterogenized Ionic Liquids

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Project

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For the Degree of

Master of Technology
In
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By
Khushbu Bhalodiya
(13MCHE14)

Guided By
Dr. Rajshekhar Ghosh & Dr. R. K. Mewada

DEPARTMENT OF CHEMICAL ENGINEERING
INSTITUTE OF TECHNOLOGY
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AHMEDABAD - 382481
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This is to certify that

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2. Due acknowledgment has been made in the text to all other material used.

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Abstract

Oxidation of olefins founds a vital research area and represents the leading variety of chemical process for manufacturing bulk and fine chemicals. Immobilization of homogeneous catalysts using ionic liquids has received important concern in development of new strategies in various chemical reactions. This organic- inorganic hybrid material has inorganic POM containing kegging anions and room temperature ionic liquid.

In this present work, fabrication of 12-tungstophosphoric acid- imidazolium cation ionic complexes encapsulated during SBA-15 formation. This includes prehydrolyzation of tetraethoxysilane in the presence of surfactant P123, addition of 1-butyl-3-methy limidazolium chloride and successive addition of heteropoly tungstic acid. The obtained hybrid catalyst and spent catalyst of reactions were well characterized. Powder XRD of fresh hybrid material indicates the material possessed good mesoporous character. FT-IR analysis showed that the terminal HPW- based ionic complexes have been incorporated into siliceous SBA-15 successfully with Kegging structure. Naphtha stream sample having mixture of olefins are oligomerized by reaction with activated zeolites. Using hydrogen peroxide mediated olefins oxidations in presence of different solvent and without solvent as test reactions, it was found the hybrid catalyst display best result (96.75% conversation) at synthesized catalyst to oxidant ratio of 0.028 (gm./ml) in presence of acetonitrile solvent which dissolves catalyst completely and generates biphasic system having advantage of handling, separation and reuse. Functional group present in the oxidation product was detected by FT-IR, indicates mixture of aldehyde, alcohol, acids and ethers

Keywords: Olefins, Zeolite, polyoxometalets, ionic liquid, immobilization,Oxidation.

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Nomenclatures

POM	Polyoxometalate
HPA	Heteropoly Acid
IL	Ionic Liquid
HPW	Heteropoly tungstate
TEOS	Tetraethoxysilane
XRD	X-ray diffraction
FT-IR	Fourier transform infrared
GC	Gas Chromatography
AN	Acetonitrile

Chapter 1

Introduction

Immobilization of homogeneous catalysts using ionic liquids has received important concern in development of new strategies in various chemical reactions. This organic- inorganic hybrid material has inorganic POM containing kegging anions and room temperature ionic liquid. It has been noticed that this combination has successful application in a various catalytic reactions like oxidative desulfurization, epoxidation, alcohol oxidation, hydro alkylation, esterification, trans esterification [1].

In this context, a concept is application of heterogenized catalyst for oxidation of olefins. The epoxidation of olefins founds a vital research area and represents the leading variety of chemical process for manufacturing bulk and fine chemicals. The heterogenization concept proposed important advantages in handling, separation and reuse procedures [1, 2].

Polyoxometalate (POM) is a significant part of solid acid catalytic materials with Bronsted acidity and fast reversible multi electron redox conversion under minor conditions and activation of hydrogen peroxide. These properties make them economically and environmentally eye-catching catalyst in homogeneous as well as heterogeneous systems. POMs can react with a many cationic organic clusters to form innovative functional ionic liquid, owing to their great negative charge and bulky metal-oxide structure. The field of polyoxometalate and ionic liquid hybrids is suggested with special consideration paid to their application in heterogeneous catalysis. It has grown numerously due to their environmentally benign behavior and green catalyst.

Polyoxometalate

Polyoxometalate have been familiar and used in lab for nearly 200 years but only after 1950s it is been able to gain richness of their chemistry, structure, and activity. Acid-base attraction of transition metal cations controls size and structure in polyoxometalets. It is a chemistry of metal-oxygen cluster anions, mostly based on Mo, W or V of the initial transition metal in their maximum oxidation states [1]. The maximum considered polyoxo structures formers are molybdenum (VI) and tungsten (VI). Heteropolyanions clusters contain heteroatoms such as Kegging $[XM_{12}O_{40}]$anion, where M is normally Mo or W in their highest oxidation state and X is a tetrahedral template normally phosphorous (P) or silicon (Si). Polyoxometalate chemistry is a current science with an extended and fruitful history and the number of publications has extremely increased in the past years [3, 4, 5].

Heteropoly acid catalysis has keen to the crucial role of the Kegging structure of HPA in both acid and oxidation catalysis. A heteroatom is situated in the center of the heteropoly acid molecule and the atoms bounded to the central heteroatom through oxygen atoms are called polyatoms. A structural model of the Kegging anion was shown in figure 1.1.

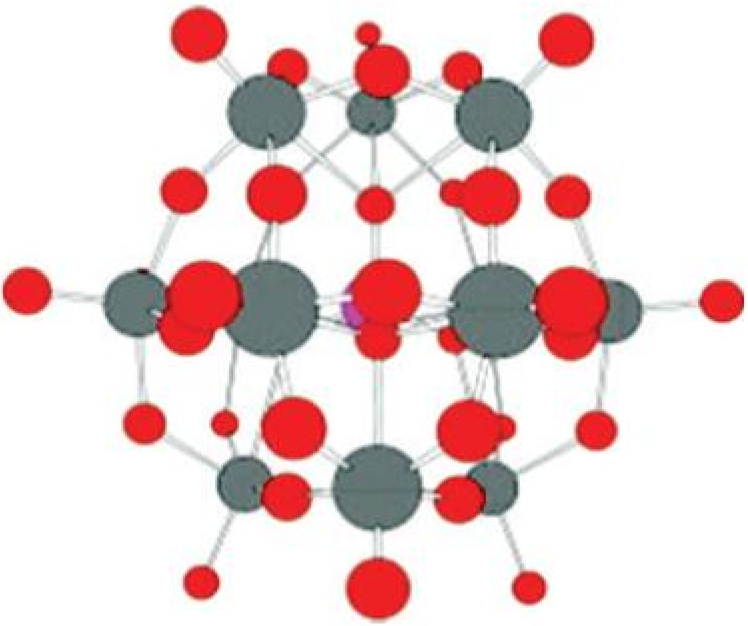


Figure 1.1: Keggin ($XM_{12}O_{40}{}^{n-}$) type polyoxometalate [1]

Polyoxometalate is not only possible to execute a new type of chemistry with the clusters in aqueous solution but also to dissolve them in organic solvents. The assemblies are ruled by the belief that all metal atom inhabits an {MOx} coordination polyhedron and the metal atom is displaced in that as a result of M-O bonding [5, 6, 7, 8, 9].

There are thousands of compounds in the polyoxometalate category which are different in their size, shape, and composition. The polyoxoanion is mostly compensated by the existence of dissimilar type of cations, inorganic or organic. The organic cations compensation approach results in a novel class of hybrid molecular arrangements. This ability offers one of the modern strategies in the material science[1].

Some of the earliest applications of polyoxometalets in general were related with their catalytic activity, and have been used as homogeneous catalyst. Active molecules would get absorbed on supporting material like organic polymer.

Ionic Liquids

Ionic liquid has been creating increasing concern in the last era. Ionic liquids are normally well-defined as salt that melt at or under 100°C and composed only of anions and cation. In several cases those are free-flowing liquids at room temperature. Those ionic liquids have real advantage of ease of handling. They display interesting variety of things which include non-volatility, great thermal stability, non-flammability, worthy electrical conductivity and broader electrochemical properties. However, the ILs in the chemical reactions can act either as a solvent, as a catalyst or a double character—solvent and catalyst or cocatalyst, solvent and support, or solvent and ligand. Those have been widely used in the combination of new hybrid materials.

An ionic liquid consist of a cation, which is usually a bulk organic structure with small symmetry. The widely used cations in ionic liquids are based on ammonium, sulfonium, phosphonium, imidazolium etc. The anion of ionic liquids may be organic or inorganic. The solubility of dissimilar types in imidazolium ionic liquids is subject to mainly on polarization and hydrogen attachment capability. Saturated aliphatic compounds are normally only thinly soluble in ionic liquids, where olefins show slightly greater solubility, and aldehyde can be totally miscible [10].

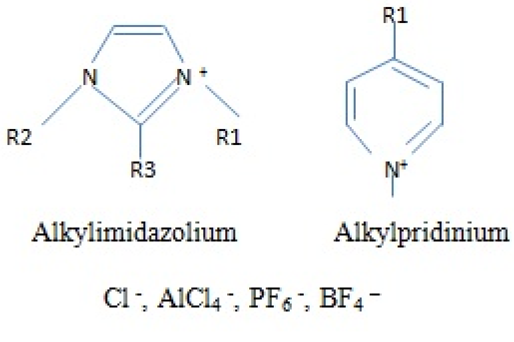


Figure 1.2: Most commonly used anions and cations of ionic liquid

Advantages of ionic liquid are,

1) Extremely low vapor pressure and virtually non-volatile.

2) It can dissolve a various organic, inorganic, polar and nonpolar substances.

3) It can have acidic and super acidic properties.

Polyoxometalate and Ionic Liquid Hybrids

The hybrid materials are shaped them in order to take benefit of both inorganic and organic parts. The strength, combined with the widely flexible molecular properties of POMs, including heteropoly acids (HPAs), make them stunning as catalysts. Proton compensated polyoxometalate anions have some benefits as heterogeneous catalyst such as strong acidity, fast redox conversion converting them to effective oxidants. The area of hybrid materials is quite beginning but it has gain quick growth, both considering new material and applications.

In despite of the benefits of the POMs, those present two major disadvantages in the catalytic system containing original heteropoly acids are, minor surface area in nonpolar solvents availability accessibility of reactants to active sites and high solubility in polar solvents having problems of reuse and separation. So. The heterogenization has been demonstrated to solve the problem, such heterogeneous HPW catalysts frequently undergo from poor accessibility of the H_2O_2 [11].

Ionic liquid as transformers in supported systems will reasonable alter the surface properties of the support and transfer IL's properties to material which is important in heterogeneous catalysis. In certain cases it has capacity of activating heteropoly acids, leading to high catalytic efficiency. HPA complexes, founded on imidazolium cations have been gained significant attention in catalysis. Ionic liquids with the special solubility and the flexible design ability have been attracted much attention[12].

1.1 Scope of the Project

The aim of this project is to oligomerize the mixture of olefins to their dimer/higher oligomer and successively oxidation reaction of these dimer/higher oligomer. Reporting the best catalyst for oligomerization out of proposed catalyst and other parameters affecting oxidation reactions are also a part of this work. The kinetics of the reactions is performed and data is fit to suitable rate equations.

Objectives

1. To find out best catalyst for oligomerization of olefins out of proposed catalyst and characterization of product as and when required.

2. To identify the components involving in the standard naphtha stream.

3. Synthesis of heterogenized catalyst as per the discussed in literature.
4. To check the effect of various parameters like the reaction temperature, the molar ratio of H_2O_2 to organic moieties, the reaction time.
5. Obtain total conversation data with respect to time and to generate kinetic data for oxidation reaction.
6. Characterization of prepared catalyst and spent catalyst of oxidation reaction.
7. Characterization of obtained product.

Chapter 2

Literature Survey

The more strict environmental rules have forced petroleum refiners and chemical manufacturing to reduce the cost for waste removal. To reduce the cost related with separation and removal of chemical waste, the process industry needs to shift from homogeneous catalyst to supported catalyst.

The oligomerization is effected by the catalyst and reaction conditions during the reaction. At initial stage olefins oligomerization was through boron trifluoride promoter complex. But boron trifluoride was found to be a pulmonary irritant and breathing effect cause health hazards.

Oligomerization of olefins by solid catalyst is a difficult reaction where textural properties of the catalyst show a major role in defining the product. Development in zeolites and their application as catalyst to oligomerize lower olefins to gasoline and disel have been reported. Acidity and pore size are important elements for maximizing oligomerization. The extent of oligomerization of olefins is found to be appereciably increased when the zeolites had higher silica/alumina ratio [13, 14, 15, 16, 17, 18, 19].

2.1 Reviews on Oxidation of Alcohol

Kegging type phosphotungstate, has usual much attention in the terms of green chemistry. Phosphotungstate have decent solubility in water so heterogenization of the homogenous catalysts is very eye-catching to overcome the difficulty of recovery. Free amino clusters adaptably attached on the imidazolium plays key role in increasing the availability of H_2O_2. Tan et al. used to immobilize the $H_3PW_{12}O_{40}$ on 1-(3-aminopropyl)-3- propylimidazolium bromine modified SBA-15. They used the ability of the SBA-15 supported ionic liquid to carry out the anionic exchange to load the $PW_{12}O_{40}{}^{3-}$ anion on the surface. Various catalyst of hybrid was more active than the kegging-type HPW, that proposed the serviceability of hybrid for charging the PW anions. PW(0.16)-NH2-IL(0.4)-SBA-15 catalyst delivered 92% of benzyl alcohol conversion with 91% of selectivity to benzaldehyde with 30% H_2O_2. Catalyst can be reused without degradation and/or leaching. Oxidation of secondary aliphatic alcohols gave good conversions to the corresponding ketones. While primary aliphatic alcohols were not oxidized efficiently under solvent free conditions. Conversion for aromatic secondary alcohols was comparatively higher than the aliphatic secondary alcohols (1-phenylethanol (97%) and Diphenylmethanol (95%)) [11].

Zhao et al. offered preparation of the hybrid by one pot synthesis. In this, hybrid is encapsulating directly during SBA-15 development. There were no practically catalytic activities of polyoxomrtalate free catalyst in oxidation of benzyl alcohol to benzaldehyde. Catalyst prepared by the one-pot procedure showed slightly lesser conversion and selectivity than prepared by multi step but show better reusability . More specially, catalyst prepared by multi step showed slow deactivation during the reuse process. These both catalysts prefer to oxidize secondary alcohols aver primary alcohols.[12].

Molecular oxygen is the finest oxidant due to low cost and environmental benefits. But, by using reducing agent (ascorbic acid), the conversion and selectivity to phenol in benzene oxidation by oxygen can be enhanced. Y. Liu et al. suggest benzene oxidation by molecular oxygen to phenol with ascorbic acid as a reducing agent to be effectively catalyzed by the transition metal exchanged phosphotungstate stabilized with quartrnary ammonium salt $[(C_4H_9)_4N]_m[XW_{11}YO_{39}H_2O]$. W- containing transition metal substituted polyoxometalete compounds efficiently catalyzed benzene oxidation with molecular oxygen. The selectivity to phenol could be enhanced by addition of sulfolane solvent in reaction scheme. [20].

Some efforts have been applied to increase the stability and lifetime of the Kegging structure through protection with organic cation as an alternative of supporting it on carrier. Combining HPAs with room temperature ILs proposed some interesting material. Ivanova et al. reported pure heterogeneous gas phase oxidation of methanol over 1-butyl, 3-methyl imidazoleum based POM hybrids ($BmimPMo_{12}O_{40}$ and $BmimPW_{12}O_{40}$). Here, special consideration was paid by authors to the thermal stability of hybrids as role of Keggin anion. The fresh hybrids do not catalyze the oxidation of methanol but after some activation procedure (carried out at 400°C) showed a high activity. The selectivity of dimethyl ether nearly 100% at 275°C for both catalysts. But hybrid constructed on phospomolybdic acid present higher activity. The partial decomposition of the hybrids in the activation process can act as precursor of catalytically active species and thus results in active and more selective catalyst. [21].

Table 2.1: Summary of alcohol oxidation reaction and hybrid applied

Reaction	**Model compound**	**Hybrid**	**References**
Alcohol Oxidation	Benzyl alcohol and H_2O_2	Immobilized the $H_3PW_{12}O_{40}$ on 1-(3-aminopropyl) -3- propylimidazolium bromine modified SBA-15	Tan et al.
	Various Benzylic alcohols and H_2O_2	Phosphotungstic based ionic liquid immobilized on mesoporous silica by one pot and multistep synthesis	Zhao et al.
	Benzene with oxygen and ascorbic acid	Transition metal exchanged phosphotungstate stabilized with quartrnary ammonium salt $[(C_4H_9)_4N]m$ $[XW_{11}YO_3.9H_2O]$	Liu et al.
	Methanol and O_2	1-butyl, 3-methyl imidazoleum based POM hybrids ($BmimPMo_{12}O_{40}$ and $BmimPW_{12}O_{40}$)	Ivanova et al.

2.2 Reviews on Epoxidation

Epoxidation is a chemical reaction in which an oxygen atom is joined to an olefinically unsaturated molecule to form a cyclic structure. The product of this reaction is known as epoxide. Epoxides and their by -products are largely utilized in industrial process and as multipurpose synthetic intermediate. Tungsten based catalyst having polyoxometalates generally show high epoxide selectivity.

Hydrogen peroxide based catalytic epoxidation has gained much importance from an environmental and economic aspects. Yamaguchi et al. suggested the immobilization of the peroxotungstate catalyst on ionic liquid modified SiO_2 as an efficient heterogeneous epoxidation catalyst with H_2O_2. Out of all soluble transition metal-based catalysts, tungsten-based catalysts with polyoxometalates indicate the high efficiency of H_2O_2 employment and the high selectivity to the epoxides. 1-Octyl-3-(3-triethoxysilipropyl)-4,5-dihydroimidazolium chloride was used as ionic liquid. Epoxidation of olefn like cis-2-octane, cis-ß-methylstyrene, cycloheptene, cyclooctene show > 99% yield of epoxide. For the epoxidation of cyclooctane, this catalyst can be recovered by the filtration and recycled at least three times with no loss of the catalystic activity and selectivity [22].

Poly et al. proposed very interesting result on immobilization of peroxophotungstate on polymeric support. They prepared various polyoxotungstate catalyst supported on amphiphilic resin by ion exchange with the help of methylimidazole and imidazole based ionic liquids using different alkyl subsitutes. The amphilic resins act as phase transfer catalyst between the H_2O_2 and the ester phase. In the epoxidation of cis methyl octadecenoate with H_2O_2 under O_2 flow, the catalytic activities of the hybrids were found to differ with the hydrophilic/lipophilic balance. The decress of the extent of alkyl chain favors the contact between reactant and oxidant agent and therefore incress in the conversion. To incress contact between the reactant and the active site, they added a spacer arm [23].

H. Li et al. presented two new catalys prepared by coupling imidazolium cation with Venturello anion. The catalyst was finely dissolve in the solvent so it can create self-separation system after the reaction ended. These were first applied to expoxidize cyclooctane without solvent. The catalyst can be recycled for next four times without noticable loss of activity. The reactnat was converted into the analogous epoxide in organic solvents dichloromethane, benzene, ethyl acetate. This catalyst can be used for five repeated catalytic cycles with slight decrease in conversion from 97% to 92%, which might be due to slight deactivation of the recovered catalyst [24].

Table 2.2: Summary of epoxidation reaction and hybrid applied

Reaction	**Model compound**	**Hybrid**	**References**
Epoxidation	Olefins and H_2O_2	Immobilization of the peroxotungstate catalyst on ionic liquid1-Octyl-3-(3-triethoxysilipropyl)-4,5 -dihydroimidazolium chloride modified SiO_2	Yamaguchi et al.
	methyl-9,10-octadecenoate and H_2O_2 , O_2	Polyoxotungstate catalyst supported on amphiphilic resin by ion exchange with the help of methylimidazole and imidazole based ionic liquids using different alkyl subsitutes	Poly et al.
	Cyclooctene and H_2O_2	POM-RILs by alkylimidazolium cation with Venturello anion	H. Li et al.
		Zwitterion phosphotungstate ($DSPIM_7$-PW_{11})	Y. Qiao et al.
		Heteropolytungstate-ionic liquid hybrids on the surface of silica coated magnetite particles	Bagheri et al.
	Oleic acid and H_2O_2	$Q_3\{PO_4[WO(O_2)_2]_4\}$	Kozhevnikov et al.

Y. Qiao et al. developed a process for epoxidation of cyclooctane over a hybrid material zwitterion-phosphotungstate. They demonstrated strong cooperative role between sodium phosphotungstate and zwitterions. This was found to be highly efficient for solvent free epoxidation at 0°C. Stable emulsion permits cyclooctene being in proper contact with the active phosphotungstate anion in the water phase. The whole catalytic system formed a stable emulsion without any other solvent during the reaction; organic solvent was needed to extract the product after reaction. The catalyst can be reused more than three times with cyclohexane as an extracting agent [25].

Bagheri et al. immobilized HPW-IL hybrids on the surface of silica covered magnetite elementss to get advantages of the separation and recycling of the material by adding the superparamagnetic properties of the magnetite. This silica covered magnetite nanoelements supported IL was synthesized by covalent connection of chloropropyl sily groups and reacted with ionic liquid on surface of silica covered magnetite nanoelements. The resulting material showed an excellent activity (84% conversion with 99% of selectivity) in the epoxidation of cyclooctene with advantages in the separation and thermal stability compared to IL-POM bare systems. The prepared catalyst can be recover and reuse in the epoxidation of cyclooctane with hydrogen peroxide [26].

Kozhevnikov et al. proposed the epoxidation of oleic acid with peroxo phosphotungstate in bi-phasic system. The employed peroxo phosphotungstate yielded 84% of epoxide at 95% of oleic acid conversion without using a chlorocarbon solvent. It was also suggested that in the reaction conditions various peroxophosphotungstate $Q_3\{PO_4[WO(O_2)_2]_4\}$ species coexist which could increase the rate of the reaction [27].

2.3 Reviews on Oxidative Desulfurization

Deep desulfurization of fuels has gained much importance due to stringent environmental regulation and fuel specification. To minimize the emission of SO_X exhaust gas from vehicle engine, the sulfur level in transportation fuel must be reduced. Conventional hydrodesulfurization (HDS) process for desulfurization have many problems like high capital investment, high temperature and high pressure leading to s high operating cost. So, Oxidation desulfurization (ODS) has paying more attention due to mild reaction conditions which give a favorable post treatment approach to the conventional hydrodesulfurization (HDS). Moreover ODS have advantages of short reaction time, high efficiency and selectivity, dibenzothiophene (DBT) and its derivatives converted into analogous sulfoxides and sulfones, which can be removed by extraction.

Metal-based surfactant-type ILs and peroxotungstate have been added to new families and creations of functionalized ILs. Zhu et al. report the preparation of various metal based surfactant type ionic liquids peroxomolybdate and peroxotungstates for the oxidative desulfurization of fuel in oil/water mixture. Catalyst could be recycled with 1 to 10 cycle with a decrease in DBT conversion from 96.2% to 85.4% respectively [28]. Li et al. used POM-IL hybrid catalyst under mild conditions [29]. W. Zhu et al. applied different POM-IL hybrid material for sulfur removal and can be recycled 8 times with slight loss in activity [30].

Table 2.3: Summary of desulfurization of oil reaction and hybrid applied

Reaction	**Model compound**	**Hybrid**	**References**
Oxidative desulfurization	Benzothiophene (BT), Dibenzothiophene (DBT), 4,6- dimethyl dibenzothiophene (4,6-DMDBT) and H_2O_2	Metal founded surfactant type ionic liquids having ammonium cation $[(CH_3)N(n\text{-}C_8H_{17})_3]^+$ combining with polyoxometalates anion	Zhu et al.
		$[Hmim]_5$ $[PMo_{10}]V_2O_{40}]]$ $(H_5PMo_{10}V_2O_{40}]$ with ionic liquid N-methylimidazolium)	Li et al.
		$[MIMPS]_3$ $PW_{12}O_{40}.2H_2O$ (1-(3-sulfonic group) propyl -3-methyl imidazolium phosphotungstate), $[Bmim]_3PW_{12}O_{40}]$ (1-butyl 3-methyl imidazolium phosphotungstate), $[Bmim]_3PMo_{12}O_{40}]$ (1-butyl 3-methyl imidazolium phosphomolybdate) and $[Bmim]_3SiW_{12}O_{40}]$ (1-butyl 3-methyl imidazolium silicotungstate)	W. Zhu et al.

Chapter 3

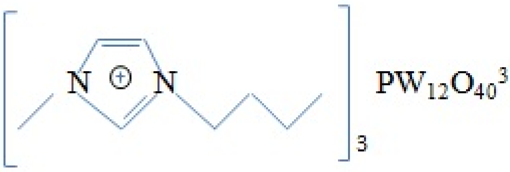
Catalyst Preparation and Characterization

Chemicals Required:

Triblock poly(ethyleneglycol)-poly(propyleneglycol)-poly(ethyleneglycol) ($EO_{20}PO_{70}EO_{20}$, P123) and 1-butyl-3-methylimidazolium chloride was procured from Aldrich and phosphotungstic acid was from Sigma-Aldrich. HCL (Labort) and tetraethoxysilane(Merck).

3.1 Catalyst Preparation

In this preparation method of $[Bmim]_3PW_{12}O_{40}$ (1-butyl 3-methyl imidazolium phosphotungstate) 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$ -HPW) and ionic liquid 1-butyl-3-methylimidazolium chloride were incorporated into SBA-15 mesoporous silicas. One pot synthesis is employed instead of using the ionic liquid modified silica support to charge the POMs by the anion exchange. As suggested by Zhao et al, it includes encapsulating directly hybrid during SBA-15 formation. Here, HPW was chosen because the utmost studied HPAs is HPW and has high stability. Tungstan based POMs displays the high efficiency of H_2O_2 utilization and the high selectivity to the epoxides.



$[Bmim]_3PW_{12}O_{40}$

Procedure

4 gm. of P123 triblock copolymer Pluronic was added to 150 ml of hydrochloride acid (1.6 M). Then solution was stirred and 9.36 gm. of tetraethoxysilane (TEOS) was added at 35°C followed by stirring at 35°C for 4 h. 0.872 gm. of 1-butyl-3-methylimidazolium chloride was added. After the mixture was stirred for time period exact 5 min, 2.10 gm. of HPW was added.

The resultant suspension was kept stirring at 35°C for 24 h and then aged at 80°C for 48 h under static condition. The resulting precipitate was filtered, washed with deionized water several times, and dried in vacuum overnight. The fine white powder was obtained. Soxhlet extraction over ethanol was performed for 48 h for removal of surfactant [12].

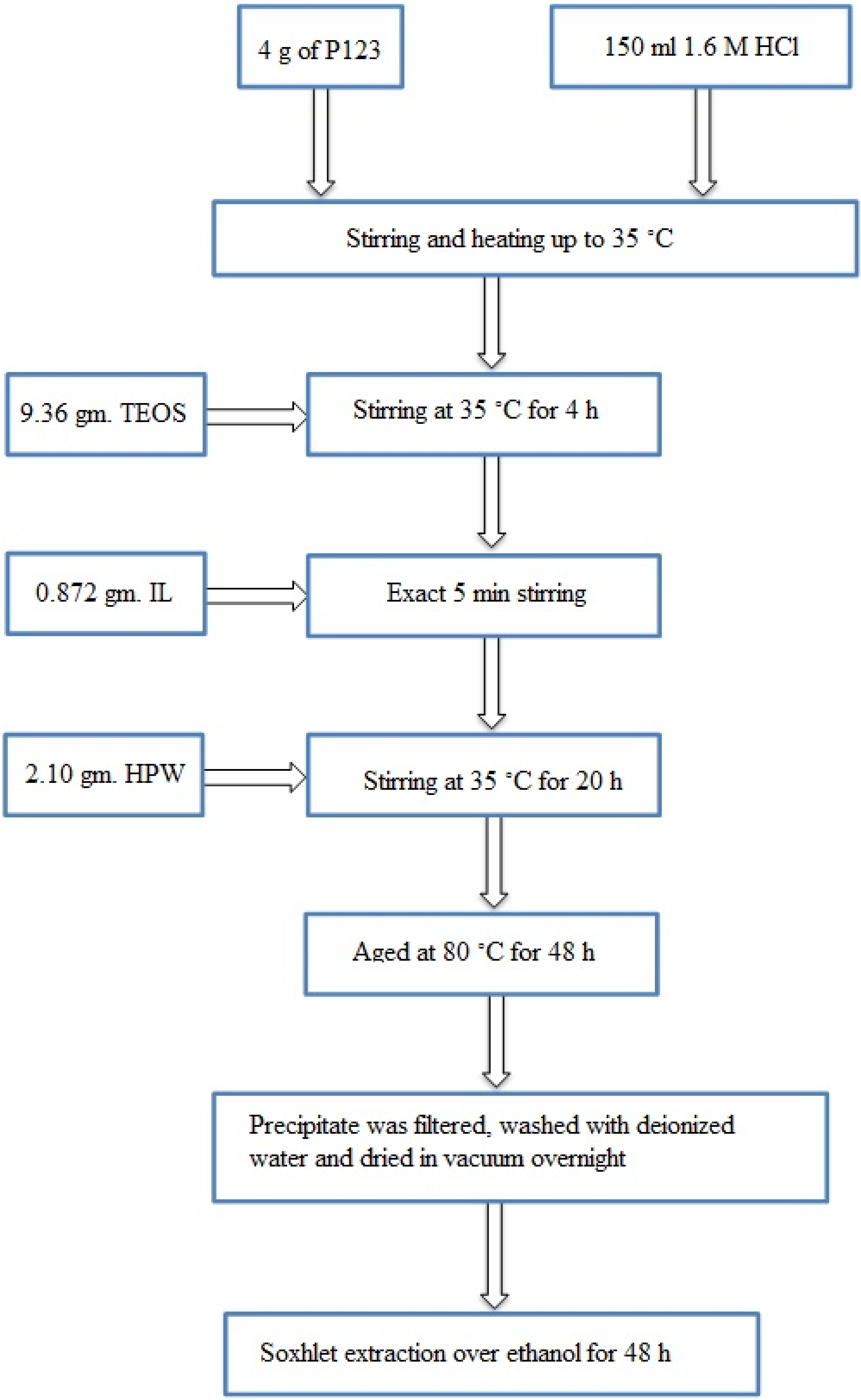


Figure 3.1: Process flow chart for heterogenized catalyst preparation

A Soxhlet extractor is lab apparatus used when the chosen compound has a partial solubility in a solvent, generally a solid material located in a thimble. Thimble was made from dense filter paper, which is kept into the Soxhlet extractor's main chamber. The extractor is located on a round bottom flask having the extraction solvent, here in this case ethanol is used as solvent. The Soxhlet is then furnished with a condenser. Ethanol is heated to reflux and vapour goes up a distillation arm, and overflows into the chamber lodging the thimble of solid. The condenser cools the solvent vapour. After several rounds the chosen compound is concentrated in the round bottom flask.

Figure 3.2: Catalyst after soxhlet extraction

3.2 Catalyst Characterization

Heterogeneous catalyst involves transfer of molecular at the interface between a catalyst and the liquid phase. This transformation contains a sequence of phenomena so, understanding and control of which needs the study of

1) How the catalyst is created in its bulk and at its surface and what alteration it suffers.

2) The nature of the interface.

Characterization provide information about Physical properties like, surface area, pore size and morphology of the carrier; and the geometry and strength of the support and Chemical propertieslike structure, composition, and nature of the carrier and the active catalytic components. Characterization of a heterogeneous catalyst states to the measurement of its 'Characteristics' which are those physical and chemical properties of the catalyst supposed to be responsible for its performance in a proposed reaction [31].

3.2.1 X-ray powder diffraction (XRD)

Powder XRD was analyzed on Bruker D8 advance with wavelength = 1.54 Å. The properties of a material have relation with the arrangement of atoms in its crystal arrangement. X-Ray powder diffraction is used to gain data about the arrangement, composition, and state of materials. X-rays are electromagnetic radiation having 100 eV- 100 keV energy. But for the deflection only small wavelength x-rays are used. The samples may be powders, solids, films or ribbons.

If a beam of X-ray is focused at a crystal material one can notices, reflection of the x-rays at different angles with reference to the primary beam. The connection between the beam wavelengthλ, diffraction angle 2θ and the distance between every planed of the crystal d, is known as Bragg equation,

$$\mathrm{n}\lambda = 2\mathrm{dsin}\,\theta$$

When Braggťs Law is satisfied Bragg reflectionť will be selected by detector scanning at that angle. The locations of those reflections express about the inner-layer spacing of atoms in the structure. Peak strengths revel information about how much X-ray smattering is contributing to that reflection [32, 33].

3.2.2 Infrared spectroscopy

Infrared spectroscopy can be used to detect materials, conclude the composition of mixtures, and provide useful information in deducing molecular structure. Fourier Transform infrared spectra were recorded using Nicolet 6700 using KBr pellets.

Analysis by infrared spectroscopy is based on the point that particles have definite frequencies of inner vibrations. These frequencies happen in the infrared area of the electromagnetic range.

When a sample is positioned in a beam of infrared radiation, it will absorb radiation frequencies equivalent to particle vibrational frequencies, but will transfer all additional frequencies. The absorbed frequencies are measured by an infrared spectrometer, and the generated graph is called infrared spectrum.

Analysis of material is possible because dissimilar materials have different vibrations and produce different infrared spectra. It is possible to detect presence of various chemical clusters from the frequencies in a proposed chemical structure. The mid-infrared, around 4000-400 cm^{-1} might be used to study the important vibrations and related rotational-vibrational structure. Fourier Transform Infrared (FT-IR) interferometer gets information from the whole range of a assumed spectrum during every time of a scan, where as a conventional spectrometer gets information from only the very contracted region [34].

Chapter 4

Component Identification

Standard naphtha stream sample was used for this project. Table shown below indicates list of most probable organic component.

Table 4.1: List of component in the standard naphtha stream

Sr.No.	**Component**	**Unit**	**Sample 1**	**Sample 2**
1	C7 np	wt%	2.02	1.98
2	C7 ip	wt%	0.31	0.33
3	C7 N	wt%	1.32	1.34
4	C7 no	wt%	0.86	0.86
5	C7 iO	wt%	0.43	0.43
6	C7 cO	wt%	1.87	2.00
7	C7 A	wt%	1.27	1.29
8	**Total C7's**	**wt%**	**8.08**	**8.23**
9	C8 np	wt%	6.15	5.66
10	C8 ip	wt%	4.14	4.05
11	C8 N	wt%	4.09	3.98
12	C8 no	wt%	3.11	2.90

Sr.No.	**Component**	**Unit**	**Sample 1**	**Sample 2**
13	C8 iO	wt%	3.12	3.08
14	C8 cO	wt%	4.44	4.60
15	C8 A	wt%	5.35	5.28
16	**Total C8's**	**wt%**	**30.40**	**29.55**
17	C9 np	wt%	6.55	6.04
18	C9 ip	wt%	4.86	4.72
19	C9 N	wt%	5.54	5.52
20	C9 no	wt%	3.07	2.88
21	C9 iO	wt%	3.50	3.33
22	C9 cO	wt%	4.24	4.18
23	C9 A	wt%	6.92	7.66
24	**Total C9's**	**wt%**	**34.68**	**34.33**
25	C10 np	wt%	3.83	4.03
26	C10 ip	wt%	4.25	4.13
27	C10 N	wt%	3.05	3.25
28	C10 no	wt%	1.77	1.89
29	C10 iO	wt%	2.60	2.32
30	C10 cO	wt%	1.47	1.40
31	C10 A	wt%	0.82	0.88
32	**Total C10's**	**wt%**	**17.79**	**17.90**
33	C11 np	wt%	0.69	0.78
34	C11 ip	wt%	1.32	1.53
35	C11 N	wt%	0.00	0.02

Sr.No.	**Component**	**Unit**	**Sample 1**	**Sample 2**
36	C11 no	wt%	0.35	0.40
37	C11 iO	wt%	0.87	0.80
38	C11 cO	wt%	0.05	0.05
39	**Total C11's**	**wt%**	**3.28**	**3.58**
40	BP>200 řC	wt%	1.39	1.49
41	PolyNapth	wt%	4.38	4.92
42	Total n_Paraffin	wt%	19.24	18.49
43	Total iso_Paraffin	wt%	14.88	14.76
44	Total n_Olefin	wt%	9.16	8.93
45	Total iso_Olefin	wt%	10.52	9.96
46	Total c_Olefin	wt%	12.07	12.23
47	Total Olefin	wt%	31.75	31.12
48	Total Naphthene	wt%	14.00	14.11
49	Total Non Aromatics	wt%	79.87	78.48
50	Total Aromatics	wt%	14.36	15.11
	TOTAL	wt%	100.00	100.00

Chapter 5

Experiments

Chemicals Used:

The used chemicals were catalyst Zeolyst CBV 600 and CBV 720 (Zeolyst International), 30 wt. % H_2O_2 (s.d.fine chemical limited), Zinc chloride (LOBA chemie), cuprous chloride (Duchem Lab Ltd.), di ethyl ether and acetonitrile (Labort) and distilled water.

Aim of this work is to first produce dimers/higher oligomer of olefins and subsequently oxidized the obtained oligomerization product by using above synthesized $[Bmim]_3$ $H_3PW_{12}O_{40}$ catalyst.

Zeolites catalysts of specifications mentioned in table 5.1 have been studied to find out the best for the oligomerizations of olefins. Dimerization reaction processed in an acidic environment so the catalyst with the hydrogen as nominal cation has been used for the reactions.

Table 5.1: Catalyst specification sheet provided by manufacturer

Zeolyst Products	SiO_2/ Al_2O_3 Mole Ratio	Nominal Cation Form	Na_2O weight %	Unit Cell Size	Surface Area (m^2/g)
CBV 600	5.2	Hydrogen	0.2	24.35	660
CBV 720	30	Hydrogen	0.03	24.28	780

5.1 Reaction Assembly

5.1.1 Reaction procedure for oligomerization

Standard naphtha stream sample contains high impurities there for, first it was vacuum distilled to extract out desired cut. Then, Zinc chloride and cuprous chloride were added to remove moisture and reduce sulfur containing impurities. Sufficient purification time of 6 hours was provided followed by filtration with simple filter paper. Zinc chloride is extremely soluble in water and hygroscopic in nature. During purification cuprous chloride oxidizes mercaptans therefore resulting bisulfides are less odorous and usually very viscous which was removed in next distillation as bottom product.

The experiments are performed on magnetic stirrer with ceramic heating plate which offers excellent chemical resistance. The typical oligomerization was carried out as follows: 195 ml of of above definite purified naphtha stream sample and specified quantity of activated Zeolyst catalyst were charged into 250 ml round bottom flask equipped with reflux condenser and magnetic bar. The flask was placed in a constant temperature oil bath to keep reaction at desired temperature. The reaction mixture was heated at 120°C for 6 h under continuous stirring.

After reaction, the catalyst was separated by vacuum filtration. The obtained filtrate was vacuum distilled on oil bath to take out desired higher oligomer product which was analyzed on Gas Chromatography.

5.1.2 Reaction procedure for oxidation

An environment benign and green process is extremely desired in research and development but, various oxidants are dangerous and explosive. From environmental and economic feature H_2O_2 is possibly best oxidant as only water is the expected by product and easy work up. Here H_2O_2 is used as oxidant for test reactions.

The oxidation was typically carried out as follows: Predefined quantity of dimer/higher oligomer product, solvent and heterogenized catalyst was charged in two-necked round bottom flask equipped with reflux condenser and magnetic bar. The flask was placed in a constant temperature oil bath to keep reaction at desired temperature. The mixture was heated to definite temperature under continuous stirring followed by adding H_2O_2 drop wise within a period of 30 min. Then, the resultant mixture was stirred at definite reaction conditions.

After completion of the reaction, the reaction mixture was extracted with ether to leave aqueous phase. The product was recovered by evaporating ether and analyzed with bromine number. This aqueous phase contains the catalyst which was recovered by evaporating.

5.2 Gas Chromatography

The GC (gas chromatography) was performed for conformation of product. In this technique, a sample is converted to the vapor state and a flowing stream of carrier gas (nitrogen) sweeps the sample into a thermally controlled column. The information obtained from a chromatographic analysis includes a chromatogram, the heights and the areas of the resolved peaks in the chromatogram.

GC analysis was carried out with 30 m capillary column of 0.53 ID and 0.25 m film thickness and FID detector. Injection sample volume was 0.8 m and injection mode was split.

5.3 Bromine Number Analysis

Bromine number is useful as a degree of aliphatic unsaturation in petroleum samples. It generally shows the concentration of double bonds existing in the sample. Bromine number is expressed as gm. of Bromine (Br_2) react with 100 gm. of sample. It uses the reaction between a ($Br^-/BrO_3{}^-$) solution and the product.

As a titrant mixture of KBr and $KBrO_3$ is used.

Titration solvent:

714 ml of acetic acid (CH_3COOH), 134 ml of dichloromethane (CH_2Cl_2), 134 ml of methanol (CH_3OH) and 18 ml of sulphuric acid (1:5, one volume of concentrated sulphuric acid with 5 volumes of distilled water) [35].

Chapter 6

Result & Discussion

6.1 Oligomerization Reaction Study

An extensive study on Zeolites and environmental benefits led us to some understanding of oligomerization. Here, for this project work Zeolites CBV 600 and CBV 720 were studied.

6.1.1 Reaction behavior study with CBV 600

Table 6.1 shows the effect of catalyst CBV 600 weight on the conversation of naphtha sample olefins mixture to respective dimer/trimer/higher oligomer.

Reaction Conditions:

Temperature 120°C , Reaction time 6 h, Sample Wt. = 195gm.

Table 6.1: Oligomerization reaction with CBV 600

Reaction No.	**Catalyst Wt. (gm.)**	**Product Wt. (gm.)**	**Overall Conversion (%)**	**Conversion with respect to Total olefins (%)**	**Conversion with respect to (n-olefin + i-olefin) %**
1	12	3.15	1.61	5.14	8.38
2	24	10.20	5.23	16.64	27.12
3	36	15.23	7.81	24.85	40.50

Table 6.2 shows the weight of reactant in trapper and in top product of vacuum distillation. As discussed in oligomerization reaction procedure of chapter 3, very low boiling components is enclosed in trapper and unconverted olefins is separated as top product in vacuum distillation.

Table 6.2: Unconverted reactant weight in CBV 600 reaction

Reaction No.	Trap Wt. (gm.)	Distillate Wt. (gm.)
1	34.7	125.03
2	22.03	105.54
3	21.40	76.61

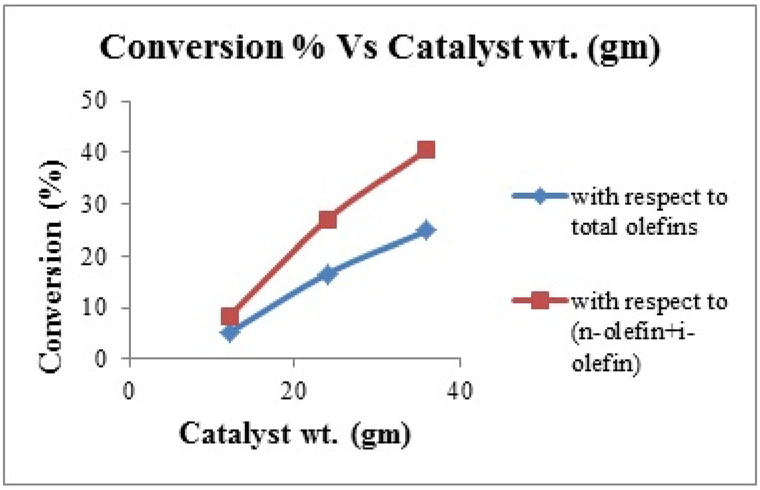


Figure 6.1: Plot of Conversion % Vs Catalyst Wt. (gm.) for CBV 600

From above figure and table it is clear that with increases in catalyst weight, conversation of olefins to dimer/trimer/higher oligomer is also increases and showing best result for 36 gm. of catalyst CBV 600 with 24.85% conversion.

6.1.2 Reaction behavior study with CBV 720

Table 6.3 shows the effect of catalyst CBV 720 weight on the conversation of naphtha sample olefins mixture to respective dimer/trimer/higher oligomer.

Reaction Conditions:

Temperature 120°C, reaction time 6 h , Sample Wt. = 195 gm.

Table 6.3: Oligomerization reaction with CBV 720

Reaction No.	**Catalyst Wt. (gm.)**	**Product Wt. (gm.)**	**Overall Conversion (%)**	**Conversion with respect to Total olefins (%)**	**Conversion with respect to (n-olefin + i-olefin) %**
4	12	10.64	5.46	17.36	28.30
5	24	15.24	7.82	24.87	40.52
6	36	14.60	7.49	23.82	38.82

Table 6.4 shows the weight of reactant in trapper and in top product of vacuum distillation in work up of reactions with CBV 720.

Table 6.4: Unconverted reactant weight in CBV 720 reactions

Reaction No.	**Trap Wt. (gm.)**	**Distillate Wt. (gm.)**
3	4.84	155.10
4	7.64	104.52
5	6.9	83.59

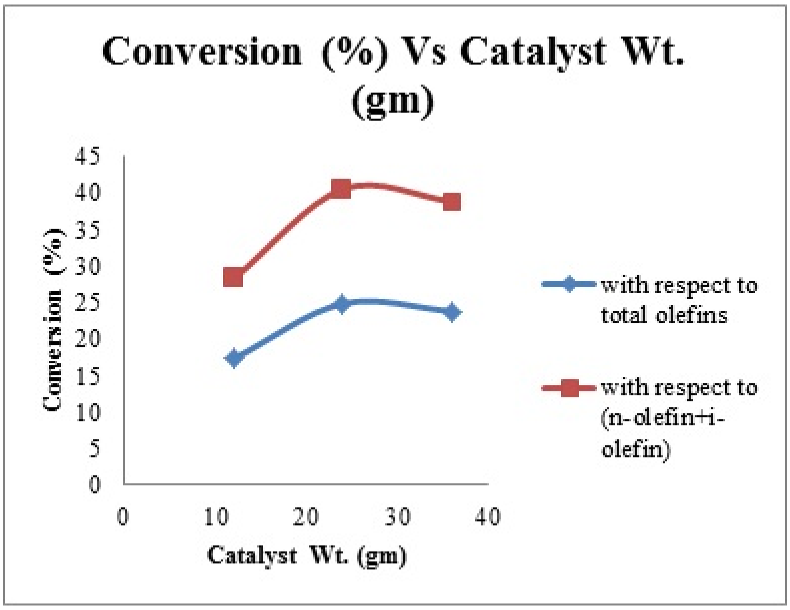


Figure 6.2: Plot of Conversion (%) Vs Catalyst Wt. (gm.) for CBV 720

From figure 6.2, it can be concluded that with increases in the catalyst weight upto 27 gm. conversion of olefins to dimer/trimer/higher oligomer is also increase but after that there is no increase in conversion was observed at proposed reaction condition. It may be due to saturation, inefficient reaction conditions, the optimum catalyst weight for CBV 720 reaction is around 27 gm.

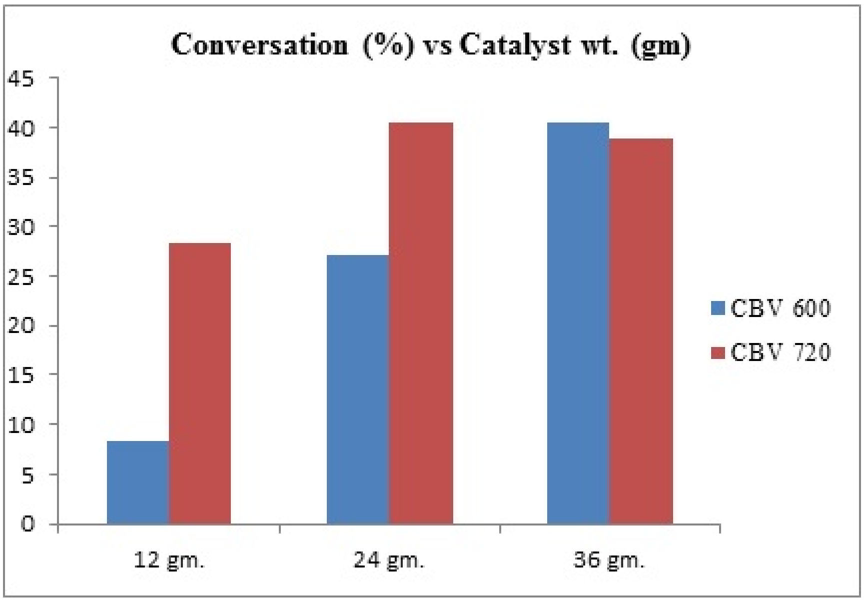


Figure 6.3: Comparison of CBV 600 and CBV 720 catalyst for oligomerization reactions

Figure 6.3 is a bar graph indicates comparation based on conversation for CBV 600 and CBV 720. For first two set up CBV 720 shows higher conversation than CBV 600 but at 36 gm. catalyst weight there is no considerable difference in conversation.

6.2 Oxidation Reaction Study

Dimer/higher oligomer obtained in oligomerization reaction is taken as reactant for oxidation reaction. In these reactions, synthesized hybrid catalyst and hydrogen peroxide are used.

6.2.1 Effect of Reaction time and temperature on conversation

In these test reactions, water is used as solvent to form aqueous phase containing catalyst as discussed in chapter 2 and determined the effect of reaction time and reaction temperature on conversation. Reaction conditions for the same are listed below.

Reaction Conditions:

Oligomer weight = 1.12 gm.(5 mmol), Catalyst weight = 0.1 gm., H_2O_2 =1.8 ml, Distilled Water = 5 ml, Reaction temperature= 100°C

Table 6.5: Effect of reaction time

Reaction No.	**Reaction Time (hr)**	**Oligomer Bromine Number**	**Product Bromine Number**	**Conversion %**
1	6	142	124	12.68
2	12	142	91	35.91
3	24	142	80	43.66

From the above table it is clear that increase in reaction time bromine number is decrease. Hence increase in conversion and still there is a perception to increase conversation by providing more reaction time.

Reaction Conditions:

Oligomer weight = 1.12 gm.(5 mmol), Catalyst weight = 0.1 gm., H_2O_2 =1.8 ml, Distilled Water = 5 ml, Reaction time = 6 hr

Table 6.6: Effect of reaction temperature

Reaction No.	**Reaction Temperature °C**	**Oligomer Bromine Number**	**Product Bromine Number**	**Conversion %**
1	100	142	124	12.68
3	120	142	124	12.68

To determine the effect of reaction temperature a reaction was placed at slight higher temperature of 120°C and keeping the other reaction parameters constant. Table 5 displays that higher reaction temperature has no effect on oligomer conversation. This gives insights that for further interpretations of data one can go for change in reaction time.

For the kinetics data and with aim to acquire maximum conversation, reactions were performed in presence of solvent and in absence of solvent and their effect are analyzed.

6.2.2 Reaction behavior of oxidation reaction with water as solvent

Reaction Conditions:

Oligomer weight = 12 gm., Catalyst weight = 1.0742 gm., H_2O_2 = 19.33 ml, Distilled Water = 53.71 ml, Reaction temperature= 100°C

After specified time interval a representative sample was taken and catalyst phase was extracted by adding ether. Then, ether was evaporated to get organic product and bromine number test was performed. Initial bromine number of the reactant was 166 and relative conversion was predicted from that.

Table 6.7: Reaction conversion data with water as solvent

Reaction Time (hr)	**Bromine Number**	**Conversion %**
6	127	23.49
12	97	41.57
24	85	48.79
36	79	52.41
48	72	56.63
60	72	56.63

From the conversion data it can be concluded that conversation is increases with increases in reaction time and maximum conversion was achieved near to 57% at 48 hrs. reaction time. After that there is no effect of reaction time on conversation this may be due to insufficient quantity of oxidant hydrogen peroxide.

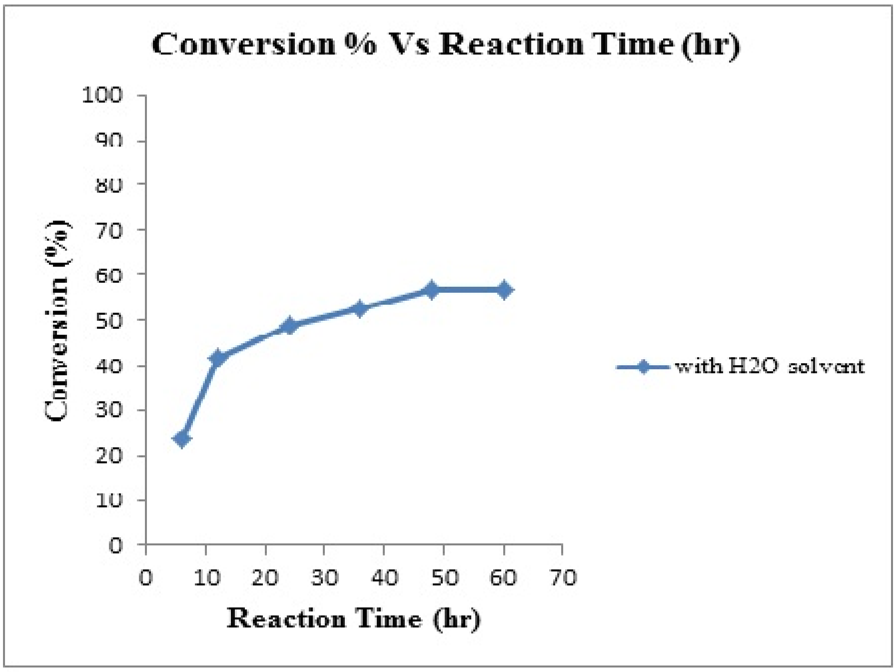


Figure 6.4: Plot of Conversion % vs. Reaction time (hr.) for oxidation reaction with water as solvent

6.2.3 Reaction behavior comparison of oxidation reaction without and with Acetonitrile as solvent

Reaction Conditions for without solvent:

Oligomer weight = 9 gm., Catalyst weight = 0.8036 gm., H_2O_2 = 29 ml, Reaction temperature= 100°C

Reaction Conditions for Acetonitrile as solvent:

Oligomer weight = 9 gm., Catalyst weight = 0.8036 gm., H_2O_2 = 29 ml, Acetonitrile = 20.1 ml, Reaction temperature= 100°C

After specified time interval a representative sample was taken and catalyst phase was extracted by adding ether. Then, ether was evaporated to get organic product and bromine number test was performed. Initial bromine number of the reactant was 185 and relative conversion was predicted from that.

Table 6.8: Reaction conversion data without and with Acetonitrile solvent

Reaction Time (hr)	**Without solvent**		**With Acetonitrile Solvent**	
	Bromine Number	**Conversion %**	**Bromine Number**	**Conversion %**
6	139	24.86	78	57.84
12	125	32.43	51	72.43
24	114	38.38	42	77.30
36	104	43.78	31	83.24
48	98	47.03	21	88.65
60	84	54.59	13	92.97
72	78	57.84	6	96.75
84	71	61.62	6	96.75

With reference to the earlier performed oxidation reaction with water as solvent it can be predicted that lower conversion was achieved due to insufficient quantity of oxidant hydrogen peroxide. So, these reactions were performed with double quantity of oxidant and to determine the effect of solvent other reaction was employed in absence of solvent.

From the table 6.8 and comparison plot for conversation, one can conclude that the reaction in presence of acetonitrile shows exceptionally reputable result as compared to without solvent. This may be cause of solvent dissolves catalyst completely and generates biphasic system which was not observed in case without of solvent.

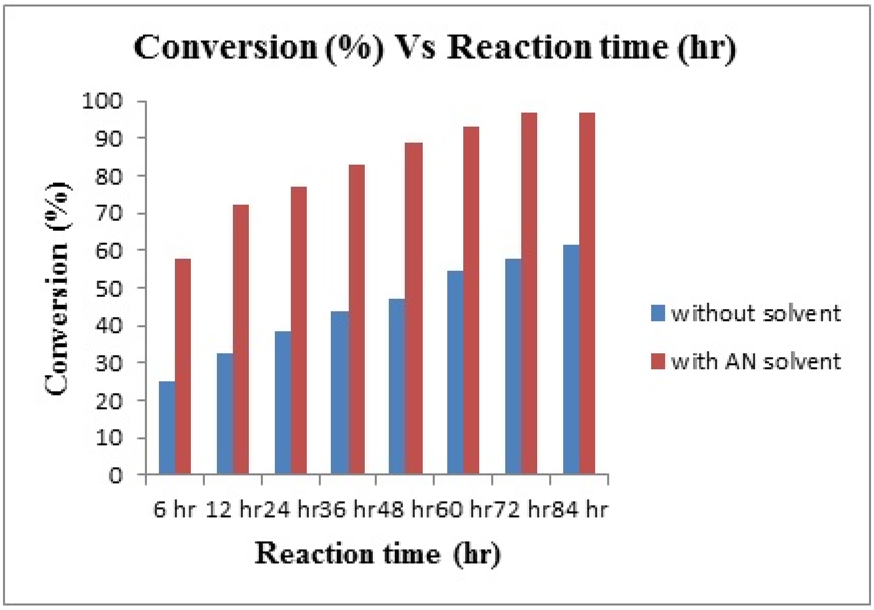


Figure 6.5: Comparison of conversion data without and with acetonitrile solvent

6.3 Oxidation Reaction Kinetics

The conversation data obtained during reaction study has been used to fit to various rate equations which give idea about some important things like the value of rate constant, correlation between conversation and rate of reaction, and the rate of reaction, effect of temperature on rate of reaction.

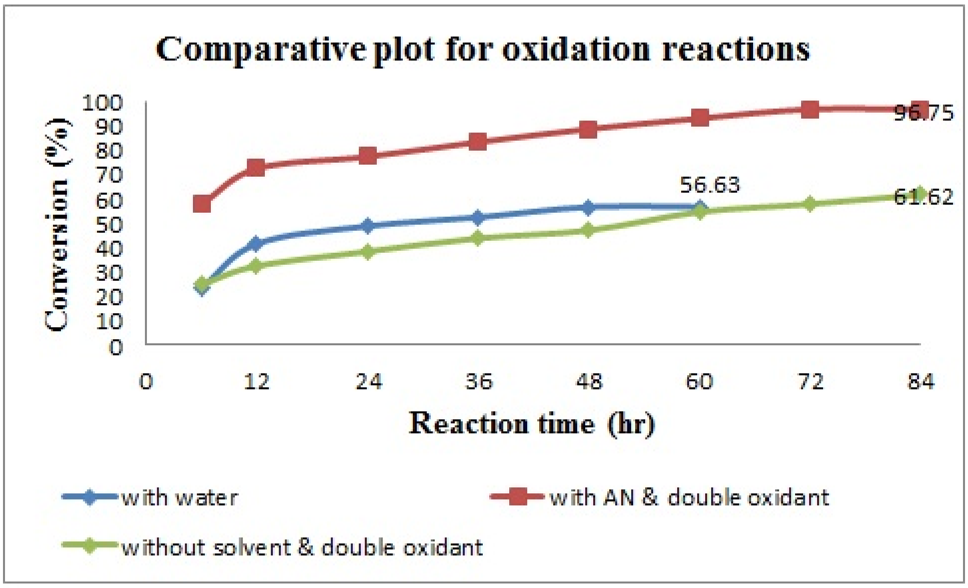
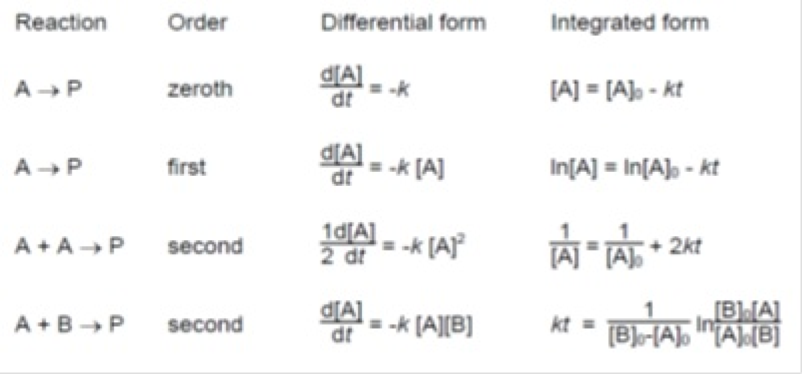


Figure 6.6: comparative plots of oxidation reactions

To measure a rate of reaction, one needs to record the concentration of any of the reactants or products with respect to time. The rate law is an expression linking the rate of a reaction to the concentrations of the chemical species. It can contain reactants, products, and catalysts. Numerous reactions follow a simple rate law,

$$r = K\ [A]^{a}\ [B]^{b}\ [C]^{c}$$

Where, K is the rate constant. The power, mainly is associated with order of the reaction with respect to specific reactant. [36].



Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k[A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \rightarrow P$	second	$\frac{1}{2}\frac{d[A]}{dt} = -k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
$A + B \rightarrow P$	second	$\frac{d[A]}{dt} = -k[A][B]$	$kt = \frac{1}{[B]_0-[A]_0} \ln\frac{[B]_0[A]}{[A]_0[B]}$

Figure 6.7: General reaction kinetic equations

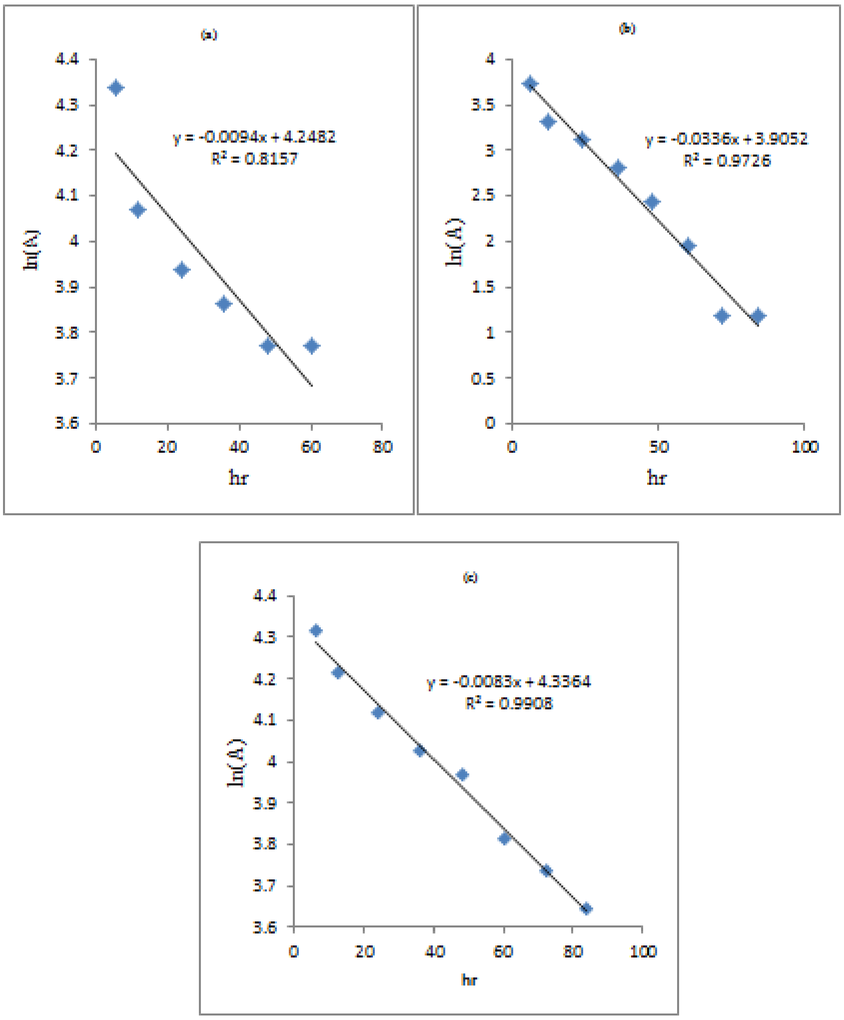


Figure 6.8: Oxidation reaction data fitting to rate equation

The kinetic data obtained during experiments were fit to a first order kinetic curve where drop in dimer/higher oligomer concentration represented by ln(A) was plotted against time. It was shown in figure6.8 like, (a) with water (b) with acetonitrile & double oxidant and (c) without solvent & double oxidant.

Table 6.9: The rate constant value for oxidation reaction

Oxidation Reaction	**Rate constant obtained, (hr^{-})**	**Order of reaction**
With An & double oxidant	3.36Œ10^{-2}	Pseudo first order
With water	0.94Œ10^{-2}	Pseudo first order
Without solvent & double oxidant	0.83Œ10^{-2}	Pseudo first order

As evident from the conversion data, the rate constant of the reaction having acetonitrile is very higher than compared to remaining two reactions. Moreover, presence of solvent plays crucial role in conversion as oxidation reaction without solvent shows lower rate constant, despite of having double quantity of oxidant in reaction.

6.4 Characterization of Catalysts

Fresh synthesized catalyst and spent catalysts were characterized by powder XRD and FTIR. In this work, bulky anion $PW_{12}O_{40}^{3-}$ is substituted in position of Cl^{-} in the imidazolium based IL pattern. The combination of Kegging anion with imidazolium cation led to the development of hybrid solid material. Figure 6.4 displays the powder X-ray diffraction (PXRD) form of silica supported 1-butyl 3-methyl imidazolium phosphotungstate hybrid material, $[Bmim]_3[PW_{12}O_{40}]$ and spent catalysts of various reactions. The PXRD pattern of hybrid material is relatively difficult and exposes dissimilar structure compared to pure PWA.

The fresh catalyst presented a design with a solid reflection at d_{100} and weaker reflections which is regulary observed for the well-ordered siliceous SBA-15. Combining IL cation with PW anions leads to peaks with a shift towards higher 2θ values due to the radiation absorption by tungsten present in PW.It was further confirmed that the synthesized heteropolyanion-based ionic liquid complex encapsulated in SBA-15 formation retained the Kegging structure. The XRD patterns of the hybrid after the reaction show the slight organic deficient hybrid. The XRD of spent catalyst with water and spent catalyst without solvent does not shows the considerable different diffraction peaks corresponding to fresh catalyst while spent catalyst with acetonitrile shows slight different pattern which is evidence of the higher conversation in case of acetonitrile reaction.

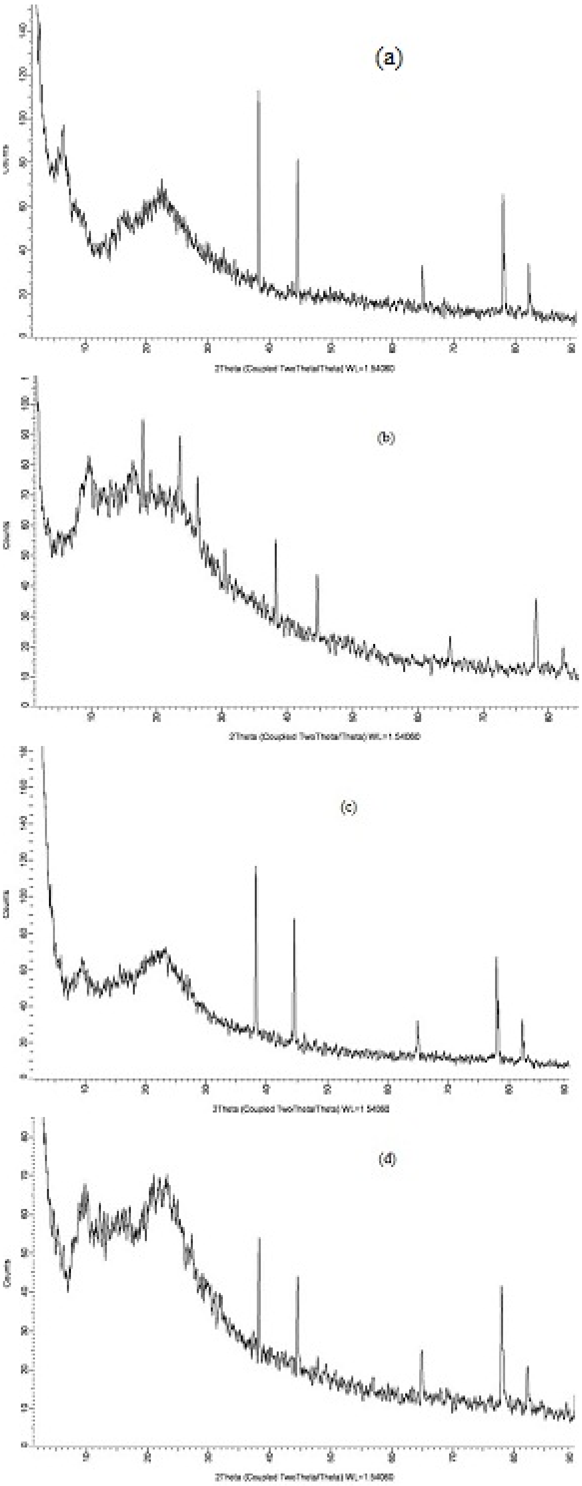


Figure 6.9: Wide-angle powder X-ray diffraction patterns of the fresh catalyst (a), spent catalyst with AN (b), Spent catalyst with water (c), and Spent catalyst without solvent (d).

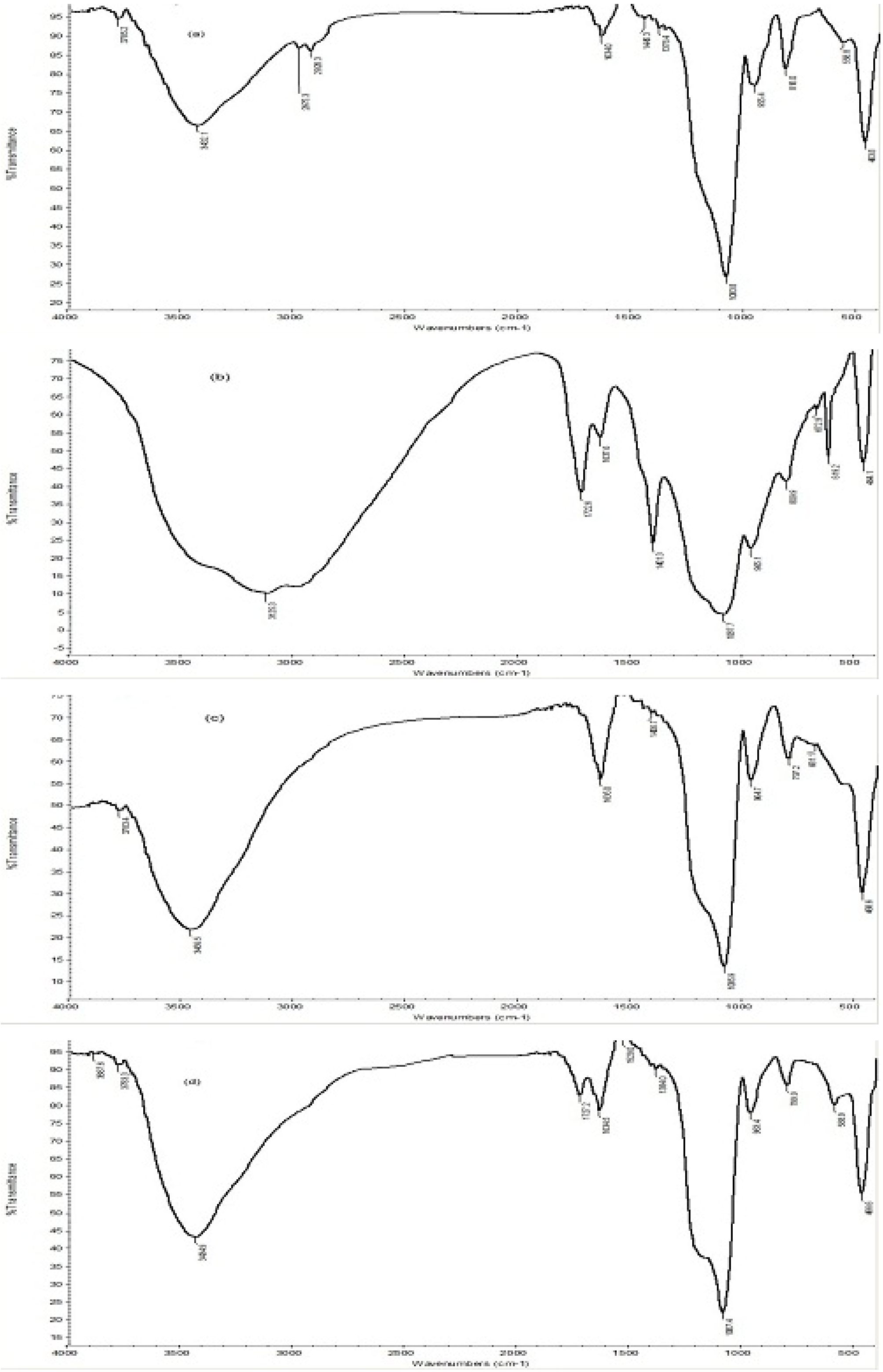


Figure 6.10: FT-IR spectra of Fresh catalyst (a), Spent catalyst with AN (b), spent catalyst with water (c), and spent catalyst without solvent (d).

The FTIR spectra are relatively beneficial to discover structural and bonding changes in the hybrid material. The Kegging structure displays typical P-O stretching (~ 1083 cm^{-}), W-O stretching (~ 955 cm^{-}), stretching of W-O$_e$-W intra bridge betwwen edge sharing WO$_6$ octahedra (~ 818 cm^{-}), woo stretching (~ 558 cm^{-}) was observed in figure (a). Edge sharing and vibrstion of P-O cannot be fixed due to their overlap with Si-O-Si stretching bannd. The above feature bands of the Kegging units in heteropoly tungstate, i.e., 955,818,558 cm^{-}, -, together with the typical bands observed for the imidazolium moieties, specify that the terminal HPW- based ionic developments have been integrated into siliceous SBA-15 mesostructures effectively. It must be observeded that the split in the C-H stretching(2928, 2975 cm-) might be the confirmation that there exist the contact between the imidazolium cations and the Kegging anions. The IR peak at 1634 cm^{-} and 1300-1500 cm^{-} were assigned to imidazole ring and imidazole C=C and C-N bending. The peaks centered at 3400-3800 cm^{-} were ascribed to water molecules.

From figure (b and c), there is absence of 558 stretching which indicate slight damage of kegging structure in spent catalysts of reaction with excess hydrogen peroxide result. After the prolong reaction time catalyst face problem of organic deficiency in spent hybrid catalyst [as shown in figure (b), (c), (d)]. FTIR of spent catalyst without out solvent shows peak at 1707 and 1856 cm^{-} which are acids group, also confirms difficulty in catalyst separation without solvent.

6.5 Oxidation Reaction Product Analysis

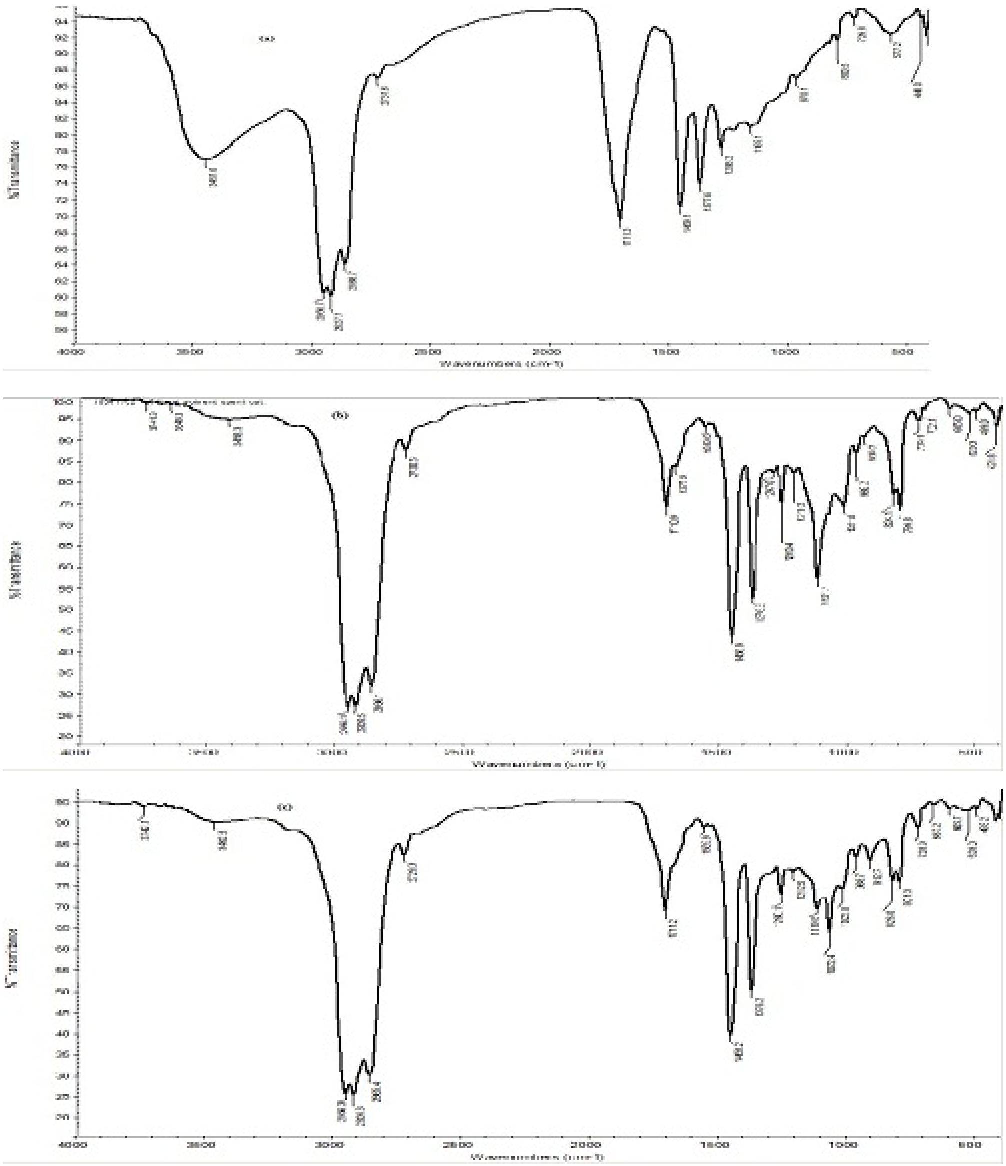


Figure 6.11: FTIR of oxidation reactions organic mixture with acetonitrile (a), without solvent (b), and with water (c)

Table 6.10: IR data of oxidation reactions organic component along with respective bond and functional group [37, 13]

Wave number (cm^{-})			**Bond**	**Functional group**
With acetonitrile reaction	**Without solvent reaction**	**With water reaction**		
729, 800,970	702,729, 799,824, 939,969	667,728, 801,826, 912,	=C–H bend and/or O-H bend	Alkenes Carboxylic acids
1165, 1288, 1327	1021, 1121, 1213, 1260, 1297	1023, 1072, 1119, 1212, 1260	C-O stretch	Alcohols, carboxylic acid, ester, ethers
1459	1456	1458	C–H bend	alkanes
1711	1559, 1677, 1710	1559, 1711	C=O stretch	Þ,ß -unsaturated aldehydes, ketones
2731, 2868, 2927, 2956	2730, 2866, 2926, 2956	2729, 2865, 2926, 2956	O–H stretch	Carboxylic acids
3451	3418	3462	O–H stretch, H–bonded	Alcohols, phenols

Above table shows obtained FT-IR wavelength of three reaction's organic product along with respective bond and probable functional groups. From figure and table it is clear that oxidation reaction product is a mixture of alcohol, aldehyde and carboxylic acid, ethers.

Chapter 7

Conclusion

The hybrid materials are shaped in order to take benefit of both inorganic and organic parts of polyoxometalate and ionic liquid. In this present work oligomerization reaction were studied for standard naphtha industry stream with different silica-alumina mole ratio of zeolyst CBV 600 and Zeolyst CBV 720 having H^+ cation form. Among these best results for oligomerization of olefins were obtained with CBV 720 due to high silica-alumina ratio. Oxidation of this higher oligomer was performed with synthesized hybrid catalyst in presence of different solvents and without solvent. The catalyst displays good conversations in case of presence of solvents because solvent dissolves catalyst completely and generates biphasic system which was not observed in case without of solvent. The best result gives 96.75% conversation at catalyst to oxidant ratio of 0.028 (gm./ml) in presence of acetonitrile solvent This also gives advantage of easy separation and reusability. Kinetics studies are performed for various reaction conditions and it was found that reaction rate is very high for above mentioned reaction. The fresh synthesized catalyst and spent catalysts were analyzed by powder XRD and FTIR. Spent catalyst of reaction with acetonitrile shows slight damage in kegging structure may be due to prolong reaction time and high oxidant. Obtained oxidation reaction product was confirmed by organic functional analysis on FTIR, which are mixture of oxides i.e. aldehydes, alcohols, ether, carboxylic acids.

Chapter 8

Future Scope

This work belongs to a very wide and growing research area for materials and its application for value addition. This can be taken to new highs in further studies:

- Reusability and reproducibility of catalyst can be studied to understand the effectiveness of catalyst.
- Reactivity of catalyst for other organic reactions can also be studied.
- Detailed study of reaction mechanism.
- Development of hybrid molecules with different ionic liquids and HPA.

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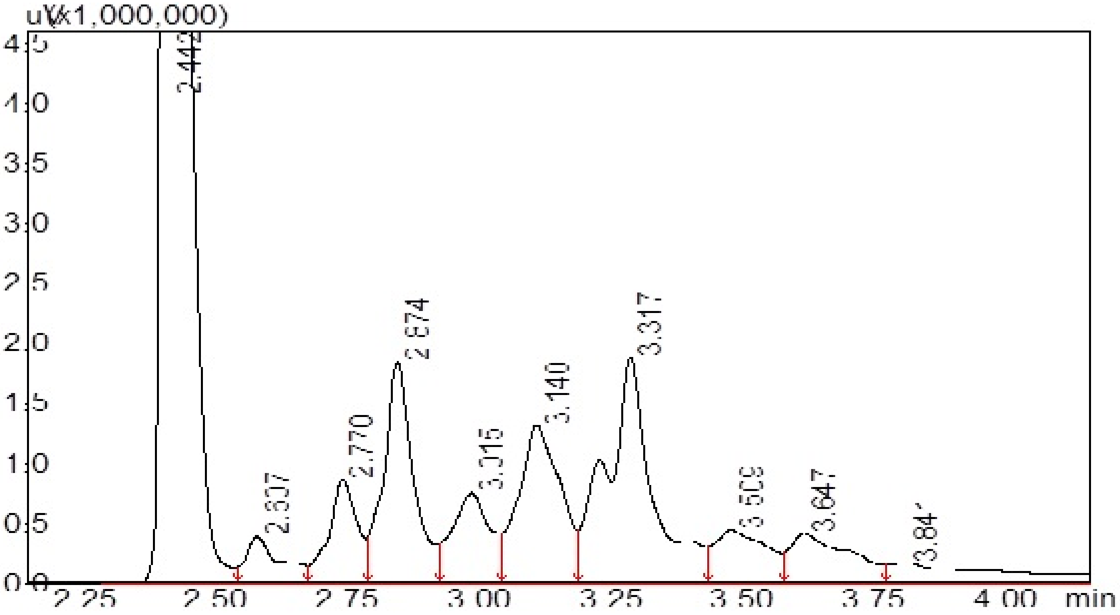
Appendix A

GC Sample Graph

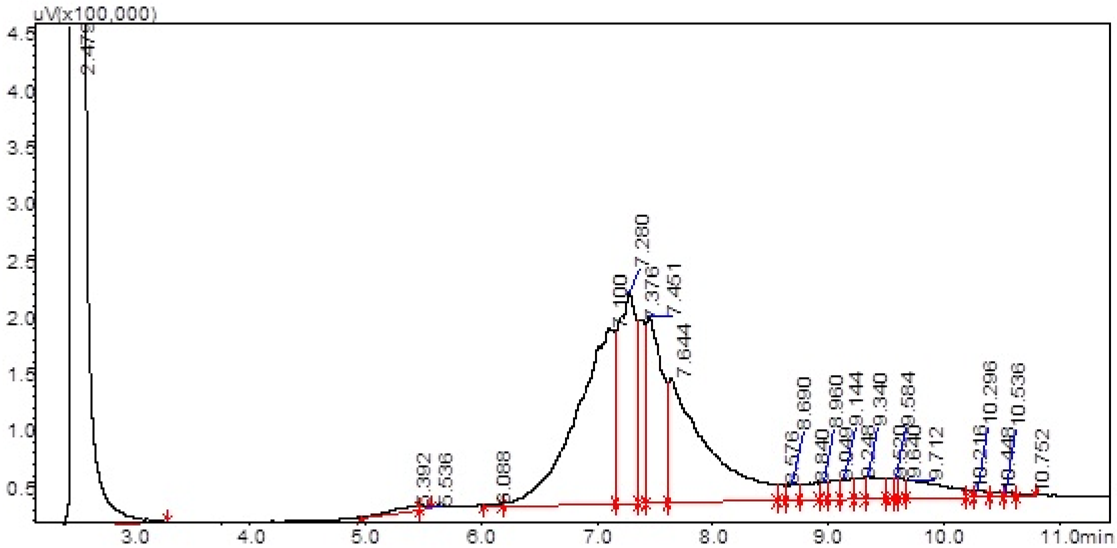
a) Chromatogram of oligomerization reaction reactant

At retention time 2.442 minutes a peak of solvent n-hexane is observed, remaining all the peaks indicates components present in the reactant sample. This program is run for 30 minutes but no further peak was observed.



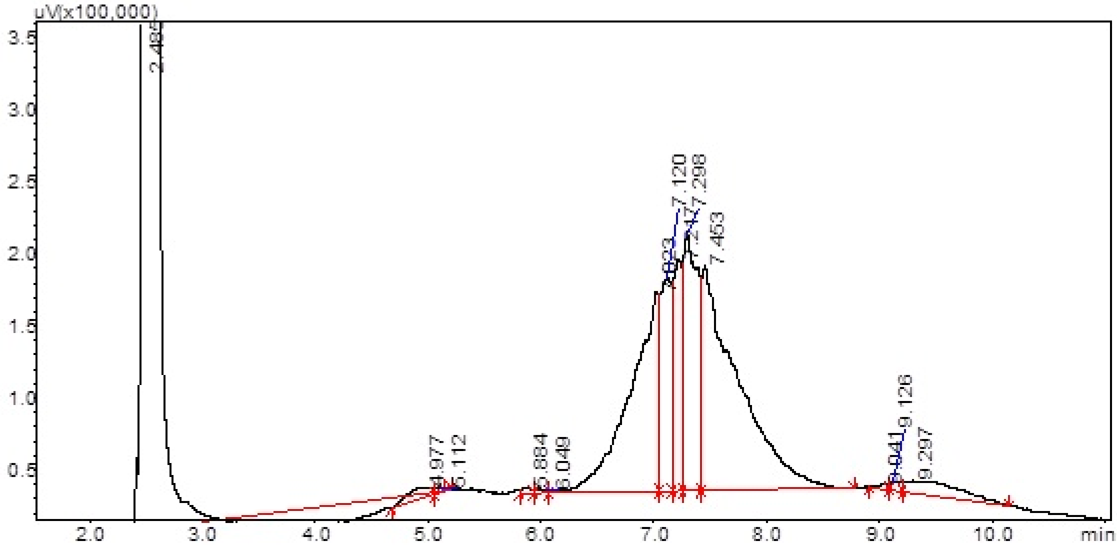
b) Chromatogram of higher oligomer product obtained in reaction-1.

At retention time 2.479 minutes a sharp peak of solvent n-hexane is observed, remaining all peaks indicates higher oligomer product obtained for reaction-1 conditions. This program is run for 30 minutes but no further peak of product was observed.



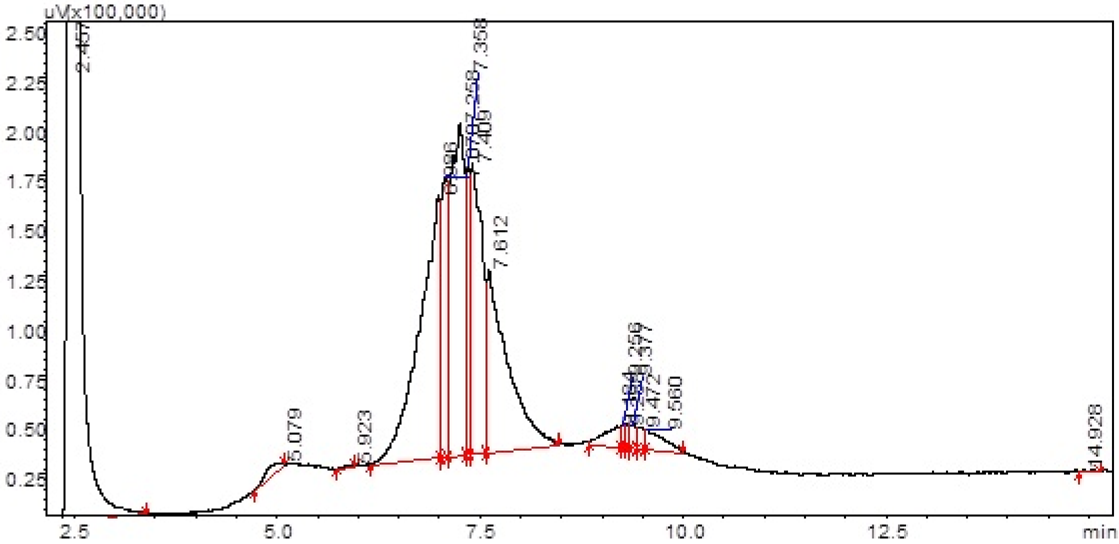
c) Chromatogram of higher oligomer product obtained in reaction-2.

At retention time 2.485 minutes a sharp peak of solvent n-hexane is observed, remaining all peaks indicates higher oligomer product obtained for reaction-2 conditions. This program is run for 30 minutes but no further peak of product was observed.



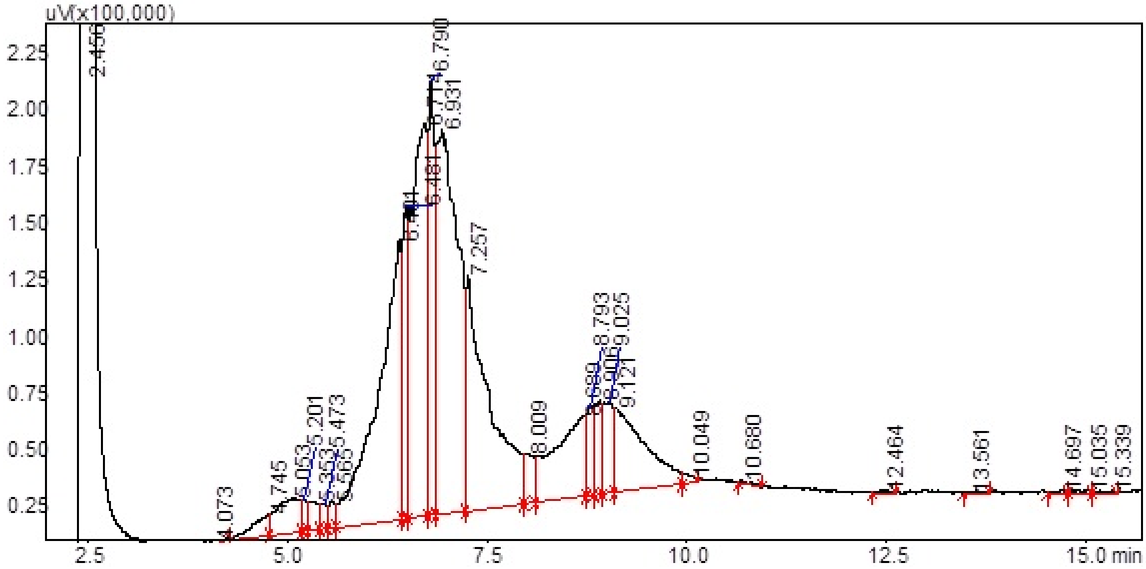
d) Chromatogram of higher oligomer product obtained in reaction-3.

At retention time 2.457 minutes a sharp peak of solvent n-hexane is observed, remaining all peaks indicates higher oligomer product obtained for reaction-3 conditions. This program is run for 30 minutes but no further peak of product was observed.



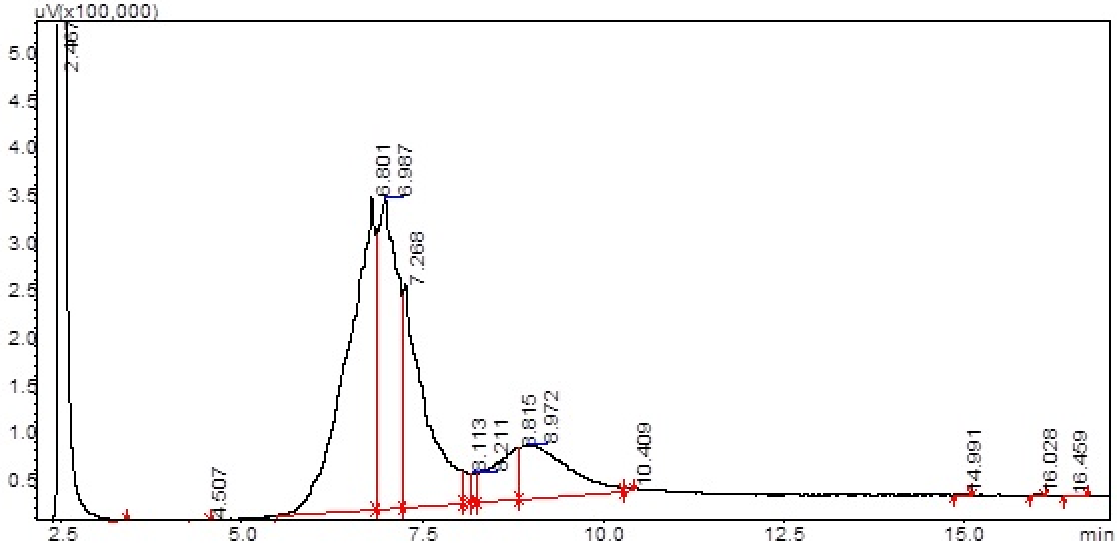
e) Chromatogram of higher oligomer product obtained in reaction-4.

At retention time 2.456 minutes a sharp peak of solvent n-hexane is observed, remaining all peaks indicates higher oligomer product obtained for reaction-4 conditions. This program is run for 30 minutes but no further peak of product was observed.



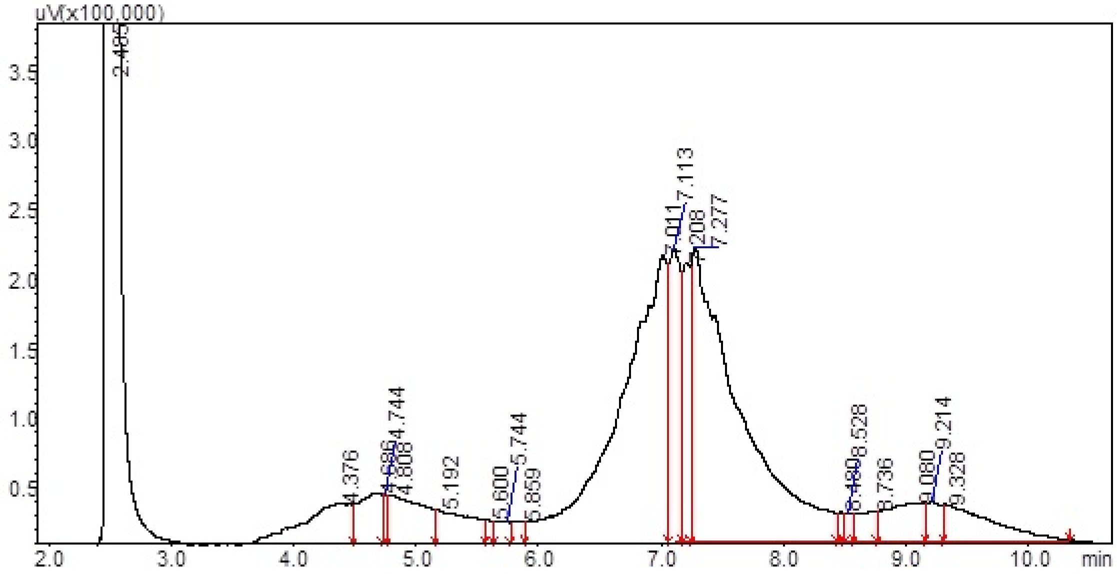
f) Chromatogram of higher oligomer product obtained in reaction-5.

At retention time 2.467 minutes a sharp peak of solvent n-hexane is observed, remaining all peaks indicates higher oligomer product obtained for reaction-5 conditions. This program is run for 30 minutes but no further peak of product was observed.



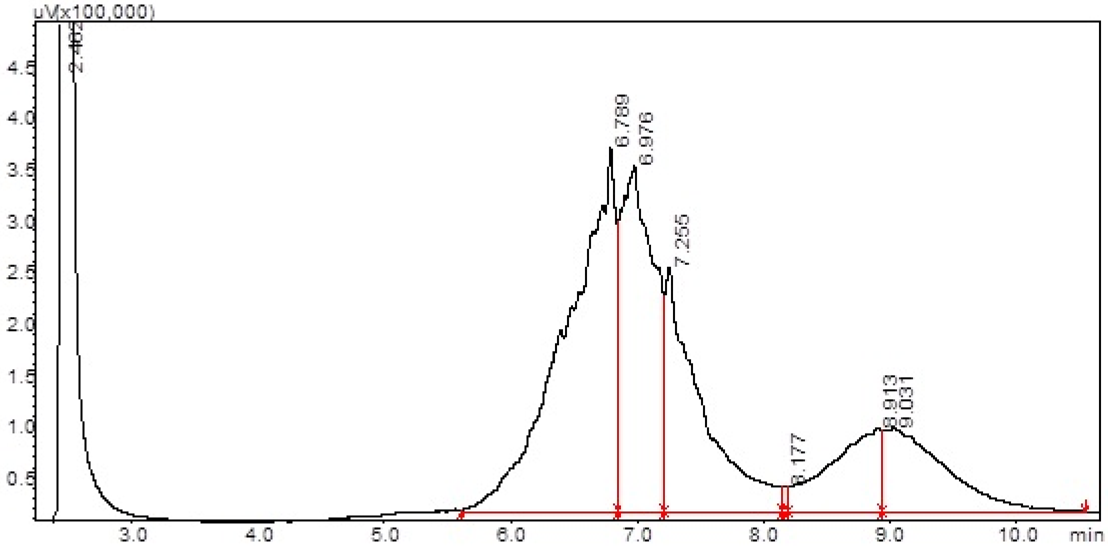
g) Chromatogram of higher oligomer product obtained in reaction-6.

At retention time 2.485 minutes a sharp peak of solvent n-hexane is observed, remaining all peaks indicates higher oligomer product obtained for reaction-6 conditions. This program is run for 30 minutes but no further peak of product was observed.



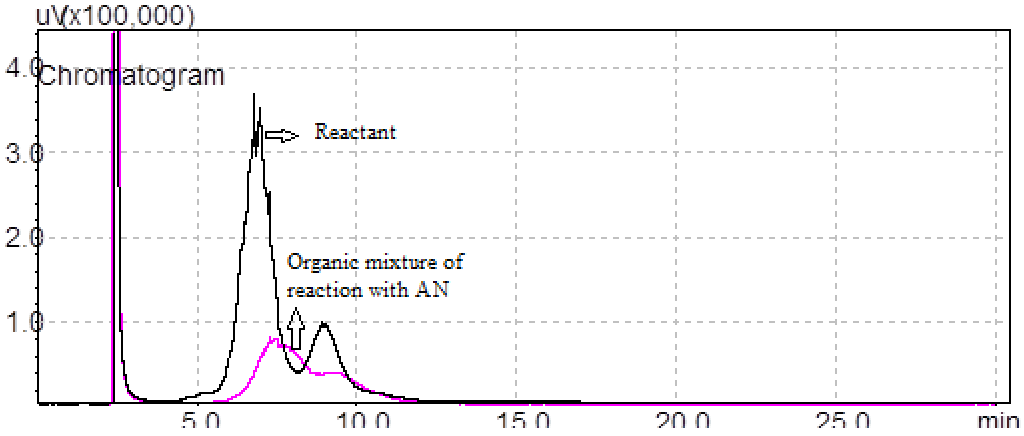
h) Chromatogram of higher oligomer taken as reactant for oxidation reaction.

At retention time 2.462 minutes a sharp peak of solvent n-hexane is observed, remaining all peaks indicates higher oligomer obtained in oligomerization reactions. This program is run for 30 minutes but no further peak of product was observed.

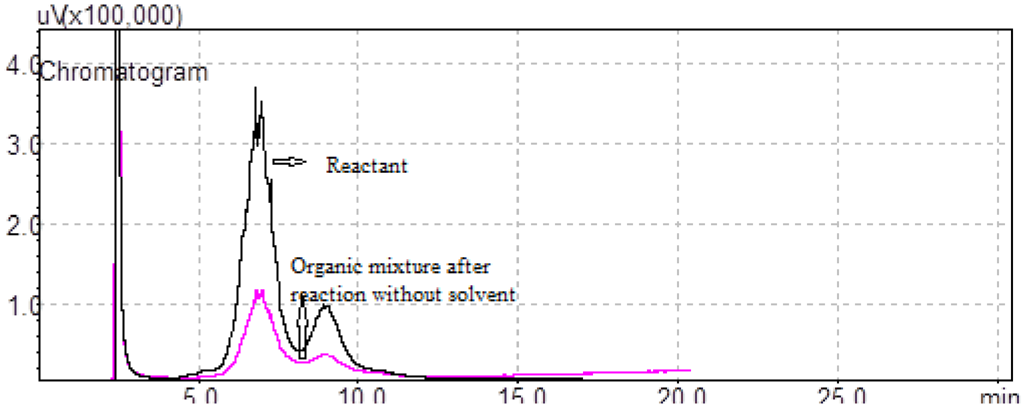


i) Overlapping of two chromatograph (i.e. oxidation reaction reactant and organic component mixture after reaction with acetonitrile)

At retention time 2.4-2.5 minutes sharp peaks of n-hexane is completely overlap and both chromatographs shows different behaviors which confirms the product of oxidation reaction with acetonitrile.



j) Overlapping of two chromatograph (i.e. oxidation reaction reactant and organic component mixture after reaction without solvent)



Appendix B

Calculation for Bromine Number

$$\begin{aligned} BromineNumber &= \frac{Burette\ Reading * Normality\ of\ KBr/KBrO3 * Factor}{Weight\ of\ Sample} \\ &= \frac{3.969*0.52*7.99}{0.116} \\ &= 142 \end{aligned}$$