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# Ammoxidation activity of *in situ* synthesized ammonium salt of molybdophosphoric acid on $VOPO_4$ catalysts

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ABSTRACT

Two isomorphous $VOPO_4$ samples were synthesized by means of well-known aqueous and organic preparation methods. These materials are further used for the *in situ* generation of ammonium salt of 12-molybdophosphoric acid (AMPA) from their solid phase phosphate components. Formation of AMPA was confirmed by XRD, FTIR, Raman and XPS analyses. The activity of the catalysts was tested in a fixed bed tubular glass reactor at atmospheric pressure for the selective ammoxidation of 2-methylpyrazine (MP) to 2-cyanopyrazine (CP). The reaction was carried out in the temperature range of 360–420 °C. Between the two mono-phosphates tested, the $\alpha$-$VOPO_4$ is observed to show somewhat better activity compared to $\beta$-$VOPO_4$. Interestingly, *in situ* synthesized AMPA catalysts displayed significantly better performance compared to their corresponding parent $VOPO_4$ solids. Among all catalysts tested, AMPA-$\alpha$-$VOPO_4$ exhibited the best performance (conversion (MP) = ca. 90%, selectivity (CP) = 65% at $T = 420$ °C). The differences in catalytic performance of the tested catalysts are ascribed to the structural differences of the used $VOPO_4$ solids.

## 1. Introduction

Vapour phase ammoxidation of different alkyl aromatics and heteroaromatics to their corresponding nitriles in a single step has become the topic of extensive research in recent times due to its usefulness as an essential commercial method. In general, these reactions have been the subject of many industrial applications for producing a variety of commercially useful chemicals. Selective synthesis of 2-cyanopyrazine (CP) from 2-methylpyrazine (MP) by means of gas phase ammoxidation (e.g. [1]) is of particular industrial importance, because the resulting nitrile (i.e. CP) is a valuable intermediate for the production of an effective anti-tubercular drug, pyrazinamide. Pyrazinamide is a prodrug that stops the growth of Mycobacterium tuberculosis. Pyrazinamide is generally used in combination with other drugs such as isoniazid and rifampicin in the treatment of Mycobacterium tuberculosis.

Vanadia based solids and vanadium phosphorus oxides (VPO) are normally used as catalysts for a variety of ammoxidation reactions [2]. Today, VPO based catalysts form a technologically most important class of solid catalysts that are checked for different partial oxidation (e.g. *n*-butane to maleic anhydride is commercialised in multi-ton scale) (e.g. [3]) as well as ammoxidation of alkyl aromatics [4]. Besides these materials, polyoxometallates or heteropoly compounds (e.g. 12-molybdophosphoric acids and their ammonium salts) are also being used as another type of low temperature ammoxidation catalysts with somewhat better selectivity [5]. However, the low thermal stability of these heteropoly compounds has become the major constraint for their applicability for rather high temperature vapour phase reactions. Thus, the efforts to develop novel catalyst systems with improved stability are highly indispensable and attractive as well.

With the ever-increasing concern towards developing eco-friendly reactions, many of the liquid phase processes, which produce harmful chemical waste, are gradually being replaced by environmental friendly vapour phase catalytic processes. Ammoxidation of 2-methylpyrazine to 2-cyanopyrazine, carried out on vanadium-containing catalysts, is one such good example. Bondareva et al. [5] reported that vanadium containing 12-molybdophosphoric acid is an active and selective catalyst and operates well at relatively lower temperatures than that of vanadia-based catalysts. In good agreement to the above, it has also been observed recently [6] that the ammonium salt of

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12-molybdophosphoric acid (AMPA) offered better selectivity than the parent acid in the aforesaid reaction. As mentioned above, the application of these AMPA solids for high temperature reactions is however problematic because of their low thermal stability as mentioned above. Even then, attempts are being made by various researchers through out the globe to increase their thermal stability particularly by means of dispersing them on different supports (e.g. $TiO_2$). On the other hand, the poor solubility of AMPA in common solvents and improper control over dispersion make the preparation of supported catalysts difficult to reproduce. Despite such growing scientific interest on developing stable materials, only a few scientific studies are dedicated in the literature to this particular type of solids. At this juncture, the method of *in situ* synthesis of AMPA by the interaction of the phosphate moieties of the solid support with the molybdenum species in the solution is indeed an alternative and highly attractive [7,8]. Since the $VOPO_4$ also contains such solid phase phosphate, it is quite interesting to generate AMPA *in situ* on such a matrix and observe its influence on the catalytic performance. In this communication, we report the possibility of synthesizing AMPA on two isomorphs of $VOPO_4$ solids (α- and β-form) and compare their performance with those of their parent compounds.

## 2. Experimental

### 2.1. Catalyst preparation

Two VPO precursors such as $VOPO_4{\cdot}2H_2O$ (VP-1) and $VOHPO_4{\cdot}0.5H_2O$ (VP-2) were prepared initially using known procedures [6,9–11]. These two precursors were further used to prepare α-$VOPO_4$ by the dehydration of VP-1 in air and β-$VOPO_4$ by oxy-dehydration of VP-2. AMPA was then impregnated separately on both α-, and β-$VOPO_4$ solids using ammonium heptamolybdate. In total four different catalysts were prepared and tested. More details on the catalyst preparation are described below:

(i) $VOPO_4{\cdot}2H_2O$ was prepared following the aqueous route by reacting 50 g of $V_2O_5$ with 37 ml of 85% $H_3PO_4$ in 120 ml of water under reflux for 24 h. The yellow solid was recovered by filtration, washed with water followed by acetone and dried in air at 120 °C for 12 h. $VOHPO_4{\cdot}0.5H_2O$, was synthesized following the organic route by suspending 50 g of $V_2O_5$ in 200 ml of benzyl alcohol and 300 ml of isobutanol. The suspension was stirred continuously and refluxed for 3 h. The slurry was cooled to room temperature with continued stirring for overnight (16 h) and then 37 ml of 85% $H_3PO_4$ was added to the cold slurry to obtain the required P:V ratio of 1. The slurry was again refluxed and stirred for 2 h. After cooling, the slurry was vacuum filtered and washed with ethanol. The residue obtained was oven dried at 120 °C for 12 h.

(ii) α-$VOPO_4$ was prepared from $VOPO_4{\cdot}2H_2O$ by dehydration in dry air at 750 °C for 17 h (at a heating rate of 4 °C/min) and β-$VOPO_4$ by oxy-dehydration of $VOHPO_4{\cdot}0.5H_2O$ at 680 °C for 4 h (with identical heating rate as above) under dry oxygen [12].

(iii) AMPA was then generated *in situ* on both the α- and β-$VOPO_4$ phases using a known quantity of ammonium heptamolybdate (2.45 g) dissolved in distilled water (50 ml) and acidified carefully using few drops of concentrated nitric acid in order to attain the desired pH of the solution (pH 1). The excess solvent was evaporated on a water bath to dryness. The catalyst mass thus obtained was first dried at 120 °C for 12 h and then calcined in air at 400 °C for 4 h. In this preparation method, 10 g of each $VOPO_4$ solid (both α- and β-phases) was used separately to generate AMPA on both these phases. The amount of AMPA in the finished catalyst was such that its nominal $MoO_3$ content would be around 20 wt%.

### 2.2. Catalyst characterization

BET surface area was determined on a Micromeritics (Auto Chem-2910) instrument using nitrogen adsorption at −196 °C.

Raman spectra were recorded using a Raman microscope (InVia Reflex, Renishaw) equipped with deep-depleted thermoelectrically cooled CCD array detector and a high grade Leica microscope (long working distance objective 20×). Raman measurements were made on the sample spot irradiated by a visible 514.5 nm argon ion laser at a fixed laser power of circa 1 mW, exposure time of 10 s and the spectral resolution of 1–1.3 $cm^{-1}$ was used.

XPS measurements of the catalysts were performed on a Kratos Axis 165 apparatus equipped with a dual anode (Mg and Al) using Mg Kα source. The carbon 1s binding energy of 284.6 eV was used as a reference for determining the binding energies. Charge neutralization of 2 eV was used to balance the charge up of the sample. The binding energy values of the samples were reproducible within ±0.1 eV.

The acidic strength of the solid samples was measured by the potentiometric titration method employing a saturated calomel electrode (SCE). A known mass of solid suspended in acetonitrile was stirred for 3 h and then the suspension was titrated with a solution of *n*-butylamine in acetonitrile (0.05N) using a flow rate of 0.05 ml/min. The initial electrode potential ($E_i$) was assumed to correspond to the maximum acid strength of the surface sites. The acid strength of surface sites was assigned as: very strong sites: $E_i > 100$ mV; strong sites: $0 < E_i < 100$ mV; weak sites: $-100 < E_i < 0$ mV and very weak sites: $E_i < -100$ mV [13].

### 2.3. Catalytic tests

Ammoxidation runs were carried out at atmospheric pressure in a fixed bed glass reactor. About 5 g of the catalyst was loaded in the reactor between two quartz plugs. A mixture of ammonia, air and MP (diluted with water) was used as the reactant feed at a molar ratio of $MP:H_2O:NH_3:air = 1:13:7:38$. The aqueous mixture of MP was admitted into the pre-heater zone of the reactor by means of a metering pump (B. Braun, Germany). The reaction was studied in the temperature range of 360–420 °C. After allowing the catalyst to attain steady state for 2 h at each reaction temperature, the product was collected for every half-an-hour and analyzed off-line by gas chromatography equipped with FID.

## 3. Results and discussion

### 3.1. BET surface areas of $VOPO_4$ and AMPA-$VOPO_4$ solids

The specific surface areas of the catalysts are given in Table 1. The surface areas of all these phosphates are found to be low, in general. However, the surface areas of ammonium salt of molybdophosphoric acid samples are comparatively higher than VOPO4 solids, which is in agreement with the literature reports

**Table 1**
BET surface areas and potentiometric titration data of $VOPO_4$ and AMPA-$VOPO_4$ catalysts

| S. no. | Catalyst | BET-SA ($m^2$/g) | Acidic strength ($E_i$, mV) |
|---|---|---|---|
| 1 | α-$VOPO_4$ | 2.2 | 798 |
| 2 | β-$VOPO_4$ | 1.4 | 528 |
| 3 | AMPA-α-$VOPO_4$ | 6.6 | 825 |
| 4 | AMPA-β-$VOPO_4$ | 2.8 | 586 |

[14]. According to Lapham and Moffat [14], for monovalent salts possessing a microporous structure, the secondary structure is altered by the translation and rotation of the anions such that the voids form a continuum of channels running both parallel and normal to the XRD (1 1 0) plane, thus producing a porous network structure and increasing the surface area. Nonetheless, in the present case, we could not notice any such drastic increase in the surface areas of AMPA samples. It is also evident from the acidity characteristics shown in Table 1 that the AMPA-α-$VOPO_4$ sample displayed higher acidity compared to all other phosphates. Catalytic results are also observed to be in line with the acidity characteristics of these samples.

### 3.2. X-ray diffraction and FTIR studies

XRD and FTIR data obtained on these isomorphous $VOPO_4$ and AMPA-$VOPO_4$ are reported earlier [6] and hence we now describe here very briefly some of the important aspects of these results. XRD patterns of parent $VOPO_4$ solids (i) closely match with those reported by Ben Abdelouahab et al. [12] and (ii) indicate the formation of the ammonium salt of molybdophosphoric acid with the general formula $(NH_4)_3PMo_{12}O_{40}{\cdot}4H_2O$. In order to show the phase composition, the XRD patterns of the spent samples are depicted in Fig. 1. It is notable that the Keggin structure [ASTM no. 9-412] is found to be intact in the spent AMPA samples, indicating good stability of AMPA solids under the reaction conditions applied during the course of the reaction. FTIR studies showed two broad bands at 1156 and 956 cm$^{-1}$ and a sharp peak at 604 cm$^{-1}$ corresponding to the asymmetric P–O stretch, V═O stretch and the asymmetric bending of O–P–O, respectively. Additionally, the respective peak positions confirm the presence of α- and β-$VOPO_4$ phases in these samples. FTIR spectra of AMPA solids display bands at 1069, 963, 884, and 782 cm$^{-1}$, which correspond well to the stretching vibrations of the (P–O), (Mo–$O_d$), (Mo–$O_b$–Mo) and (Mo–$O_c$–Mo) bonds of the popular Keggin structure [15]. Another band appeared at 1420 cm$^{-1}$, which is ascribed to ammonium ions, confirms the existence of AMPA in the *in situ* generated catalysts. Generally speaking, FTIR results gave good supporting evidence to the information obtained from XRD.

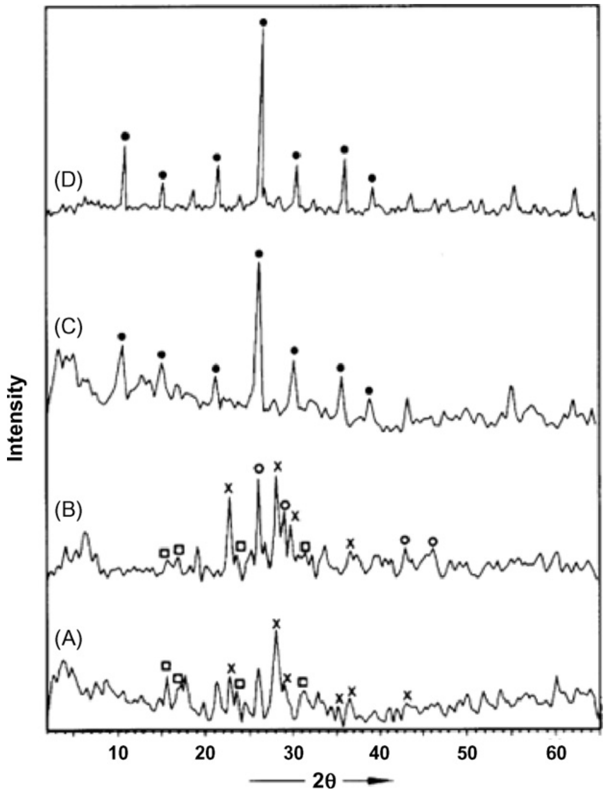

**Fig. 1.** XRD patterns of the used catalysts: (A) α-$VOPO_4$; (B) β-$VOPO_4$; (C) α-AMPA/$VOPO_4$; (D) β-AMPA/$VOPO_4$; (●) corresponds to AMPA [ASTM no.: 9-412]; (○) corresponds to β-$VOPO_4$ [ASTM no.: 27-948]; (×) corresponds to $(VO)_2P_2O_7$ [ASTM no.: 34-1381]; (□) correcponds to $(NH_4)_2(VO)_3(P_2O_7)_2$ [ASTM no.: 47-804].

### 3.3. Raman spectroscopy

Raman spectra of the fresh $VOPO_4$ and AMPA-$VOPO_4$ samples are presented in Fig. 2. As a matter of information, we would like to add below some general information concerning the appearance of Raman bands in different regions for the present type of catalysts. Generally, the vanadium-containing compounds of present type exhibit Raman bands in two distinct ranges such as (i) below 700 cm$^{-1}$ and (ii) between 850 and 1200 cm$^{-1}$ [16–18]. The first range relates to bending modes, coupled vibrations and collective modes of crystal lattice, while the second one corresponds to stretching modes of P–O and V–O bonds [12]. It can be seen from Fig. 2 that the intense Raman bands are located in the range of 850–1200 cm$^{-1}$ wave number range. The appearance of strong signals (Fig. 2, spectrum-a) at 943 and 1032 cm$^{-1}$ as well as other bands at 990, 694, 538, and 281 cm$^{-1}$ are typical for α-$VOPO_4$ [12]. The V═O stretching frequency for $V_2O_5$ is at 994 cm$^{-1}$ in the Raman spectrum [19] suggesting that the band at 996 cm$^{-1}$ of β-$VOPO_4$ can be assigned to this mode. The bands at 655, 894, 985, and 1073 cm$^{-1}$ can be attributed to P–O stretching and bending of the $PO_4$ units-both symmetric and asymmetric modes [20]. The bands from 278 to 461 cm$^{-1}$ are assigned to coupled V–O and P–O bending vibrations, where as those below 278 cm$^{-1}$ are a result of skeletal vibrations of $VO_6$ and $PO_4$ units. The assignment of these bands discussed here are in agreement with those of Bhargava and Condrate [21]. The spectra of AMPA catalysts showed bands at 1016, 988, 922, 873, 598, 615 and 243 cm$^{-1}$. The main characteristic features of the Keggin structure were observed at 988 cm$^{-1}$ ($\nu_s$ Mo–$O_d$), 919–877 cm$^{-1}$ ($\nu_{as}$ Mo–$O_b$–Mo) and 598–615 cm$^{-1}$ ($\nu_{as}$ Mo–$O_c$–Mo) with an important bridge stretching

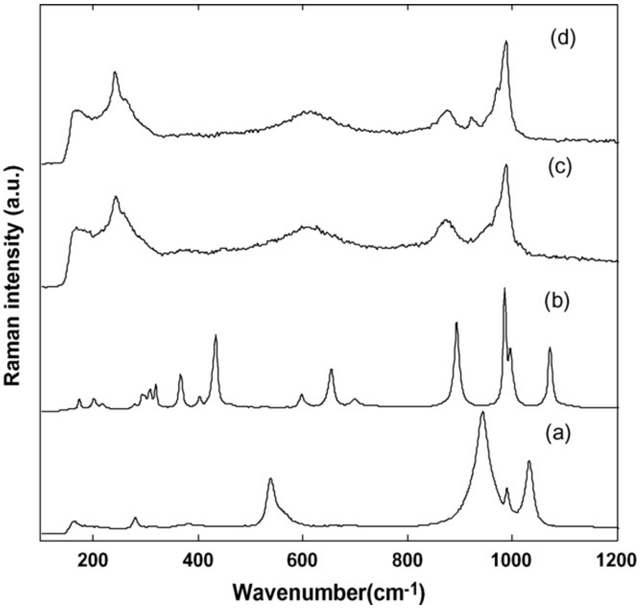

**Fig. 2.** Raman spectra of the fresh $VOPO_4$ and AMPA-$VOPO_4$ catalysts. (a) α-$VOPO_4$; (b) β-$VOPO_4$; (c) AMPA-α-$VOPO_4$; (d) AMPA-β-$VOPO_4$.

character. The spectra agreed well with those values reported in the literature [22]. Thus the information obtained from the Raman data also confirms the formation of AMPA on the $VOPO_4$ materials. Various Raman bands exhibited by the present catalysts are listed in Table 2.

### 3.4. XPS results

Fig. 3 depicts XP spectra of V 2p of pure vanadium phosphate and AMPA-$VOPO_4$ catalysts. The major peaks at 517.5 and 521.5 eV that correspond to the V $2p_{3/2}$ and V $2p_{1/2}$ states could be seen from Fig. 3. The binding energy (BE) values observed for all these catalyst samples are shown in Table 3. The value of V $2p_{3/2}$ binding energy of $VOPO_4$ catalysts lay in between 517.4 and 517.6 eV, which corresponds to the value expected for $V_2O_5$ in +5 oxidation state [23]. Formation of AMPA does not give rise to changes in AMPA-α-$VOPO_4$ (Table 3); but BE value shifted to 519 eV in the case of AMPA-β-/$VOPO_4$. This is an indication that only one type of vanadium oxide species with +5 oxidation state is present in all the catalysts. It is also evident from Table 3 that the formation of AMPA in the solids showed considerable influence on the surface composition particularly in the surface V/P ratios. Both α-, and β-AMPA-$VOPO_4$ catalysts exhibited low V/P ratios compared to their corresponding parent compounds. This is simply due to the differences in their phase composition (i.e. in the first case, they are pure phases and in the second case AMPA was generated by the interaction of phosphate moieties on the solid support). In addition, if the comparison is made between α-, and β-AMPA-$VOPO_4$ samples, α-form exhibited high V/P and Mo/P ratios than the β-form, which indicates that there is a clear surface enrichment of both vanadium and molybdenum in α-AMPA-$VOPO_4$ solid. This difference also seems to be responsible for such higher activity of the α-$VOPO_4$ containing catalysts than their β-analogues.

From the XPS analysis, the binding energies of Mo $3d_{3/2}$ and Mo $3d_{5/2}$ (Fig. 4) are found to be 233.4 and 234 eV, respectively, for both the AMPA-α-$VOPO_4$ and AMPA-β-$VOPO_4$ catalysts. These values are in agreement with those reported for $Mo^{6+}$ [24]. XPS P 2p spectra of all these four phosphate samples are depicted in Fig. 5. The binding energy values of P 2p, which remained almost constant (between 133.2 and 134.5 eV) confirm that the phosphorus is present in the form of phosphate tetrahedra ($PO_4^{3-}$). The O 1s spectra portrayed in Fig. 6 exhibit two peaks with binding energies at 530.23 and 532.91 eV. A shift of +0.76 is observed for the AMPA catalysts. The species assigned to 530.23 eV are related to the oxomolybdenum species and the ones correspond to 532.91 eV peak are due to OH groups. The characterization data derived from XPS technique also confirms the formation of the Keggin ion of AMPA on $VOPO_4$ supports.

**Table 2**
Raman peaks of the fresh $VOPO_4$ and AMPA-$VOPO_4$ catalysts

| Catalyst | Experimental |
|---|---|
| α-$VOPO_4$ | 1032 (S); 990 (M); 943 (vS); 694 (vW) 538 (S), 380 (vW, br), 281 (M) |
| β-$VOPO_4$ | 1073 (S), 996 (M, sh), 985 (Vs), 894 (S), 798 (vW), 736 (vW), 698 (W), 654 (M), 598 (M), 461 (W), 433 (S), 404 (W), 367 (M), 334 (vW), 320 (M), 308 (M), 294 (M), 278 ((W), 227 (vW), 217 (vW), 201 (W), 139 (vW) |
| AMPA-α-$VOPO_4$ | 988 (vS), 873 (M), 598 (M, br), 243 (S) |
| AMPA-β-$VOPO_4$ | 988 (vS), 922 (W), 875 (M,), 615 (M, br), 241 (S) |

vS: very strong; S: strong; M: medium; W: weak; vW: very weak; sh: shoulder; br: broad.

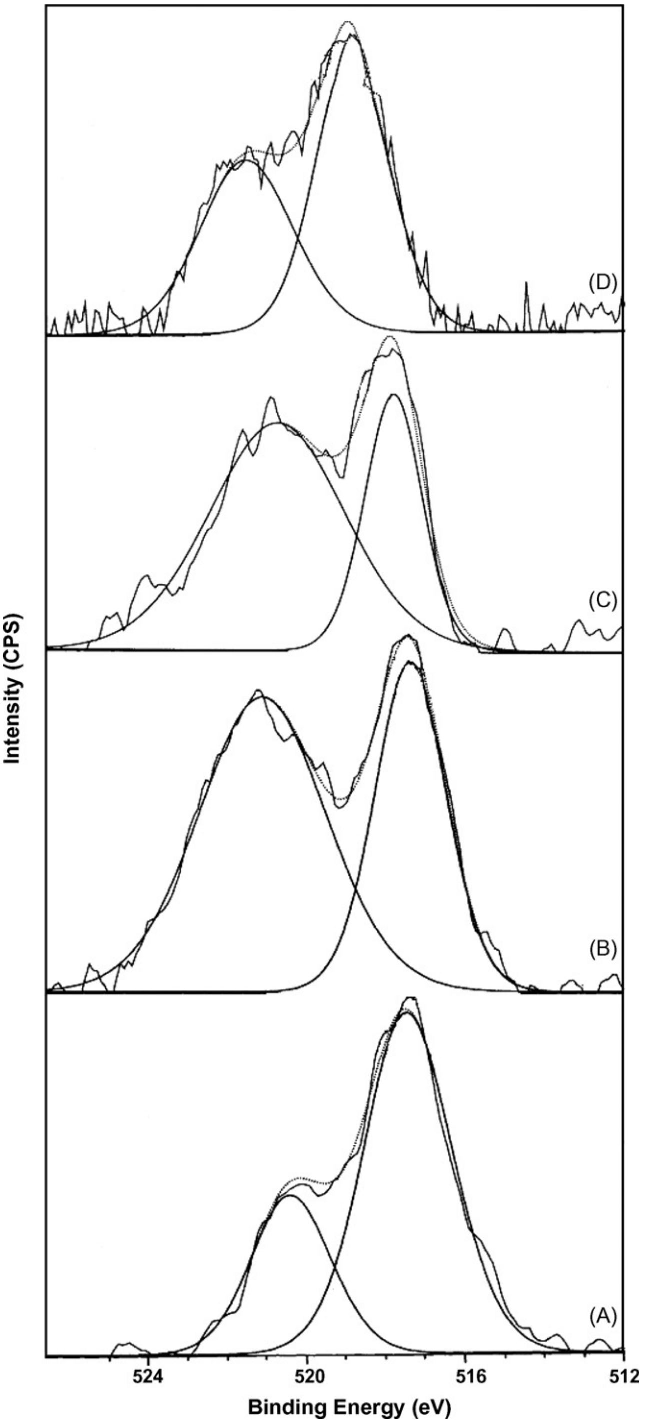

**Fig. 3.** XPS V 2p spectra of fresh $VOPO_4$ and AMPA-$VOPO_4$ catalysts. (A) α-$VOPO_4$; (B) β-$VOPO_4$; (C) AMPA-α-$VOPO_4$; (D) AMPA-β-$VOPO_4$.

### 3.5. Acidity measurements

The acidity measurements of the catalysts were carried out by means of potentiometric titration with *n*-butyl amine and presented in Fig. 7. It is evident from Fig. 7 that the catalysts possess very strong acid sites, as the *E* value falls in the range of 700–830 mV. The acidic strength of sites present in these catalysts

**Table 3**
Results of X-ray photoelectron spectroscopy of $VOPO_4$ and AMPA-$VOPO_4$ samples

| Sample | Position and FWHM of V 2p | Position and FWHM of Mo 3d | Position and FWHM of P 2p | Surface V/P ratio | Surface Mo/P ratio |
|---|---|---|---|---|---|
| $\alpha$-$VOPO_4$ | 517.4 (2.57) | – | 134.4 (2.05) | 2.52 | – |
| $\beta$-$VOPO_4$ | 517.3 (2.13) | – | 133.2 (1.82) | 3.52 | – |
| AMPA-$\alpha$-$VOPO_4$ | 517.9 (1.92) | 233.4 (1.91) | 134.2 (2.13) | 1.12 | 2.03 |
| AMPA-$\beta$-$VOPO_4$ | 519.0 (2.51) | 234.0 (1.72) | 134.9 (2.02) | 0.79 | 1.21 |

seems to be comparable for similar type of catalysts, i.e. no remarkable differences between $\alpha$-$VOPO_4$ & AMPA-$\alpha$-$VOPO_4$ and $\beta$-$VOPO_4$ & AMPA-$\beta$-$VOPO_4$ solids. However, $\alpha$-$VOPO_4$ & AMPA-$\alpha$-$VOPO_4$ exhibit much higher acid strength compared to $\beta$-$VOPO_4$ & AMPA-$\beta$-$VOPO_4$.

### *3.6. Catalytic results*

Influence of reaction temperature on the conversion of 2-methyl pyrazine is shown in Fig. 8a. All four different samples (two $VOPO_4$ ($\alpha$- and $\beta$-) and two AMPA-$VOPO_4$ solids) were tested in the present study. Fig. 8a clearly demonstrates that the reaction temperature has a promotional effect on the conversion of 2-methyl pyrazine irrespective of the nature of catalyst applied. It is also obvious that there is a distinct influence of *in situ* synthesized AMPA samples on the catalytic performance compared to their corresponding analogues. Both the AMPA-containing materials ($\alpha$- and $\beta$-) exhibited considerably superior performance in comparison with their parent $\alpha$- and $\beta$-$VOPO_4$ samples. Another interesting observation is that between these AMPA-containing solids, $\alpha$-form of AMPA displayed better performance compared to its $\beta$-form. In a similar way, between the two monophosphates tested, the $\alpha$-$VOPO_4$ is observed to show somewhat higher activity than $\beta$-$VOPO_4$.

It is reasonable to assume that the differences in the activity of these two monophosphates could be due to the differences in the structure of these $VOPO_4$ solids, i.e. $\alpha$-$VOPO_4$ consists of a layered structure whereas $\beta$-$VOPO_4$ shows a three-dimensional one. In addition, the acidity characteristics of the catalyst samples are also another possible reason for such deviations in their catalytic performance. For instance, the highly acidic samples of this study such as AMPA-$\alpha$-$VOPO_4$ and $\alpha$-$VOPO_4$ exhibit higher activity and selectivity and support the above assumption that acidity plays a critical role on the catalytic performance. It can be deduced that the presence of AMPA enhances the Brønsted acidity of the catalysts. Such enhancement in the Brønsted acidity in turn increases the ammonia adsorption capacity of the catalysts. This seems to be the more probable reason for the increased activity of the AMPA-$VOPO_4$ catalysts.

On the whole, it can be stated that among four different catalysts tested, AMPA-$\alpha$-$VOPO_4$ displayed the highest conver-

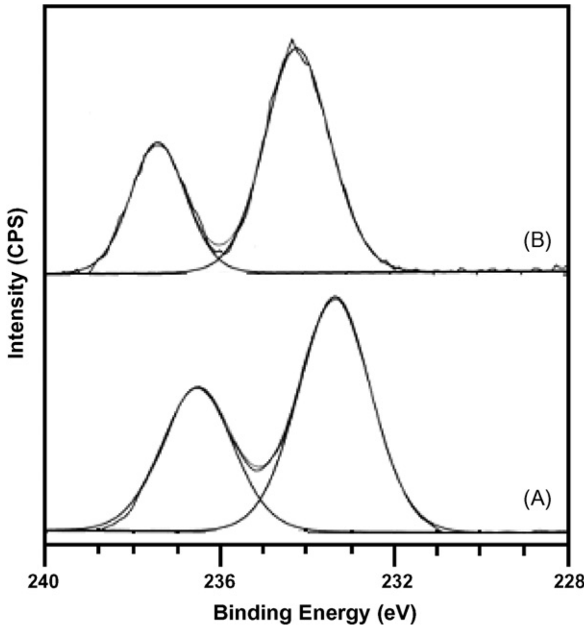

**Fig. 4.** XPS Mo 3d spectra of fresh AMPA-$VOPO_4$ catalysts. (A) AMPA-$\alpha$-$VOPO_4$; (B) AMPA-$\beta$-$VOPO_4$.

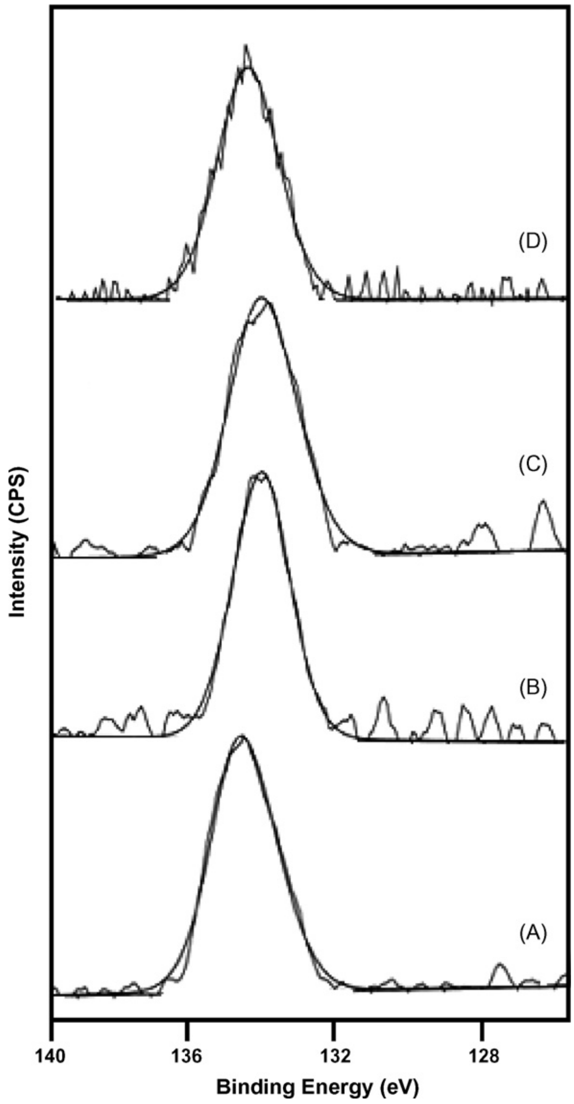

**Fig. 5.** XPS P 2p spectra of fresh $VOPO_4$ and AMPA-$VOPO_4$ catalysts. (A) $\alpha$-$VOPO_4$; (B) $\beta$-$VOPO_4$; (C) AMPA-$\alpha$-$VOPO_4$; (D) AMPA-$\beta$-$VOPO_4$.

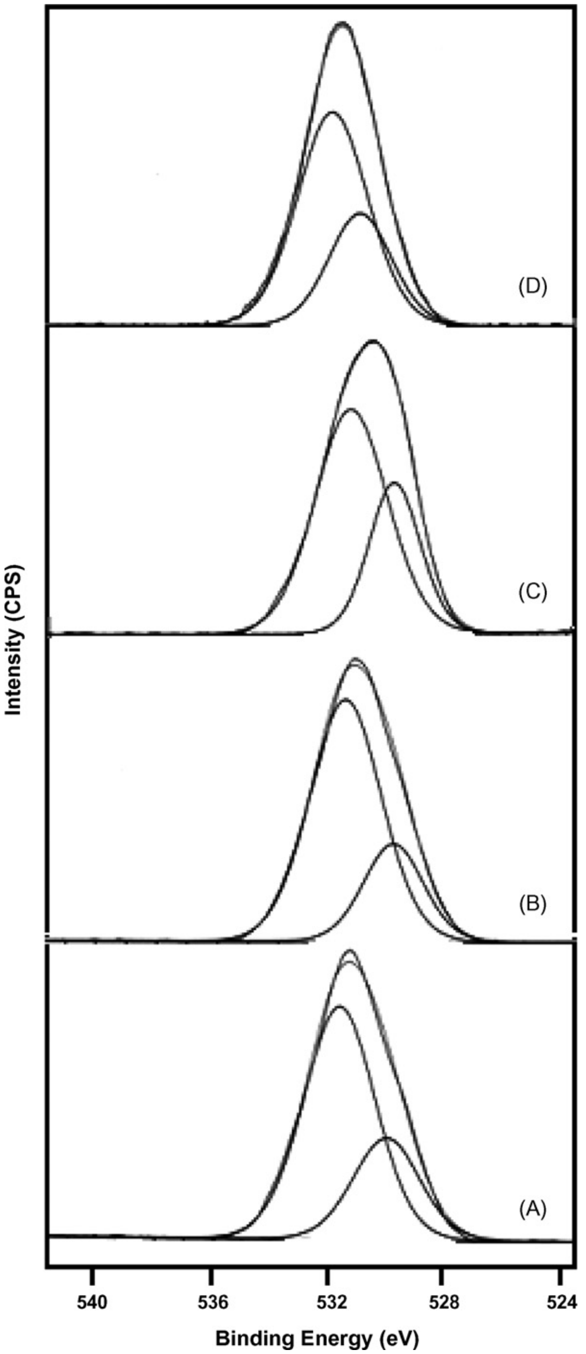

**Fig. 6.** XPS O 1s spectra of fresh $VOPO_4$ and AMPA-$VOPO_4$ catalysts. (A) α-$VOPO_4$; (B) β-$VOPO_4$; (C) AMPA-α-$VOPO_4$; (D) AMPA-β-$VOPO_4$.

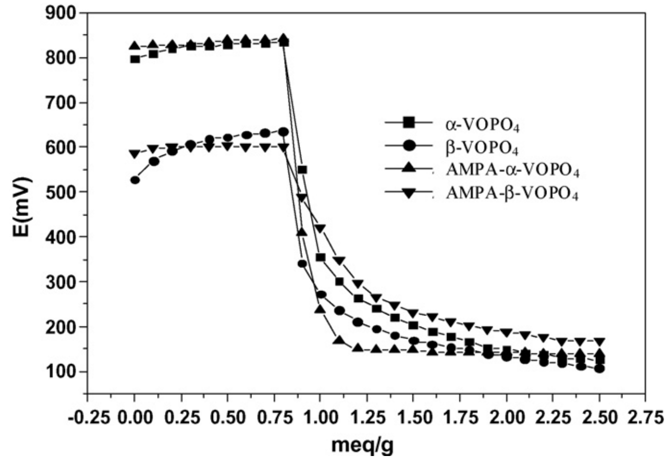

**Fig. 7.** Potentiometric titration profiles of the fresh $VOPO_4$ and AMPA-$VOPO_4$ catalysts.

sion of MP (X-MP = ca. 90% at 420 °C), while β-$VOPO_4$ exhibited the lowest at almost all temperatures applied in the current study.

Variation of CP selectivity as a function of reaction temperature is illustrated in Fig. 8b. Temperature of the reaction showed a clear influence on the selectivity of cyano pyrazine. β-$VOPO_4$ exhibited the highest selectivity (S-CP = $\geq$95%) but only at very low degree of conversion (X-MP = $\leq$5%). However, with rise in conversion levels, the CP selectivity is significantly decreased. The AMPA catalysts disclose a slightly lower selectivity (S-CP = 60–70%) but remarkably higher conversions (X-MP = ca. 55–90%) than the pure $VOPO_4$ catalysts (S-CP = 60–95% & X-MP = <5–30%). Overall, the better yields were obtained over *in situ* synthesized AMPA-containing $VOPO_4$ solids compared to their corresponding analogues.

XRD and the FTIR data obtained on the spent samples revealed that the $VOPO_4$ catalysts were partly getting transformed into the ammonium-containing vanadium phosphates, such as $(NH_4)_2(VO)_3(P_2O_7)_2$, during the course of the reaction [6]. A comparison of an absorption band appeared at 1420 cm$^{-1}$ (corresponds to $NH_4^+$ ion) in both the $VOPO_4$ catalysts, it seems plausible that the aforesaid ammonium complex formation is more facile in the case of α- than in the β-isomorph.

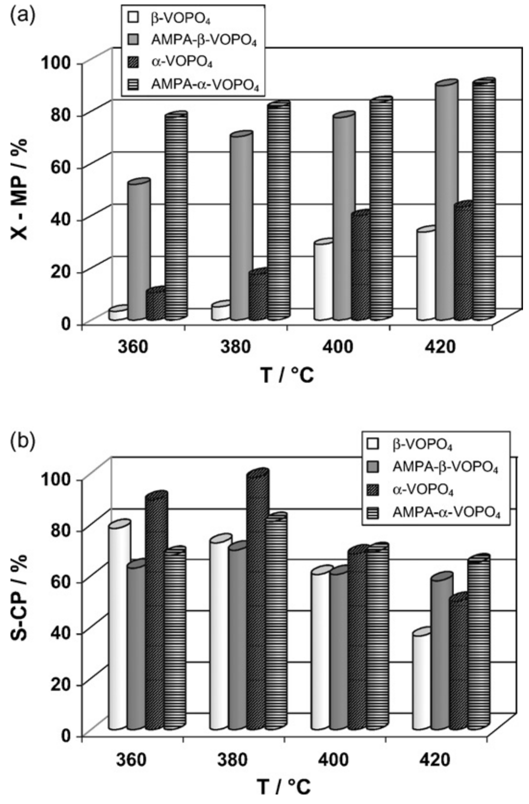

**Fig. 8.** (a) Influence of reaction temperature on the catalytic performance of $VOPO_4$ and AMPA-$VOPO_4$ catalysts. (b) Variation of CP selectivity as a function of reaction temperature over $VOPO_4$ and AMPA-$VOPO_4$ catalysts.

## 4. Conclusions

The results revealed that ammonium salt of the 12-molybdophosphoric acids could be successfully synthesized *in situ* on two isomorphs of $VOPO_4$ materials. Formation of AMPA on both the $VOPO_4$ solids was confirmed from XRD, FTIR, Raman and XPS. Interestingly, the *in situ* synthesized AMPA-containing catalysts exhibited higher activity than their parent monophasic phosphate catalysts. Between the two isomorphs of $VOPO_4$, the $\alpha$-form of the monophosphate displayed higher activity and selectivity in the selective ammoxidation of 2-methylpyrazine to 2-cyanopyrazine.

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## References

[1] V.M. Bondareva, T.V. Andrushkevich, E.A. Paukshtis, N.A. Paukshtis, A.A. Budneva, V.N. Parmon, J. Mol. Catal. A: Chem. 269 (2007) 240.
[2] A. Martin, B. Lücke, Catal. Today 57 (2000) 61.
[3] G. Centi, F. Trifiro, J.R. Ebner, Chem. Rev. 88 (1988) 55.
[4] A. Martin, V.N. Kalevaru, B. Lücke, D. van Deynse, M. Belmans, F. Boers, WO 03/101939 A2 (2003) (Tessenderlo Chemie S.A.).
[5] V.M. Bondareva, T.V. Andrushkevich, L.G. Detushera, G.S. Latvak, Catal. Lett. 42 (1996) 113.
[6] Ch. Srilaxmi, N. Lingaiah, A. Hussain, P.S. Sai Prasad, K.V. Narayana, A. Martin, B. Lücke, Catal. Commun. 5 (2004) 199.
[7] Ch. Srilakshmi, K. Narasimha Rao, N. Lingaiah, P.S. Sai Prasad, Catal. Lett. 83 (2002) 127.
[8] M. Santhosh Kumar, K. Narasimha Rao, N. Lingaiah, I. Suryanarayana, P.S. Sai Prasad, Green Chem. 4 (2002) 344.
[9] F. Cavani, G. Centi, F. Trifiro, Appl. Catal. 9 (1984) 191.
[10] F. Cavani, G. Centi, F. Trifiro, A. Vaccari, Stud. Surf. Sci. Catal. 21 (1985) 287.
[11] G.J. Hutchings, T.M. Sananes, S. Sujata, J.C. Kiely, A. Burrows, J.I. Ellison, J.C. Volta, Catal. Today 33 (1997) 161.
[12] F.B. Abdelouahab, R. Olier, N. Guilhaume, F. Lefebvre, J.C. Volta, J. Catal. 134 (1992) 151.
[13] P. Vazquez, L. Pizzio, C. Caceres, M. Blanco, H. Thomas, E. Alesso, L. Finkielsztein, B. Lantano, G. Moltrasio, J. Aguirre, J. Mol. Catal. 161 (2000) 223.
[14] D. Lapham, J.B. Moffat, Langmuir 7 (1991) 2273.
[15] R. Belanger, J.B. Moffat, Catal. Today 40 (1998) 297.
[16] T.P. Moser, G.L. Schrader, J. Catal. 92 (1985) 216.
[17] M.E. Lashier, G.L. Schrader, J. Catal. 128 (1991) 113.
[18] R.N. Bhargava, W. Kiefer, Appl. Spectrosc. 28 (1974) 279.
[19] C. Sanchez, J. Livage, G. Lucazeau, J. Raman Spectrosc. 12 (1982) 68.
[20] D.E.C. Corbridge, E.J. Lowe, J. Chem. Soc. 4555 (1954).
[21] R.N. Bhargava, R.A. Condrate, Appl. Spectr. 31 (1977) 230.
[22] C. Rocchiccioli-Deltcheff, A. Aouissi, M.M. Bettahar, S. Launay, M. Fournier, J. Catal. 164 (1996) 16.
[23] K.V.R. Chary, G. Kishan, C. Praveen Kumar, G. Vidya Sagar, J.W. Niemantsverdriet, Appl. Catal. A: Gen. 245 (2003) 303.
[24] S. Damyanova, M.L. Cubeiro, J.L.G. Fierro, J. Mol. Catal. A: Chem. 142 (1999) 85.