CHAPTER - I
General Introduction

Due to global and domestic compulsions, catalytic scientists have to draw new strategies and plans relevant to basic research that would help them develop and produce competitive catalysts and catalytic technologies in the global market. Catalytic research is fast growing in the areas of production of fine chemicals and environmental pollution abatement [1]. In order to achieve this objective there has been a new focus on invoking new methodologies and exploration of new materials. Renewed interest has been laid on modifying and fine tuning the existing materials, like the polyoxometalates. These compounds, also popularly called as heteropoly compounds (HPCs), have recently been identified as very active catalysts in the development of environmentally benign processes. The catalytic functionalities of HPCs, which are acidic and redox in nature, are used in solution as well as in the solid state [2]. An enormous amount of work has been done on the preparation, characterization and evaluation of these catalysts for various industrially important reactions including dehydrogenation and selective oxidation [2]. Concerted efforts have been directed towards developing more efficient heteropolyacid catalysts to be used in other reactions like the ammoxidation of aromatic and heteroaromatic compounds.

1.1 Heteropolyoxometalates:

HPCs were first discovered in the 19th century [3]. Their interesting properties have been exploited in diverse areas such as analytical, medicinal chemistry, photochemistry and solid-state devices [4-7]. The HPCs contain a group of peripheral atoms (mostly Mo or W) interlinked with oxygen atoms along with hydrogen atoms. At the center of these polyoxometalates, there is a central or heteroatom linking with these groups again with oxygen atoms. More than sixty-five elements from all groups of the periodic table can be found incorporated as heteroatoms [3].
The classification of heteropoly compounds is based on the ratio between polyatom and heteroatom present in the total structure and their structural arrangement. Some typical structures of heteropoly ions are shown in Figure 1.1.

![Figure 1.1: Structures of heteropoly ion](image)

(a) Keggin, (b) Wells-Dawson, and (c) Anderson

1.2 The Keggin structure and its isomers:

The Keggin type HPCs, with the general formula $X_nM_{12}O_{40}^{(n+)}$ ($MX=12$) are the most studied compounds for catalytic applications, due to their ease of preparation, relatively high thermal stability and redox and acidic properties. The central atom, $X$, is usually either $P^{5+}$ or $Sf^{4+}$ and the heteroatom, $M$, is usually $W^{6+}$ or $Mo^{6+}$. Some examples of heteropolymolybdate anions are listed in Table 1.1.

The first polyanion prepared by Berzelius [8] was the phosphomolybdate, $[PMo_{12}O_{40}]^3-$ ion. The structure of a similar compound, i.e., $[PW_{12}O_{40}]^3-$ was determined about 100 years later using X-ray diffraction. The complex acidic anion is a coordinated structure consisting of a central $PO_4$ group surrounded by twelve $MO_6$ groups as a shell, linked together by shared oxygen atoms. The Keggin anions can be viewed from two perspectives, focusing on the central atom and considering it as ligated by 12 octahedra or, in contrast, imagining a cage formed by 12 octahedra that is then filled up by the central atom.
Table: 1.1 Different heteropoly molybdates

<table>
<thead>
<tr>
<th>Chemical Formula (M=Mo)</th>
<th>Heteroatom(X)</th>
<th>Structure (X : M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Xⁿ⁺M₁₂O₄₀]ₙ⁻</td>
<td>P⁵⁺,As⁵⁺,Si⁴⁺,Ge⁴⁺</td>
<td>1:12 Keggin [9]</td>
</tr>
<tr>
<td>[Xⁿ⁺M₁₁O₃₈]₁₁⁻</td>
<td>P⁵⁺,As⁵⁺,Si⁴⁺,Ge⁴⁺</td>
<td>1:11 lacunary Keggin</td>
</tr>
<tr>
<td>[X₂⁺M₁₃O₆₂]₁₂⁺</td>
<td>P⁵⁺,As⁵⁺</td>
<td>2:18 Dawson [10]</td>
</tr>
</tbody>
</table>

These polyions are known to exist in α, β, γ, δ and ε isomeric forms (Figure 1.2), which differ, in the spatial arrangement of the edge-shared M₃O₁₃ triplets. The first among the series is the most exploited one in terms of its applications including heterogeneous catalysis [12]. A ball and stick representation of the Keggin anion is shown in Figure 1.3.
1.3 Primary, secondary and tertiary structures:

The hierarchical structure of solid HPCs is important for understanding the nature of the species formed and the corresponding functionality of the catalysts [13, 14]. The schematic models of the primary, secondary & tertiary microstructures of the heteropolyacid are shown in Figure 1.4. The primary structure is the Keggin structure. The secondary structure is a three-dimensional (usually regular) arrangement consisting of polyanions, counter cations and additional molecules. The secondary structure is flexible to different extents depending on the counter cation and the structure of the polyanion, and is the basis for bulk-type catalysis of solid HPC catalysts [13]. The tertiary structure represents the manner in which the secondary structure assembles into solid particles and relates to the properties such as particle size, surface area and pore structure and plays an important role in heterogeneous catalysis.

1.4 Importance of Mo and W containing Keggin structure compounds:

In general, heteropoly anions exhibit varied structures with the ability to catalyze a wide range of industrially and biologically significant reactions [15]. The applications of heteropoly compounds are based on their unique properties including size, mass, electron
and proton transfer/storage abilities, thermal stability, and mobility of lattice oxygen and high Bronsted acidity [14].

HPCs are also attracting much academic interest as potential catalyst materials because they possess dual catalytic functions of strong acidity and high oxidizing ability. Many known and new HPCs have been used for a variety of reactions like the formation of carboxylic acids from the corresponding aldehydes, as well as the dehydrogenation of alcohols, aldehydes and carboxylic acids to form C=C and C=O bonds [16]. They have also been widely involved in heterogeneous catalytic oxidation processes such as commercial vapor phase oxidation of methacrolein, which produces 80,000 tons of methacrylic acid per year [17]. The bifunctional HPC catalysts can be used for sequential hydroformylation and oxidation of olefins [18]. HPCs also display homogeneous oxidative catalytic activity such as water splitting processes and oxygen transfer to alkanes [19]. The oxidation of alkanes and the coupling of aromatics utilize molybdovanadates as the
reoxidant, known as the Wacker process [20]. Catalysts containing polyoxomolybdates are widely used for hydrodesulfurization, hydrodenitrification of fossil fuels [21]. The latest commercial process, the direct oxidation of ethylene to acetic acid catalyzed by palladium and HPC produces 100,000 tons per year of the product [22]. There is another rapidly growing area, which is the heteropoly compound photochemistry and photo catalysis. Heteropoly compounds provide a variety of specialized oxidizing agents and recently their usefulness in bleaching or wood pulp via oxidative delignification has been reported [23]. Molybdenum based heteropoly compounds are better catalysts for oxidation reactions than their tungsten counterparts. Other applications as ion-exchange materials, ion-selective membranes and inorganic resistant materials have also been reported [24]. It is evident that the research activity on heteropoly compounds is very intensive and still growing.

The reasons for the heteropoly compounds to be suitable materials for both theoretical design and practical processes are listed below;

(i) Systematic variations of acid and redox properties.
(ii) Molecular nature of solid heteropoly compounds originating from heteropoly anion molecules enabling precise design of catalysts and molecular description of catalytic process.
(iii) The availability of a variety of reaction fields for catalytic processes, for example they can be bifunctional metal acid catalysts.
(iv) Their pseudoliquid phase character by means of which they can act as phase transfer catalysts.
(v) The soft basicity of the polyion in stabilizing the reaction intermediates [25].

Although practical applications of heteropoly compounds have been derived for a long time, the chemical properties, the structure and catalytic functionalities of these compounds have been interrelated only recently.
1.5 Ammonium salts of heteropoly acids:

Berzelius [8] discovered the first heteropoly compound in 1826, which is now known as ammonium 12-molybdophosphate. It has been used successfully to separate cesium present in the nuclear waste containing fission products. Very few studies have been reported on the catalysis and structural chemistry of the ammonium salt. The arrangement of \( \text{NH}_4^+ \) ion in heteropoly acid salt is shown in Figure 1.5.

![Figure 1.5: The Keggin unit of AMPA with the position of \( \text{NH}_4^+ \) ion.](image)

Notation of oxygen atoms: \( \text{O}_a \), inner oxygen atom forming P-O bond; \( \text{O}_b \), bridging oxygen atoms on the common corners of neighboring \( \text{MoO}_6 \) octahedra; \( \text{O}_c \), oxygen atom joining the structural subunits of three \( \text{MoO}_6 \) octahedra connected by common edges; \( \text{O}_d \), terminal oxygen atoms, frequently considered as double bonded as in \( \text{Mo}=\text{O} \).

Several methods are reported in literature to prepare the ammonium salts of heteropolyacids, which have been described in Chapter 3. All these methods have used the transformation of the hydrogen ions of the parent acid to the ammonium ions. But these methods are not suitable for getting pure ammonium salt without any residual protons or any other impurity. So, there is a necessity for the development of methods to prepare pure ammonium salt.
1.6 Characterization of the ammonium salt using different techniques:

Characterization of the ammonium salt using different techniques such as XRD, FTIR, TGA and $^{31}$P NMR is the usual approach to understand the physico-chemical properties of the salt and to correlate these properties with its catalytic functionality. XRD and FTIR are essential techniques to elucidate the primary and secondary structure of the Keggin heteropoly compounds [2,3]. The HPCs loose their structural stability at higher temperatures, the salt being thermally better stable than the parent acid. It is also known that with increase in temperature, the salt takes the form of different intermediates, like the lacunary structure, before finally decomposing into the oxides of Mo and P [26]. Further, the surface area of the bulk acid/salt, when calcined to higher temperatures (>300°C), is very low (<10 m$^2$/g). In order to increase the surface area and also to reduce the salt content, the HPCs are normally deposited on various supports. The nature of the support HPC species depends on the acid-base property of the support as well as on the extent of loading. The $^{31}$P MAS NMR technique is an essential tool to identify the different species formed during the temperature treatment. It is also successfully used to determine the salt-support interaction in the case of supported systems [27]. Since no specific characterization technique can completely describe the above characteristics, there is a need to use several techniques to complement one another for the structural characterization. Whereas standard methods are available for other catalysts like the supported oxides of V and Mo for measuring the dispersion of the active species, no technique has been standardized yet for the determination of dispersion of the heteropoly compound on various supports. It is, therefore, necessary to develop a reliable technique for the determination of the salt dispersion on the support.
1.7 The role of ammonium salt of 12-molybdophosphoric acid in the ammoxidation reaction.

The importance of ammoxidation reaction is described in the next section. However, it is necessary to discuss the need to develop low temperature active catalysts for the ammoxidation. Extensive work has been carried out on the V-based catalysts, such as V$_2$O$_5$ either alone or in combination with other metals like, Bi, Sb, Nb particularly supported on TiO$_2$ [28]. However, all these catalysts are active at high reaction temperature (>430°C). In an exothermic reaction like that of ammoxidation, high reaction temperature leads to drastic reduction in product selectivity. Effective control of the exothermic reaction temperature is very critical, since there is every chance for reactor run away [29]. Efforts have been consistently made to develop low temperature active catalysts, for which the 12-molybdophosphoric acid is found to be very effective. However, it is observed that the acid gets transformed into its ammonium salt during the reaction in the presence of ammonia and water [30]. Application of the ammonium salt itself appears to be the right proposition to achieve the goal.

1.8 Synthesis of aromatic and hetero aromatic nitriles by ammoxidation:

Aromatic and hetero aromatic nitriles are important synthetic intermediates used in pharmaceutical, pesticide, dyestuffs, liquid crystal and polymer syntheses [31]. The syntheses of hetero aromatic nitriles have attracted considerable attention. Several methods to prepare these materials have been reported. However, these processes are very complex; the starting materials such as acids, aldehydes, amides, acetamides, benzylamine, aromatic Grignard reagents, are expensive, and in several cases special reagents such as NaN$_3$, 2-pyridyl cyanate are used. As raw material for the synthesis of nitrile, methyl aromatic compounds are cheaper than the corresponding derivatives mentioned above. In particular, the conversion of methylaromatics into their nitriles by catalytic processes is a good proposition in terms of economics as well as environmental aspects [32].
1.9 Importance of 2-cyanopyrazine:

2-cyanopyrazine is an important intermediate in the production of 2-amidopyrazine, popularly called Pyrazinamide, an effective anti-tubercular drug [29]. Several routes are available in literature to produce pyrazinamide, but two routes viz.; the non-catalytic (glyoxal) and the catalytic route (methyl pyrazine) are frequently employed for the production of pyrazinamide [33].

1.10 The Non-catalytic route:

Phenylenediamine is initially reacted with glyoxal to get quinoxaline, which is subjected to permanganate oxidation to pyrazine dicarboxylic acid. Pyrazine dicarboxylic acid is carefully converted into its monocarboxylic acid, which is subsequently converted to pyrazine amide in the presence of ammonia. This route has certain disadvantages that include high material cost, high solubility of the acid in water leading to difficulty in the isolation of intermediates, production of large volumes of used catalyst sludge for disposal and low purity of the product.

1.11 Catalytic route:

In the catalytic route (Scheme 1.1), 2-methylpyrazine is first synthesized from ethylenediamine and propylene glycol by a vapor phase cyclodehydrogenation in presence of a mixed zinc-chromium oxide based catalyst operating at atmospheric pressure and in the temperature range of 400-450°C.

2-methylpyrazine is then converted to 2-cyanopyrazine by the vapor phase ammoxidation using various transition metal oxide based catalysts operating at 360-450°C temperature and atmospheric pressure. Cyanopyrazine is subsequently hydrolyzed to amidopyrazine or pyrazinamide [33].
1.12 Advantages of catalytic process:

The conventional process (described in 1.10) is highly cumbersome and is environmentally not suitable. Yields are also very low. The catalytic process offers many advantageous, like increase in the rate of reaction and thus obtaining high conversions.

**Scheme 1.1:** Three different steps involved in catalytic route in the production of Pyrazinamide.

1. Ammoxidation:
   \[ \text{Pyrazine} + 1.5 \text{O}_2 + \text{NH}_3 \rightarrow \text{Pyrazine cyanide} + 3 \text{H}_2\text{O} \]

2. Oxidative Dealkylation:
   \[ \text{Pyrazine} + 1.5 \text{O}_2 \rightarrow \text{Pyrazine} + \text{CO}_2 + \text{H}_2\text{O} \]

3. Total Combustion:
   \[ \text{Pyrazine} + 6.5 \text{O}_2 \rightarrow 5 \text{CO}_2 + 3 \text{H}_2\text{O} + \text{N}_2 \]

**Scheme 1.2:** Three possible reactions during ammoxidation of 2-MP.
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and selectivity, reduction in time, energy and the amount of reagents used in the reaction. Among the three steps of the total process, the second step i.e. catalytic ammoxidation of 2-MP to CP is the key and crucial step. Because of its exothermic nature, the control of reaction temperature is difficult.

Vapor phase ammoxidation of methyl pyrazine is a nucleophilic oxidation reaction. Even though it is the most simple and economically most profitable route for the production of 2-cyano pyrazine [34], other reactions involving production of byproducts also take place.

1.13 Aims and Objectives:

Design of heterogeneous catalysts to carry out reactions under milder conditions, leading to high selectivity to the required product is one of the problems in the ammoxidation reaction, which cannot be achieved by the multi-component transition metal oxide catalysts. The present work examines the applicability of the ammonium salt of 12-molybdophosphoric acid for achieving this goal.

Since the acid form of this HPC eventually turns into the salt during the reaction, it is interesting to see the applicability of the salt directly in place of the acid. An effort is made in this direction.

Synthesis of the ammonium salt by a multi-step process like the preparation of acid first and its subsequent transformation into the ammonium salt leads to formation of non-stoichiometric compounds. Further, the utilization of phosphoric acid during the preparation needs corrosion resistant contact equipment. Synthesis of the salt by avoiding the corrosive media is another objective of this work. Attempts have also been made to synthesize the salt by avoiding the non-stoichiometric species, as far as possible, for which various methods of preparation have been examined. Identification of the best procedure for the preparation of the salt is another objective of the present work.

Though extensive work has been reported in the literature on supported HPCs in their acid form, detailed studies on the supported salt systems are very scarce.
Examination of the effect of dispersion of the salt on various supports has been actively pursued in the present work. As has already been discussed above, very few reports are available on the characterization of the supported salt systems, particularly with reference to the nature of interaction of the salt with the support, which is expected to vary with the acid-base property of the support. By means of selection of supports, which vary in their nature of surface sites, this thesis examines the nature of salt-support interaction. A thorough characterization of the catalysts is carried out to identify the nature of the species formed by the application of spectroscopic techniques.

This thesis also aims at development of a suitable technique for the determination of dispersion of the salt on the support as a function of loading. For this purpose, the FTIR spectra of the catalysts have been made use of.

While a great deal has already been achieved in the ammoxidation catalysis, there is still ample scope for further improvement. Since the process is not thermodynamically limited, it is theoretically possible to attain optimum (close to 100 %) nitrile selectivity. Design and development of a composite catalyst, which can offer high nitrile selectivity with good yields at lower reaction temperature, is yet another objective of this work. Particular attention has been paid to obtain high selectivity even at the cost of reduced conversion, to make the process environmentally benign.

1.14 Scope of the thesis:

Heteropoly acid and its salts are known as topics of research for a long time. Of late bismuth phosphomolybdate has been used for the preparation of acrylonitrile. Many published papers and patents have disclosed the effective utilization of heteropoly acids and their salts as oxidation catalysts. However, the application of ammonium salt of 12-molybdophosphoric acid (AMPA) for ammoxidation has not been reported in the literature.

In this thesis, the synthesis of AMPA (which is more stable, active and selective than its parent acid) using different preparation procedures is described. A thorough
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characterization is carried out to identify the presence of ammonium salt, its degradation and regeneration of products into active component.

It was also found that salt-support interaction in the case of supported AMPA catalysts results in higher activity and selectivity in the ammoxidation of MP. The activity and selectivities obtained are more than that of the bulk catalyst. The FTIR half-band width analysis and $^{31}$P MAS NMR techniques are used for characterizing the extent of interaction and correlating it with the performance of the catalyst.

The results of the present investigation reveal that there can be ample scope for planning strategic basic innovative research for the preparation and development of AMPA based catalysts for the production of industrially important nitriles by ammoxidation of hetero aromatic hydrocarbons and other selective oxidation reactions.

1.15 Structure of the thesis:

The contents of this thesis can be divided into seven chapters

Chapter 1 Application of AMPA for the first time.

This chapter presents a brief introduction on the heteropoly compounds and their importance. A particular emphasis has given to ammonium salts of heteropoly acids and their characteristic properties to catalyze redox type reactions. The Importance of development of a catalyst for the ammoxidation of methylpyrazine is discussed.

Chapter 2 Identification of the best preparation technique, literature survey and characterization of catalysts by XRD, FTIR, TGA, $^{31}$P MAS NMR, temperature programmed desorption of ammonia and SEM analysis.

General methods for the preparation of bulk, supported and metal incorporated MPA and its ammonium salt are discussed. (iii) Characterization of these materials by various techniques like nitrogen gas adsorption, X-ray diffraction, FTIR, TGA, $^{31}$P MAS NMR, temperature programmed desorption of ammonia and SEM analysis are reviewed. The importance of these techniques in understanding the physico-chemical properties like the formation of Keggin structure and its stability, the extent of salt-support interaction and the formed species presented during the pretreatment of catalyst are presented in this survey.
Chapter 3 (iii) The experimental procedures used.

The detailed procedures for catalyst preparation, adopting different approaches are explained. The basic concepts and the experimental producers of spectroscopic techniques are described. The methodology followed to evaluate the catalysts in the ammoxidation of methylpyrazine is discussed.

Chapter 4 Study on the bulk ammonium salt of 12-molybdophosphoric acid. It comprises three sections. Section 1 deals with a comparison of the structure and reactivity of MPA and its ammonium salt pretreated at different temperatures. This study was performed to understand the suitability of ammonium salt of MPA as ammoxidation catalyst. The influence of pretreatment temperature on the stability of MPA, AMPA and the effect of reaction temperature on the activity and selectivity are discussed. Section 2 deals with solid-solid wetting method to prepare the ammonium salt. The effect of calcination temperature on the secondary structure and its influence on activity and selectivity are also discussed. Section 3 presents the influence of phosphorous precursor on the synthesis of AMPA, the nature of thermolysis products formed after subsequent treatment at high temperature and finally their ammoxidation functionality.

Chapter 5 (v) Studies on the effect of supports.

This chapter consists of five sections. Section 1 describes the effect of acidity of the Nb$_2$O$_5$ support to interact with AMPA, the nature of the interacted species and their behavior in ammoxidation of MP. Section 2 describes the results of physico-chemical properties and the reactivity of SiO$_2$ supported AMPA catalysts. Section 3 presents the effect of salt-support interaction in ammoxidation of methylpyrazine over TiO$_2$ supported ammonium salt catalysts. FTIR half-band width analysis method in characterizing the extent of interaction is described and a correlation is drawn with the performance of the catalyst. Section 4 describes the different Keggin species formed when AMPA was supported on ZrO$_2$ at different loadings. The species responsible for activity and selectivity in the ammoxidation reaction are also described. Section 5 describes the physico-chemical properties of γ-Al$_2$O$_3$ supported AMPA catalysts and their ammoxidation functionality.
Chapter 6 (vi) Incorporation of metal ions

This chapter contains three sections. Section 1 represents a study on the V metal modified AMPA catalysts. Section 2 contains results on Bi metal modified AMPA catalysts and Section 3 describes the effect of Sb metal addition to AMPA catalysts on their structural stability.

Chapter 7 consists of conclusions drawn from the results obtained in the present work.
1.16 References:


