CHAPTER - VI
Transition metal modified ammonium salt of 12-
molybdophosphoric acid catalysts

6.0 Introduction:

The Keggin type heteropoly compounds are known to possess the unique feature of strong intrinsic acidity as well as oxidizing properties [1]. Both the features can be suitably modified, by the variation of the cationic composition as well as by substitution of either molybdenum or tungsten in peripheral positions in the anion with other transition metals such as V, Sb, Fe, Ti etc [2, 3]. The addition of transition metals to heteropoly compounds is an important approach to control their redox properties which is also proved to improve their thermal stability [3]. Metals can be coordinated with a heteropoly ion in three different ways to form metal coordinated polyions [4], which show unique catalytic activities for various reactions. The first method is the simple combination of metal salts with heteropoly ion. The second is the use of lacunary anion as ligand for transition metal ions i.e., transition metal substituted polyion. The third is the use a polyion to support transition metals i.e., heteropoly ion supported transition metal. The first method is the most commonly used method to prepare the transition metal modified heteropoly compounds. It has been reported that the protonic form, $\text{H}_3\text{PMO}_{12}\text{O}_{40}$, catalyze oxidation of lower alkanes and that the substitution of V$^{6+}$ for Mo$^{6+}$ improves the catalytic activity and selectivity [5]. The catalytic performance is much enhanced by the addition of transition metals. Iron and copper have been the most widely used additives for enhancing the catalytic activity of heteropoly compounds as reported in the literature [6]. Among the transition metals, the effect of vanadium, iron, zinc, chromium and nickel in both cationic and anionic positions, on the catalytic performance of heteropoly compounds in gas phase oxidations has been studied [2]. Catalysts containing V in combination with these elements are known to be effective for the ammoxidation of hydrocarbon reactions [7].

The present chapter describes the preparation of ammonium salt of 12-
molybdophosphoric acid modified by transition metals such as V, Bi and Sb. The effect
Chapter: VI

Studies on transition metal modified AMPA catalysts

of these ions in the stabilization of the structure of AMPA has been studied by using different characterization techniques like XRD, FTIR, $^{31}$P MAS NMR and SEM. The structural stability of metal substituted AMPA is correlated with the ammoxidation functionality.

Section: 1

Studies on vanadium substituted 12-molybdophosphoric acid catalysts

6.1.1 Introduction:

Heteropoly compounds containing mixed molybdenum – vanadium ions are active for several selective oxidation reactions in both homogeneous and heterogeneous systems [2]. The main component of the commercial catalyst for the oxidation of methacrolein to methacrylic acid is the Cs/Na$_4$ salt of MPA [8]. High activity and stability of the catalyst is governed by good reoxidation of the catalyst by air and the mobility of lattice oxygen. It is expected that, vanadium in the Keggin unit reduces the acid strength and increases the redox nature of the catalyst. So, this system has been found to be a promising catalyst for reactions like ammoxidation. Fujibayashi et al [9] studied the catalytic activity of ammonium salt of molybdovanadophosphates for different organic transformations. Marchal-Roch et al [10] synthesized the ammonium salt of vanadomolybdophosphate and employed it for oxidative dehydrogenation of isobutyric acid. Bondareva et al [11] employed the vanadium molybdophosphoric acid and its sodium salt for the ammoxidation of 2-methylpyrazine and reported that the presence of vanadium enhances the ammoxidation functionality. Although various studies of mixed metal coordinated HPA catalysts have been reported, their stability and redox properties remain controversial [12]. The present section deals with the preparation of vanadium substituted ammonium salt of MPA and the influence of number of vanadium atoms on its physico-chemical properties and the ammoxidation functionality.

Two series of catalysts were prepared by incorporating 1 and 2 vanadium atoms in AMPA and subsequently decreasing the Mo atoms from 12 to 11 and from 11 to 10 respectively, maintaining the stoichiometry of the Keggin unit. The two catalysts are
likewise designated as AMPV\textsubscript{1} and AMPV\textsubscript{2} respectively. The detail of the preparation of
the catalysts has been described in chapter 3 under section 2.3.4.

6.1.2 Results and discussion:
6.1.2a Nitrogen adsorption for BET surface area:

The surface areas of the AMPV\textsubscript{1} and AMPV\textsubscript{2} catalysts calcined at different
temperatures in the range of 300-500\degree C, are tabulated in Table 6.1. The surface
area of the catalysts decreases with increase of vanadium content. In general, the
ammonium salt after precipitation and drying possess meso pores. Incorporation of the
metal inside these pores might have led to decrease of surface area. Increase of
calcination temperature also leads to loss of mesopores resulting in the drastic decrease
of surface area of the catalysts [13].

Table 6.1: BET surface area values of AMPV\textsubscript{1} and AMPV\textsubscript{2} catalysts

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Catalyst</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AMPV\textsubscript{1}-300</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>AMPV\textsubscript{1}-350</td>
<td>40</td>
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<tr>
<td>3</td>
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<tr>
<td>4</td>
<td>AMPV\textsubscript{1}-450</td>
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<td>5</td>
<td>AMPV\textsubscript{1}-500</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>AMPV\textsubscript{2}-300</td>
<td>45</td>
</tr>
<tr>
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</tr>
<tr>
<td>8</td>
<td>AMPV\textsubscript{2}-400</td>
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</tr>
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<td>AMPV\textsubscript{2}-450</td>
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</tr>
<tr>
<td>10</td>
<td>AMPV\textsubscript{2}-500</td>
<td>4</td>
</tr>
</tbody>
</table>

6.1.2b X-ray diffraction (XRD) studies:

The XRD patterns of AMPV\textsubscript{1} and AMPV\textsubscript{2} catalysts calcined at different
temperatures in the range of 300-500\degree C are shown in Figures 6.1.1 & 6.1.2 respectively.
The AMPV\textsubscript{1} calcined at 300 to 400\degree C possessed a stable cubic secondary structure
similar to that of (NH\textsubscript{4})\textsubscript{3}PMo\textsubscript{12}O\textsubscript{40}. 4H\textsubscript{2}O. In the case of catalysts calcined at 450-500\degree C,
the XRD patterns showed diffraction lines corresponding to MoO\textsubscript{3} (JCPDS File No.5-
508) indicating the decomposition of ammonium salt [14]. The AMPV\textsubscript{2} catalyst showed diffraction lines due to the presence of MoO\textsubscript{3} at 400°C itself and these lines became more sharper as the temperature increased to 450°C.

A comparison of the catalysts calcined at 400°C reveals that the ammonium salt exists in AMPV\textsubscript{1} whereas the AMPV\textsubscript{2} sample showed its decomposition. This indicates that increase of vanadium content decreases the thermal stability of ammonium salt. It may be expected that the presence of guest metals remarkably affects the structure of
Mo in the primary as well as secondary frameworks. Accordingly, vanadium might replace molybdenum in the peripheral positions of the Keggin anion or act as cation replacing the ammonium in the secondary structure. Diffraction lines relative to vanadium oxide phases were not observed even for the high vanadium content catalyst. However, there is a possibility of vanadium forming a segregated phase, which may exist as amorphous or microcrystalline phase [16], not detected by XRD technique.

Figure 6.1.2: XRD patterns of AMPV₃ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C. ▲, ■ Correspond to AMPA and MoO₃ phases respectively.
Inumaru et al [17] suggested that thermal treatment of 1-vanado-11-molybdophosphoric acid at 350°C in oxygen caused the elimination of vanadium atom from the Keggin anion and formed undefined polymeric and monomeric vanadium species. From the XRD results it seems that the expelled vanadium atoms might be replacing the ammonium atoms causing the collapse of the cubic secondary structure. In the present work this effect seems to be more feasible in AMPV₂ samples because these materials contain more vanadium atoms.

Figure 6.1.3: XRD patterns of used AMPV₁ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C. ▲, ■ Correspond to AMPA and MoO₃ phases respectively.
The XRD patterns of used AMPV₁ and AMPV₂ catalysts are shown in Figures 6.1.3 & 6.1.4 respectively. The catalysts calcined at 300-400°C showed perfect cubic secondary structure similar to that of (NH₄)₃PMo₁₂O₄₀.₄H₂O. Catalysts calcined at 450-500°C showed peaks due to both ammonium salt and MoO₃. These results indicate that regeneration of the decomposed oxides into the ammonium salt in the presence of ammonia and water vapor might have occurred, though not completely [18]. Interestingly, in qualitative terms it can be observed that the extent of formation of ammonium salt by regeneration is less in the case AMPV₂ than in AMPV₁ as observed from the intensities of the XRD peaks. This also suggests that the amorphous vanadium oxide may be inhibiting the regeneration of MoO₃ and P₂O₅ in to ammonium salt in the vanadium rich sample.

Figure 6.1.4: XRD patterns of used AMPV₂ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C. △, ■ Correspond to AMPA and MoO₃ phases respectively.
6.1.2c Fourier Transform Infrared (FTIR) spectroscopic studies:

The FTIR spectra of the fresh AMPV₁ and AMPV₂ catalysts are shown in the Figures 6.1.5 & 6.1.6 respectively. AMPV₁ catalyst calcined at temperature in the range of 300 to 400°C showed strong bands at 1605, 1405, 1050, 950, 855 and 770 cm⁻¹ and small peaks at 590 and 495 cm⁻¹.

Figure 6.1.5: FTIR spectra of AMPV₁ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C
Figure 6.1.6: FTIR spectra of AMPV$_2$ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

Bielanksi et al [19] observed slight negative shifts, of the order of 9 to 10 cm$^{-1}$ wave numbers, for the P-O and Mo=O bands when vanadium was substituted into the Keggin structure. In the spectrum of AMPV$_1$, the P-O and Mo=O bands were shifted by 5cm$^{-1}$ compared to the standard sample, indicating that the vanadium atom might have been incorporated into the Keggin ion. Further increase of calcination temperature to 450-500°C, the AMPV$_2$ sample showed the bands at 982, 863 and 595 cm$^{-1}$ due to MoO$_3$. 

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indicating the collapse of primary as well as secondary structures. It appears that, the incipient destruction of the secondary structure occurs beyond 400°C. For the pure AMPA also, the loss of ammonium cations was observed close to this temperature. A comparison of these results indicates that, incorporation of vanadium into the Keggin ion initiates the loss of secondary structure. The spectra of AMPV_2 sample show bands just like AMPV_1 sample between the 300 and 350°C. Interestingly, no significant difference in peak positions was observed between the AMPV_1 and the AMPV_2 samples implying that the Keggin units in the two samples are nearly identical. Had there been extra vanadium ions added to the Keggin ion, there would have been more shift in the positions of P-O and Mo=O bands of IR spectrum of AMPV_2. Therefore it appears that the extra vanadium was not substituted into the Keggin unit [20] of AMPA.

Figure 6.1.7: FTIR spectra of used AMPV_1 catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C
Upon increasing the temperature to 450 and 500°C, a total collapse of the primary as well as secondary structures was observed. The extra vanadium might have formed into amorphous segregates.

The FTIR spectra of used AMPV₁ and AMPV₂ samples are presented in Figures 6.1.7 & 6.1.8 respectively. The AMPV₁ samples calcined at 300-400°C showed perfect appearance of all the IR bands due to the Keggin structure and the bands due to ammonium ion. Even though the fresh AMPV₁ samples calcined at 450 and 500°C
showed the bands due to MoO₃, the used samples showed the bands corresponding to AMPA, confirming the regeneration of decomposed oxides into the Keggin units. FTIR spectra of used AMPV₂ samples calcined at 300 to 350°C show clear bands due to AMPA. However, bands due to MoO₃ were more dominant in the case of high temperature (400-500°C) calcinated samples. These results support the XRD data, that the extent of regeneration was less in the case of AMPV₂ samples.

6.1.2d \(^{31}\)P MAS NMR spectroscopic studies:

The \(^{31}\)P NMR spectral data are useful to study the nature of the primary and secondary structures. \(^{31}\)P MAS NMR spectra of AMPV₁ and AMPV₂ calcined between 300 and 500°C are shown in Figure 6.1.9. The two samples calcined at 300°C show a single peak at -4.45ppm. According to Black et al [21] (NH₄)₃PMo₁₂O₄₀ reflects a single chemical shift at -4.45ppm. Mestle et al [22] deduced that H₄PMo₁₁V₁O₄₅.8H₂O show at least three types of species with different levels of hydration. In the present case, the presence of a single sharp resonance peak reveals that the catalyst is in a undissociated phase. Casarini et al [23] interpreted the presence of only one species in the single V substituted sample and the presence of multiple resonances in the NMR spectrum of two V atom substituted samples as to the formation of stereo isomers and not to oxoanion with different degree of substitution of metal, which is not possible in the case of V₁ sample. The AMPV₁ sample calcined at 500°C showed two unresolved peaks at 10.00 and -2.80ppm and a sharp resonance peak at -3.73ppm respectively. It is known that the latter two peaks can be assigned to dehydrated Keggin species [24]. The peak at 10.00ppm could not be identified as the species was formed at high calcination temperature. The AMPV₂ sample calcined at 500°C showed a small hump at 10.00ppm a sharp signal at -3.64ppm and a broad signal at -10.07ppm respectively. According to Iwamoto et al [25] the peak at -10.00ppm can be assigned to a mono phosphate formed during calcination. These results suggest that AMPV₁ sample after calcination at 500°C consists of fragmented and dehydrated Keggin ion species with slight indication of decomposed products revealing that the addition of vanadium is showing a sustainable
affect in stabilizing the Keggin ion. Appearance of broad band at -10.0 ppm in AMPV₂ sample reveals that the decomposition is more prominent in the vanadium rich sample.

Figure 6.1.9: $^{31}$P MAS NMR spectra of (a) AMPV₁ - 300°C (b) AMPV₂ - 300°C (c) AMPV₁ - 500°C (d) AMPV₂ - 500°C
6.1.2 Scanning Electron Microscopic (SEM) studies:

The SEM photographs of AMPV₁ and AMPV₂ catalysts are shown in Figures 6.1.10 & 6.1.11 respectively. The AMPV₁ sample calcined at 300 and 350°C showed spherical crystallites with uniform size (2.5 μm) and they appeared to be in a single phase. The sample calcined at 400 and 450°C contained big crystals along with small spherical aggregates. Besides, an amorphous material appeared to have covered the crystals. This morphology was dominant in the case 450°C calcined catalysts than the sample calcined at 400°C. Very big crystals with roughness on the surface were clearly observed in sample calcined at 500°C.

Figure 6.1.10: SEM photographs of catalysts AMPV₁ calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

Ji.Hu et al [26] observed the presence of spherical aggregates corresponding to the ammonium salt at lower calcination temperatures. The large crystals in the above
figures might correspond to MoO$_3$, since XRD results showed a reminiscent peak of MoO$_3$. Similarly the number of big crystals increased in sample calcined at 450°C, where the formation of MoO$_3$ is confirmed from XRD and FTIR results. At 500°C, the sample showed a different morphological behavior. A condensed matter was observed besides the crystals of MoO$_3$.

![SEM photographs of catalysts AMPV$_2$ calcined at various temperatures](image)

**Figure 6.1.11**: SEM photographs of catalysts AMPV$_2$ calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

The morphology of AMPV$_2$ catalysts is totally different from that of the AMPV$_1$ catalysts. The samples calcined at 300 and 350°C showed spherical aggregates of different sizes. An amorphous phase formation was observed in the sample calcined at 400°C besides the presence of irregular aggregates. The samples calcined at 450 and 500°C showed complete coverage of amorphous mass over the aggregates. It is known that expulsion of vanadium as oxovanadium (VO)$_2^+$ cations from the Keggin ion is possible. These species may be covering the aggregates of AMPA and MoO$_3$. XRD and
FTIR results also indicated that decomposition of AMPA would start beyond 410°C. But the sample calcined at 400°C showed the amorphous material also suggesting that there was another phase formation other than MoO₃ and P₂O₅.

6.1.2f Ammoxidation of 2-methylpyrazine:

The product distribution patterns in the ammonoxidation of 2-methylpyrazine reaction over AMPV₁ and AMPV₂ catalysts are shown in Figures 6.1.12 & 6.1.13. The AMPV₁ catalyst calcined at 300°C showed 50% MP conversion with 95% selectivity to CP at a typical reaction temperature of 360°C. With the increase in calcination temperature from 300 to 500°C, the conversion dropped from 62 to 48% and the selectivity to CP marginally dropped from 93 to 90% at a reaction temperature of 380°C. It appears that the increase of calcination temperature led to destruction of the Keggin ion, which in turn, decreased the ammonoxidation functionality. An interesting observation is that, the vanadium substituted AMPA catalysts showed a remarkable activity and selectivity when compared with the pure AMPA catalysts. The pure AMPA catalyst calcined at 500°C showed a maximum conversion of 10% with 98% selectivity to CP at a reaction temperature of 400°C, but the AMPV₁ catalyst calcined at 500°C showed 60% conversion with 88% selectivity to CP. This fact can be explained on the basis of increase in redox properties of the AMPV₁ catalyst and the vanadium atoms from the Keggin ions might have formed into V⁺⁺⁺ atoms on the surface of the catalysts [28, 29]. The latter species are more active for the ammonoxidation reaction, and also upon exposure of water the Mo and P oxides formed during the calcination were reconstructed into the Keggin ion which may also be helpful to get more activity.

The AMPV₂ catalysts showed a similar behavior with increase in calcination temperature. The decrease in conversion and increase in the selectivity was observed in these catalysts when compared with AMPV₁ catalysts. Expulsion of vanadium atoms from the Keggin unit even at lower calcination temperatures appears to be more in the case of AMPV₂ than that of AMPV₁ samples. Presence of additional vanadium atoms in these catalysts may be responsible for this behavior.
Figure 6.1.12: Product distribution in ammoxidation of 2-MP reaction as a function of calcination temperature over AMPV₁ catalysts at different reaction temperatures (A) conversion of MP (B) selectivity to CP (C) selectivity to pyrazine
Figure 6.1.13: Product distribution in the ammoxidation of 2-MP as a function of calcination temperature over AMPV2 catalysts at different reaction temperatures (A) conversion of MP (B) selectivity to CP (C) selectivity to pyrazine
Section: 2
Studies on bismuth substituted 12-molybdophosphoric acid catalysts:

6.2.1 Introduction:

Over the past 20 years several generations of multi component bismuth molybdate catalysts have been developed for the ammoxidation reactions [30]. The primary function of bismuth in these systems is to activate the surface adsorbed reactive substrate through the abstraction of a α-hydrogen atom. This is the first and an important step in the ammoxidation reaction [31]. There are several reports on the effect of addition of bismuth phosphate to molybdate systems for oxidation and ammoxidation reactions. Rodriguez et al [32] reported the synthesis of bismuth phosphomolybdate catalyst and its application towards synthesis of nitriles from formamides. Hence, it is relevant to study the effect of incorporation of this metal into the Keggin type heteropoly compounds on the activity and examine the changes in the physico-chemical properties of these compounds. The present section describes the physico-chemical properties of bismuth modified AMPA. The influence of addition of bismuth atoms to AMPA was studied by comparing their ammoxidation functionality with that of the pure AMPA.

Two series of catalysts were prepared by incorporating 1 or 2 atoms of bismuth into the Keggin structure simultaneously decreasing the Mo atoms from 12 to 11 and 11 to 10, to maintain the stoichiometry of the Keggin unit. The catalysts are designated as AMPBi₁ and AMPBi₂ representing AMPA containing 1 and 2 bismuth atoms respectively. The details of preparation have been presented in Chapter3 under section 2.3.4.

6.2.2 Results and discussion:

6.2.2a Nitrogen adsorption for BET surface area:

The surface areas of the AMPBi₁ and AMPBi₂ catalysts calcined at different temperatures in the range of 300-500°C are tabulated in Table 6.2. It may be observed that with increase in bismuth content as well as increase in calcination temperature the surface area of the catalysts decreased. Precipitation and drying at 120°C allows the catalysts to possess mesopores contributing to high surface area, but calcination at higher temperature leads to dehydration of the salt with a consequence collapse of the
medium pores [13]. Formation of metal oxides due to the decomposition of the salt further decreased the surface area.

Table 6.2 BET surface area values of AMPBi₁ and AMPBi₂ catalysts

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
</tr>
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<tr>
<td>1</td>
<td>AMPBi₁-300</td>
<td>47</td>
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<tr>
<td>2</td>
<td>AMPBi₁-350</td>
<td>39</td>
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<td>3</td>
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<td>AMPBi₂-500</td>
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</table>

6.2.2b X-ray diffraction (XRD) studies:

The XRD patterns of AMPBi₁ and AMPBi₂ catalysts calcined at different temperatures in the range of 300-500°C are shown in Figures 6.2.1 & 6.2.2 respectively. The AMPBi₁ catalysts calcined at 300 to 400°C clearly showed the diffraction peaks corresponding to the cubic structure of (NH₄)₅P₂Mo₁₇O₄₅.4H₂O (JCPDS File No.9-412). The samples calcined at 450 and 500°C showed diffraction lines due to MoO₃. These results reveal that the decomposition of ammonium salt started at a temperature between 400 to 450°C. In comparison, the diffraction pattern of AMPA showed diffraction lines due to MoO₃ beyond 400°C, thus the addition of bismuth metal to the salt appeared to have no negative effect on the thermal stability of the salt. It is known that Bi salts of HPA are less thermally stable than that of the parent acid [3]. It is also known that the redox properties of molybdenum-based heteropoly compounds can be remarkably affected by the presence of guest metals in the primary framework [33], as well as by the nature of the metal cations in the secondary framework. Hence, bismuth might play a crucial role also in the stabilization of the structure of AMPA.
Figure 6.2.1: XRD patterns of AMPBi catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

\( \Delta, \Box \) Correspond to AMPA and MoO\(_3\) phases respectively

The sample AMPBi\(_2\) calcined at 300 and 350°C showed the diffraction lines due to AMPA and bismuth phosphomolybdate with the formula Bi\(_4\)P\(_{12}\)O\(_{42}\) (d = 3.18, 3.056 and 4.88, JCPDS file No. 30-193). The intensity of the diffraction lines corresponding to Bi\(_4\)P\(_{12}\)O\(_{42}\) increased with increase in temperature from 300 to 350°C.
Figure 6.2.2: XRD patterns of AMPBi2 catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

△, ■, O Correspond to AMPA, MoO3 and Bi9PMo12O49 phases respectively

Upon increasing the temperature to 400°C, the peaks corresponding to AMPA disappeared and the diffraction lines due to MoO3 were observed along with lines due to Bi9PMo12O49.
These results indicate that during the preparation of the catalysts, the excess (more than 1 Bi atom) bismuth nitrate in the solution increased the bismuth atoms in the mixture, which might have reacted with phosphorous leading to the formation of the Bi₉PMo₁₂O₄₀ phase. There was no change in the intensity of the diffraction lines corresponding to this phase with increase in temperature of calcination from 400 to
500°C. Because of the formation of bismuth phosphomolybdate, the extent of formation of ammonium salt also decreased (evidenced by the decrease of intensity of diffraction peaks).

Figure 6.2.4: XRD patterns of used AMPBi catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

▲, ■, ○ Correspond to AMPA, MoO₃ and Bi₆PMo₁₂O₄₀ phases respectively

The XRD patterns of used AMPBi₁ and AMPBi₂ catalysts are shown in Figures 6.2.3 & 6.2.4 respectively. The used catalysts of AMPBi₁ samples calcined between 300
and 500°C showed perfect cubic structure of $\text{(NH}_4\text{)}_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$. It may be construed that, the regeneration of ammonium salt from the decomposed oxides is more favorable in the case of single bismuth atom incorporated compounds. The used samples of AMPBi$_2$ calcined at 300 and 350°C showed diffraction lines due to both the AMPA and Bi$_9$PMo$_{12}$O$_{52}$ phases. The catalysts calcined at high temperatures (400-500°C) showed the diffraction lines corresponding to MoO$_3$ and Bi$_9$PMo$_{12}$O$_{52}$, the disappearance of diffraction lines due to AMPA reveal that the regeneration of MoO$_3$ and P$_2$O$_5$ into AMPA was not happening in these catalysts. Formation of stable Bi$_9$PMo$_{12}$O$_{52}$ might have inhibited the regeneration of the decomposed oxides.

6.2.2c Fourier Transform Infrared (FTIR) spectroscopic studies:

The FTIR spectra of the fresh AMPBi$_1$ and AMPBi$_2$ catalysts calcined at different temperatures are shown in the Figures 6.2.5 & 6.2.6 respectively. The IR spectrum of the unmodified ammonium salt calcined at 300-350°C shows the bands at 1065, 964, 887, 790 and 1410 cm$^{-1}$ corresponding to $v_{as}(\text{P-O})$, $v_{as}(\text{Mo-O})$, $v_{as}(\text{Mo-O}_5\text{Mo})$, $v_{as}(\text{Mo-O}_2\text{Mo})$ and NH$_4^+$ vibrations of the Keggin ion respectively [10]. The AMPBi$_1$ samples calcined at temperature in the range of 300 to 400°C showed all the characteristic bands of the Keggin ion as well the band at 1410 cm$^{-1}$ due to the ammonium ion. These results offer a clear evidence for the stability of cubic ammonium salt. Further increase in temperature to 450 and 500°C, AMPBi$_1$ samples showed the bands at 982 863 and 595 cm$^{-1}$ due to MoO$_3$. The FTIR spectral data of AMPBi$_1$ samples showed no differences in the structure due to the bismuth addition with respect to the pure salt. From these results it can be assumed that bismuth did not replace molybdenum in the peripheral positions of the Keggin anion. If it had happened, there would have been a certain shift in the characteristic bands of the Keggin ion [19, 20]. These results indicate that the bismuth added might be acting as cation in the secondary structure. Stabilization of the Keggin structure is more pronounced when the bismuth content corresponded to one atom per Keggin unit.
Studies on transition metal modified AMPA catalysts

The AMPBi samples calcined at 300 and 350°C showed all the bands corresponding to AMPA. Even though the bismuth phosphomolybdate observed in XRD patterns of these catalysts is also a condensed phase of heteropoly acid, there were no
bands corresponding to this phase in the IR spectrum. The spectra of AMPBi2 samples calcined at 400 to 500°C showed the peaks due to MoO3 along with a hump at 1060 cm⁻¹, corresponding to P-O stretching vibration. These results indicate that the formation of bismuth phosphomolybdate leads to low temperature destruction of Keggin ion of AMPA in AMPBi2 samples when compared with that in AMPBi1 samples.

Figure 6.2.6: FTIR spectra of AMPBi2 catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C
The FTIR spectra of used AMBi₁ and AMBi₂ samples are shown in the Figures 6.2.7 & 6.2.8 respectively. Interestingly all the AMBi₁ samples show the characteristic bands of the Keggin structure and a high intense band at 1410 cm⁻¹ due to ammonium ion. The intensity of the latter ion band was more in the used catalysts than in the fresh catalysts.

Figure 6.2.7: FTIR spectra of used AMBi₁ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C
Even though fresh AMPBi2 samples calcined at 450 and 500°C showed the bands due to MoO₂, the used samples displayed the bands corresponding to AMPA, revealing that the regeneration of decomposed oxides into the Keggin units is possible. The FTIR results are supporting the fact that the regeneration of ammonium salt is
possible even after complete destruction of the Keggin unit, which was not observed in the case of other metal substituted AMPA catalysts. The FTIR spectra of used AMPBi₂ samples calcined at 300 to 400°C showed clear bands due to AMPA. However, bands due to MoO₃ are more dominant in the case of 450 and 500°C calcinated samples. Appearance of small bands at 1410, 950 cm⁻¹ and a doublet at 1060 cm⁻¹ indicate the presence of bismuth phosphomolybdate. Even though there was AMPA formation, it was not as intense as it was in the AMPA pure sample. These results are in accordance with the XRD results, indicating that the extent of regeneration is restricted in bismuth rich samples.

6.2.2d $^{31}$P MAS NMR studies:

$^{31}$P NMR spectral data are useful to study the nature of the species formed during the preparation and the changes occurring during calcination. $^{31}$P MAS NMR spectra of AMPBi₁ and AMPBi₂ samples calcined at 300 and 500°C are shown in Figure 6.2.9. The AMPBi₁ sample calcined at 300°C showed a single resonance peak at -4.49ppm, whereas the sample of AMPBi₂ calcined at 300°C showed two sharp resonance peaks with very little margin in chemical shift i.e., at -3.73 and -4.38 ppm and two small peaks at -12.48 and 3.51ppm respectively. According to Black et al [21] $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ reflects a single chemical shift at -4.45ppm. The resonance peak at -4.38ppm can be assigned to AMPA and the other at -3.73ppm to the presence of Bi₉PMo₁₂O₄₂. The appearance of this peak in the lower fields also indicates that this compound exhibits the Keggin type structure. The XRD pattern of the AMPBi₂ sample calcined at 300°C also showed the presence of Bi₉PMo₁₂O₄₂ phase. The other peaks at -12.48 and 3.518ppm can be assigned to the dehydrated and fragmented species. The AMPBi₁ sample calcined at 500°C showed three sharp resonance peaks at 0.383, -3.814 and -6.396ppm respectively. It is known that the peak at -3.81ppm is due to the appearance of Bi₉PMo₁₂O₄₂. Partial fragmentation of the Keggin ion occurs at this temperature, the fragmented AMPA species, reflecting at -6.396ppm. The AMPBi₂ sample calcined at 500°C showed a broad peak composed of two unresolved peaks at -3.284 and -4.059ppm, which could be assigned to the different dehydrated Keggin
species. From these results, it may be inferred that even at 500°C the Keggin unit exists with slight modification, in the AMPBi₁ sample.

The peak at −0.383 ppm may be due to P₂O₅ formed during the decomposition of the Keggin unit at this temperature [25]. These results indicate that AMPBi₂ sample
calcined at 500°C consists of decomposed and fragmented Keggin ion species. It may be expected that the addition of excess of bismuth leads to formation of unwanted species showing negative affect in the stabilization of the Keggin ion.

6.2.2e Scanning Electron Microscopic (SEM) studies:

The SEM photographs of AMPBi$_1$ and AMPBi$_2$ catalysts are shown in Figure 6.2.10 & 6.2.11. The AMPBi$_1$ sample calcined at 300 and 350°C showed spherical aggregates with uniform size (2.5 μm) and they appeared to be of single phase. The sample calcined at 400°C contained big agglomerates. Besides, there was an amorphous material covering the crystals in these samples. The catalysts calcined at 450 and 500°C showed big crystals, which may correspond to MoO$_3$, since the XRD results revealed formation of MoO$_3$ as a major component at these temperatures. The nature of the amorphous matter however could not be established.
The morphology of AMPBi₂ catalysts was quite different from that of the AMPBl₁ samples. The catalysts calcined at 300°C showed highly dispersed small aggregates along with needle type crystalline material. From the XRD and FTIR results, it was observed that this may because of the Bi₅PMo₁₂O₄₅ phase. With increase of temperature from 350 to 450°C, the catalysts showed amorphous material covered on the surface of the crystallites, it may because of formation non-stoichiometric compounds composed of Bi, Mo and P. The catalyst calcined at 500°C showed the two types of crystals with different sizes. The needle type crystals might belong to Bi₅PMo₁₂O₄₅ and the other may be because of MoO₃ formed due to decomposition of AMPA [27].

Figure 6.2.11: SEM photographs of AMPBi₂ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

6.2.2f Ammoxidation of 2-methylpyrazine:

The product distribution in the ammoxidation of 2-methylpyrazine reaction over AMPBl₁ and AMPBi₂ catalysts are shown in Figures 6.2.12 & 6.2.13.
Figure 6.2.12: Product distribution in ammoxidation of 2-MP reaction as a function of calcinations temperature over AMPBi, catalysts at different reaction temperatures (A) conversion of MP (B) selectivity to CP (C) selectivity to pyrazine.
Figure 6.2.13: Product distribution in ammoxidation of 2-MP reaction as a function of calcinations temperature over AMPBi\textsubscript{c} catalysts at different reaction temperatures (A) conversion of MP (B) selectivity to CP (C) selectivity to pyrazine
The AMPBi₁ catalysts calcined at 300 and 350°C showed 45% conversion of MP with 92% selectivity to CP at reaction temperature of 360°C. With increase in reaction temperature the conversion of MP increased to 94% at 420°C and the selectivity to CP decreased to 85%. It was already explained that at high conversion levels, the selectivity to CP decreases, which may due to the non-catalytic reaction, i.e., conversion of CP to pyrazine via formation of carboxylic acid in the presence of air and its decarboxylation leading to pyrazine formation. With increase in calcination temperature from 400-500°C, a small increase in conversion of MP and decrease in selectivity to CP was observed at all reaction temperatures. This behavior may be because of presence of bismuth in the samples which might have been segregated into unidentified mixed oxides. This type of amorphous materials can enhance the redox nature of the catalysts.

The AMPBi₂ catalysts calcined at 300 and 350°C showed 50% conversion of MP with 90% selectivity to CP at typical reaction temperature of 360°C. With increase of calcination temperature to 400 to 500°C, both the conversion and selectivity to CP decreased. This may be due to the lesser extent of formation of AMPA in this case because of the formation of bismuth phosphomolybdate during the catalyst preparation. The regenerability of AMPA is also less when compared with AMPBi₁ catalysts. These two factors seems to have affected the ammoxidation functionality of these catalysts.
Section: 3

Studies on antimony substituted ammonium salt of 12-molybdophosphoric acid catalysts

6.3.1 Introduction:

Very few studies [34, 35] have been devoted to study the effect of antimony on the properties of heteropoly compounds in catalysis reactions of selective oxidations and ammoxidation, even though antimony is a well-known component of catalysts for this class of reactions. Cavani et al [35] reported that the addition of antimony ions to a mixture of potassium/ammonium salts of 12-molybdophosphoric acid considerably improves the structural stability of the compound. They claimed that the addition of at least one atom of antimony per Keggin unit increases the starting temperature of structural decomposition by 80-100°C. Cavani et al [35] reported that the addition of antimony led to decrease in the performance of the catalysts. To improve the catalytic performance they added other promoter metals like Cr, Fe, Cu etc. However, the variation of catalytic performance with structural stability is still ambiguous because antimony metal is associated with many kinds of metals under various reaction conditions. Hence, one cannot come to a conclusion with the existing information [36]. To clarify the above queries, a study has been undertaken on preparation of selective antimony metal doped ammonium salt of 12-molybdophosphoric acid, its structural stability and catalyst performance in the ammoxidation of 2-methylpyrazine, is presented in this section.

Three series of catalysts, each subjected to precalcination at different temperatures in the range 300-500°C with increasing amounts of antimony atoms from 1 to 3 and a consequence decrease of Mo atoms from 11 to 9 to maintain the stoichiometry of the Keggin unit, were prepared. The catalysts are designated as AMPSb₁, AMPSb₂ and AMPSb₃ for 1 to 3 antimony atoms respectively. The preparation procedure was given in Chapter 3 under section 3.3.4.
6.3.2 Results & discussions:

6.3.2a Nitrogen adsorption for BET surface area:

The surface areas of the AMPSb₁, AMPSb₂ and AMPSb₃ catalysts calcined at different temperatures in the range of 300-500°C are tabulated in Table 6.3. With increase in antimony content and the calcination temperature, the surface area of the catalysts decreased. In general, dried ammonium salts possess meso pores. Decrease in surface area with the addition of metal contributing to high surface coverage implies pore blockage. Increase in calcination temperature decreases the ammonium content, which leads to formation of metal oxides resulting the drastic decrease of surface area of the catalysts.

6.3.2b X-ray diffraction (XRD) studies:

The XRD patterns of AMPSb₁, AMPSb₂ and AMPSb₃ catalysts calcined at different temperatures in the range of 300-500°C are shown in Figures 6.3.1, 6.3.2 & 6.3.3 respectively. All the catalysts calcined at 300 and 350°C possessed stable cubic secondary structure of (NH₄)₃PMo₁₂O₄₀. 4H₂O (JCPDS File No.9-412). At 400°C, the decomposition of ammonium salt started in the case of AMPSb₁ and AMPSb₂, since 400°C is very close to the temperature of incipient decomposition for the ammonium salt [15]. But the sample AMPSb₃ calcined at 400°C showed (NH₄)₃PMo₁₂O₄₀. 3H₂O (ASTM File No.16-181). It was also observed that with the increase of antimony composition corresponding from 1 to 3 atoms the intensity of diffraction peaks of the ammonium salt increased.
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Figure 6.3.1: XRD patterns of AMPS₅₅ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

▲, □ Correspond to AMPA and MoO₃ phases respectively

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Table 6.3 BET surface area values of AMPSb₁, AMPSb₂, and AMPSb₃ catalysts at different calcination temperatures

<table>
<thead>
<tr>
<th>S.No</th>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AMPSb₁-300</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>AMPSb₁-350</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>AMPSb₁-400</td>
<td>24</td>
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<tr>
<td>4</td>
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<td>6</td>
<td>AMPSb₂-300</td>
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<td>33</td>
</tr>
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<td>8</td>
<td>AMPSb₂-400</td>
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<td>9</td>
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<tr>
<td>15</td>
<td>AMPSb₂-500</td>
<td>4</td>
</tr>
</tbody>
</table>
Figure 6.3.2: XRD patterns of AMP-Sb catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

▲,■ correspond to AMPA and MoO₃ phases respectively.
Figure 6.3.3: XRD patterns of AMPSb$_2$ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

- - Correspond to AMPA and MoO$_3$ phases respectively

At 450 and 500°C the AMPSb$_1$ and AMPSb$_2$ samples showed complete decomposition of the salt. On the other hand AMPSb$_2$ sample showed small diffraction peaks corresponding to the ammonium salt. This is a clear evidence for the enhancement of thermal stability of ammonium salt by the addition of higher amount of antimony atoms.
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Figure 6.3.4: XRD patterns of used AMPSb catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

▲, ■ Correspond to AMPA and MoO₃ phases respectively

This indicates that the nature of interaction between antimony ion and molybdenum is different in the samples. It is known that the redox properties of molybdenum, based
heteropoly compounds can be remarkably affected by the presence of guest metals in the primary framework, as well as by the nature of the metal cations in the secondary framework. Accordingly antimony might replace molybdenum in the peripheral positions of the Keggin anion or act as cation replacing the ammonium in the secondary structure [17]. Diffraction lines relative to antimony oxide phases were not observed even for high antimony containing ammonium salt. There is a possibility of formation of segregated phase of antimony, such as dispersed/amorphous or microcrystalline phases.

![XRD patterns of used AMPSb\textsubscript{2} catalysts calcined at (a) 300\textdegree C (b) 350\textdegree C (c) 400\textdegree C (d) 450\textdegree C (e) 500\textdegree C.](image)

*Correspond to AMPA and MoO\textsubscript{3} phases respectively.*
Cavani et al [38] mentioned that with the increase of antimony content the ammonia content decreases in the secondary structure in the case of potassium-ammonium salt of 12-molybdophosphoric acid. But in the present case, the results are quite reverse. This difference could be due to the presence of another atom i.e., potassium in the secondary structure, which is more stable than the ammonium cation.

Figure 6.3.6: XRD patterns of used AMPoSb catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

▲, □ Correspond to AMPA and MoO₃ phases
They also mentioned that antimony atom could act as a cation replacing the ammonium in the secondary structure. With increase of antimony content and calcination of the salts at higher temperature, antimony replaces ammonia and the expelled ammonia comes out of the secondary structure as nitrogen or ammonia gas [37]. But in the present case only ammonium ions were present in the secondary structure. In the case of AMPSb2 the antimony might have been held at some other positions in the secondary structure leading to high thermal stability of the salt, which needs to be identified. The variation of intensity of the MoO3 diffraction peaks corresponding to the planes of (020), (040) and (060) might be due to the change in the crystallinity of the samples.

The XRD patterns of used AMPSb1, AMPSb2 and AMPSb3 catalysts are shown in Figures 6.3.4, 6.3.5 & 6.3.6 respectively. The used catalysts of all the samples calcined at 300-400°C showed perfect cubic secondary structure of \((\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}\). Catalysts calcined at 450-500°C showed peaks due to ammonium salt and MoO3. These results indicate the regeneration of the decomposed oxides into the ammonium salt in the presence of ammonia and water vapor. Interestingly AMPSb3 catalyst calcined at 500°C did not show clear diffraction lines due to the ammonium salt. This may be because of its peculiar behavior in decomposition of ammonium salt. The formed amorphous antimony oxide may be inhibiting the regeneration of MoO3 and P2O5 in to ammonium salt.

6.3.2c Fourier Transform Infrared (FTIR) spectroscopic studies:

The FTIR spectra of the fresh AMPSb1, AMPSb2 and AMPSb3 catalysts calcined at different temperatures are shown in the Figures 6.3.7, 6.3.8 & 6.3.9 respectively. The IR spectra of the ammonium salt pretreated at 300-400°C show the bands at 1065, 964, 887, 790 and 1420 cm\(^{-1}\) corresponding to \(v_{\text{as}}(\text{P-O}_2)\), \(v_{\text{as}}(\text{Mo-O}_7)\), \(v_{\text{as}}(\text{Mo-O}_6-\text{Mo})\), \(v_{\text{as}}(\text{Mo-O}_5-\text{Mo})\) and \(\text{NH}_4^+\) vibrations respectively, of the Keggin ion.
These results offer a clear evidence for the stability of cubic ammonium salt up to 400°C. At 450-500°C calcination temperatures, AMPSb₁ and AMPSb₂ samples showed the bands at 982 863 and 595 cm⁻¹ due to MoO₃. But the AMPSb₃ sample showed the bands due to the Keggin ion even at 500°C; however the band due to ammonium ion disappeared at 450-500°C calcination. These results indicate that the Keggin structure is
stable below 450°C in the case of AMPSb₁ and AMPSb₂, but it is stable above 450°C in case of AMPSb₃ sample. The FTIR spectral data showed no differences in the structure due to the antimony addition with respect to the pure salt. From these results one can assume that antimony did not replace the molybdenum in peripheral positions in the Keggin anion. If it had happened, there would have been certain shift occurring in the characteristic bands of the Keggin ion. This observation implies that antimony may be present as a cation in the secondary structure or remaining as an amorphous segregated oxide phase [36].

![Figure 6.3.8: FTIR spectra of AMPSb₃ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C](image-url)
Stabilization of secondary structure was more pronounced in the case of catalysts containing 3 Sb atoms per the Keggin unit. In the XRD patterns of AMPSb₁ and AMPSb₂, the formation of MoO₃ was observed in samples calcined above 400°C, but the FTIR spectra of these catalysts showed the characteristic bands of the Keggin ion at this temperature. This contradiction can be interpreted either by assuming that the loss of ammonium does not lead to the decomposition of the Keggin ion, since a proton or an antimony atom can effectively act as a cation in the secondary structure [38].

![FTIR spectra of AMPSb₃ catalysts calcined at different temperatures](image)

**Figure 6.3.9:** FTIR spectra of AMPSb₃ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C
The FTIR spectra of the used AMPSb₁, AMPSb₂ and AMPSb₃ catalysts are shown in Figures 6.3.10, 6.3.11 & 6.3.12 respectively. The used AMPSb₁, AMPSb₂ and AMPSb₃ samples calcined at 300-450°C showed all the bands corresponding to the ammonium salt. These results are also revealing that the regeneration of the ammonium salt from its decomposed oxides took place in the case of these catalysts.

Figure 6.3.10: FTIR spectra of used AMPSb₁ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C
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Figure 6.3.11: FTIR spectra of used AMPSb₂ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

The catalysts of used AMPSb₁ and AMPSb₂ calcined at 500°C showed strong bands corresponding to the ammonium salt and weak bands due to MoO₃ indicating that regeneration was not complete. Interestingly the sample AMPSb₃ calcined at 500°C showed typical IR spectrum containing a strong band at 1410 cm⁻¹ due to ammonium ion and bands due to MoO₃ with splitting. This is indicative of a strong interference of antimony, which is more in case of AMPSb₂ sample to regenerate the Keggin ion. These results are quite in corroboration with the XRD results.
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Figure 6.3.12: FTIR spectra of used AMPSb₃ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

6.3.2d $^{31}$P MAS NMR spectroscopic studies:

Even though an examination by X-ray diffraction and FTIR gave valuable information, these are, in general, not sufficiently sensitive to show either the presence of mixed heteropoly anions or structural changes which occur as a consequence of calcination. $^{31}$P NMR spectral analysis is useful for elucidating the nature of the primary and secondary structures. $^{31}$P MAS NMR spectra of AMPSb₁, AMPSb₂ and AMPSb₃
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calcined at 300 and 500°C are shown in Figure 6.3.13. The three samples calcined at 300°C showed a single peak at -4.41 ppm.

Figure 6.3.13: $^{31}$P MAS NMR spectra of (a) AMPSb₁ - 300°C (b) AMPSb₂ - 300°C (c) AMPSb₂ - 300°C (d) AMPSb₁ - 500°C (e) AMPSb₂ - 500°C (f) AMPSb₂ - 500°C
According to Black et al. [21], (NH₄)₃PMo₁₂O₄₀ reflects a single chemical shift at -4.45 ppm. It is known that any metal substitution in the Keggin ion can lead to mixtures containing a variety of species with differing degrees of substitution. From these results, one can conclude that antimony was not substituted into the Keggin ion. The AMPSb₁ and AMPSb₂ samples calcined at 500°C showed a broad peak composed of at least three peaks appearing at -11.00, -13.00 and -18.00 ppm respectively. According to Iwamoto et al. [25], these peaks can be assigned for mono and polyphosphates formed during the calcination. But the spectrum of AMPSb₂ calcined at 500°C showed a single resonance peak at -18.27 ppm. The multiple bands represented by the AMPSb₁ and AMPSb₂ samples indicate the uneven decomposition of the Keggin unit into different species. In contrast, AMPSb₃ sample showed a uniform polymeric phosphorus oxide species suggesting the effect of the presence of more antimony. This might be the reason for the absence of the Keggin ion bands in the FTIR spectrum, of used AMPSb₃ catalyst.

### 6.3.2e Scanning Electron Microscopic (SEM) studies:

The SEM images of AMPSb₁, AMPSb₂ and AMPSb₃ catalysts calcined at different temperatures are shown in Figures 6.3.14, 6.3.15 & 6.3.16 respectively. SEM images at lower calcination temperatures (300-400°C) showed that the samples containing (NH₄)₃PMo₁₂O₄₀ are well formed, spherical aggregates of 2.5 μm average diameter. After increasing the calcination temperature to 450-500°C the salts showed large irregular block like crystals of varying sizes (4-5 μm) with roughness. An amorphous mass on the surface of the crystallites was also observed suggesting the presence of decomposition products. It is noteworthy to mention that the amounts of amorphous mass as well as the size of the metal oxide crystals are more in the case of AMPSb₃ sample than in other series of samples at higher calcination temperatures.
Figure 6.3.14: SEM photographs of AMSb₁ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C
Figure 6.3.15: SEM photographs of AMSb$_2$ catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C
Figure 6.3.16: SEM photographs of AMSb\(_3\) catalysts calcined at (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

6.3.2f Ammoxidation of 2-methylpyrazine:

The production distribution in the ammoxidation of 2-methylpyrazine reaction over AMPSb\(_1\), AMPSb\(_2\) and AMPSb\(_3\) catalysts are shown in Figures 6.3.17, 6.3.18 & 6.3.19 respectively. AMPSb\(_1\) calcined at 300°C offered 54% conversion with 92% selectivity to CP at 380°C, whereas by increasing the antimony atom content to 2 and 3 the conversion decreased to 45-20%. However, selectivity to CP increased to 97-100%. Similar behavior was observed in other reaction temperatures also. With the increase of reaction temperature increase in conversion and decrease in selectivity to CP was
observed. With increase of calcination temperature from 300 to 500°C, all the samples exhibited increase in conversion and a slight decrease in selectivity to CP. This fact can be explained by taking the hypothesis proposed by Cavani et al [36] that with the increase of calcination temperature, the amount of ammonia expelled out from the secondary structure increases, increasing the amount of antimony going into the secondary structure. It is known that due to the redox reaction between the [PMo$_{12}$O$_{40}$]$^{3-}$ and the residual Sb$^{3+}$ ions the oxidation state of Mo reduces from 6 to 5. The extent of reduction is directly proportional to the antimony content. From this discussion we can say that the sample AMP$\text{Sb}_2$ has more amount of Mo$^{5+}$ species. The presence of higher amounts of reduced molybdenum species (Mo$^{5+}$), which are known to be more active in redox type reactions is the reason for getting high conversions and yields of CP.
Figure 6.3.17: Product distribution in ammoxidation of 2-MP reaction as a function of calcinations temperature over AMPSb<sub>i</sub> catalysts at different reaction temperatures (A) conversion of MP (B) selectivity to CP (C) selectivity to pyrazine
Figure 6.3.18: Product distribution in ammoxidation of 2-MP reaction as a function of calcinations temperature over AMPs\textsubscript{2} catalysts at different reaction temperatures (A) conversion of MP (B) selectivity to CP (C) selectivity to pyrazine
Figure 6.3.19 Product distribution in ammoxidation of 2-MP reaction as a function of calcinations temperature over AMPSb$_3$ catalysts at different reaction temperatures (A) conversion of MP (B) selectivity to CP (C) selectivity to pyrazine
6.4 References:

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