

# Antimony Substituted Ammonium 12-Molybdophosphoric Acid Catalysts for Gas Phase Chlorobenzene Oxidation

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## Abstract

Antimony (Sb) substituted Keggin structured ammonium salt of 12-molybdophsphoric acid (AMPA) materials were synthesized by acid precipitation method. The samples were obtained by increase of Sb atoms from 1 to 3 and corresponding decrease of Mo atoms from 11 to 9. The synthesized materials were thermal treated in the range of 300–500 °C. The catalytic performance of thermally treated Sb incorporated AMPA materials were examined for oxidation of chlorobenzene and the catalytic activity of Sb-AMPA samples was compared with activity of bulk AMPA. The materials were thoroughly analyzed by different techniques such as elemental analysis, TG, powder XRD, FTIR, SEM, N<sub>2</sub>-physisorption, <sup>31</sup>P MAS NMR, XPS, DR UV–Vis and H<sub>2</sub>-TPR techniques. The characterization results clearly indicated that Sb-AMPA samples possessed high thermal stability, relatively large surface area and easy reducibility compared to bulk AMPA. The synthesized samples also possessed high content of surface adsorbed oxygen species, which are responsible for superior catalytic activity.

## **Graphic Abstract**



**Keywords**  $(NH_4)_3[PMo_{12}O_{40}] \cdot Sb$  incorporation  $\cdot$  Chlorobenzene  $\cdot$  Gas phase oxidation

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Extended author information available on the last page of the article

## 1 Introduction

Degradation of chlorinated organic molecules to  $CO_2$ , HCl and H<sub>2</sub>O have gained tremendous importance due to the fact that chlorinated organic compounds are toxic to human beings even in low concentrations and also they are responsible for the lessening of the ozone layer in the stratosphere [1, 2]. The destructive removal of chlorinated organic compounds by using catalytic oxidation is well used process because it is not only effective but also economical. It is a challenge to develop a catalyst that could destruct a wide range of chlorinated organic compounds with different concentrations and exhibit high selectivity towards the formation of harmless products at relatively low reaction temperatures [3].

Catalysts contained noble metals such as Pt, Pd [4] and transition metal oxides such as V, Cu, Ni, Fe and Mn oxides [5] were used for the decomposition of chlorinated molecules. In fact, noble metal based catalysts are highly active at low temperature, they suffer from disadvantages such as they are more expensive and deactivate with in few hours of reaction. However, it was realized that metal oxide catalysts are less expensive and are more resistant to deactivation, but they suffer from less activity [6]. Literature reports indicated that the mixed oxide based catalysts such as V-Ti, V-Mo and V-W oxides showed better catalytic activity and selectivity than the single oxide catalysts [7, 8].

Keggin structured AMPA salt is thermally more stable and efficient selective oxidation catalyst than its parent acid;  $H_3PMo_{12}O_{40} \cdot xH_2O$  [9]. It was previously reported that expulsion of  $NH_4^+$  ions from the secondary structure and decomposition of primary  $[PMo_{12}O_{40}]^{3-}$  (Keggin ion) into parent Mo and P oxides beyond 380 °C is responsible for lower performance in gas phase catalytic reactions [10]. Incorporation of transition metals such as V and Cu metal ions into Keggin structure is a well reported method to enhance the thermal stability of AMPA [10]. Heteropoly acids based materials could be an effective catalysts for decomposition of chlorinated organic molecules as these materials were used in many acid-catalyzed and oxidation reactions both in liquid and gas phase conditions [11]. It was previously reported that the incorporation of transition metals showed substantial influence over the redox and acid-base characteristics of heteropoly compounds [12]. Decades ago, Cavani et al. [13] observed that incorporation of Sb into AMPA enhanced the thermal stability of the Keggin structure. The authors claimed that incorporation of one Sb atom in the Keggin structure of AMPA shifted the structure degradation temperature by 100 °C and it was also observed that Sb atom was replaced some of the K<sup>+</sup> or  $NH_4^+$  ions in the secondary structure of AMPA. However,

it is unclear whether the observed structural stability is due to presence of doped Sb or K atoms which were already presented in the secondary structure of AMPA. Recent reports [14, 15] concluded that Sb in the primary structure of heteropolyacid could improve the thermal stability (higher than 400  $^{\circ}$ C) and catalytic functionality.

In this work, Sb incorporated Keggin structured AMPA samples were synthesized by a simple acid precipitation method. The synthesized materials were used as heterogeneous catalysts for gas phase oxidation of chlorobenzene. A thorough catalyst characterization was performed by using TG, XRD, FT-IR, <sup>31</sup>P MAS NMR, SEM, N<sub>2</sub>-physisorption, XPS and H<sub>2</sub>-TPR techniques. The performance of the catalysts in gas phase oxidation of chlorobenzene was correlated with their chemical and structural properties.

# 2 Experimental

## 2.1 Materials

The analytical grade chemicals utilized for the synthesis of materials and gas phase oxidation reaction are obtained from Aldrich, UK and the reagents were used as received without adapting any purification procedures.

## 2.2 Synthesis of Sb Incorporated AMPA Catalysts

Acid precipitation method was used to synthesize Sb incorporated AMPA catalysts and the typical procedure is as follows. A calculated amounts of ammonium heptamolybdate and diammonium hydrogen orthophosphate were dissolved in minimum amount of distilled water by heating at the aqueous solution at 80 °C. Stoichiometric quantity of SbCl<sub>3</sub> in dil. HCl solution was added drop wise to the previously prepared solution and the pH of the solution was maintained around 1. During the addition of dil. HCl, the color of the solution progressively changed from green to light blue at the same time, a precipitate was obtained. The total contents were refluxed at 100 °C for 4 h, The precipitate was then filtered and washed with distilled water for four times and dried at 120 °C for 12 h. The dried powder was thermally treated at different temperatures in the range from 300 to 500 °C for 4 h. The atomic ratio of Mo:Sb has been varied from 11:1, 10:2 and 9:3 for AMPSb1, AMPSb2 and AMPSb3 series of catalysts. For comparison study, bulk AMPA with out Sb was prepared by acidification of stoichiometric amounts of ammonium heptamolybdate, orthophosphoric acid, and the excess amount of ammonium nitrate with nitric acid. The resulting suspension was evaporated to dryness and the solid thus obtained was thermally treated at the temperature range of 300–500 °C for 4 h.

#### 2.3 Catalyst Characterization

The chemical composition (atomic ratios of Mo, Sb, and P) of the samples was measured by using Perkin-Elmer ICP-MS instrument. The thermogravimetric patterns of the samples were obtained using Netsz thermal analyzer. The XRD patterns of the samples were recorded using Bruker D8 Advance X-ray diffractometer using Ni filtered Cu Ka radiation ( $\lambda = 1.5405$  Å). The FT-IR spectra of the samples were recorded using Bruker D70 spectrometer. The nitrogen physisorption measurements were carried out using Quantachrome Autosorb ASiQ instrument. The SEM analysis of the samples was carried out using JEOL Model JSM-6390LV microscope. The XPS spectra of samples were obtained using a PHI Quantera Scanning XPS Microprobe operating in its large area mode. The <sup>31</sup>P MAS NMR spectra of the samples were recorded in a 400 MHz Bruker spectrometer. The DR UV-Vis spectra of the synthesized samples were obtained using Thermo-Scientific evolution spectrophotometer equipped with an integrating sphere in the wavelength range of 200-800 nm. The H<sub>2</sub>-TPR measurements of the samples were carried out using Quantachrome CHEMBET-3000 instrument.

# 2.4 Catalytic Oxidation of Chlorobenzene

Oxidation of chlorobenzene was carried in a continuous, fixed bed micro-catalytic reactor (made of quartz, 8 mm inner diameter, 30 cm long) and heated in an electric furnace. The flow rates of air and nitrogen gases were measure using calibrated mass flow controllers. Catalyst sample (250 mg diluted with 500 mg of quartz pellets) was placed between two layers of the quartz wool in the reactor. Chlorobenzene was introduced into the reactor by N<sub>2</sub> gas flow through a saturator. The saturated stream was then mixed with O<sub>2</sub> and N<sub>2</sub> gases to achieve the desired concentrations, and preheated before entering into the reactor. The concentration of chlorobenzene in the reactor feed is about 1300 ppm, unless otherwise stated. The total gas flow was 133 mL min<sup>-1</sup>, 85% N<sub>2</sub> and 15% O<sub>2</sub> along with 1300 ppm chlorobenzene. An excess O2 was utilized to insure complete oxidation of chlorobenzene. The gas hour space velocity was maintained at 8000  $h^{-1}$ . The reaction was carried out at a different temperature range from 150 to 350 °C. The reaction temperature was maintained by means of PID temperature controller and a thermocouple placed co-axially with the catalyst bed. The product stream was then collected for every half an hour under steady state conditions obtained after a few hours of operation. The formed HCl and Cl<sub>2</sub> were both trapped at the exit of the reactor in a bubbler containing 0.1 M aqueous KI solution. The product analysis was carried out using GC equipped with four columns, one methanizer, two FID and one TCD allowed to quantify

benzene, chlorobenzene,  $O_2$ , CO,  $CO_2$ ,  $N_2$  components and to detect other hydrocarbons and chlorinated hydrocarbons. The obtained data is accurate within a range of about 1% (in relative) for the conversion of chlorobenzene.

# **3** Results and Discussion

The thermal behavior of three dried Sb incorporated AMPA materials was studied by thermogravimetric and differential scanning calorimetry (TG/DSC) analyses. The TG patterns of dried AMPSb1, AMPSb2 and AMPSb3 samples are shown in Fig. 1. The TG results indicated that major weight loss was occurred in two stages in all the samples. The first weight loss occurred between 140 and 360 °C could be attributed to the removal of structural H<sub>2</sub>O molecules and expulsion of NH<sub>4</sub> ions from the Keggin structure. The second weight loss between 360 and 540 °C is due to the complete destruction of Keggin structure to form Mo and P oxides.

It is well known that complete destruction of Keggin structure in bulk AMPA generally occurs between 390 and 400 °C [16]. The TG results indicating that thermal decomposition process is clearly delayed in Sb doped AMPA samples; this is most probably due to the substitution of Sb atoms in the secondary structure (in place of NH<sub>4</sub> cations). This phenomenon is observed in three synthesized Sb substituted AMPA materials, however it is high in case of AMPSb3 material. The total weight loss observed for AMPSb1, AMPSb2 and AMPSb3 samples is 20%, 18% and 14% respectively. The total weight loss in Sb substituted AMPA materials is higher than bulk AMPA (around 11%). This is probably due to high hydration levels of Sb [17] presented in the samples and increase of Sb atoms in AMPA samples resulted the increase of H<sub>2</sub>O molecules. The DSC curves of AMPSbx samples exhibited an endothermic peak in the temperature range of 180-250 °C. The maximum temperature of peak is at 210 °C indicating the loss of physically adsorbed water in the pores of microcrystalline AMPA structure. Presence of a broad endothermic peak in the range of 400-540 °C could be attributed to destruction of secondary structure of AMPA by losing the crystalline H<sub>2</sub>O and NH<sub>4</sub><sup>+</sup> cations. A short exothermic process presented in the range of 600-630 °C could be due to the exothermic crystallization of P, Mo and Sb oxides through destruction of Keggin structure. The area under the exothermic and endothermic peaks assigned to the losses of mass corresponding to the H<sub>2</sub>O and NH<sub>4</sub><sup>+</sup> species. These results could be related with both number and nature of cations in the AMPA structure. Thus, the complete decomposition of Sb incorporated AMPA salts occurred 600 °C, 610 °C and 630 °C for AMPSb1, AMPSb2 and AMPSb3 samples respectively, which corresponds to the broad exothermic effect with maxima for AMPSb3 sample.



Fig. 1 TG/DSC patterns of as synthesized Sb incorporated AMPA samples

These observations indicating the presence of Sb enhanced the thermal stability of AMPA structure.

The powder XRD patterns of AMPSb1, AMPSb2 and AMPSb3 samples thermally treated in the range of 300-500 °C are shown in Fig. 2. The catalysts thermally treated at 300 and 350 °C exhibited the reflections due to crystalline cubic structured AMPA [(NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·4H<sub>2</sub>O, JCPDS File No.9-412]. Presence of narrow intense reflections due to highly crystalline  $\alpha$ -MoO<sub>3</sub> [molybdenite, JCPDS 35-0609] phase was observed in case of AMPSb1 and AMPSb2 samples calcined at 400 °C along with minor reflections corresponding to AMPA phase. This is observation is indicating that decomposition of AMPA has started in AMPSb1 and AMPSb2 samples at 400 °C. It is known that the cubic structure of bulk AMPA is preserved until 380 °C and beyond this temperature the ammonium cations evolves out from the Keggin structure [18]. The AMPSb3 sample thermally treated at 400 °C showed diffraction peaks corresponding to AMPA phase and did not showed any reflections corresponding to  $\alpha$ -MoO<sub>3</sub> phase. At 450 °C and 500 °C, AMPSb1 and AMPSb2 materials exhibited major reflections attributed to  $\alpha$ -MoO<sub>3</sub> due to the destruction of Keggin structure. In contrast, AMPSb3 material shown major reflections due to AMPA at 450 °C. The results from XRD studies are revealing that the incorporation of Sb was delayed the degradation of Keggin structure of AMPA. These observations are in accordance with the results of TG experiments. It was previously indicated that the incorporated foreign metal ions either could substitute Mo in peripheral positions in Keggin anion (primary structure) or act as cation by removing the  $NH_4^+$  ions in the secondary structure [19]. Marchal-Roch et al. [20] performed XRD analysis of V incorporated AMPA [inside primary Keggin ion,  $(NH_4)_4[PMo_{11}V^VO_{40}]$  sample and the cubic phase is stable up to 410 °C. However, the authors observed that the cubic phase is stable only up to 390 °C, when the V was substituted in the secondary structure of the Keggin compound { $(NH_4)_{3-2x}(V^{VI}O)_x[PMo_{12}O_{40}]$ }. The temperature difference is not huge, however it was proposed that in case of  $(NH_4)_4$ [PMo<sub>11</sub>V<sup>V</sup>O<sub>40</sub>], the V atoms were removed from the Keggin anion after thermal treatment at 210 °C and the expelled V cations occupied the counter-cation position.

FT-IR analysis is one of the important analytical tool to analyze the structural features of synthesized Sb-AMPA samples. The FT-IR spectra of AMPSb1, AMPSb2 and AMPSb3 samples thermally treated in the range of 300–500 °C are shown in Fig. S1 (electronic supplementary information). It was reported that the FT-IR spectrum



Fig. 2 Powder XRD patterns of a AMPSb1 b AMPSb2 and c AMPSb3 samples thermally treated at (a) 300 °C (b) 350 °C (c) 400 °C (d) 450 °C and (e) 500 °C

of bulk AMPA calcined at 300 °C generally exhibits the IR bands at 1060, 960, 890, 795 and 1425 cm<sup>-1</sup> attributed to asymmetric stretching vibrations for (P–O<sub>d</sub>), (Mo–O<sub>t</sub>), (Mo–O<sub>b</sub>–Mo), (Mo–O<sub>c</sub>–Mo) and NH<sub>4</sub><sup>+</sup> functional groups respectively [21]. The Sb substituted AMPA materials thermally treated at 300, 350 and 400 °C exhibited the characteristic bands due to Keggin ion along with a band at 1425 cm<sup>-1</sup> corresponding to NH<sub>4</sub><sup>+</sup> ions (secondary structure). This observation indicating that the Keggin structure is intact up to 400 °C in all the Sb substituted AMPA materials. At 450 °C, AMPSb1 sample did not show IR absorption band corresponding to NH4<sup>+</sup> ion and bands attributed to  $MoO_3$  at 982 cm<sup>-1</sup>, 863 cm<sup>-1</sup> and 595 cm<sup>-1</sup> are dominant, however, AMPSb2 and AMPSb3 catalysts exhibited bands related to Keggin and NH<sub>4</sub><sup>+</sup> ions. At 500 °C, AMPSb1 and AMPSb2 samples showed only bands due to MoO<sub>3</sub> phase and AMPSb3 catalyst exhibited low intense IR bands corresponding to Keggin structure and the band corresponding to NH<sub>4</sub><sup>+</sup> groups was vanished. These observations revealing that the Keggin ion is intact up to 450 °C for AMPSb1, 500 °C for AMPSb2 and above 500 °C for AMPSb3 material. Therefore, the FT-IR spectral data also indicating that incorporation of Sb into AMPA resulted increase of thermal stability of Keggin structure, however it is important to understand the location of the incorporated Sb atoms. It was previously reported that if any metal ion is substituted in the peripheral position of Mo of the Keggin structure, it would bring changes in the frequencies of IR vibrations of Keggin structure due to decrease of the PO<sub>4</sub> symmetry [22]. Therefore, if Sb atoms occupied in place of Mo, a shoulder generally appears in (P–O<sub>d</sub>) band. However no shoulder was observed in 1060 cm<sup>-1</sup> band in the FT-IR spectra of Sb-AMPA samples. From these results, it is clear that Sb atoms were not replaced the Mo in the peripheral positions of Keggin anion, but could have accommodated in the secondary structure or segregated as isolated amorphous phase.

To obtain precise information about the location of Sb atoms, <sup>31</sup>P MAS NMR analysis of the samples was performed. Solid state <sup>31</sup>P MAS NMR spectra of representative Sb-AMPA samples are shown in Fig. 3. The Sb-AMPA samples thermally treated at 300 °C showed three resonance peaks; a major sharp peak at -4.5 ppm, and two broad peaks at -5.8 ppm and 2.1 ppm. All the samples exhibited three P resonance peaks at low temperature treatment, clearly indicating that the Sb-AMPA samples possessed three different species. Black et al. [23] reported that pure AMPA [(NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·4H<sub>2</sub>O] phase exhibits a single <sup>31</sup>P MAS NMR peak at -4.45 ppm. The peak observed



Fig. 3 <sup>31</sup>P MAS NMR spectra of representative Sb-AMPA samples

at -4.5 ppm in the samples could be attributed to bulk AMPA phase. The resonance peak appeared at -5.8 ppm, is due to AMPA with different degree of hydration, due to high hydration levels of Sb [24] presented in the samples and increase of Sb atoms. It was also reported that the <sup>31</sup>P MAS NMR peaks are sensitive to the number of crystalline H<sub>2</sub>O molecules presented in Keggin structure, for instance, chemical shift for  $H_3PMo_{12}O_{40}$ ·30 $H_2O$  is - 3.9 ppm, while it is shifted to -2.9 ppm for H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> [25]. Loss of H<sub>2</sub>O molecules in the crystal structure resulted NMR peak shift towards positive ppm, however in case of Sb-AMPA samples the peak shifted towards negative ppm, indicating that the synthesized samples also contained Keggin structure compound with more number of H<sub>2</sub>O molecules. These results are in quite accordance with TG and FT-IR results. The peak at 2.1 ppm could be due to presence of  $Sb(PO_4)$  as the intensities of both peaks at 2.1 ppm and -5.8 ppm are increasing with increase of Sb atoms.

The AMPSb1 sample thermally treated at 450 °C exhibits a broad peak consists two resonances at 0.5 ppm and 0 ppm. It is well known that the phosphorous oxides such as isolated  $PO_4^{3-}$  and  $P_2O_5$  species appears positive ppm scale [26], the peaks appeared at 0.5 ppm and 0 ppm could be assigned to oxides of P generated due to degradation of Keggin unit. This sample also shows a small broad resonance at - 8.3 ppm, which is due to the lacunary Keggin ions (forms after expulsion of MoO<sub>6</sub> octahedral species). In contrast, AMPSb2 sample showed two resonance peaks, first one at - 4.5 ppm and another one at 0 ppm due to presence of AMPA and phosphorous oxide. On other hand, AMPSb3 sample showed very broad resonance peak centered at - 3.3 ppm due to Keggin species with different stoichiometry. The obtained observations revealing that a prominent degradation was happened in AMPSb1 material, however increase of Sb atoms to 2 and 3 resulted existence of Keggin structure even at 450 °C thus proves the stabilization role of Sb atoms.

The morphology of Sb-AMPA samples was studied using SEM analysis. The SEM images of AMPSb1, AMPSb2 and AMPSb3 samples thermally treated at 300, 400 and 500 °C are shown in Fig. S2. The samples calcined at 300 °C exhibited small, spherical particles ranging from 10 to 20 nm in diameter. It was previously reported that cubic structured AMPA nanoparticles exhibits spherical morphology due to isotropic crystal growth [27]. Increase of treat temperature to 400 °C resulted in rise in particle size, as the three samples clearly showed the presence of relatively large particles due to agglomeration. However, it is interesting to observe that the extent of agglomeration is less in case of AMPSb3 sample compared to AMPSb1 and AMPSb2 samples, indicating the influence of Sb stoichiometry on the size and morphology of the AMPA. In contrast, the Sb-AMPA samples thermally treated at 500 °C exhibited large irregular block-like crystals with large size (around 100–150 nm), which are mainly composed of decomposed Keggin structure AMPA, to form Mo, P and Sb oxides. These results are in consistent with the XRD and FT-IR results.

The N<sub>2</sub>-physisorption measurements were carried out to study the textural properties of the synthesized samples. The N<sub>2</sub> adsorption–desorption isotherms of synthesized materials are presented in Fig. 4. The three Sb-AMPA materials thermally treated at 300 °C showed type IV isotherms (IUPAC standards), which is a representative of mesoporous solids. It is well known that bulk AMPA possesses majorly micro pores [28], but the Sb incorporated AMPA samples treated at 300 °C exhibited sharp increase of adsorption at low pressures. The Sb incorporated AMPA samples treated at 400 °C samples exhibited the type H4 hystereses, which is related to presence of narrow pores. On other hand, the samples treated at 500 °C exhibited type H2 hystereses, which relates to presence of inkpot-shaped pores with narrow necks and large spaces. These observations are in accordance with results reported in the literature [29] that Keggin salts with large cations such as Cs<sup>+</sup>, NH<sub>4</sub><sup>+</sup> are mesoporous in nature.

The BET surface area, pore volume and average pore radius for the AMPSb1, AMPSb2 and AMPSb3 catalysts thermally treated at different temperatures are tabulated in Table 1. It was previously observed that the pure AMPA possesses high surface area (around  $150 \text{ m}^2 \text{ g}^{-1}$ ) with micro pore radius of 13 Å due to its microporous nature and has

 Table 1
 The textural properties of Sb-AMPA samples treated at different temperatures

Catalyst	Surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Average pore radius (Å)	
AMPSb1-300	124	0.124	24	
AMPSb1-400	69	0.110	20	
AMPSb1-500	6	0.028	10	
AMPSb2-300	103	0.113	20	
AMPSb2-400	55	0.100	14	
AMPSb2-500	8	0.019	8	
AMPSb3-300	89	0.104	15	
AMPSb3-400	43	0.070	8	
AMPSb3-500	5	0.012	6	



Fig. 4 N<sub>2</sub> adsorption–desorption patterns of the Sb-AMPA samples thermally treated at different temperatures

average meso pore radius of 35 or 45 Å [30]. A decrease in the surface area of the samples observed with Sb incorporation and also the thermal treatment from 300 to 500 °C (85–10 m<sup>2</sup> g<sup>-1</sup>), similar to that reported in the literature [31]. It was previously reported that the expulsion of  $NH_4^+$ ions from the secondary structure of the Keggin after thermal treatment at high temperature leads to decrease of specific surface area [29]. A huge loss in surface area was also noticed due to the complete degradation of Keggin unit that occurs at very high temperatures. The loss of surface area in case of Sb substituted AMPA samples could also due to degradation of Keggin structure and pore blockage because of Sb surface coverage.

High energy resolution X-ray photoelectron spectra for AMPSb samples were collected for all the elements to observe their chemical state as the quantity of Sb was increased. As shown in the Fig. 5, substituting Sb for Mo creates a second Mo chemical state. The Mo  $3d_{5/2}$  peak for AMPA and the primary peak for the other samples occurred at approximately 233 eV. Confirmation of Mo<sup>6+</sup> in the pure AMPA (Fig. S3) can be obtained from sharpness of the signals of Mo  $3d_{5/2}$  and Mo  $3d_{3/2}$  levels in the XPS spectrum [32]. As Sb is incorporated for Mo, the Mo concentration decreases and a new Mo peak appears at approximately 232 eV. The intensity of this new peak increases as the quantity of Sb increases. A similar effect is observed for the samples treated at 400 and 500 °C. The new peak at 232 eV could be due to presence of reduced Mo(V) species, as reduced Mo in heteropolyacid salts and oxides generally show broad peaks at lower binding energy [33]. These results are quite corroborating with the thermolysis pathway described in the literature [34]. The increase of the intensity peak at 232 eV could be attributed to the rise in the number of Mo(V) ions in the Sb substituted AMPA materials as per electron exchange occurring as follows:  $Sb^{III} + 2Mo^{VI} \leftrightarrow Sb^{V} + 2Mo^{V}$ .

The fitting results of Sb3d and O1s peaks of AMPSbx samples are also shown in Fig. 5. Due to the overlapping of  $Sb3d_{5/2}$  with O1s peak, its binding energy could not be determined accurately. All Sb $3d_{3/2}$  XP peaks were correctly fitted by Gaussian parameters with binding energy maximum of 540.8 eV and it could be attributed to Sb(V) species [35]. The intensity of the peak at 540.8 eV increased with increase of Sb atoms in the Keggin structure, revealing that the number of Sb(V) species were increased with rise of Sb(III) atoms in AMPA. According to Zeng et al. [36], Sb  $3d_{3/2}$  peak corresponding to Sb(III) appear at 539.7 eV. The absence of this peak suggesting that even though Sb(III) is the starting material used for preparation of AMPSbx samples, it is readily oxidizing to Sb(V) during the preparation of catalysts. It is clear that during the thermal treatment below 450 °C, formation of [PMo<sub>5</sub><sup>5+</sup>Mo<sub>7</sub><sup>6+</sup>O<sub>40</sub>]<sup>8-</sup> and expulsion of Sb atoms from Keggin structure occurs. The expelled Sb(V) atoms are occupying the vacant cationic position due to release of  $NH_3$  and water from AMPA structure.

Liu et al. [37] observed that AMPA structure composed of  $[PMo_{12}O_{40}]^{3-}$  lattices with large cavities and channels also exists in between the crystal lattices. Therefore, there is clear possibility for free movement of metal cations in between the crystal lattices and substitute  $NH_4^+$  ions. Thus, substitution of Sb(V) ions is possible all through the AMPA crystal lattice and not limited to the surface. The XPS data is also used to determine the elemental concentrations at the surface of the Sb incorporated samples. The quantitative data in the Table 2 shows the Sb concentration increasing in concentration from samples AMPSb<sub>1</sub>, AMPSb<sub>2</sub> and AMPSb<sub>2</sub> for all the samples calcined at 300, 400 and 500 °C. The data also shows the Mo concentration is decreasing in concentration when looking at samples 1 through 3. Due to an overlap with O1s and the Sb $3d_{5/2}$  peaks, curve fitting was used to isolate the O1s peak area prior to making quantitative calculations. The elemental concentrations of the catalysts also measured using ICP-MS (Table 2) and compared with the surface composition. The bulk and surface composition of the samples are almost equal; this could be due to homogeneous nature of the materials.

The diffusive reflectance UV-Vis (DR UV-Vis) spectral analysis was performed to distinguish the electronic properties of the Mo and Sb atoms in the Keggin compounds. The DR UV-Vis spectra of the samples (Fig. S4) exhibited ligand-metal charge transfer bands  $[O^{2-} \rightarrow Mo^{6+}]$  in the range of 215-225 nm, 280-300 nm and 380-400 nm due to the different types of metal-oxygen ligands in the AMPSbx compound structure. Presence of more than one UV-Vis bands for metal incorporated Keggin structured heteropoly compounds was previously reported other researchers [38]. Cavani et al. [39] suggested that the size and position of the lower charge transfer bands was influenced by the composition of the cations of the Keggin secondary structure. It is clear from the spectra that lower charge transfer band is shifted in case of AMPSbx samples indicating that composition of secondary structure is different in these samples compared to bulk AMPA sample. In addition, another large charge transfer band was observed above 700 nm for AMPSbx samples, which could be assigned to the d-d transition band of Mo<sup>5+</sup> species in octahedral coordination [40]. This observation indicating that reduction of M<sup>6+</sup> to Mo<sup>5+</sup> by the Sb<sup>3+</sup> in AMPSbx samples  $[Sb^{3+} + Mo^{6+} \rightarrow Sb^{5+} + Mo^{5+}].$ 

The intensity of band at 700 nm is increasing with increase of Sb content in the sample, which is indicating that the extent of Mo reduction is a function of the Sb content; more the Sb content, the higher the concentration of Mo<sup>5+</sup> species [41]. The formation of Mo<sup>5+</sup> species as a function of the calcination temperature was also studied using DR UV–Vis spectral analysis. The spectra of AMPSb3 sample



Fig. 5 Deconvoluted X-ray photoelectron spectra of Sb-AMPA samples thermally treated at different temperatures

calcined at different temperatures shows that the extent of Mo reduction increases with increase of calcination temperature; higher the calcination temperature the band at 700 nm becomes dominant. These observations are supporting the results observed from XRD, FT-IR and  $^{31}P$  MAS NMR studies.

The  $H_2$ -TPR profiles for AMPA and Sb incorporated AMPA samples calcined at 300 °C are shown in Fig. 6.

 Table 2
 Bulk and surface elemental composition of Sb incorporated

 AMPA catalysts calcined at different temperatures

Catalyst	Bulk com (ICP-MS)	Bulk composition (ICP-MS)		Surface composition (XPS)	
	P/Mo ratio	P/Sb ratio	P/Mo ratio	P/Sb ratio	
AMPSb1-300	0.092	0.981	0.091	0.979	
AMPSb1-400	0.091	0.980	0.091	0.980	
AMPSb1-500	0.090	0.980	0.090	0.980	
AMPSb2-300	0.101	0.493	0.100	0.490	
AMPSb2-400	0.102	0.495	0.100	0.493	
AMPSb2-500	0.102	0.495	0.101	0.493	
AMPSb3-300	0.112	0.333	0.111	0.332	
AMPSb3-400	0.111	0.331	0.111	0.331	
AMPSb3-500	0.111	0.332	0.111	0.332	



Fig. 6  $\,H_2\text{-}\mathrm{TPR}$  patterns for AMPA and Sb incorporated AMPA samples calcined at 300  $^\circ\mathrm{C}$ 

The bulk AMPA sample showed a major reduction peak at 650 °C. However the Sb contained AMPA samples exhibited a small reduction peak around 530 °C with major reduction peak in the range of 655–665 °C. As the heteropoly acids generally decompose above 500 °C, the reduction peaks could be attributed to the reduction of Mo and Sb oxides formed by the degradation of the Keggin ion during the H<sub>2</sub>-TPR experiments.

Sun et al. [42] reported that the reduction peak in the range of 640–690 °C for metal substituted heteropoly

compounds could be attributed to the reduction of Mo<sup>6+</sup> to Mo<sup>4+</sup>. As shown in Fig. 6, with increasing Sb content, the center of the major peak shifting to high temperatures suggesting that the replacement of  $NH_4^+$  ions by Sb, as it is well known that the reducibilities of heteropoly compounds were considerably influenced by their counter cations. The AMPASb<sub>3</sub>-300 catalyst is more stable than other samples because its reduction temperature is higher, at which the heteropoly compound was decomposed to Mo, P and Sb oxides. The TG-DSC analysis of the synthesized samples indicating that Keggin structure is decomposed completely degraded to form crystalline oxides when temperature was above 600 °C. Therefore, a small reduction peak appeared around 530 °C could be assigned to the reduction of the segregated Sb oxide. A similar observation was reported in case of vanadium incorporated heteropolyacid catalysts, in which the authors found a H2-TPR peak below 600 °C due to reduction of vanadium oxide species [43]. The hydrogen consumption values were obtained from the H2-TPR analysis and the highest value was observed for the AMPSb3-300 sample (supporting information, Table S1).

The catalytic activity for the AMPA and Sb containing AMPA samples treated at different temperatures was tested for the oxidation of chlorobenzene reaction. The activity tests were also performed for bulk AMPA samples for comparison purpose. A blank test was performed to investigate the thermal decomposition of chlorobenzene using quartz pellets and only 2% chlorobenzene conversion was observed. Figure 7 shows the temperature dependency of the conversion over the investigated catalysts. It is found that the catalytic activity is greatly affected by the reaction temperature. The conversion of chlorobenzene is gradually increased with increasing the reaction temperature in all the catalysts.



Fig. 7 Conversion of chlorobenzene of over AMPA and Sb incorporated AMPA samples thermally treated at different temperatures

As shown in Fig. 7, among the investigated catalysts, AMPSb3-300 is found to possess the superior activity for oxidation of chlorobenzene. The chlorobenzene conversion reached to 90% at 350 °C. At this temperature, AMPA-300 sample offered chlorobenzene conversion of 26%, and is about 50% and 70% for AMPSb1-300 and AMPSb2-300 catalysts respectively. For AMPSb3-300 catalyst, the complete chlorobenzene conversion was achieved at 375 °C, however AMPSb1-300 and AMPSb2-300 catalysts needs minimum 450 °C, which is 75 °C greater than that for AMPSb3-300 sample. All the investigated Keggin structured catalysts in this study offered around 99% selectivity to CO<sub>x</sub> and no other measurable by-products were obtained. The observed trend in the Sb-AMPA catalysts is guite dissimilar from that of Pt, Pd supported on alumina and alumina pillared clays [44, 45], where large quantities of polychlorinated benzenes were formed during oxidation of chlorobenzene. The change in the catalytic activity of Sb incorporated AMPA catalysts thermally treated in the range of 300-500 °C is due to the fact that these samples possessed different redox properties as a result of treatment temperature; a similar observation was reported by Predoeva et al. [46] in case of vanadium incorporated heteropolyacid samples.

Influence of Sb atoms in the Keggin structured AMPA catalysts over gas phase oxidation of chlorobenzene was investigated. The catalytic activities AMPASb catalysts calcined at different three different temperature are compared in Fig. 8a. The highest activity was found in case of the catalysts calcined at 300 °C. With the increase of Sb atoms in AMPA structure, the catalytic activity is increased linearly. When Sb atom reaches 3, the total conversion is reached to 70% at 300 °C. The results clearly indicated increase in catalytic activity of AMPA catalysts in chlorobenzene oxidation after Sb atoms substitution and the catalyst with

more number of Sb atoms is the highly active. It is mainly due to the fact that Keggin structured polyoxometalates are multi-electron oxidants and Sb-containing heteropoly compounds are the strongest oxidants [47]. Previously, Cavani et al. [48] reported that substitution of one or more Sb atoms in the Keggin compounds resulted in improvement in the oxidizing capability of heteropoly compound because of Sb redox potential. It can be concluded that the Sb containing AMPA catalysts offers dominant activity due to modification of redox properties of heteropolyacid framework by the Sb atoms.

The conversion of chlorobenzene at different chlorobenzene concentrations over representative AMPSb3-300 catalyst is shown in Fig. 8b. This study is essential majorly due to the fact that the concentration of hazardous materials usually changes in the industrial emissions. As shown in figure, the chlorobenzene conversion was decreased with increase of concentration of chlorobenzene from 1300 to 5200 ppm. However, increase of reaction temperature from 150 °C to 350 °C resulted gradual increase of chlorobenzene conversion. A similar trend was observed in case of all the investigated catalysts. Further, the stability of the Sb incorporated AMPA samples under the reaction conditions was investigated.

The Fig. 9 shows the chlorobenzene conversion at 300 °C over AMPSb1-400, AMPSb2-400 and AMPSb3-400 catalysts for continuous 15 h. A minor decline of activity was observed in the catalysts, however the extent of loss of activity is very small in case of AMPSb3-400 catalysts compared to AMPSb1-400 and AMPSb2-400 catalysts. The substituted Sb atoms are enhancing the Keggin structure stability and also assisting for the generation of the surface interactive Sb–O–Mo groups (XPS results). In addition to the structural stability at high temperatures, the redox ability of incorporated Sb–O–Mo groups



Fig. 8 a Influence of Sb atoms in AMPA catalysts over gas phase oxidation of chlorobenzene b Chlorobenzene conversion at different chlorobenzene concentrations over representative AMPSb3-300 catalyst



Fig. 9 Time on stream analysis of the Sb incorporated AMPA samples

could expedite the direct involvement of Sb in activation of  $O_2$  and chlorobenzene molecules.

The stable chlorobenzene conversion levels in case of AMPSb3-300 catalyst during time-on-stream analysis may be because of presence of more number of Sb-O-Mo species in the catalyst. The slight decrease of the activity could be due to surface reduction of Sb-AMPA catalyst during catalytic reaction as HCl and Cl<sub>2</sub> are the products and they usually make catalysts deactivated because of surface decomposition. Paul et al. [49] reported that lattice oxygen plays a crucial role in the selective oxidation reaction and with increase of number of Mo<sup>5+</sup> species could accelerate the migration of the lattice oxygen, and lead to high selectivity to oxygenated products. It was reported in the literature that the oxygen source for Keggin structured heteropoly compounds catalyzing oxidation reactions is actually originating from the Keggin anion (bridging oxygen atoms of the  $[PMo_{12}O_{40}]^{3-}$  ion), which is eventually replenished by the  $O_2$  in the reactants stream [50]. Therefore, the catalyst which contained maximum surface redox sites would be the best oxidation catalyst. From the characterization data it is clear that the Sb-AMPA samples possessed high thermal stability, considerably high surface area and easy reducibility. The AMPSb3-300 sample possessed more number of Sb-O-Mo interactive species on the surface of the catalyst, which are responsible for superior chlorobenzene oxidation activity.

# **4** Conclusions

In this work, Sb (atoms from 1 to 3) incorporated Keggin structured ammonium salt of 12-molybdophosphoric acid (AMPA) catalysts were synthesized and the three series of catalysts were thermally treated at different temperatures in the range of 300-500 °C. The synthesized catalysts were analyzed by elemental analysis, thermogravimetric analysis, X-ray diffraction, Fourier transformed infrared spectroscopy, scanning electron microscopy, N<sub>2</sub>-physisorption, <sup>31</sup>P MAS NMR, X-ray photoelectron spectroscopy, DR UV-Vis and H<sub>2</sub>-temperature programed reduction techniques. The characterization results indicated that AMPA samples maintained the Keggin structure after incorporation of Sb atoms and the introduction of Sb influenced the thermal stability and redox properties of the AMPA catalysts. The catalytic performance of the thermally treated Sb incorporated AMPA catalysts were examined for the gas phase oxidation of chlorobenzene and the performance of the synthesized samples was compared with activity of bulk AMPA samples. The incorporation of three Sb atoms enhanced the chlorobenzene conversion. Among the studied catalysts, AMPSb3-300 catalyst offered the best results; 90% conversion at 350 °C with 100% selectivity to CO<sub>x</sub>. The improvement in catalytic activity is mainly due to change in the redox properties as the XPS and H<sub>2</sub>-TPR results indicated that the electron transfer between  $Sb^{3+}$  and  $Mo^{5+}$  caused increase in surface oxygen species. The observed results revealed that the chlorobenzene oxidation activity is influenced by redox nature and Keggin structure stability of Sb substituted AMPA catalysts.

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