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Synthesis and Characterization of Zirconia Supported Vanadium Incorporated Ammonium Salt of 12-molybdophosphoric Acid Catalyst for Aerobic Oxidation of Benzyl alcohol

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Abstract A series of zirconia supported ammonium salt of molybdophosphoric acid (AMPV) catalysts with and with out vanadium incorporation are prepared in a single step adopting wet impregnation method. These catalysts are characterized by BET surface area, XRD, FT-IR and potentiometric titration. XRD and FT-IR techniques suggest the formation of Keggin ion on zirconia support. The high resolution FT-IR analysis reveals the incorporation of vanadium into the primary structure of Keggin ion. The catalytic functionalities of these catalysts are tested for the aerobic oxidation of benzyl alcohol. The vanadium containing AMPV results in higher selectivity towards the oxidation product compared to the catalyst without vanadium incorporation.

Keywords Molybdophosphoric acid · Vanadium · Zirconia · Oxidation · Benzyl alcohol

1 Introduction

Heteropoly acids (HPAs) are well known green catalysts for oxidation [1] and acid catalyzed reactions [2]. The salts of these HPAs, which are more thermally stable than their parent acids [3], are also extensively used as catalysts to obviate solubility problems during reactions. The deposition of HPAs on solid supports is important for catalytic applications, as the surface areas of unsupported ones are low. In deed, the most important restriction to the use of these materials for heterogeneous gas phase applications is their low thermal stability [4, 5]. It is well known that the catalytic functionalities of HPAs depend on their acidic and redox properties, which are tunable [1, 6]. It is also well reported that partial substitution of vanadium for molybdenum is expected to enhance the oxidizing ability [7, 8]. The effect of vanadium substitution for molybdenum in molybdophosphoric acid has been the subject of study by various authors [9–11]. A few reports are available on the synthesis of bulk vanadium substituted molybdphosphoric acid and its ammonium salt [12, 13].

To enhance the thermal stability and surface area of the HPA further, their salts are supported on various acidic or neutral supports such as active carbon, ion-exchange resins, SiO_2 and TiO_2. These supports are found to be suitable as they can preserve the Keggin ion up to higher temperatures [14]. A number of researchers have focused attention on the thermal stability of HPAs by supporting them on various acidic or basic substrates [5, 15–19]. In recent years much attention has been focused on the amphoteric zirconium dioxide (ZrO_2) as an outstanding catalyst and catalyst support. Several HPAs and their salts have already been supported on ZrO_2. Lopez-Salinas et al. [20] reported that 12-tungstophosphoricacid (TPA) supported on hydrated ZrO_2 is stable up to 400 °C. Introduction of ZrO_2 into the SiO_2 support is reported to change the catalyst character from acidic to redox nature [21].

Oxidation of alcohols to aldehydes, in particular benzyl alcohol to benzaldehyde, is an important organic transformation. Benzaldehyde is a very valuable chemical, which has widespread applications in perfumery, dyestuff and agro chemical industries [22]. Selective oxidation of alcohols has been extensively studied using various kinds of reagents like the stiochiometric oxidants such as manganese and chromium salts. However their toxicity is the

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main limitation. From the standpoint of atom economy and environmental demand much attention has been paid to the development of metal based catalysts, using clean oxidants, in liquid phase [23, 24]. Pd and Ru complexes, supported on metal oxides and hydrotalcites are also frequently used for this purpose [25–30].

Of late, there has been sporadic interest on the vapor phase oxidation of alcohols [31]. An attempt in this direction is the work reported by Hayashibara et al. using alkali promoted Cu-Na-ZSM-5 catalyst tested at 400 °C [32]. In vapor phase reaction the control of selectivity towards partial oxidation product is the main problem, which has to be achieved mainly by regulating the reaction temperature. However, low reaction temperatures lead to decrease in oxidation activity of the catalyst. Hence, it is important to develop a catalyst system, which is highly active and selective at low reaction temperatures.

There are a few reports wherein this objective is achieved over HPAs. Peng et al. studied the oxidation of benzyl alcohol over a series of Cs salts of molybdophosphoric acid and vanadomolybdo phosphoric acid using H_2O_2 as oxidant; but the reaction was carried out in the liquid phase [33]. Olaofe and Viswanathan carried out the vapor phase oxidation over molybdophosphoric acid and its salts [34]. Heteropoly acids like 12-molybdophosphoric acid (MPA) and 12-tungstoposphoric acid (TPA) are not stable in benzyl alcohol atmosphere as they are highly soluble in this organic reactant medium. Even though, the salts of HPA are relatively stable their activity is limited. This leaves enough scope for the development of thermally stable and chemically active catalysts.

Two factors, which affect the activity and selectivity in the oxidation reaction, are the acidity and redox property of the catalysts. Addition of transition metals like V is expected to influence these properties considerably, particularly when it is incorporated in the primary structure of the Keggin ion. In our previous publication [35] we have reported that the vanadium incorporated ammonium salt of molybdophosphoric acid (AMPV) offers higher benzaldehyde selectivity than the parent acid and bulk AMPA. The focus of present investigation is two fold (i) to synthesize ZrO_2-supported AMPA and vanadium containing AMPA catalysts by a simple wet impregnation method and (ii) to understand the effect of vanadium and its characteristics in the selective oxidation of benzyl alcohol to benzaldehyde.

2 Experimental

All the reagents, acids and $(NH_4)_6Mo_6O_{24} \cdot 4H_2O$ were supplied by S.D. Fine Chemicals, India. $(NH_4)_2HPO_4$, NH_4VO_3, 12-molybdophosphoricacid (MPA) and 12-tungstophosphoricacid (TPA) were obtained from Loba Chemie, India. The ZrO_2 support was supplied by Zircon, India.

2.1 Preparation of Catalysts

AMPA was prepared by the precipitation method. Required quantities of ammonium heptamolybdate and diammonium hydrogen orthophosphate were dissolved in minimum amount of water. This solution was first refluxed at 100 °C for 6 h. Then the pH of the solution was adjusted to one by adding dilute HNO_3 to precipitate on yellow compound, which, was filtered, dried at 120 °C and calcined in air at 350 °C. The preparation of ZrO_2 supported AMPA catalysts are obtained by wet impregnation technique. The required quantities of AMPA solution is added to the support and the pH of the solution was adjusted to 1 by adding dilute HNO_3 and the resultant solution was evaporated to dryness. Later the catalyst mass was dried at 120 °C and calcined finally in air at 350 °C for 4 h.

The preparation of AMPV (vanadium incorporated ammonium salt of MPA) and the supported AMPV catalysts were similar to the described above except taking calculated amount of ammonium metavanadate to the correspondingly reduced amount of molybdenum salt.

X-ray diffraction (XRD) patterns of the catalysts were recorded on a Siemens D-5000 diffractometer using CuK_α radiation. The FTIR spectra were recorded on a Nicolet 740 spectrometer using the KBr disc method. The splitting of 1050 cm^{-1} peak in AMPV1 catalyst was recorded on Digilab FTIR with a resolution of 0.1 cm^{-1}. The specific surface areas of the catalyst samples were calculated from N_2 adsorption data acquired on a Autosorb-1 instrument (Quantachrome, USA) at liquid N_2 temperature. The powders were first outgassed at 473 K 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 area using the method of Brunauer, Emmet, and Teller (BET).

The acid strength of the catalysts was measured by using the potentiometric titration method. This method was proposed initially by Cid and Pecchi [36], Blanco et al [37, 38] used it to determine the acidity of the catalysts with *n*-butyl amine as the titrant. In all the communications, it was mentioned that the strength of acid sites is indicated by the initial electrode potential and the value at the plateau region of the curve (meq/g of the solid) as the total number of acid sites of the titrated solid. In this method a known amount of catalyst (about 0.1 g) was suspended in acetonitrile and stirred for about 3 h. Later, the suspension was titrated with a solution of 0.05 N *n*-butyl amine in acetonitrile at a flow rate of 0.5 mL/min using a micro-processor controlled titrater (Schott, Germany). The variation in electrode potential, while adding the *n*-butyl amine solution, was measured using a double junction electrode. They classified the strength of the acid sites into the following scale: $E > 100$ mV (very strong sites); $0 <E> 100$ mV (strong sites); $-100 < E < 0$ mV (weak sites) and $E < -100$ mV (very weak sites).

Vapor phase air oxidation of benzyl alcohol was carried out in a fixed bed micro reactor at atmospheric pressure. In a typical experiment about 1 g of catalyst (crushed to a particle size of 18/25 BSS mesh to avoid mass transfer limitations), diluted with same size and volume of quartz beads, was loaded in a micro reactor. The catalyst was initially pretreated in air (60 mL/h) at 300 °C for 1 h. The reactant, benzyl alcohol, was fed into the reactor at a flow rate of 2 mL/h using a microprocessor based syringe pump (B. Braun, Germany). Pre-heated air was also introduced at a rate of 60 mL/min. The reaction was carried out in the temperature range of 250–310 °C. After the system had attained steady state over a period of 1 h, the liquid product collected (by cooling it to −10 °C) was analyzed by gas chromatography with SE-30 column and a flame ionization detector.

3 Results and Discussions

The surface areas of the pure support and supported AMPA and AMPV are shown in Table 1. The surface area of pure ZrO_2 is 65 m^2/g. The surface area values of supported catalysts have decreased by increasing the loading of AMPA and AMPV on the support.

Powder X-ray diffraction patterns of the ZrO_2-supported AMPA and AMPV catalysts along with support ZrO_2 are shown in Figs. 1 and 2 respectively. The low loaded (5 wt.%) sample has not revealed any diffraction peaks of the active component other than that of the support. This indicates that the Keggin units might have been well dispersed on the zirconia surface. Vazquez et al. [39] have observed that the hydroxyl groups bonded to the titania surface are protonated in the acidic solution, thereby creating positively charged surface hydroxyl groups. These groups can bind a complex anion like that of the Keggin $[PMo_{12}O_{40}]^{3-}$ ion by electrostatic attraction leading to strong interaction of the HPA with the support surface. There is a possibility for the existence of a similar phenomena in the present case as well, leading to the formation of an interactive species of the salt on the surface. The XRD patterns of 10–30 wt.% catalysts, on the other hand, have shown the major lines related to crystalline phase of AMPA with the formula

Table 1 BET surface values and acidity values by potentiometry method

Catalyst	BET surface area (m^2/g)	Acid strength E_i (mV)
ZrO_2	65	263
5% AMPA/ZrO_2	41	294
10% AMPA/ZrO_2	36	356
15% AMPA/ZrO_2	31	472
20% AMPA/ZrO_2	24	490
25% AMPA/ZrO_2	19	546
30% AMPA/ZrO_2	13	470
5% AMPV/ZrO_2	61	245
10% AMPV/ZrO_2	58	308
15% AMPV/ZrO_2	56	424
20% AMPV/ZrO_2	48	458
25% AMPV/ZrO_2	43	518
30% AMPV/ZrO_2	35	497

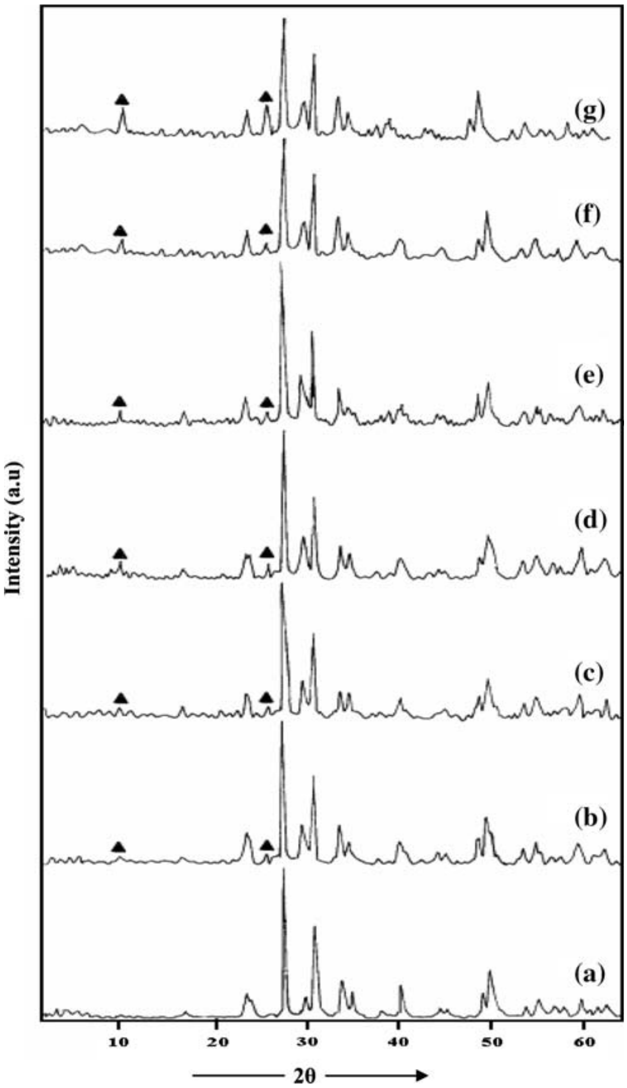

Fig. 1 XRD patterns of pure ZrO_2-AMPA/ZrO_2 catalysts: (**a**) support (**b**) 5 wt.% (**c**) 10 wt.% (**d**) 15 wt.% (**e**) 20 wt.% (**f**) 25 wt.% (**g**) 30 wt.%; (▲) Keggin ion

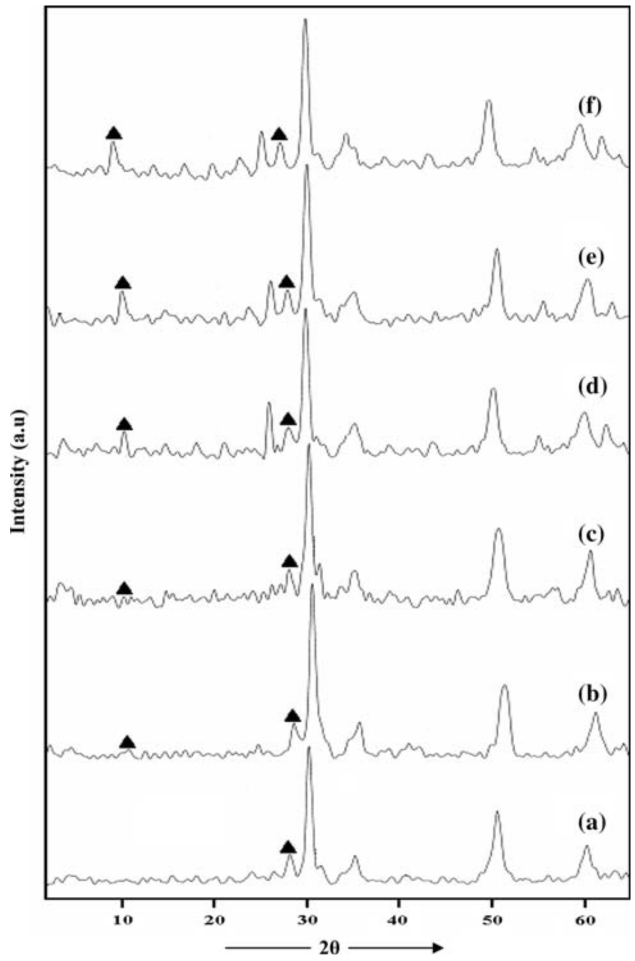

Fig. 2 XRD patterns of AMPV/ZrO_2 catalysts (**a**) 5 wt.% (**b**) 10 wt.% (**c**) 15 wt.% (**d**) 20 wt.% (**e**) 25 wt.% (**f**) 30 wt.%; (▲) Keggin ion

$(NH_4)_3PMo_{12}O_{40} \cdot 4H_2O$. The intensities of the two peaks corresponding to the salt have increased with increase in AMPA loading. Similar patterns have also been observed in the AMPV/ZrO_2 samples.

The FTIR spectra of the AMPA/ZrO_2 catalysts are shown in Fig. 3. The IR spectra of pure AMPA has shown the bands at 1410, 1065, 960, 873 and 786 cm^{-1} that are assigned to stretching vibrations of NH_4^+ ion, (P–O_d), (Mo–O_t), (Mo–O_b–Mo), and (Mo–O_c–Mo), respectively [40]. The pure support shows strong bands at 1600, 750 and 500 cm^{-1}. The catalyst with 5 wt.% AMPA impregnated on the support has shown strong and clear bands at 1620, 1060, 980 and 870 cm^{-1} in which the first one corresponds to an OH stretching vibration of the support and the latter bands are the characteristic bands of Keggin ion. A doublet between 1395 cm^{-1} and 1410 cm^{-1} (shown in inset of the figure) is observed contrary to the general appearance of a single peak at 1410 cm^{-1}. The appearance of a doublet could be related to the formation of interactive species of the type $(ZrOH_2)^+(NH_4)_2[PMo_{12}O_{40}]$ or $(ZrOH_2)_2^+(NH_4)[PMo_{12}O_{40}]$ in addition to AMPA. The strong band at 789 cm^{-1} due to the support overlapped the characteristic band at 786 cm^{-1} corresponding to Mo–O_c–Mo stretching vibration. From these results, one can say that there is a definite modification in the secondary structure of the heteropoly compound. Even though the XRD pattern has not shown any diffraction lines due to ammonium salt, the FTIR spectra reveal the fingerprint bands corresponding to the Keggin ion.

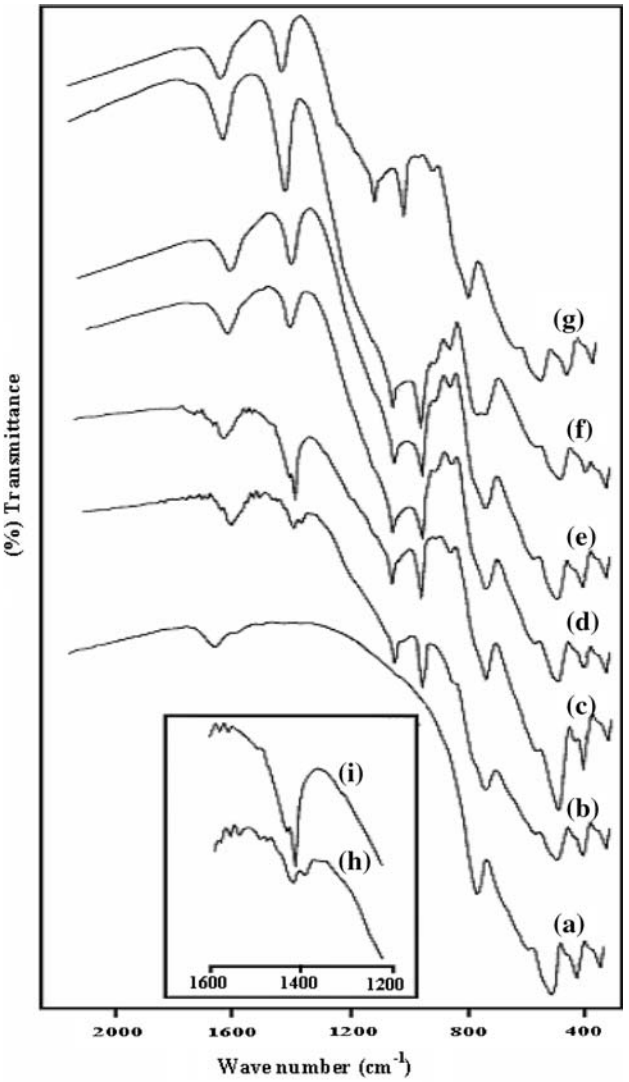

Fig. 3 FTIR patterns of pure ZrO_2-AMPA/ZrO_2 catalysts (**a**) support (**b**) 5 wt.% (**c**) 10 wt.% (**d**) 15 wt.% (**e**) 20 wt.% (**f**) 25 wt.% (**g**) 30 wt.% (Inset) The doublet of 1410 cm^{-1} peak corresponds to NH_4^+ ion; (**h**) 5 wt.% (**i**) 10 wt.% catalysts

As the loading increases to 10 wt.%, the intensity of 1395 cm^{-1} peak of the doublet decreased while that of 1410 cm^{-1} is found to increase noticeably. The increase of intensity of the 1410 cm^{-1} peak may be due to the increase in the content of bulk AMPA at higher loadings. On a further increase of AMPA loading to 15–30 wt.%, the doublet between 1395 cm^{-1} and 1410 cm^{-1} has become a single peak at 1410 cm^{-1} with increase in intensity. It is noteworthy that the broadening of the characteristic bands of the Keggin ion is a consequence of a direct interaction between AMPA and the support [21]. This broadening indicates weakening of interaction of bonds between the atoms in the heteropoly ion. The FTIR spectra of AMPV/ZrO_2 samples are shown in Fig. 4. For these catalysts the same characteristic patterns are observed as that of the AMPA/ZrO_2 samples. The difference is in the band of P–O_d at 1063 cm^{-1}. The peak at 1063 cm^{-1} was resolved further using a resolution of 0.1 cm^{-1} and it is shown in the inset of Fig. 4. The splitting of P–O_d band was observed for the samples with the presence of vanadium in the Keggin structure. It is known that the introduction of a metal other than Mo in the Keggin ion induces a decrease in the Mo–O_t stretching frequency and a possible splitting of the P–O_d band [41]. This splitting suggests the incorporation of V into the Keggin ion. These data suggest that the Keggin structure has been formed on zirconia during the synthesis. The intensity of the peaks related to Keggin ion are weak at lower loading but showed an increase with increasing loading, similar to the observations made in the case of XRD.

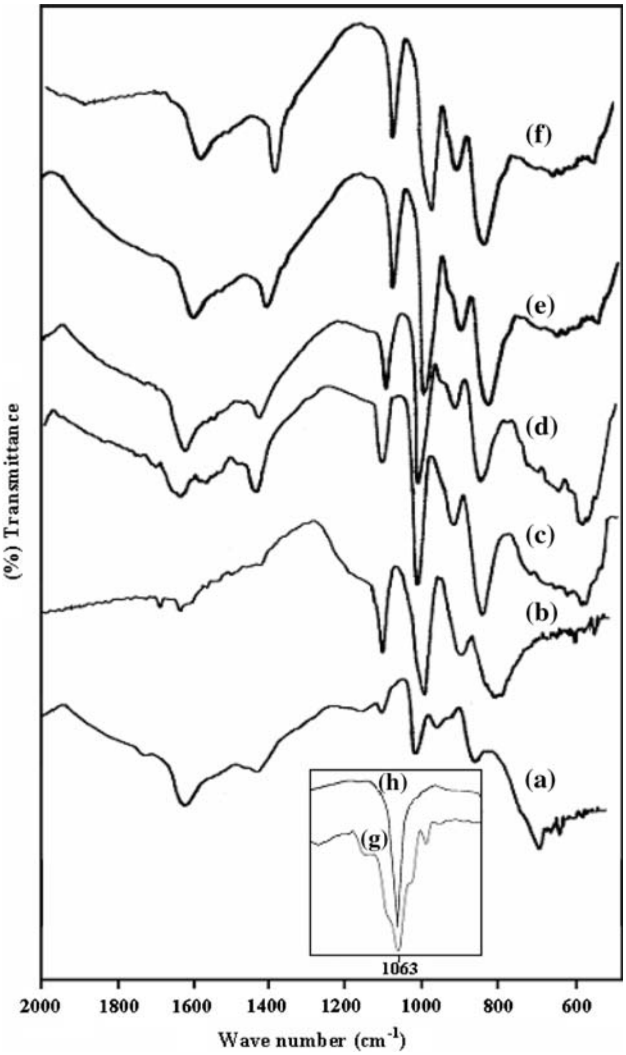

Fig. 4 FTIR patterns of AMPV/ZrO_2 catalysts (**a**) 5 wt.% (**b**) 10 wt.% (**c**) 15 wt.% (**d**) 20 wt.% (**e**) 25 wt.% (**f**) 30 wt.%; (Inset) splitting of 1063 cm^{-1} peak (**g**) AMPV (**h**) AMPA

The acidity of the samples was estimated by potentiometric titration method and the results are shown in Table 1. Pure zirconia support, when titrated with butyl amine in acetonitrile, took very little quantity (0.6 mL) for neutralization and showed an initial EMF of 263 mV. This indicates that pure zirconia has moderate acidity. When 5% AMPA was impregnated on the support, the EMF value increased to 294 mV and as the proportion of AMPA loading increased on zirconia, the value increased further up to 546 mV at 25 wt.%. At 30 wt.% it reduced due to the attainment of the bulk nature. The acidity of these compounds is mainly due to the presence of residual protons resulting from incomplete stoichiometric during salt formation. Nowinska et al. [42] observed that the acidity of ammonium salt of HPAs is close to the acid strength of typical superacids due to the residual protons. The compositions of the residual protons in the present catalysts were estimated using FTIR spectroscopy and elemental analysis following the procedure reported by Highfield and Moffat [43]. Even though those 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 25 wt.% AMPV/ZrO_2 was calculated as $(NH_4)_{3.16}H_{0.84}PMo_{11}V_1O_{40}$. Similar composition may exist in all the catalysts. The acidity of AMPV/ZrO_2 samples also displayed the same trend increasing acid strength up to 25 wt.% and of decreasing thereafter. However, the acid strength values are lower than the supported AMPA catalysts.

Benzyl alcohol undergoes different transformations based on the nature of catalyst. The main reactions are:

$$2C_6H_5CH_2OH + O_2 \rightarrow 2C_6H_5CHO + 2H_2O \quad (1)$$

$$2C_6H_5CH_2OH \rightarrow C_6H_5CH_2OCH_2C_6H_5 + H_2O \quad (2)$$

$$2C_6H_5CH_2OH \rightarrow C_6H_5CHO + C_6H_5CH_3 + H_2O \quad (3)$$

The formation of benzaldehyde depends on the oxidation ability of the catalyst. The formation of dibenzyl ether and the disproportionation of benzyl alcohol depend on the acidic nature of the support.

The benzyl alcohol conversion over ZrO_2 supported AMPA and AMPV catalysts, as a function of salt loading at different reaction temperatures, are shown in Fig. 5. In both the catalyst systems the conversion of benzyl alcohol increased with increasing the active component loading up to 25 wt.%. Further increase of the loading up to 30 wt.% the conversion decreased marginally. This might be due to attainment of bulk nature. These results indicate that the active component is dispersed on ZrO_2 up to 25 wt.% and attained bulk nature beyond that composition. The main products observed during the partial oxidation of benzyl alcohol were benzaldehyde and toluene. With the substitution of one V into AMPA a considerable increase in the conversion of benzyl alcohol was observed compared to the AMPA.

The selectivity of benzaldehyde and toluene as a function of AMPA and AMPV loading at a reaction temperature of 290 °C are shown in Fig. 6. The selectivity to benzaldehyde increased with increase in the active component and attained a maximum value at 25 wt.%. The vanadium containing catalysts showed better selectivity to benzaldehyde compared to AMPA catalysts. It is known that the presence of vanadium enhances the redox property of the catalysts. It is reported that the reduction potential approaches its maximum when one vanadium is incorporated into molybdophosphoric acid. It is interesting to see that the selectivity towards toluene, a disproportiantion product, is high for the AMPA catalysts compared to vanadium containing counterparts. The formation of toluene is facile on acidic sites whereas benzaldehyde depends on the oxidizing ability of the catalysts. The acid strength measured from potentionmetric titration method suggests the increased acidic strength of the AMPA catalysts compared to AMPV catalysts. The vanadium containing catalysts are less acidic as they possess redox properties thus leading to more oxidation product.

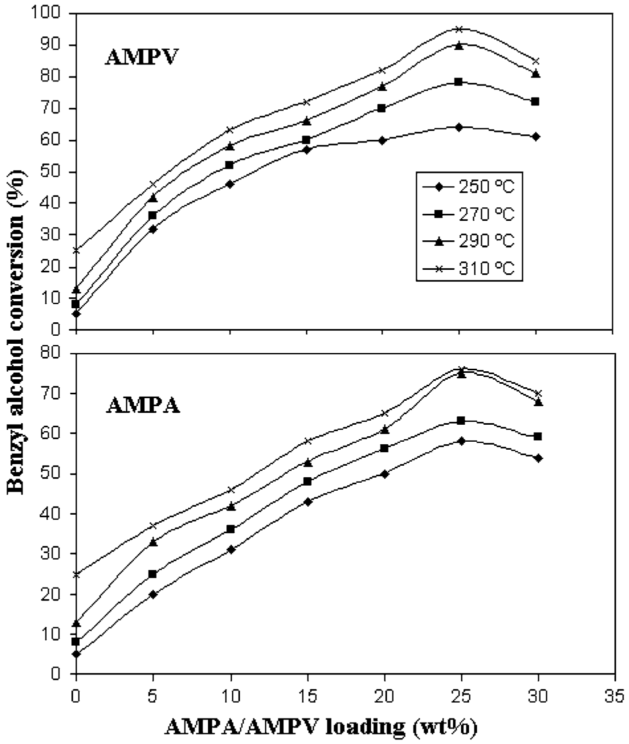

Fig. 5 Conversion of benzylalcohol using AMPA/ZrO_2 and AMPV/ZrO_2 as a function of different loadings with different temperature

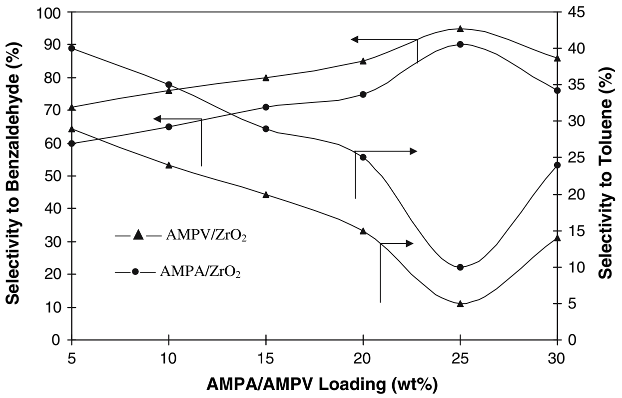

Fig. 6 Selectivity to benzaldehyde as a function of AMPA/AMPV loading at 290 °C

The activity of the best 25 wt.% AMPV/ZrO_2 catalysts was compared with bulk AMPA, bulk AMPV and 25 wt.% AMPA/ZrO_2. The selectivity towards the main product benzaldehyde and the reaction rates at a reaction temperature of 290 °C are shown in Fig. 7. The zirconia supported AMPV catalyst showed the better activity and selectivity to oxidation product compared to the rest of the catalysts. The performances of the catalysts are in the following order: AMPV/ZrO_2 > AMPA/ZrO_2 > AMPV > AMPA. The high activity of 25 wt.% AMPV/ZrO_2 catalyst might also be a manifestation of increased redox nature of the catalyst.

In conclusion, zirconia supported ammonium salt of 12-molybdophosphoric acid and vanadium incorporated ammonium salt of 12-molybdophosphoric acid are prepared in a single step by simple impregnation.

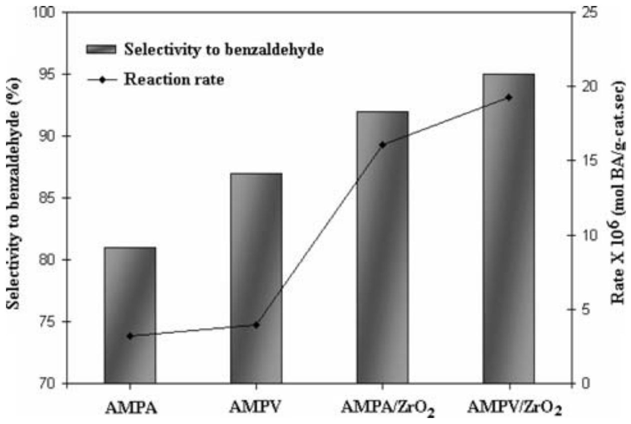

Fig. 7 Comparison of selectivity and reaction rates of different catalysts at 290 °C

Characterization techniques suggest the incorporation of vanadium into the primary Keggin structure of AMPA. Zirconia supported vanadium containing AMPA catalyst is highly active for oxidation of benzaldehyde. Vanadium incorporation leads to high selectivity to bezaldehyde due, to enhanced redox nature of catalysts.

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