A comparison of structure and catalytic functionality of 12-molybdophosphoric acid and its ammonium salt in the ammoxidation of 2-methylpyrazine to 2-cyanopyrazine*

K. Narasimha Rao, N. Lingaiah, I. Suryanarayana, and P.S. Sai Prasad†

Catalysis and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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Two series of catalysts have been prepared by calcination of 12-molybdophosphoric acid or its ammonium salt at various temperatures, in the region of 300–500 °C. The catalysts have been characterized by nitrogen adsorption, XRD, FTIR spectroscopy and TG/DTA analysis to delineate changes in the solid phase associated with high-temperature treatment. Ammoxidation of 2-methylpyrazine has been carried out on these catalysts in a continuous, vapor phase, fixed-bed reactor, in the reaction temperature range of 360–420 °C. The used catalysts have also been subjected to characterization to ascertain the extent of formation of the salt from its decomposition products. The ammonium salt has shown higher activity, selectivity and better stability, when compared with its parent acid, up to a calcination temperature of 450 °C. However, at temperatures higher than the decomposition temperature the activity of the salt decreases considerably, possibly due to the formation of an undesired species mediated by Mo in the reduced state, thus setting a limit to the calcination temperature.

KEY WORDS: 12-molybdophosphoric acid; ammonium salt of 12-molybdophosphoric acid; ammoxidation of 2-methylpyrazine.

1. Introduction

With the ever-increasing concern for environmental protection, many of the conventional acid catalysts, for example, sulfuric and nitric acids, are progressively replaced by solid acid-type environmentally friendly catalysts [1]. Heteropolyacids, particularly the 12-molybdophosphoric acid (MPA) and the 12-tungstophosphoric acid possessing strong acidic and redox properties, are found to be very attractive alternatives to the conventional catalysts [2]. These compounds, exhibiting the popular Keggin structure, with a tetrahedral PO_4 ion surrounded by 12 edge sharing MO_3 ($M = Mo$ or W) octahedra, are found to be highly effective in catalyzing reactions like olefin hydration, alcohol dehydration, hydrocarbon oxidation and methanol conversion to hydrocarbons [3].

Of late, the heteropolyacids have also been found to be applicable as catalysts for the synthesis of fine chemicals. An example in this direction is the catalysis by MPA in the ammoxidation of 2-methylpyrazine (MP) to 2-cyanopyrazine (CP) [4]. CP is an important intermediate in the preparation of amidopyrazine (popularly called pyrazinamide), which is an effective antitubercular drug. This process is emerging as a viable alternative, environmentally as well as economically [5], to the conventional route starting from phenylene diamine and propylene glycol, wherein huge amounts of by-products are liberated. Ammoxidation of MP to CP is very crucial in this process, since the reaction carried out in vapor phase is highly exothermic and the facile formation of pyrazine (as the main by-product due to oxidative dealkylation) and the oxides of carbon (due to total combustion), which greatly affect the selectivity to CP (figure1). V-based catalysts, like the V-Sb oxide [6,7] and the V-P oxide [8], have been found to be active for the ammoxidation. However, their activity is more pronounced at high reaction temperatures (close to 430 °C) where thermal runaway of the reactor could occur, as the highly exothermic oxidation of ammonia starts dominating under these conditions.

In order to moderate the reaction conditions, Mo-based catalysts have been adopted for this reaction and the heteropolyacid system is found to be attractive. Bondareva *et al.* [9] have employed vanadium containing 12-molybdophosphoric acid as the catalyst and achieved about 75% CP yield at lower reaction temperatures (380–390 °C). They have noticed the formation of the ammonium salt of the 12-molybdophosphoric acid (AMPA) in the used catalysts. A recent American patent [10] also proposes Mo-phosphate-based catalytic system for achieving higher selectivity. However, structural details of the catalyst are not disclosed in this case. Recently, we have proposed that better activity and selectivity could be achieved if AMPA is used in place of its parent acid [11]. A considerable amount of research work has been carried out on AMPA catalysts and their activities in different

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* IICT Communication No. 021108

† To whom correspondence should be addressed.
E-mail: saiprasad@iict.ap.nic.in

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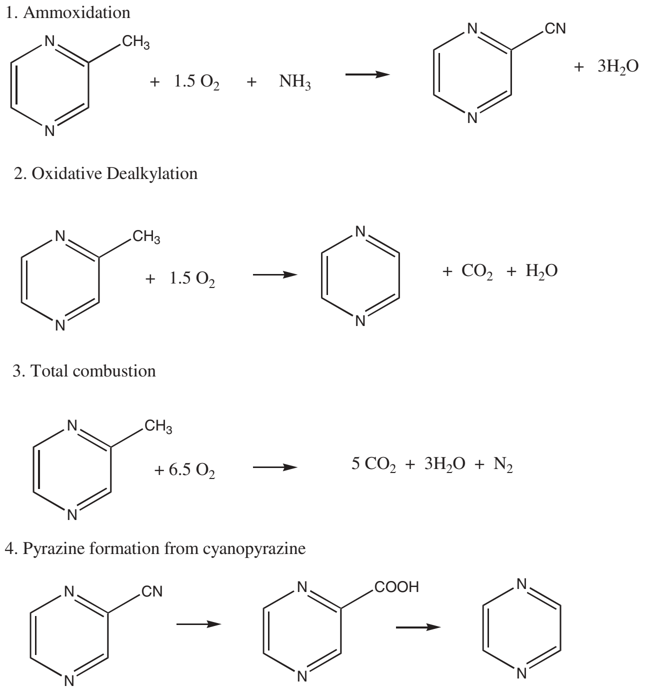

Figure 1. The plausible reactions during vapor-phase ammoxidation of MP to CP.

reactions. Hayashi *et al.* [12] are the first to prepare an ammonium salt of the heteropolyacid, showing that this catalyst has a substantially higher surface area than the parent acid. They have also demonstrated that the salt exhibits superior properties in the conversion of methanol to hydrocarbons than the parent acid. McMonagle *et al.* [13] in their study on preparation and characterization with X-ray diffraction (XRD), nitrogen adsorption and mercury porosimetry have shown that AMPA possessed a high surface area and is microporous. McMonagle *et al.* [14] have also carried out the effects of calcination temperature of the catalyst on the conversion of ethanol. A series of papers by Nayak *et al.* [15] have also reported on a comparison of the sorption in and diffusion through heteropolyacids and their ammonium salts by a variety of organic molecules. The ion-exchange properties of MPA and AMPA have been studied [16], their pore structure elucidated and a comparative study on their catalytic activity is made [17] in the oxidative dehydrogenation of isobutyric acid to methacrylic acid. The results of a comparative study of the microporosity of the ammonium and cesium salts of 12-molybdophosphoric acid, among others, were reported by Bonardet *et al.* [18]. In the light of the above observation, it is imperative to understand the structure-activity relationship by preparing the catalysts at different temperatures of calcinations, in an important reaction like the ammoxidation.

An important problem associated with the heteropolyacids is their low thermal stability. If the catalysts are meant for vapor-phase application during which they are subjected to high reaction temperature, an examination of their thermal stability is the prime requisite. Highfield *et al.* [19] and McMonagle *et al.* [13] have reported that AMPA is more thermally stable than MPA. Beyond a particular calcination temperature, the heteropoly compounds are reported to decompose into their component oxides. However, they get regenerated to the parent structure when subjected to treatment under moisture. In the particular case of ammoxidation, it is also interesting to observe the ease of regeneration of AMPA from its decomposition species in the presence of water as well as ammonia.

With these objectives in mind, a detailed study has been undertaken that involves preparation of MPA and AMPA catalysts with pretreatment at different calcinations temperatures; their physicochemical characterization by XRD, FTIR, TG/DTA techniques and nitrogen adsorption for the BET surface area and activity evaluation in the ammoxidation of MP. A comparison of the performance of the two catalysts is made and conclusions are drawn on the applicability of the catalysts under different operating conditions.

2. Experimental

AMPA was prepared by dissolving ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] and diammonium hydrogen orthophosphate [$(NH_4)_2H(PO_4)$] in the stoichiometric ratio ($Mo/P = 12/1$) in minimum amount of water. The aqueous solution was refluxed at 100 °C for 6 h and then the pH of the solution was adjusted to 2 by adding dilute nitric acid. The addition of acid led to the precipitation of a yellow compound. It was filtered, washed with deionized water and dried at 120 °C. Catalyst samples were collected after calcining this compound, under flowing air for 4 h each, at different temperatures in the range of 300–500 °C. MPA was purchased from a commercial source (Loba Chemie, India, G R Grade) and was used after calcination as described above.

BET surface areas of the catalyst samples were determined using a conventional all-glass high-vacuum apparatus by adsorbing nitrogen at liquid nitrogen temperature. The XRD patterns of the catalysts were obtained on a Siemens D-5000 diffractometer using Cu Kα radiation. The Fourier transform infrared (FTIR) spectra were recorded on a Biorad −175 C (USA) spectrophotometer using the KBr disc method. Simultaneous TG/DTA data were obtained on a Mettler Toledo Star system in the temperature range of 30–600 °C with a ramping rate of 16 °C/ min.

Ammoxidation of MP was carried out at atmospheric pressure, in vapor phase. About 5 g of catalyst (crushed to 18/25 BSS mesh) was fixed between two quartz plugs in a 20-mm i.d. and 300 mm long glass tubular reactor provided with a concentric thermowell. The reactor was kept at the required temperature using a PID controller. A mixture of ammonia, air and MP (diluted with water) was used as the feed at a molar ratio of MP : water : ammonia : air = 1 : 13 : 7 : 38. The liquid feed was admitted into the preheater part of the reactor by means of a metering pump (B. Braun, Germany) at a flow rate of 2 mL/h. The reaction was studied in the temperature range of 360–420 °C. After allowing the catalyst to attain steady state at each reaction temperature for 30 min, the product samples were collected (condensing in a series of traps cooled by dry ice- acetone mixture) for 10 min and were analyzed by gas chromatography, separating on OV-17 column using an FID. From the analysis of the noncondensable exit gas mixture, it was confirmed that the presence of organic species or the oxides of carbon was negligible.

3. Results and discussion

Table 1 provides the surface area data of the catalysts after calcination at various temperatures. The BET surface areas of all the catalysts are found to be less than 5 m^2/g. This observation is in agreement with the results reported by Lapham and Moffat [20] who have explained the decrease in surface area from a high value (200 m^2/g for the 120 °C dried salt) to less than 5 m^2/g due to loss of mesopores below, and micropores above, 300 °C. The bulk MPA catalyst normally possesses very low surface area even at low temperatures. Besides, the surface area values have also decreased with increase in calcination temperature, obviously due to structural transformations associated with pore collapse. Calcination at temperature above 300 °C resulted in catalysts mainly with macropores of diameter in the range of 2000–4000 Å.

The XRD patterns of AMPA catalysts pretreated at different temperatures are similar to those reported in our previous publication [4] giving the conclusions, *viz.*, (i) the low-temperature-calcined (300–400 °C) catalysts show the formation of $(NH_4)_3PMo_{12}O_{40} \cdot 4H_2O$, agreeing with the data presented by Marchal-Roch *et al.* [21] and Albonetti *et al.* [22] and (ii) samples calcined at temperatures 450 °C and above show peaks due to MoO_3, with the release of ammonia either as such or in the form of nitrogen or its oxides, as also suggested by Damyanova *et al.* [23] and Hodnett *et al.* [24]. The decomposition of the Keggin ion of AMPA started at a temperature between 400–450 °C and its complete decomposition occurred at about 500 °C. No traces of peaks due to $MoOPO_4$ are observed. This deviation from the earlier publication is probably due to the change in the method of preparation (solid–solid wetting in the case of reference [4] and liquid-phase precipitation in the present case). However, existence of other species in low concentration or with crystallite size less than 40 Å cannot be ruled out.

Table 1

Surface areas of AMPA and MPA catalysts heat-treated at various temperatures

Catalyst	Surface Area (m^2/g)	Catalyst	Surface Area (m^2/g)
AMPA-300[a]	70	MPA-300	5
AMPA-350	66	MPA-350	3.7
AMPA-400	35	MPA-400	2.2
AMPA-450	15	MPA-450	1.6
AMPA-500	5	MPA-500	0.8

[a] The numeral indicates the temperature (°C) at which the catalyst was pretreated.

In the case of MPA, the XRD patterns of catalysts treated at 300 and 350 °C (figure 2) show characteristic peaks at $d = 11.2$ 9.8 and 3.21 Å corresponding to its monoclinic structure. Peaks due to MoO_3 are observed in the sample calcined at 400 °C as against 450 °C in the case of AMPA. This implies that the structure of the Keggin ion begins to decompose at a temperature between 350 and 400 °C with partial reduction and distortion of the Keggin unit, as also shown by Tsigdinos [25]. Further increase in the calcination temperature to 450 and 500 °C resulted in samples with the presence of MoO_3 phase only. Thus, the thermal stability of MPA is lower compared to AMPA, closely agreeing with what has been reported by McMonagle *et al.* [14].

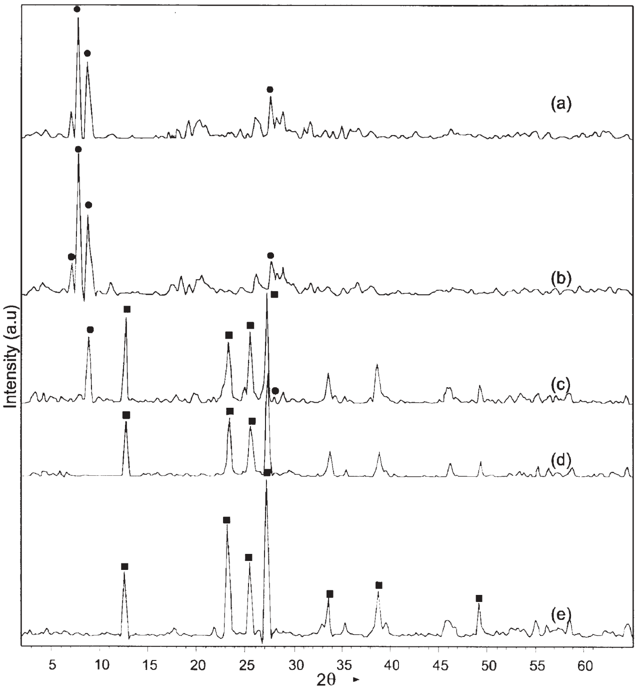

Figure 2. X-ray diffraction patterns of fresh MPA samples pretreated at (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, and (e) 500 °C (●) $H_3PMo_{12}O_{40} \cdot xH_2O$, (■) MoO_3.

The FTIR spectra of the fresh AMPA samples subjected to thermal treatment at 300–400 °C are also similar to those presented in our previous publication [4]. The characteristic peaks due to the Keggin ion, the presence of ammonium ion and a significant shift in the Mo–O_b–Mo band to an extent of 15 cm^{-1} reveal the formation of AMPA, as also reported by Rocchiccioli-Deltcheff *et al.* [26]. At 450 °C, the formation of MoO_3 has appeared. Calcination at 500 °C has resulted in total disappearance of AMPA and the domination of bands due to MoO_3.

The FTIR spectra of the MPA catalysts calcined at lower temperatures (figure 3) i.e., 300–350 °C, show characteristic bands of the Keggin ion without any distortion. Upon increasing the pretreatment temperature to 400 °C, a broadband between 600–1000 cm^{-1} due to formation of MoO_3, has appeared. The peak at 790 cm^{-1} corresponding to ν_{as}(Mo–O_c–Mo) also becomes very weak, confirming the distortion of the Keggin structure. After calcination at 450–500 °C the MPA spectra clearly show characteristic bands of MoO_3, indicating complete destruction of the Keggin ion.

Figure 4 shows the thermogravimetric curves of MPA and AMPA as (a) and (b) respectively. In order to observe the decomposition pattern of AMPA, the thermogram is obtained on the sample precalcined at 300 °C. The endothermic peak spanning between 400 and 470 °C represents the decomposition of AMPA into its component oxides. The weight loss has agreed well with that expected for the three ammonium ions corresponding to the molecular formula of the AMPA structure. The thermogravimetric pattern of hydrated MPA shows that most of the water of hydration is lost before 150 °C. Between 150 and 270 °C, there is a plateau region showing a gradual but very small loss of water. Beyond this temperature, probably up to 370 °C the loss in weight is again considerable. It may be envisaged that the MPA has existed in the amorphous form during this region. Above 370 °C the molecule appears to have decomposed into its component oxides, the process continuing up to 500 °C. From the thermograms of the two samples, the better thermal stability of AMPA over its parent acid is clearly recognized.

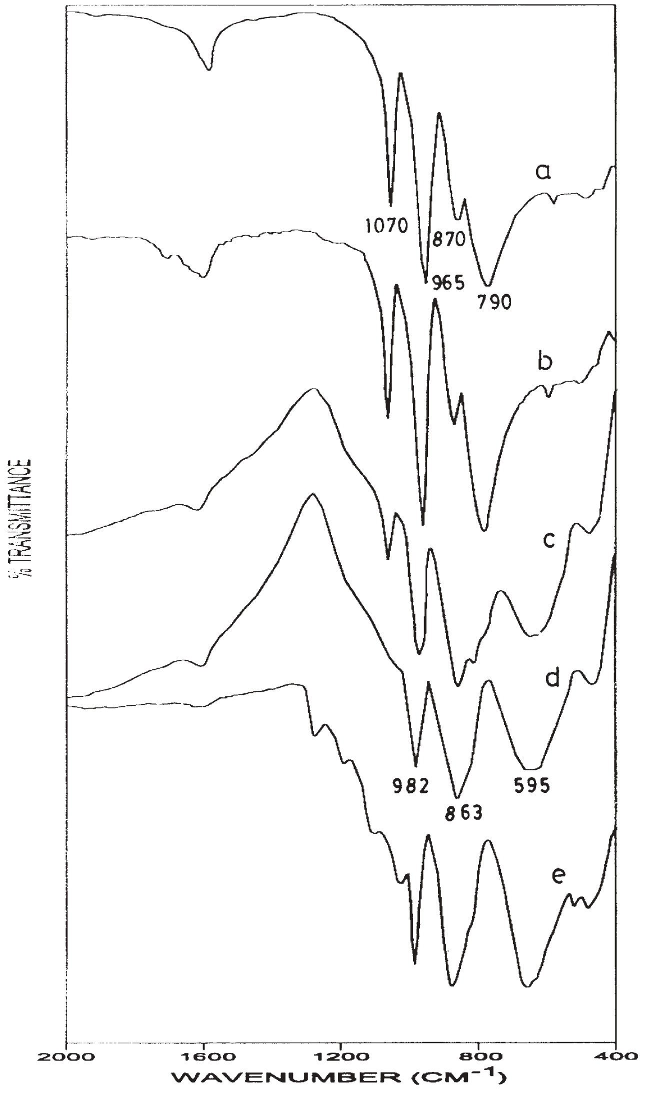

Figure 3. FTIR spectra of fresh MPA samples pretreated at (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, and (e) 500 °C.

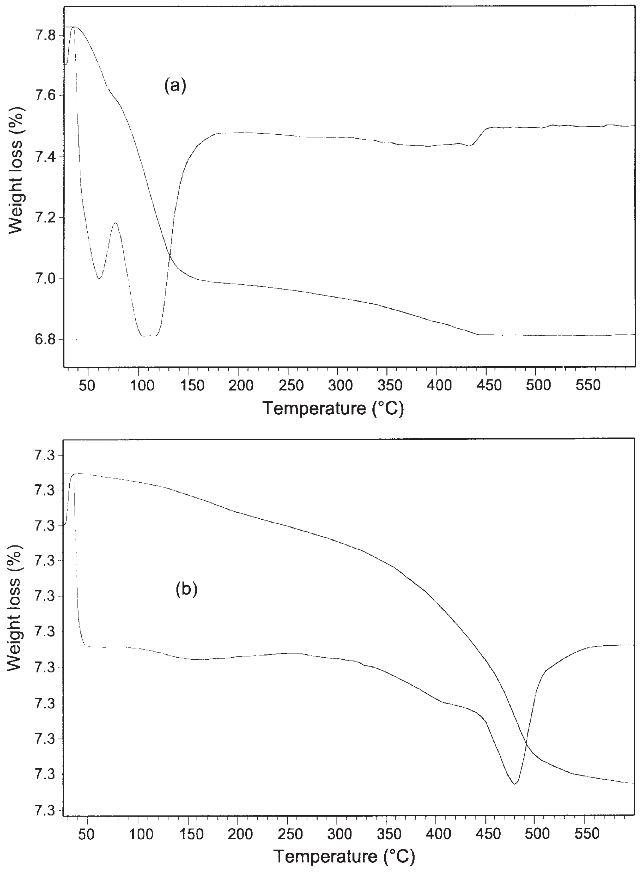

Figure 4. TG/DTA patterns of (a) MPA uncalcined and (b) AMPA calcined at 300 °C catalysts.

Variations in the activity and selectivity of AMPA catalyst against the temperature of pretreatment and the reaction temperature are shown in figure 5. The catalysts pretreated in the temperature region of 300–450 °C show stable activity, reflected in terms of overall conversion, at all reaction temperatures in the region of 360–420 °C. Further, the conversion has reached a value of 80% at the reaction temperature of 360 °C increasing further with increase in temperature, to a value close to 100% at 420 °C. This kind of very high, stable activity and high CP selectivity (varying in the region of 75–95%) of AMPA in the ammoxidation reaction at low reaction temperature is a significant observation. Higher activity of the ammonium salt, than that of the acid, is also observed in the formation of methacrylic acid from isobutyric acid [17]. Studying the conversion of methanol to hydrocarbons, Hayashi *et al.* [12] observed a similar effect in the case of the ammonium salt of TPA. The effect of the cation is related either to its electronegativity affecting the Mo oxidation state or to the modification of acidity. The activity patterns also reveal that the AMPA catalyst offers the flexibility of conducting the reaction either at maximum conversion by limiting the selectivity or at maximum selectivity by limiting the conversion, the latter being environmentally highly attractive. However, the pyrazine levels have increased (from 5–25%) with increase in calcination temperature. Increase in pyrazine selectivity could also result from "after oxidation" (figure 1), particularly when the MP conversion exceeds 80%, as suggested by Bondareva *et al.* [27].

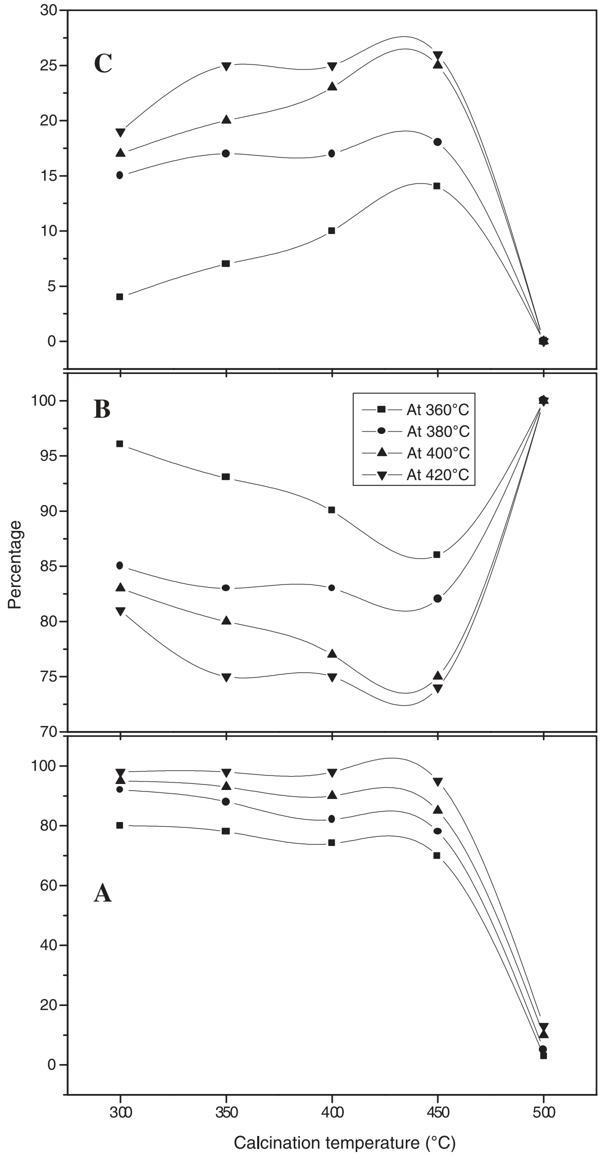

Figure 5. Product distribution (A) conversion (B) yield of CP, and (C) yield of pyrazine at various reaction temperatures of AMPA catalysts pretreated at different temperatures.

An important observation is the drop in activity of AMPA to a very low value when the pretreatment temperature is 500 °C. From the XRD and FTIR results, it may be noted that the catalyst has retained the structure of AMPA, at least partially, up to 450 °C, beyond which there is complete destruction of the Keggin unit with the release of ammonia and the formation of oxides of molybdenum and phosphorous. However, if the species formed are only the oxides of Mo and P, they should be regenerable to AMPA during the reaction. It is necessary to understand why the high-temperature-calcined AMPA shows drastic reduction in activity. This aspect will be discussed later.

The product distribution in the ammoxidation reaction over MPA catalysts is shown in figure 6. The catalysts display low conversion in the beginning, which gradually increases from 30–75% when the pretreatment temperature increases from 300–500 °C. Even though the MPA catalyst exhibits a facile decomposition at a lower temperature compared to that of AMPA, the increase in conversion with increase in calcination temperature could be attributed to the gradual transformation of the oxides into the AMPA structure during the reaction. This observation is evident from the XRD and FTIR data of used MPA catalysts (figures 7 and 8, respectively). The XRD patterns of the samples exhibit well-crystallined $(NH_4)_3PMo_{12}O_{40} \cdot 4H_2O$ phase. The IR spectra also show bands corresponding to AMPA with their characteristic Keggin bands, corroborating the observations made in the case of XRD patterns.

A comparison of the IR spectra of the 500 °C calcined fresh MPA (figure3(e)) and AMPA catalysts (figure 9(c)) reveals the formation of a new phase in the case of the latter, which is not found in the former. Bondareva *et al.* [27] have also reported the formation of an additional phase, which they have provisionally assigned to molybdenyl phosphate. The XRD pattern of the used AMPA catalyst, previously calcined at 500 °C, is shown in figure 9(b). The main peaks do not correspond to that of the standard ones given in JCPDS file No. 9-412 of AMPA. A comparison of this pattern with the corresponding one of MPA given in figure7(e) reveals

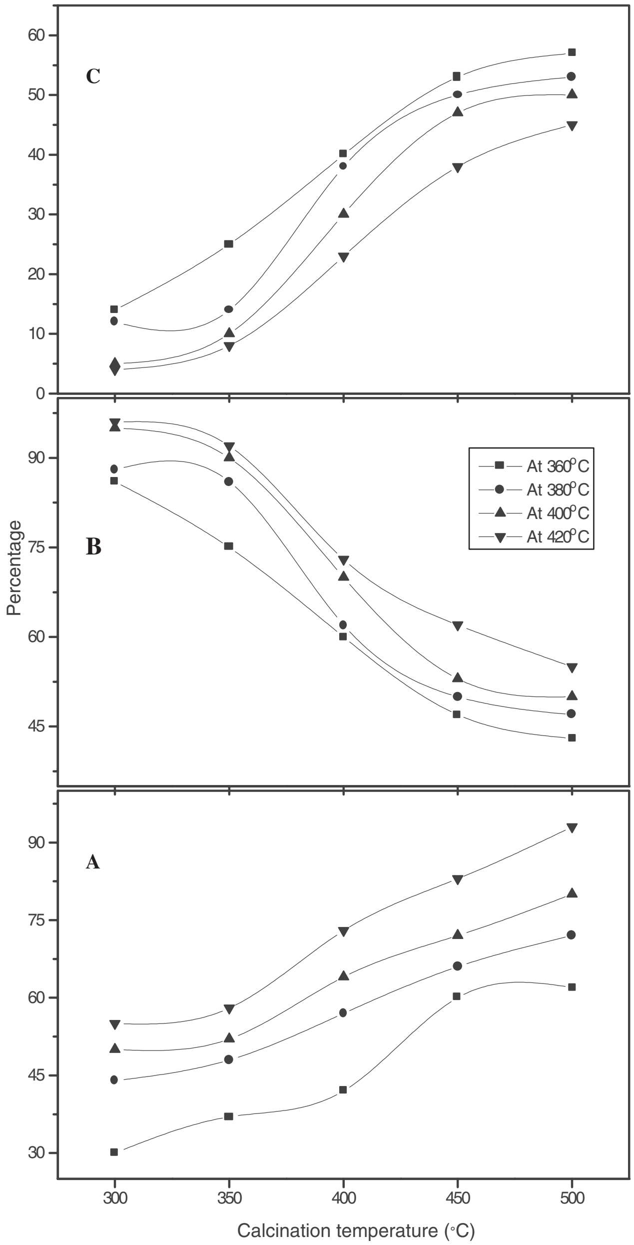

Figure 6. Product distribution (A) conversion, (B) yield of CP, and (C) yield of pyrazine at various reaction temperatures of MPA catalysts pretreated at different temperatures.

an interesting observation. The used MPA catalyst contained AMPA phase, implying good regenerability of oxides into the salt. Such a clear indication of regenerability is not observed in the case of XRD patterns of the used AMPA catalyst. This could be due to the presence of a non-regenerable species in the fresh catalyst (figure 9(a)). A similar result could be derived from the FTIR spectra of the two catalysts after use (figures 9(d) and 8(e)). A significant decrease in the intensities of the bands due to the Keggin unit is observed, revealing the presence of only a small proportion of AMPA, the majority of it containing new species, which could not be identified.

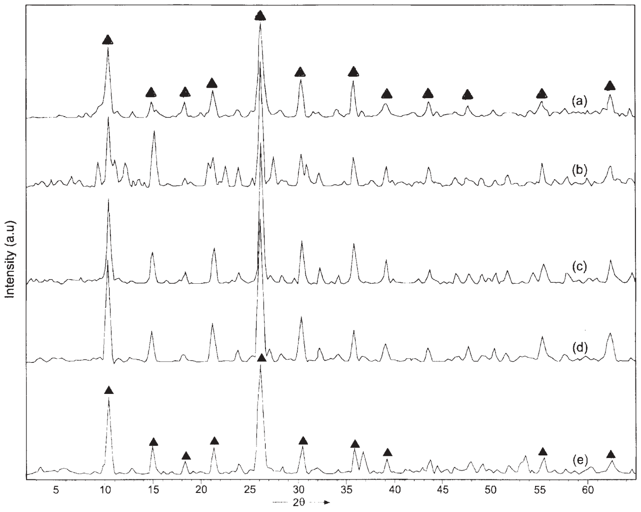

Figure 7. X-ray diffraction patterns of used MPA samples pretreated at (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, and (e) 500 °C (▲) $(NH_4)_3PMo_{12}O_{40} \cdot 4H_2O$.

Formation of non-regenerable species might be responsible for the sudden decrease in activity of AMPA precalcined at 500 °C. One possibility is the formation of a surface phosphide species mediated by Mo in its reduced state, which in turn is formed by the high-temperature passivation, in hydrogen, of AMPA, as described below.

$$(NH_4)_3PMo_{12}O_{40} \rightarrow 3NH_3 + H_3PMo_{12}O_{40}$$

$$NH_3 \rightarrow 1/2N_2 + 3/2H_2$$

$$H_2 + H_3PMo_{12}O_{40} \rightarrow H_2O + HPA_{\text{reduced}}$$

Whereas the first two reactions are well documented in literature, Katamura *et al.* [28] elucidated the nature of species formed when MPA is subjected to reduction in hydrogen.

It should, however, be noted that in spite of the ability for regeneration of the Mo and P oxides into AMPA during the reaction, the overall activity of the MPA catalysts cannot match the activity of AMPA catalysts.

4. Conclusions

AMPA offers higher activity and selectivity compared to its parent acid, MPA, in the ammoxidation of MP. The catalyst also affords tunable performance to achieve high activity or selectivity, depending upon the requirement. The salt is thermally more stable than the acid. Even though these heteropolycompounds decompose into their component oxides during their preparation when subjected to higher calcination temperatures, they get regenerated in the course of reaction. However, at very high calcination temperatures, of the order of

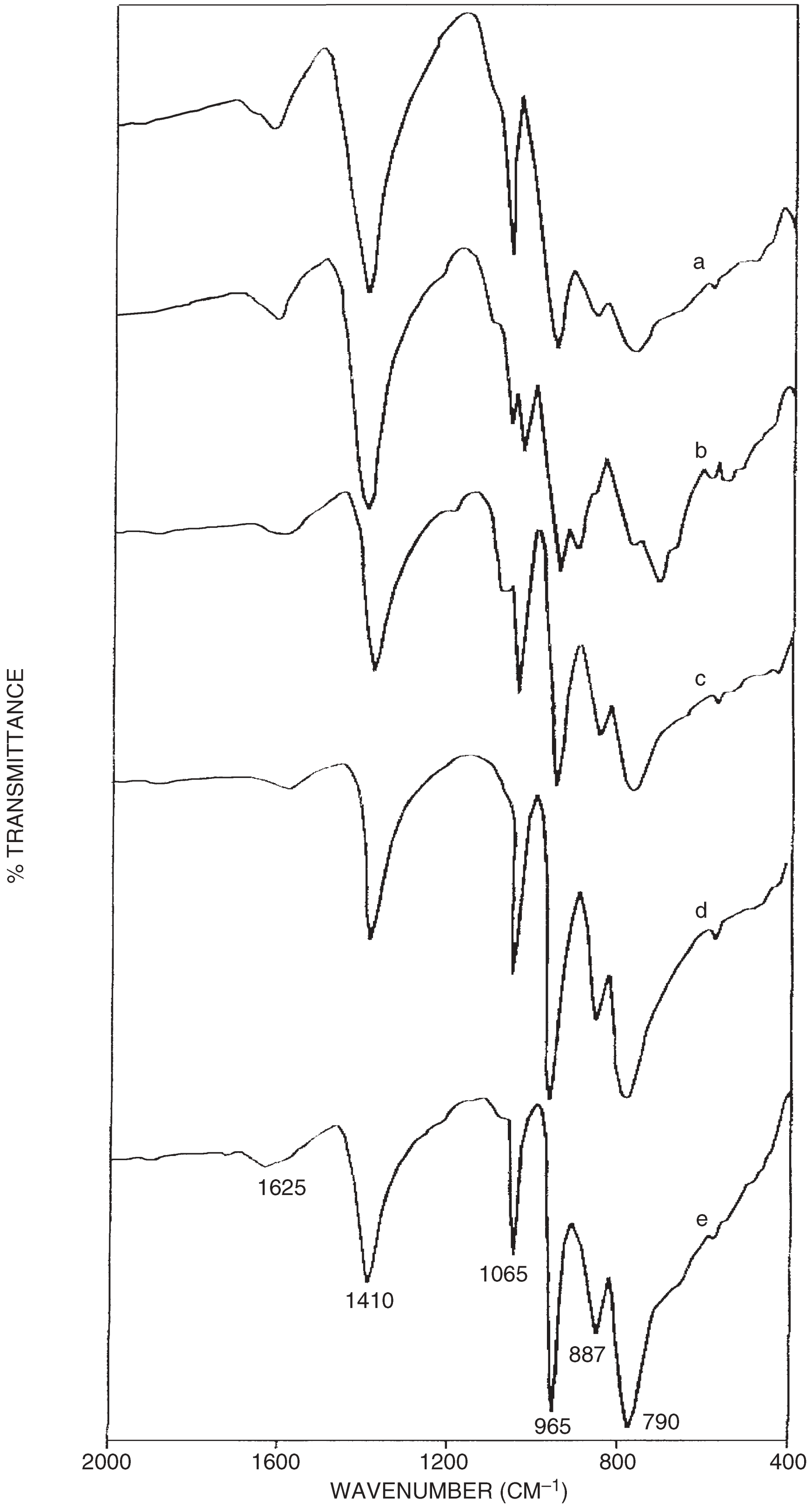

Figure 8. FTIR spectra of used MPA samples pretreated at (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, and (e) 500 °C.

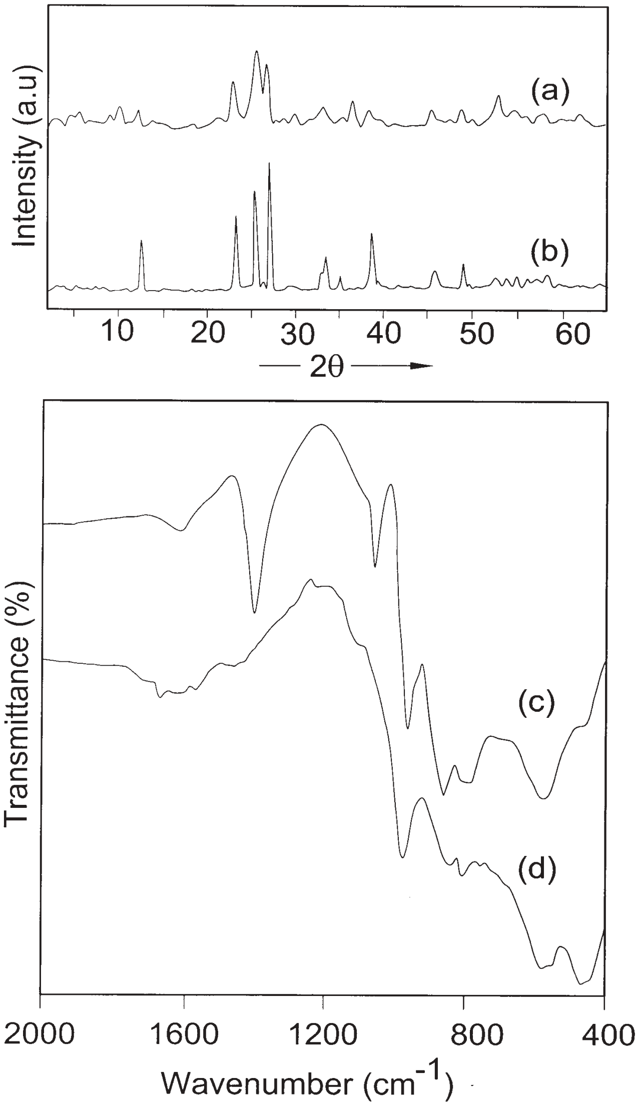

Figure 9. Fresh and used XRD and FTIR patterns of AMPA catalyst pretreated at 500 °C.

500 °C, AMPA decomposes, at least partially, into non-regenerable, inactive species, thus limiting the maximum temperature of pretreatment.

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