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Synthesis, Characterization and Ammoxidation Functionality of Silica Supported Vanadium Incorporated Ammonium Salt of 12-Molybdophosphoric Acid Catalyst

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Abstract A series of silica supported vanadium incorporated ammonium salts of 12-molybdophosphoric acid (AMPV) catalysts, with 5–25 wt% of active component were prepared. These catalysts were characterized by XRD, FTIR, BET-Surface Area, TGA/DTA and acidity by potentiometry techniques. The characterization data derived from XRD, FT-IR techniques reveal that the AMPV on silica support exists in the form of Keggin structure. These catalysts are studied for the vapor phase ammoxidation of 2-methyl pyrazine (MP) to cyanopyrazine (CP). The conversion of methyl pyrazine increased with increase in loading on silica showing a maximum value of conversion at 20 wt% AMPV loading. The ammoxidation activity of these catalysts with and without vanadium is studied and the vanadium incorporation led to substantial improvement in the cynopyrazine selectivity.

Keywords Ammonium salt of 12-molybdophosphoric acid · Vanadium incorporation · Silica · Ammoxidation · 2-Methylpyrazine · 2-Cyanopyrazine

1 Introduction

Heteropoly compounds have been studied as bulk catalysts as well as in supported form. The deposition of heteropoly acids on solid supports is important for catalytic applications, as the surface area of unsupported ones is low. In deed, the most important restriction to the use of bulk materials for heterogeneous gas phase applications is due to their low thermal stability [1, 2]. The heteropoly-acids (HPA) are finding potential applications in the synthesis of fine chemicals particularly in acid or mild oxidation catalyzed reactions [3, 4]. The catalytic functionalities of HPAs depend on their acidic and redox properties [5, 6]. The salts of heteropoly acids are more stable than the free acids, but they possess low surface area. The effect of vanadium substitution for molybdenum in molybdophosphoric acid has been the subject of study by various authors [7–9]. A few reports are available on the synthesis of bulk vanadium substituted molybdphosphoric acid and its ammonium salt [10, 11]. Use of support improves the thermal stability and the catalytic activity. The activity and selectivity depends upon the constituent elements, structure and the interactive species generated on the support surfaces [12, 13]. Supported heteropoly acids present a greater number of surface acid sites than their bulk components and the acidity depends mainly on the support and the extent of loading [2, 14]. Supports such as SiO_2, ZrO_2 and carbon etc. are most widely examined [15–22]. In general, the acidity at low loadings is weaker and less uniform than for the bulk solid and some decomposition of the heteropoly acid may also be observed [23]. As the loading increases, the acid strength also increases [24]. It is worth mentioning here that all the studies so far made were only with the heteropoly acids especially 12-molybdophosphoric acid and 12-tungstophosphoric acid on different supports. The results obtained and the conclusions drawn in some cases, like 12-molybdophosphoric acid on silica as mentioned by Claude Rocchccioli-Deltcheff [25] are quite contradictory. It is reported that the thermal stability of MPA decreased when

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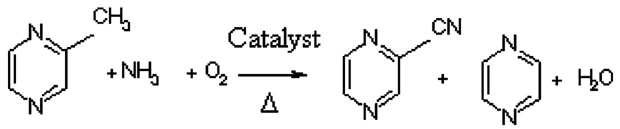
it is supported on silica and the stability of catalyst is less at lower concentration of MPA [26, 27]. Servicka et al. [28] concluded that deposition on silica lowers the stability of MPA. Moffat and his group [29, 30] gave the opposite conclusion that MPA is strongly stabilized by the support, and is found to be stable up to 580–600 °C when supported on silica. J.B. Black et al. [31, 32] consider that this stabilization is only apparent, since the starting material is easily rebuilt from the decomposition products after exposure to water vapor and this reconstruction is facilitated on the silica surface.

The application of heteropolyacids as catalysts has now been extended to the synthesis of fine chemicals like drugs and drug intermediates. Preparation of 2-cyanopyrazine (CP) by the ammoxidation of 2-methylpyrazine (MP) is one such example, wherein higher CP selectivity could be derived by enhancing the redox property of the catalyst. Cyanopyrazine is an intermediate in the production of 2-amidopyrazine, an effective anti-TB drug. Conventionally, Vanadia based catalysts, (particularly the V–Ti–O catalysts) have been used for the ammoxidation. Even though very active, giving close to 100% conversion, they operate at high reaction temperature (>430 °C) and their CP selectivity is low. Besides, the exothermic oxidation of ammonia starts dominating under the conditions of the reaction leading to under-utilization of ammonia for CP synthesis.

It is a general observation that the VPOs need high activation time to reach equilibrium state. The second and the new class of low temperature ammoxidation catalysts includes the 12-molybdophosphoric acid and its ammonium salt. Bondareva et al. [33] have suggested the use of V-containing heteropoly compounds as catalysts for the ammoxidation of MP and obtained a maximum CP selectivity of ca. 70% at 90% conversion. In the case of these catalysts low thermal stability is the main deterrent in their applicability for vapor phase reactions.

In the present investigation, an attempt is made to synthesize the vanadium incorporated ammonium salt of molybdophosphoric acid impregnated on silica in a single step. The catalysts have been characterized in order to understand the stability of ammonium salt when vanadium is incorporated into the structure and their catalytic functionality has been studied in the ammoxidation of MP to CP (Scheme 1).



Scheme 1 Overall reaction scheme of ammoxidation of 2-methyl pyrazine

2 Experimental

A series of silica (Sigma: CAS 112945-52-5) supported ammonium salt of 12-molybdoposphoric acid (AMPA) and vanadium incorporated ammonium salt of 12-molybdoposphoric acid (AMPV) catalysts with 5–25 wt% loading of active component were prepared by impregnation of the support with a mixture of required quantities of aqueous solutions of ammonium heptamolybdate, ammonium metavanadate and diammonium hydrogen orthophosphate, generating the Keggin ion in one step. For the preparation of AMPA catalysts, required quantities of ammonium heptamolybdate and di ammonium hydrogen orthophosphate were dissolved in minimum amount of water. This solution was first refluxed at 100 °C for 6 h and then the required quantity of this solution was added to the support. After the addition, the pH of the solution was adjusted to 1 by adding dilute HNO_3. These catalysts were designated as AMPA/SiO_2. The procedure adopted for the preparation of AMPV catalysts was the same as the preparation of AMPA except the addition of calculated amount of ammonium metavanadate by reducing corresponding amount of molybdenum salt (such that the Mo/V atomic ratio 11/1). These catalysts were designated as AMPV/SiO_2. Finally these catalysts were calcined in air at 350 °C for 4 h.

X-ray diffraction (XRD) patterns of the catalysts were obtained on a Rigaku Miniflex diffractometer using CuK_α radiation. FTIR spectra were recorded on a DIGILAB (USA) spectrometer, with a resolution of 1 cm^{-1} using KBr disc method. The specific surface areas of the catalyst samples were calculated from N_2 adsorption–desorption data acquired on a autosorb-1 instrument (Quantachrome, USA) at liquid N_2 temperature. The powders were first outgassed at 200 °C to ensure a clean surface prior to construction of adsorption isotherm. A cross-sectional area of 0.164 nm^2 of the N_2 molecule was assumed in the calculations of the specific surface areas using the method of Brunauer, Emmet, and Teller (BET). Elemental analysis of the heteropoly acid samples were estimated by inductively coupled plasma atomic emission spectroscopy (ICP-MAS). The samples were digested using aquaregia and the elements to be analyzed are phosphorus, molybdenum and vanadium. The TGA/DTA analysis was carried out on a Mettler–Toledo apparatus. With a sample weight of ca. 30–40 mg, the tests were performed under nitrogen flux in the temperature ranging from 25 to 800 °C and at a heating rate of 10 °C/min.

The acidity of the solid samples was measured by the potentiometer titration method. A known mass of solid, suspended in acetonitrile, was stirred for 3 h and then the suspension was titrated with a solution of 0.05 N n-butyl amine in acetonitrile, at a flow rate of 0.05 ml/min. The variation in the electrode potential was measured with an instrument having a digital pH meter, (Automatic titrator, Schott GmbH, Germany) using a standard calomel electrode. The potentiometric titration was performed with a glass electrode. The instrument was calibrated using standard buffer solutions. The acidity of the catalysts measured by this technique enables determination of the total number of acid sites and their strength [34, 35].

Ammoxidation of MP was carried out in a micro reactor at atmospheric pressure in the temperature range of 360–420 °C. In a typical experiment about 5 g of the catalyst (crushed to 18/25 BSS sieve to eliminate mass transfer limitation and diluted with equal quantity of quartz beads) was loaded in the reactor suspending it between two quartz plugs. The feed with a molar ratio of MP: Water: ammonia: air = 1:13:7:38 was fed into the preheater portion of the reactor. The aqueous mixture of MP was metered using a microprocessor based feed pump (B. Braun, Germany), at a flow rate of 2 ml/h. After allowing the catalyst to attain steady state for 30 min, at each reaction temperature, the liquid product was collected for 30 min and it was analyzed by gas chromatography, separating it on an SE-30 column (2 m long, 3 mm dia) using an FID detector.

3 Results and Discussion

3.1 Surface Area

The surface areas of silica support, bulk AMPV and silica supported AMPV catalysts are shown in Table 1. The surface area of the pure support was 358 m^2/g. Bulk AMPV showed low surface area compared to the supported catalysts. The surface area decreased gradually as the loading of active component (AMPV) increased from 5 to 25 wt% on the silica support. Decrease in the surface area may be partly due to a decrease in the relative support content and/or the interaction of active species with hydroxyl groups of the silica support (≡Si–OH). In Table 1, the results of elemental analysis for silica supported catalysts are compared to pure ammonium salt of phosphomolybdic acid (AMPA). The Mo/P ratio of AMPA catalyst was 12.4, indicating a relatively pure phase of the heteropolyacid. The Mo/P ratio in our synthesized pure AMPV catalyst is 11.1. The pure AMPV catalyst consist slightly lower contents of Mo in the Keggin units due to partial substitution of Mo by V. Indeed, the V/P ratio in this sample is 0.93. The Mo/P ratios for 5–25 wt% supported catalysts, 10.6, 10.92, 11.0, 11.2 and 11.1 respectively. Since elemental analysis provide supporting information for these solid samples.

Table 1 BET surface area of bulk and SiO_2 supported AMPV catalysts

S.No.	Catalyst	BET surface area (m^2/g)
1	SiO_2	358
2	AMPA	66
3	AMPV	40
4	5 wt% AMPV/SiO_2	262
5	10 wt% AMPV/SiO_2	233
6	15 wt% AMPV/SiO_2	204
7	20 wt% AMPV/SiO_2	182
8	25 wt% AMPV/SiO_2	158

3.2 Powder X-ray Diffraction Studies

The XRD patterns of AMPV/SiO_2 catalysts calcined at 350 °C are shown in Fig. 1. The powder diffraction method of identification was adopted by number of research workers as a routine method of identification of the crystalline phase of heteropoly acids [12–14]. When a heteropoly acid is impregnated on a support, the pattern should show the reflections due to AMPV and as well as the support. The XRD pattern of pure support showed a broad peak at 2θ value of 20–30° indicating the amorphous nature of the support. With increase in AMPV content on

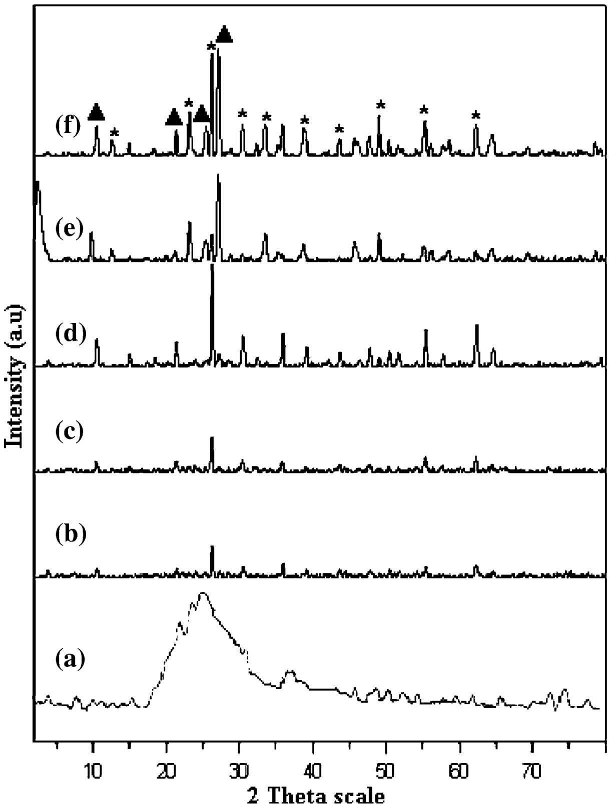


Fig. 1 XRD patterns of SiO_2 and AMPV/SiO_2 catalysts (**a**) support (**b**) 5 wt% (**c**) 10 wt% (**d**) 15 wt% (**e**) 20 wt% (**f**) 25 wt%; (▲) Keggin ion; (*) SiO_2 phase

SiO_2, the samples showed crystalline nature. The 5 wt% AMPV/SiO_2 catalyst showed clear diffraction lines due to tridymite silica phase (JCPDS file No.14-260 and ICDD No. 88-2488). At higher loadings, the main diffraction lines correspond to Keggin ion (JCPDS file No.9-412) was clearly observed. As the loading increased from 5 to 25 wt%, the intensity of the diffraction lines due to tridymite silica phase are substantially decreased and the diffraction lines corresponds to Keggin ion were increased. These results are in good agreement with the observations made by Soled et al. [36]. Thus, the XRD data revealed the formation of AMPV Keggin ion the support.

3.3 Fourier Transform Infrared (FTIR) Studies

The FTIR spectra of AMPV/SiO_2 catalysts were shown in Fig. 2. Pure silica support exhibited three main bands at 1,100 cm^{-1} (broad and very strong), 800 cm^{-1} (medium) and 470 cm^{-1} (strong), which partly overlap with the characteristic bands of the Keggin unit [37]. It is well known that the bulk AMPA reveals characteristic bands of the $[PMo_{12}O_{40}]^{3-}$ Keggin ion at 1,060, 960, 860 and 790 cm^{-1} corresponding to the stretching vibrations of P–O_a, Mo–O_d, Mo–O_c–Mo, Mo–O_b–Mo of the Keggin unit respectively and a band at 1,410 cm^{-1} is ascribed due to N–H vibration mode of ammonium ion [30, 38]. In the present case, the strong bands of silica masked the band at 1,060 cm^{-1} is due to Keggin ion vibration in supported AMPV catalysts. However, information can still be obtained from the less affected regions, which show an increase in intensity. The bands placed at 963 and 790 cm^{-1} can be ascribed due to Keggin ion. These small non-overlapped bands also confirm the presence of the Keggin ion on the support. Similar observations were made on titania and zirconia supported AMPA catalysts wherein some of the bands due to Keggin ion are masked by the support [37, 38]. The FTIR data also, confirms the formation of Keggin ion on the support during the synthesis. These results are in agreement with the observations made by XRD.

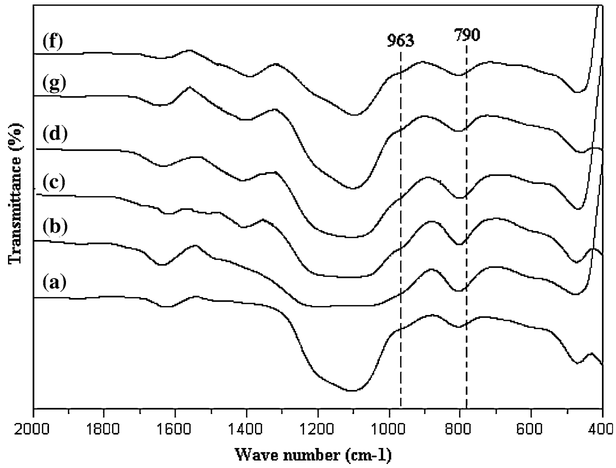


Fig. 2 FTIR spectra of AMPV/SiO_2 catalysts (**a**) support (**b**) 5 wt% (**c**) 10 wt% (**d**) 15 wt% (**e**) 20 wt% (**f**) 25 wt%

The presence of vanadium in Keggin ion can be confirmed by FTIR analysis, which gives a shoulder at 1,055 cm^{-1}. As this band is marked by strong vibrations of silica support. However, the presence of V in Keggin ion is observed for pure AMPV catalyst. In order to find about the presence of vanadium a similar preparation method is followed for the synthesis of AMPV with out silica support. The bulk catalyst is characterized by FT-IR and showed a split in P–O stretching vibration at 1,055 cm^{-1}, which is due to the presence of vanadium in Keggin ion primary structure [39]. Other supporting evidence is made from ICP-MAS analysis. Where it showed Mo/P ratio as 11.1 for AMPV and 12.4 for with out vanadia (AMPA).

3.4 Thermogravimetric/Differential Thermal Analysis (TG/DTA) Studies

One of the earliest studies on the stability of the heteropoly acids was employing thermogravimetric (TG) and differential thermal analysis (DTA). The TG/DTA curves of bulk AMPV and AMPV/SiO_2 catalysts are shown in Fig. 3. The thermal behavior of metal salts can be discussed by dividing them into two groups. The first group consists of the salts of small metal ions like Na^+ and Cu^{2+}, which are soluble in water. In the other group, the salts of larger ions such as Cs^+, Ag^+, NH_4^+ etc. The salts of first group resemble the acid forms in several respects. Water evolving near 200 °C for divalent metal salts may be due to water coordinated to the metal ion. In the case of second group, the water content is low and is released at lower temperature. Thermal stability also depends on the surrounding environment of the catalyst. Bulk AMPV has shown an endothermic peak at 200 °C and an exothermic peak at 410 °C. The TG/DTA analysis of the 5 and 10 wt% silica supported samples, showed weight loss at 250 °C, is due to the loss of constitutional water. As the loading increased to 15–25 wt% the weight loss observed in two stages; the one at 250 °C is due to the loss of constitutional water, and other is at 460 °C due to weight loss of the crystallization of the oxides resulting from the decomposition of the Keggin unit. Therefore, silica supported AMPV catalysts are thermally stable compared to the bulk AMPV. The endothermic and exothermic peaks are shifted towards higher temperatures ($\geq$50 °C) than the bulk AMPV catalyst. This may be due to a part of the supported catalyst was thermally stabilized while the rest, probably forming multi-

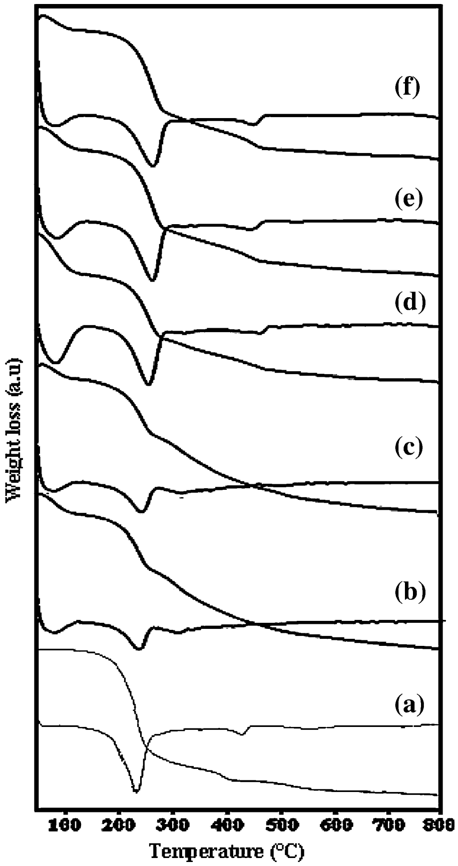


Fig. 3 TG/DTA profiles of bulk and supported catalysts (**a**) bulk AMPV (**b**) 5 wt% (**c**) 10 wt% (**d**) 15 wt% (**e**) 20 wt% (**f**) 25 wt%

layered clusters on SiO_2 surface, preserved the properties characteristics of the unsupported acid. This observation is inline with the work of Marchal-Roch et al. [12] who reported the TG analysis of $(NH_4)_3PMo_{12}O_{40}$ and mixed ammonium and Cs salts. Bruckman et al. [26] have also reported the thermal behavior of pure and silica-supported vanadium substituted MPA catalysts and revealed that the thermal stability is high with supported catalyst compared to that of the bulk catalyst.

3.5 Acidity by Potentiometry

The potentiometric titration curves obtained for the catalysts during the n-butyl amine titration are shown in Fig. 4. Pizzio et al. recommended this technique to evaluate the strength and the total number of acid sites on catalyst surface [35]. According to them the initial electrode potential (Ei) be taken as the acid strength of the surface sites and the range where the plateau is reached as the total number of acid sites. The replacement of Mo^{6+} by V^{5+} in the Keggin structure weakens the $V–O_a$ interaction and the protons reside mainly in the bridging water moieties forming $H_5O_2^+$. This modification changes the charges on the different oxygen atoms of Keggin primary structure, mainly O_b, leading to higher acid strength of a new proton [39]. Figure 4 clearly indicates that the acid strength values were increased from 573 mV to 730 mV as the loading increases from 5 to 20 wt% and slightly decreases to 720 mV for 25 wt% AMPV catalyst. This indicates that the AMPV is well dispersed up to 20 wt% on the support. Nowinska et al. [40] observed that the acidity of ammonium salt of HPAs is close to the acid strength of typical super acids and they explained that the acidity of ammonium salts of HPA is due to the residual proton resulting from incomplete stoichiometry of the salts. In the present study, it expected that the salt of the heteropoly acid would not contain three molecules of ammonia. Therefore, the compositions of the residual protons in the catalysts were estimated using FT-IR spectroscopy and elemental analysis following the procedure reported by Highfield and Moffat [41]. Even though the spectra of the support at low loadings masked the peaks due to AMPV, a good measure of the peaks and the composition of the samples could be obtained reliably at higher loading. The composition of the 20 wt% AMPV/SiO_2 was calculated as $(NH_4)_{3.12}H_{0.88}PMo_{11}V_1O_{40}$. Similar type of composition may exist in all the catalysts.

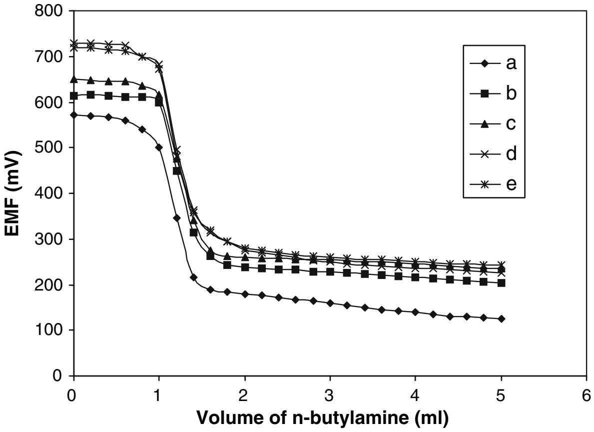


Fig. 4 Potentiometric titration profiles of AMPV/SiO_2 catalysts (**a**) 5 wt% (**b**) 10 wt% (**c**) 15 wt% (**d**) 20 wt% (**e**) 25 wt%

3.6 Activity: Ammoxidation of 2-Methyl Pyrazine

The ammoxidation activity over AMPV/SiO_2 catalysts as a function of different loadings and different reaction temperatures are shown in Fig. 5. Pure silica support has shown only 15–25% MP conversion with low selectivity towards CP. The MP conversion gradually increased with increase in AMPV loading. The highest conversion (close to 100%) was achieved for the 20 wt% AMPV/SiO_2 catalyst. The conversion of MP increased as acid strength of the catalyst increases. It is interesting to note that, there is a more or less proportionality existing between acid strength

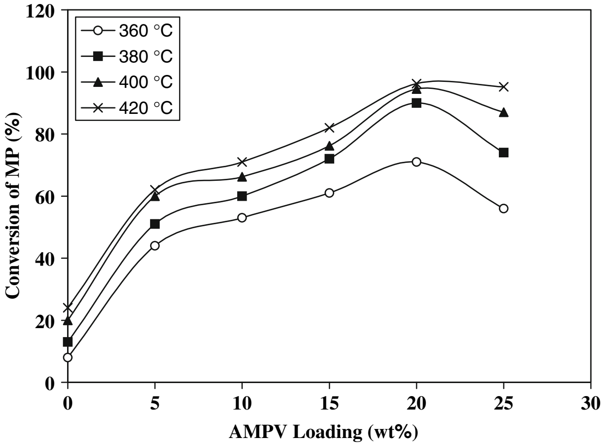


Fig. 5 Effect of AMPV loading on the conversion of MP at different reaction temperatures

and activity. The high activity of 20 wt% AMPV catalyst may be due to its high acid strength and/or availability of more number of active sites on the support.

The product distribution over the most active catalyst 20 wt% AMPV/SiO_2 is compared with the catalysts without vanadium in the Keggin structure i.e. AMPA/SiO_2 and the results are shown in Fig. 6. The conversion increased with increase in the reaction temperature (360–400 °C) and there after it remains almost constant. The vanadium containing catalyst showed higher selectivity than that of without vanadium containing catalyst. This is a significant observation reiterating the importance of incorporation of vanadium into the ammonium salt of 12-molybdophosphoric acid leads to substantial improvement in the selectivity towards CP, by minimizing the formation of pyrazine with high conversion of MP. The enhancement in CP selectivity can be attributed to the induced redox property of the transition metal ion in the catalyst.

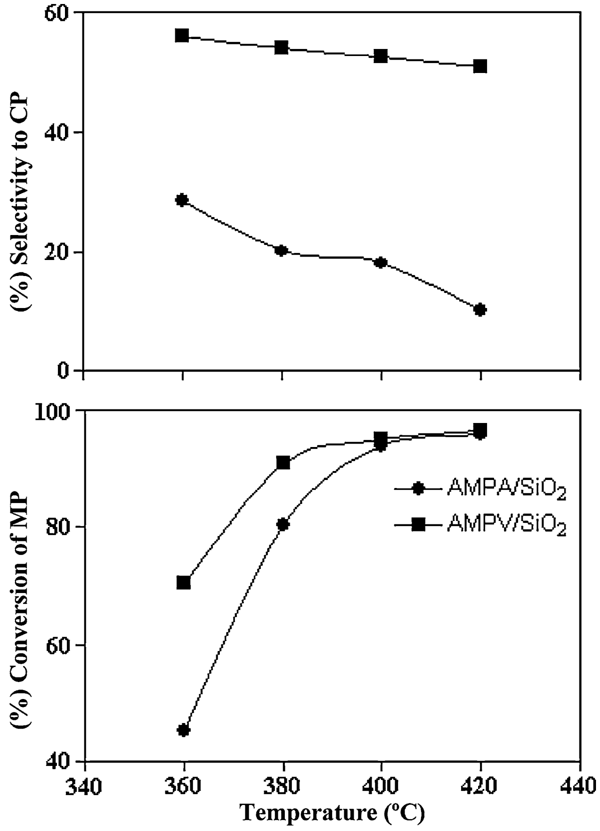


Fig. 6 Comparison of activity and selectivity of 20 wt% silica supported AMPA/ AMPV catalysts at different reaction temperatures

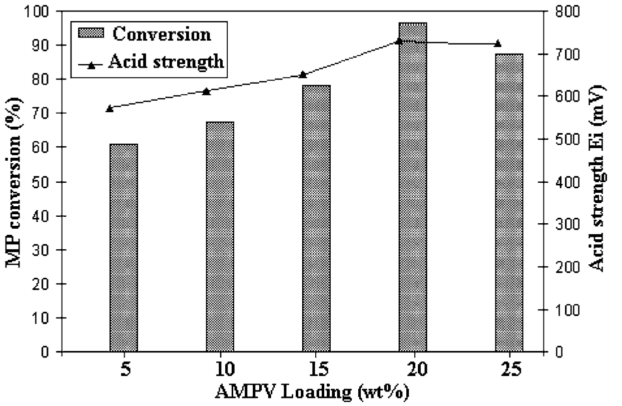


Fig. 7 Comparison of activity and acid strength values of AMPV/SiO_2 catalyst at 400 °C

The influence of acidity on the ammoxidation activity of the AMPV/SiO_2 catalysts was investigated. The total acidity and the acidic strength are the two parameters used in comparing the activity of the catalysts. A good proportionality was noticed between the acidic strength and the activity. Figure 7 shows a linear relationship between the acid strength and conversion of MP. This shows that the activity depends on the acidic strength of the catalyst, which in turn depends on the loading of active component (AMPV) on the support.

In conclusion, silica supported vanadium incorporated ammonium salt of 12-molybdophosphoric acid catalysts were prepared in a single step with Keggin structure. The acid strength of these catalysts is found to be proportional to the activity. Vanadium incorporation in to the Keggin structure increases the redox nature of the catalyst and that leads to desired high nitrile selectivity.

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