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In situ synthesis of the ammonium salt of 12-molybdophosphoric acid on niobium phosphate by salt-surface interaction: The ammoxidation functionality of the catalyst in the transformation of 2-methylpyrazine to 2-cyanopyrazine[†]

Ch. Srilakshmi, K. Narasimha Rao, N. Lingaiah, I. Suryanarayana and P.S. Sai Prasad[*]

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

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The ammonium salt of 12-molybdophosphoric acid (AMPA) has been synthesized, *in situ,* on niobium phosphate by interacting the phosphate of the support with the molybdenum of the salt. The formation of AMPA, with the popular Keggin structure, is confirmed by X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. The *in situ* synthesized catalysts exhibited higher ammoxidation activity than the bulk AMPA, showing optimum conversion at 10 wt% Mo loading. The selectivity to nitrile increased with increasing loading.

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

1. Introduction

12-molybdophosphoric acid (MPA), an important heteropolycompound, has been extensively used as a catalyst for a variety of chemical reactions [1]. The activity of this catalyst can be attributed to its beneficial acidic and redox properties. Bulk MPA exhibits the popular Keggin structure [2] with 12 MoO_6 octahedra surrounding the central PO_4 tetrahedron. In spite of the widespread importance of MPA as a catalyst, its extensive application is restricted because of its complexity, poor reproducibility of the methods of synthesis, and low thermal stability. For example, apart from the calcination temperature, the rate at which the temperature is reached also affects the final structure [3]. Several methods have been reported for preparation of the salts of the heteropolyacid exhibiting the Keggin structure. Some of the important routes are: dissolving the right amounts of the precursor salts in water, precipitation at controlled pH followed by extraction with a suitable solvent like ether [4], and direct precipitation through the addition of either stoichiometric or non-stoichiometric amounts of cations in the solution containing the dissolved acids [5]. In a recent review [6], Moffat has well documented the surface and catalytic properties of heteropoly compounds. Rodrigo *et al.* [7] have reported the formation of molybdosilicic acid (HSiMo) on the SiO_2 surface by reacting it with an aqueous solution of ammonium paramolybdate, during the preparation of Mo/SiO_2 catalysts at lower Mo loadings (<1 wt%). However, upon increasing the Mo loadings (5–10 wt%), the polymolybdate species and crystalline MoO_3 species have been observed. It is known that the stability of HSiMo is very low when compared with other heteropoly acids and is not recommended for high-temperature vapor-phase reactions. A few other reports have also revealed the formation of heteropoly compounds by reacting the fluid phase with one or more of the species in the solid phase [8–10]. MPA is often used by dispersing it on different supports. However, the acidity of the support plays a vital role in its stabilization. On supports like alumina the stability of MPA is found to be poor, suggesting that the acidic supports are favorable. Some researchers have studied the activity of the catalyst by preparing its ammonium or mixed metallic salts. These salts are used either directly or by depositing them on oxide supports. It is interesting to examine the possibility of generating the salts of MPA, in their Keggin structure, by interacting the phosphate of the support with the Mo of the salt.

Recently, the catalytic usage of MPA has been extended to synthesis of fine chemicals as well. For example, Bondareva *et al.* [11] have suggested MPA as a catalyst in the ammoxidation of 2-methylpyrazine (MP) to 2-cyanopyrazine (CP). The ammoxidation is an important component step in the synthesis of 2-amidopyrazine, an effective anti-tubercular drug. With the growing concern for environmental safety, this route has become highly competitive compared to the older process involving phenylene diamine and glyoxal. Ammonium salt of 12-molybdophosphoric acid (AMPA), exhibiting

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[†] IICT Communication No. 4670.

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

the Keggin structure, has been studied for the oxidative dehydrogenation of isobutyric acid to methacrylic acid by McGarvey and Moffat [12]. In a recent publication [13], it has been reported that the AMPA offers better CP selectivity than the parent acid itself in the ammoxidation of MP. Hence, a lot of attention is now focused on the synthesis of AMPA by novel techniques, using acidic supports.

Presently, acidic niobium compounds are extensively used as heterogeneous catalysts [14]. Niobium containing mixed oxides is found to be highly active and selective in the ammoxidation of propene [15] and ethane [16] to their respective nitriles. Niobium oxide is also used for dispersing MoO_3. It is observed that the addition of H_3PO_4 to Nb_2O_5 increases its acidity and stability towards phase transformation [17], thereby offering enhanced activity in reactions like 1-butene isomerization, dehydration of cyclohexanol and alkylation of benzene. However, studies on the synthesis of AMPA on niobium phosphate are scarce. Secondly, no detailed study has been reported yet on the possibility of an *in situ* synthesis of AMPA on niobium or any other phosphate supports. It is also interesting to examine the extent of formation of AMPA with the surface phosphate species and correlate it with the ammoxidation functionality.

In the present investigation, we report the *in situ* synthesis of AMPA (exhibiting the Keggin structure) by interacting the phosphate ion of the support with the molybdenum species of the salt. An attempt has also been made to correlate the extent of formation of AMPA with the activity and the selectivity of the catalysts in the transformation of MP to CP.

2. Experimental

A series of catalysts with varying AMPA loading were prepared by impregnating the niobium phosphate (CBMM, Brazil) support with known quantities of ammonium heptamolybdate (Loba Chemi, GR) by the wet impregnation method. The amount of Mo in the impregnating solution was selected such that the nominal MoO_3 content varies between 5 wt% (designated as Mo-5) and 20 wt% (Mo-20) in the finished catalysts. The impregnated samples were first dried at 120 °C, after evaporating the solution in a water bath. The dried mass was then carefully calcined in air at 400 °C over a period of 6 h and kept at that temperature for 4 h. X-ray diffraction (XRD) patterns of the catalysts were obtained on a Siemens D-5000 diffractometer using Cu K_α radiation. FTIR spectra were recorded on a Nicolet 740 spectrometer using the KBr disc method. Scanning electron micrographs of the catalysts were obtained in a Hitachi S-520 electron microscope at an accelerated voltage of 10 kV. Samples were mounted on aluminum stubs using double adhesive tape and were gold-coated in a Hitachi HUS-5GB vacuum evaporator. The EDX analysis was performed using Oxford Link ISIS-300 at an accelerated voltage of 20 kV. Total pore area, intrusion volume and the average pore diameter were obtained on a Micromeritics (AutoChem-2910) mercury porosimeter. The ammoxidation reaction was studied taking 3 g (18/25 BSS mesh size) of catalyst in a tubular reactor, placed between two quartz plugs and passing a mixture of MP, water, ammonia and air in the molar ratio 1 : 13 : 7 : 38 respectively (at a liquid flow rate of 4 ml/h), in the temperature range 360–400 °C. The liquid product collected, after the catalyst had attained a steady state, was analyzed by gas chromatography. From the analysis of the non-condensable exit gas mixture, it was confirmed that the presence of any organic species or the oxides of carbon was negligible. The niobium phosphate support was also evaluated for the sake of comparison.

3. Results and discussion

The XRD patterns of the catalysts, along with that of the niobium phosphate, are given in figure 1. The NbP is found to be amorphous in nature. Martins *et al.* [18] have also reported the amorphous nature of niobium phosphate up to a calcination temperature of 700 °C. The formation of the ammonium salt of 12-molybdophosphoric acid (AMPA) with the d-lines matches closely that of $(NH_4)_3PO_4(MoO_3)_{12}$. $4H_2O$ (ASTM Card No. 09-412) can be clearly observed from the XRD patterns of Mo-5 to Mo-20 catalysts, the intensity of the lines increasing with an increase in Mo loading. The XRD patterns of Mo-10 and Mo-20 catalysts exhibit some small diffraction lines other than peaks related to AMPA are unable to detect clearly may be due to the formation of mixed Mo and Nb oxides. The crystallographic properties of AMPA also agree with those of the values reported by McMonagle and Moffat [19]. The present observation is very significant in the sense that the formation of AMPA, exhibiting the Keggin structure, occurs by the participation of the surface phosphate of the support, contrary to the general methods of preparation of AMPA, wherein the phosphate species is added in the form of phosphoric acid or its ammonium salts along with the Mo salt.

The FTIR spectra of the pure niobium phosphate and the Mo-5 to Mo-20 catalysts are shown in figure 2. The infrared spectrum of the niobium phosphate support shows strong absorption at 1629 cm^{-1}, which can be attributed to adsorbed water. The very broad and strong band spanning between 1000 and 1200 cm^{-1} is due to the asymmetric stretching mode of the phosphate ion, as also observed by Martins *et al.* [12]. The Mo-5 catalyst shows strong bands at 1624, 1404–1410, 1164, 1064, 1012, 970, 870 and 792 cm^{-1}. Particular attention may be focused on bands at 1064, 970 and 870 cm^{-1}, which are due to the Keggin structure present in the

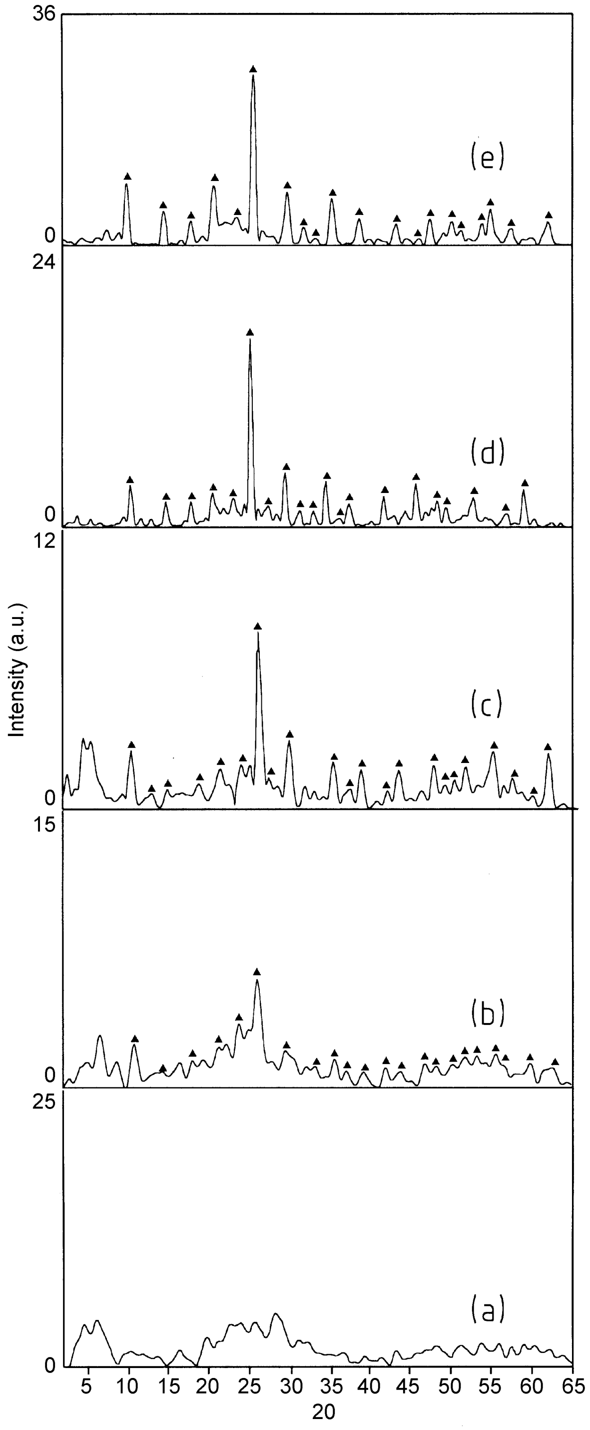

Figure 1. X-ray diffraction patterns of the catalysts prepared with different Mo content. (a) Support; (b) Mo-5; (c) Mo-10; (d) Mo-15; (e) Mo-20 and (▲) $(NH_4)_3PMo_{12}O_{40}.4H_2O$.

moiety. The band at 1404–1410 cm^{-1} is due to the ammonium ion. It can also be observed that the intensity of these bands has increased as the AMPA content in the catalyst increases. This observation corroborates the increased intensity of crystallization of AMPA, from Mo-5 to Mo-20, as observed in the XRD patterns of the catalysts. Thus, the information obtained from the FTIR data also confirms the *in situ* formation of AMPA on the support.

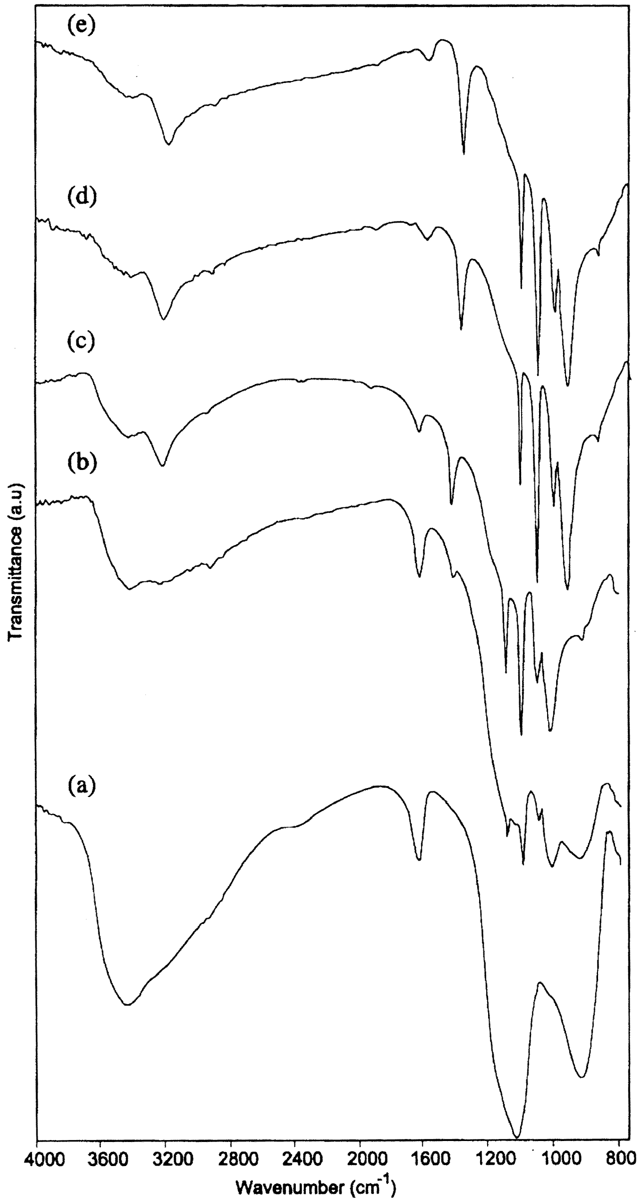

Figure 2. FTIR spectra of the catalysts prepared with different Mo content. (a) Support; (b) Mo-5; (c) Mo-10; (d) Mo-15; (e) Mo-20.

A continuous decrease in the total pore area and the intrusion volume and a gradual increase in average pore diameter can be observed from the data given in table 1. This implies that the micropores are progressively filled up with an increase in loading. The decrease in surface Nb and P contents of the catalysts with a simultaneous increase in the Mo content can also be observed by the EDX analysis given in table 1, which also supports the above observation. The ion exchange and reduction studies of AMPA by Hodnett and Moffat [20] and morphological studies by Lapham and Moffat [21] suggest similar type of result.

Table 1
Variation of textural properties and Mo, P and Nb contents with Mo loading.

Catalyst	Total pore area (m^2/gm)	Intrusion volume (ml/g)	Average pore diameter (A°)	Mo content (atomic percent)	P content (atomic percent)	Nb content (atomic percent)
Support	146	0.41	113	–	9.5	44.6
Mo-5	85	0.34	160	18.0	6.0	29.4
Mo-10	79	0.29	145	25.9	5.1	22.6
Mo-15	41	0.20	196	32.9	2.8	16.9
Mo-20	34	0.17	196	39.0	2.2	13.5

It is interesting to know whether the formation of AMPA, with the Keggin structure, is limited to the surface of niobium phosphate or niobium enters into the primary structure of the Keggin unit. A comparison of the positions of the characteristic FTIR bands due to the Keggin ion reported in the literature [22] with those of the values observed in the present work reveals that there is no noticeable shift in these bands. Hence, it may be considered that the formation of AMPA is confined to the surface of niobium phosphate only and Nb is not incorporated in the primary structure of the Keggin unit. If the niobium has modified the Keggin structure, the characteristic bands of the polyion would have been shifted to lower frequencies, as in the case of Mo-V heteropolyacid salt catalysts reported by Marchal-Roch *et al.* [23]. From XRD and FTIR, results reveal that the niobium in the solid phase interacts with ammonium heptamolybdate fluid and forms an amorphous solid.

Figure 3 displays the variation of the ammoxidation activity (expressed as percent conversion of MP) of the catalysts as a function of Mo loading at different reaction temperatures. The observations made on the niobium phosphate are also included. The MP conversions have been consistently higher than that of the bulk AMPA (40–45%, as reported in our earlier publications [13,24]). The activity of the catalysts increased with an increase in Mo loading up to Mo-10, and from then on showed a decreasing trend. It appears that the AMPA exists as a dispersed phase up to an Mo loading of 10 wt%, during which the activity increases with loading. Further addition of Mo might have led to the formation of bulk-like AMPA offering diffusional resistance to the reacting species. Forni [25] has also observed that despite reducing the particle size to the minimum, it is difficult to eliminate the diffusion resistance during the ammoxidation reaction.

The selectivity of the catalysts to CP formation, as a function of Mo loading, is shown in figure 4 along with the selectivities obtained on niobium phosphate. The niobium phosphate support has displayed high selectivity to pyrazine, a byproduct formed because of oxidative dealkylation of MP, which could be due to the high surface acidity of the niobium phosphate. Okazaki and Wada [26], in their studies on commercial amorphous niobium phosphate, have reported that the catalyst possesses strong surface acidity and hence promotes acid-catalyzed reactions. However, it may be noticed that with an increase in Mo content the selectivity to pyrazine has decreased and that of CP increased. This may be an effect of the formation of AMPA on the support and simultaneous neutralization of the acid centers. This is in conformity with our earlier observation [24] that AMPA is highly selective to CP formation. On AMPA/TiO_2 catalysts [27] we have also noticed a surface-induced enhancement in the activity and selectivity. Figure 5 is a typical representation of the variation of activity of the catalyst as a function of reaction temperature for the catalyst containing 10 wt% Mo.

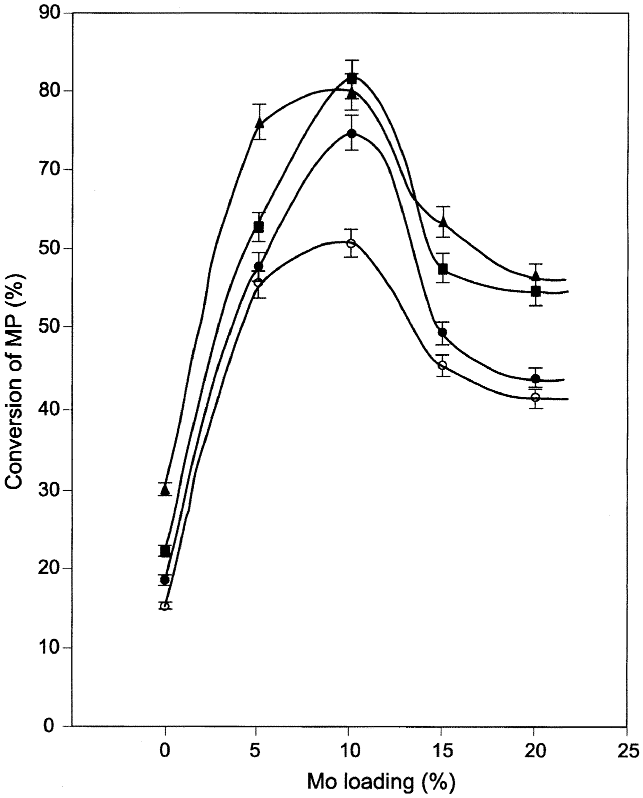

Figure 3. Variation of the ammoxidation activity of the catalysts as a function of Mo loading at different reaction temperatures. (Mo loading 0% corresponds to that of support.) (○) 360 °C; (●) 380 °C; (■) 400 °C; (▲) 420 °C.

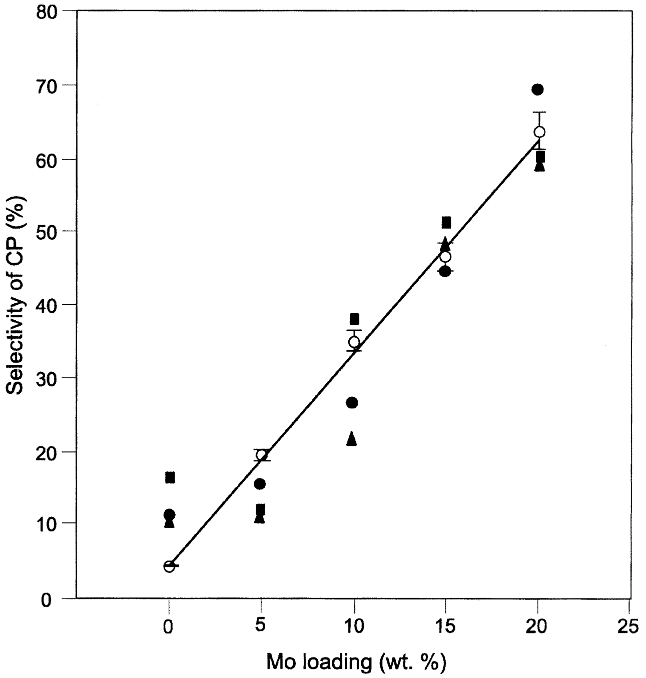

Figure 4. Variation of selectivity to CP as a function of Mo loading at different reaction temperatures. (Mo loading 0% corresponds to that of support.) (○) 360 °C; (●) 380 °C; (■) 400 °C; (▲) 420 °C.

The conversion increased continuously up to 400 °C, and from then on showed a decreasing trend. It appears that the AMPA is stable up to 400 °C. Further increases in temperature cause partial decomposition of the ammonium salt into ammonia (or nitrogen) first and subsequently into the oxides of Mo and P. This phenomenon is discussed in detail in the literature [3].

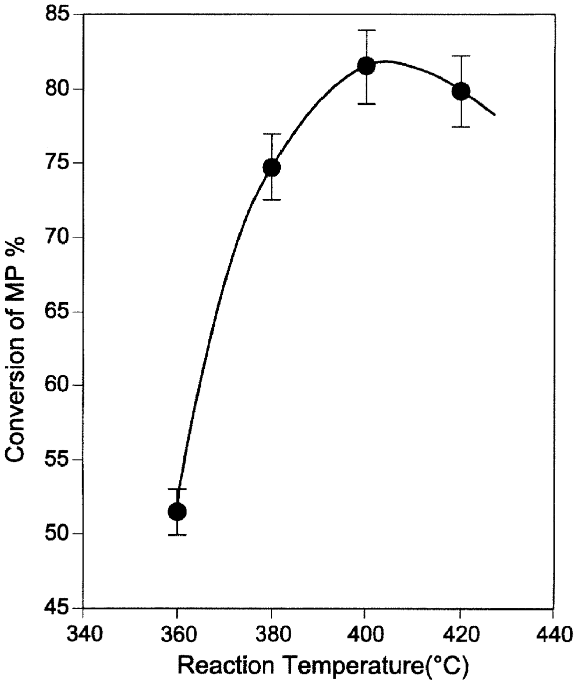

Figure 5. Effect of the reaction temperature on the ammoxidation activity of Mo-10 catalyst.

4. Conclusions

It may be concluded that the synthesis of AMPA is possible by interacting the molybdenum compound with the phosphate species on the surface of the solid phase, thus offering a new single-step synthesis of the ammonium salt of 12-molybdophosphoric acid. The behavior of the AMPA thus generated *in situ* is comparable with that of the AMPA prepared by conventional methods during the ammoxidation reaction. Further experiments are in progress to compare the thermal stability of AMPA prepared by the present method and that obtained by conventional techniques.

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