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Nature and mode of addition of phosphate precursor in the synthesis of aluminum phosphate and its influence on methanol dehydration to dimethyl ether

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Abstract

Four aluminum phosphate catalysts with Al/P = 1 were prepared by precipitation of mixture of aluminum nitrate and phosphate precursor (either phosphoric acid or diammonium hydrogen phosphate) with NH_3 and precipitation of aluminum nitrate with NH_3 followed by impregnation of phosphate precursor (either phosphoric acid or diammonium hydrogen phosphate). The catalysts were characterized, using different physico-chemical methods viz., BET-S.A., XRD, FT-IR, and NH_3-TPD. ^{27}Al and ^{31}P MAS NMR spectroscopy was used to characterize selected catalysts in order to find out the presence of Al and P environments. The catalytic conversion of methanol to dimethyl ether was conducted over these catalysts in a temperature range of 448–548 K at atmospheric pressure. $AlPO_4$ prepared by precipitating the mixture of aluminum nitrate and $(NH_4)_2HPO_4$ with aq. NH_3 generated more number of moderate acid sites and showed higher methanol dehydration activity with 100% selectivity to DME at 548 K.

Keywords: Aluminum phosphate; Methanol; Dimethyl ether; Dehydration; NH_3-TPD; ^{27}Al and ^{31}P MAS NMR

1. Introduction

In recent times, dimethyl ether has been receiving much attention as an alternative clean fuel due to its thermal efficiency being equivalent to traditional diesel fuel, lower NO_x formation, near zero smoke and with less engine noise [1,2]. Moreover, DME is a building block for the synthesis of many chemicals viz., methyl acetate, dimethyl sulfate, gasoline and aromatics [3]. Dimethyl ether (DME) has been increasingly used as a propellant in aerosol formulations to replace chlorofluorocarbons, which are found to destroy the ozone layer of the atmosphere [4,5]. The growing demand for DME as a clean, alternative fuel and as an aerosol led to search for the production of DME in large quantities. At present DME is commercially produced by the dehydration of methanol using acidic porous materials such as zeolites, silica–alumina and γ-Al_2O_3 as the catalysts [6]

$$2CH_3OH \xrightarrow{\text{Catalyst}} CH_3\text{–}O\text{–}CH_3 + H_2O. \qquad (1)$$

Ether synthesis from alcohol is known to be an acid catalyzed reaction. However, most of the solid-acid catalysts due to the presence of strong acid sites produce undesirable products such as hydrocarbons [4,7]. Although γ-Al_2O_3 is an excellent catalyst for the methanol dehydration, it undergoes a fairly rapid, irreversible deactivation. In order to avoid the formation of coke and to increase the selectivity of DME to 100%, the strength of

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acid sites must be reduced. It has been reported that 1 wt% titania modified γ-Al_2O_3 catalyst shows an even better performance by increasing dehydration rate, minimizing coke formation and reducing the amount of by-products compared with a phosphoric acid–alumina catalyst [8]. However, the optimum operating temperature over titania modified γ-Al_2O_3 is 673 K which is considerably higher than the temperature employed in the syngas to methanol process.

It has been reported that methanol dehydration takes place on the modified alumina catalysts with phosphorous to reduce the amounts of coking and by-products [9]. The catalytic activity of $AlPO_4$ is strongly dependent on the method of preparation, chemical composition (Al/P ratio) and activation temperature [10,11]. In the present study, the catalytic dehydration of methanol to DME has been performed over aluminium phosphates ($Al/P = 1$) prepared by co-precipitation and impregnation methods with either phosphoric acid or diammonium hydrogen phosphate as phosphate precursor and NH_3 solution as precipitating agent. The effects of nature and mode of addition of phosphate ion in the synthesis of $AlPO_4$ has been investigated. These catalysts are evaluated in a temperature range of 448–548 K and at feed rate of 2 ml/h of methanol, in order to find out the most promising methanol dehydration catalyst.

2. Experimental

2.1. Preparation of catalysts

Aluminum phosphates with $Al/P = 1$ were prepared by following four different methods. To the mixture of 10 wt% aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$ and H_3PO_4 (of 88% purity) kept under vigorous stirring at room temperature, 5% ammonia solution was added dropwise to precipitate aluminum phosphate at a pH of 9.0. The precipitate was filtered and washed with distilled water. The filtered mass was dried at 383 K for 12 h and calcined at 923 K for 2 h in air and the catalyst designated as AP-I. Catalyst AP-III was prepared same as in the case of AP-I by replacing the phosphate precursor with $(NH_4)_2HPO_4$. The other two catalysts were prepared by addition of 5% ammonium solution dropwise to a 10 wt% aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$ kept under vigorous stirring at room temperature to get aluminum hydroxide precipitate at a pH of 9. The precipitate was filtered and washed with distilled water. The filtered mass was dried at 383 K for 12 h and calcined at 923 K for 2 h in air. The calcined Al_2O_3 thus obtained was made in two parts and the first part was impregnated with H_3PO_4 (of 88% purity) followed by drying in oven at 383 K and calcined in air at 923 K for 2 h and the catalyst was designated as AP-II. The second part is impregnated with $(NH_4)_2HPO_4$ followed by drying in oven at 383 K and calcined in air at 923 K for 2 h and the catalyst was designated as AP-IV.

2.2. Characterization techniques

BET-surface areas of the catalysts were obtained on an all glass high vacuum unit capable of yielding 10^{-6} Torr vacuum with N_2 as adsorbate at liquid nitrogen temperature. X-ray powder diffraction (XRD) patterns of fresh and used (after reaction) catalysts were recorded on a Rigaku Miniflex (M/s. RIGAKU Corporation-Japan) instrument using Ni filtered Cu Kα radiation, with a scan speed of 2°/min and a scan range of 10–70° at 30 kV and 15 mA. The FT-IR spectra of $AlPO_4$ catalysts were recorded on a Perkin-Elmer, Spectrum GX FTIR spectrometer using KBr pellet method.

Acidity measurements were performed by temperature programmed desorption of ammonia (TPD-NH_3) conducted on Auto Chem 2910 (Micromeritics, USA) instrument. In a typical experiment, about 100 mg of oven dried sample was taken in a U-shaped quartz sample tube. Prior to TPD studies, the catalyst sample was pretreated at 473 K for 1 h by passing pure helium (99.999%), at a rate of 50 ml/min. After pretreatment, the sample was saturated with 10% anhydrous ammonia balance helium mixture at 353 K for 1 h. TPD analysis was carried out from ambient temperature to 1023 K at a heating rate of 10 K/min. The amount of NH_3 desorbed was calculated using GRAMS/32 software.

High-resolution magic-angle spinning (MAS) NMR studies of ^{27}Al and ^{31}P were carried out on a Bruker DRX-500 spectrometer operating at a magnetic field of 11.7 T. Spectra were recorded at a sample rotation of 9 kHz for ^{27}Al and 7.2 kHz for ^{31}P using 4 mm zirconia rotors. Chemical shifts of ^{27}Al and ^{31}P were referenced using $Al(H_2O)_6^{3+}$ and ortho phosphoric acid (85%), respectively.

2.3. Activity studies and product analysis

Catalytic dehydration of methanol was carried out in a fixed bed quartz reactor (200 mm long and 8 mm i.d.). About 1 g of the catalyst sample (18-25 BSS mesh), was packed at the center of the reactor between two plugs of quartz wool mounted in an electrically heated furnace. The reaction was carried out starting from 448 to 548 K in N_2 flow at atmospheric pressure. Methanol was fed on to the catalyst using syringe pump (Perfusor FT, B. Braun, Germany) at a rate of 2 ml/h. Prior to the experiment, the sample was activated in situ at 473 K for 2 h in a flow of nitrogen. The reaction products were analyzed at 3rd h feeding of methanol using on-line GC equipped with FID through a 6-port sampling valve using a Porapak-Q column (3 m long × 1/8″ dia.). The product lines were heated electrically in order to avoid unwanted condensation of methanol and water. Product Confirmation was done using GC–MS (M/s. Shimadzu, Model: QP-5050) with electron ionizer and quadrupole mass analyzer. The rate of conversion of the feed methanol was calculated as follows:

$$\text{Rate of conversion of methanol} = \frac{\text{Fractional conversion} \times \text{Flow rate of methanol (m mol/h)}}{\text{Weight of the catalyst (g)}}$$

3. Results and discussion

3.1. Catalyst characterization

Fig. 1A represents the XRD patterns of the fresh aluminum phosphate catalysts. The patterns clearly indicate that the catalysts AP-I, AP-II and AP-III are amorphous in nature. Only a very broad hump is found in the range of 15–35° which is centred at 26° (2θ), characteristic of the tetrahedral structure in amorphous $AlPO_4$ [23]. AP-IV catalyst shows signals at $d = 4.36$, 4.08 and 2.53 Å. The band at $d = 4.36$ Å observed is found to be incompatible with the orthorhombic symmetry of α-crystobalite. The same observation by El-Hakam et al. [12] and Flork and Lachenmayer [13,14] has been related to the presence of structural defects in the α-crystobalite phase. The other two d lines at 4.08 and 2.53 Å can be identified with that of α-crystobalite phase [ICDD No. 82-0512]. The XRD patterns of used catalysts (Fig. 1B) indicate no change in AP-I, AP-III and AP-IV even after the reaction as they remained in amorphous form except for AP-IV, which maintained the same crystalline α-crystobalite phase. However, used catalyst of AP-II showed the presence of an additional phase of berlinite along with α-crystobalite phase. This transformation of amorphous phase of aluminum phosphate, AP-II to crystalline phases of

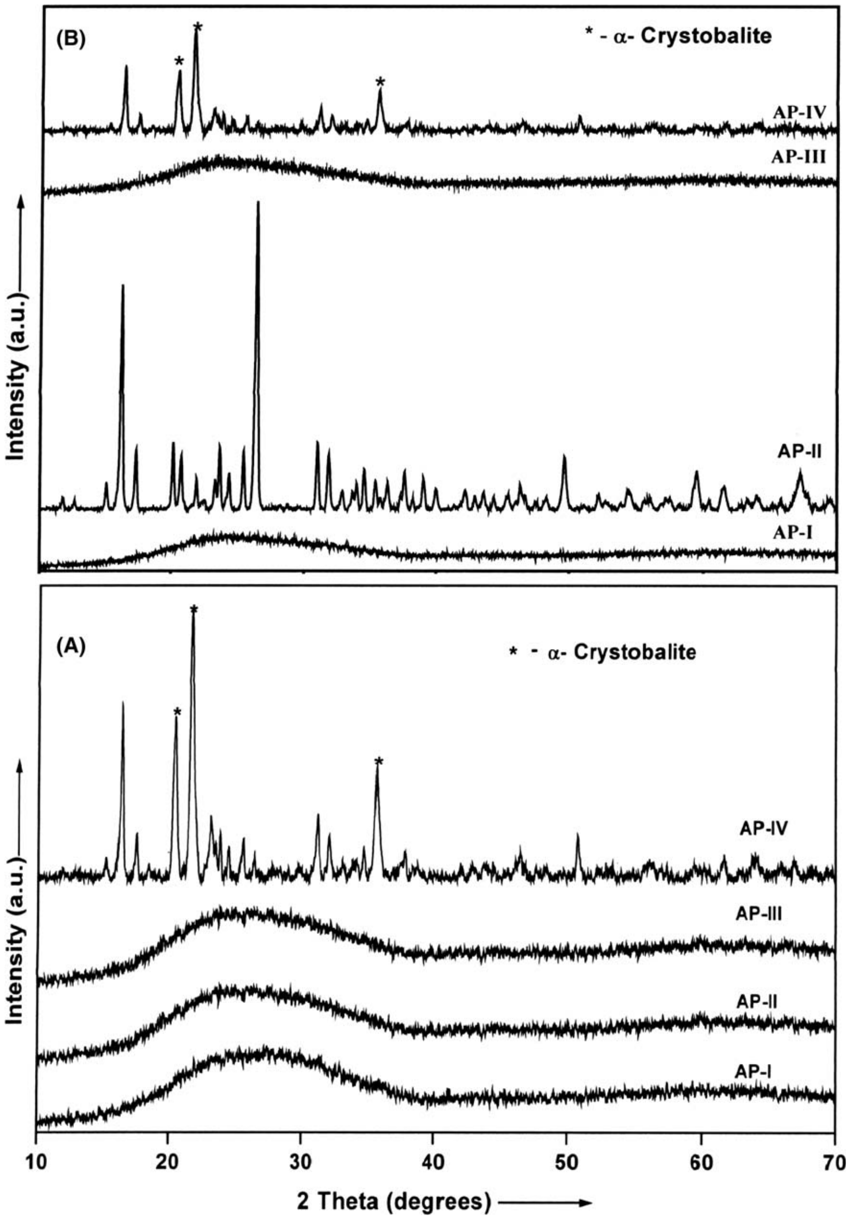

Fig. 1. (A) X-ray diffraction patterns of fresh $AlPO_4$ catalysts; (B) X-ray diffraction patterns of used $AlPO_4$ catalysts.

α-crystobalite and Berlinite may be attributed to a surface reconstruction that may be taking place during the course of the reaction.

Table 1 presents the BET-Surface areas and the acidities measured by the TPD of NH_3 of the fresh $AlPO_4$ catalysts studied. The surface areas of AP-I to AP-IV catalysts are in the range of 20–40 $m^2\ g\ catalyst^{-1}$. This is a clear indication that these catalysts possess either large pores (macro) or mesopores. From Table 1 and Fig. 2, the catalysts obtained by the addition of phosphate ion first, followed by hydrolysis with NH_3, yield higher acidities viz., 51 and 55 $ml\ STP\ g\ catalyst^{-1}$ in AP-I and in AP-III, respectively in comparison to catalysts prepared by the incorporation of phosphate ion at the end by impregnation viz; AP-II and AP-IV. In case of AP-II and AP-IV, addition of acidic phosphate ion to a hydroxide gel resulted in yielding aluminum phosphate. Since, the amount of hydroxide and phosphate ions are in 1:1 mole ratio, one can expect the formation of a crystalline aluminum phosphate catalyst and also the bulk changes in this method. XRD results also support the formation of crystalline $AlPO_4$ in AP-IV. May be the crystallites of $AlPO_4$ in AP-II (not big enough to show XRD signals) become crystalline on exposure to reaction conditions. In the catalysts AP-I and AP-III, addition of phosphate ion in the beginning yields an aluminum precursor interacted with phosphate ion present in it. These materials after hydrolyzing with NH_3 may probably result in the generation of materials containing partly OH^- and partly PO_4^{3-}, which are amorphous in nature. From the T_{max} values (ranging from 498 to 573 K), it is clear that the nature of acid sites in all the four catalysts is moderate. Thus the catalysts present in this work are more suitable for selective dehydration of methanol to get DME, as these catalysts possess moderate acid sites. Catalysts AP-II and AP-IV contain a smaller number of acid sites in moderate region. Hence, they may not be active for formation of DME.

Table 1
BET S.A. and TPD NH_3 data of $AlPO_4$ catalysts

Catalyst	TPD		BET S.A. (m^2/g)
	NH_3 uptake (ml/g STP)	T_{max} (K)	
AP-I	51.14	573	33.0
AP-II	21.08	573	24.0
AP-III	55.06	498	37.0
AP-IV	17.85	573	27.0

Fig. 3 represents the FT-IR spectra of the fresh $AlPO_4$ catalysts. A broad band in the OH stretching vibration region of 3700–2900 cm^{-1} centered at ~3500 cm^{-1} can be evidenced from the Fig. 3, which is present in all the samples. This has been attributed by several authors to the stretching vibrations of the surface hydroxyl groups of phosphorous both free and perturbed by a hydrogen bridge

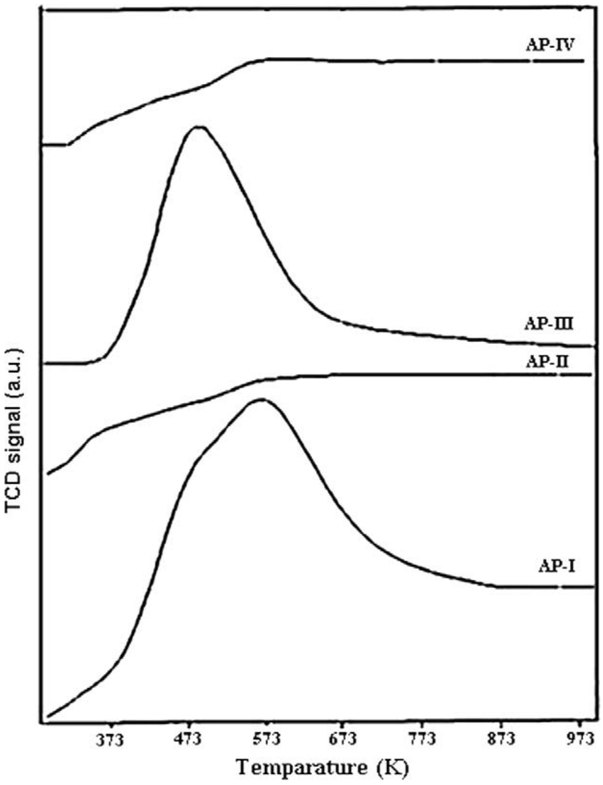

Fig. 2. TPD-NH_3 profiles of fresh $AlPO_4$ catalysts.

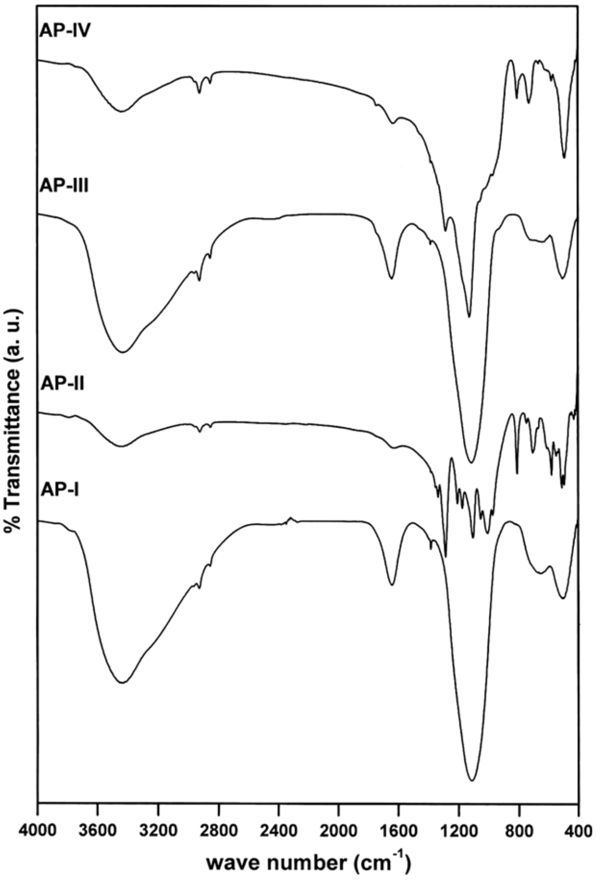

Fig. 3. FT-IR spectra of fresh $AlPO_4$ catalysts.

band from a surface hydroxyl band [15,16]. Peri ascribed these hydroxyl groups to isolated geminal OH attached to the phosphorous atom or to single P–OH groups that are more difficult to remove [17]. The hydroxyl groups on the phosphorus atom are stated by Moffat et al. to be acidic and their acidity to have been further enhanced by H-bonding to Al–OH groups [18]. Weaker acidity has been associated with aluminium atoms while P–OH sites have been associated to stronger acidity [18]. The shoulders that appear as sharp bands centered at ~2850 and ~2935 cm^{-1} in case of AP-IV probably indicate the presence of –OH groups of various strengths attached to phosphorous in these samples.

The vibrations corresponding to H_2O molecules (HOH) are observed in the form of a smaller band centered at ~1650 cm^{-1} in almost all the samples. The other two main regions in the range of 1400–900 cm^{-1} and 800–400 cm^{-1} can be seen as broad bands in unresolved form in the spectra of the samples except for AP-IV, where these bands seemed to appear as two groups of multiple peaks, i.e., the bands in resolved form. A number of bands evidenced in the region of 1400–900 cm^{-1} (centered at 1130, 1080,1030 and 920 cm^{-1}) and at 480 cm^{-1} are attributed by Bautista et al. to the triply degenerate P–O stretching vibration v_3 mode of tetrahedral $(PO_4)^{3-}$ and to the triply degenerate O–P–O bending vibration v_4 mode of $(PO_4)^{3-}$ tetrahedral, respectively, where as the bands at ~720 and 890 cm^{-1} to the stretching vibrations of Al–O bonds in combination with P–O bonds [16]. The bands in the range of 800–400 cm^{-1} are assigned to the asymmetric and symmetric stretching frequencies of Al–O–P bonds, which correspond to non-stoichiometric aluminum phosphates [19]. The bonds are attributed to the PO_2 in a chain structure with two oxygen atoms from phosphorous coordination sphere bonded to aluminum atoms while the other two corresponding to the P=O bonds [19].

The fresh catalysts with highest and lowest acidities viz., AP-III and AP-IV, respectively are characterized by ^{27}Al and ^{31}P NMR in order to find out the differences in Al and P environments. As may be seen from the Fig. 4A, ^{27}Al MASNMR shows three peaks in the range of 39–41, 8–15 and −6 to −14 ppm. Peaks in the range of 39–41 ppm are assigned to aluminium in tetrahedral environment, where as peaks in the range of 8–15 ppm are assigned to penta coordinated aluminium and peaks in the range of −6 to −14 ppm are assigned to hexa coordinated (octahedral) aluminium [20,21]. AP-III has very broad peaks, unlike in case of crystalline $AlPO_4$'s, where the sample gives much narrow peaks as a result of long-range order. Though relatively a large proportion of aluminium is present in octahedral form, significant content of it is in tetrahedral form. Presence of pentavalent aluminium has been reported in crystalline aluminum phosphates. However, further investigations are required to understand the pentavalent aluminium in these samples, as the coordinating groups are very clear. Surprisingly, the sample (AP-IV) that was prepared by precipitation of $Al(NO_3)_3$ with ammonia followed by deposition of phosphate precursor has a large proportion of aluminium in tetrahedral environment and peak widths are also much less compared to those in AP-III sample. Peak corresponding to hexa coordinated (octahedral) is much less intense in this sample.

Proton decoupled ^{31}P MASNMR spectra (Fig. 4B) indicates the presence of broad peak at −19 ppm for AP-III sample, while a peak at −27 ppm along with a shoulder at −36 ppm is observed for AP-IV. Usually, peaks in the region of −10 to −20 ppm are assigned to phosphorus in amorphous phase [22]. In crystalline aluminum phosphates, the peak at −19 ppm is assigned to occluded phosphate groups in the pores. These occluded phosphates have weak acidity and as a result may be active in reactions that are less demanding in acid strength, like methanol dehydration to DME. Among the peaks at −36 and −27 ppm in case of AP-IV, the peak at −27 ppm might have originated during initial stages of crystallization of aluminum phosphates, which is assigned to a reactive intermediate during crystallization [23]. The intense shoulder at −36 ppm can be unambiguously assigned to phosphorus in tetrahedral environment, suggesting that phosphorus present in reactive intermediate (peak at −27 ppm) is getting condensed during heating at higher temperatures leading to the presence of crystalline tetrahedral coordinated environment. This condensation might have lead to a reduction in the P–OH groups; hence catalytic activity of this sample might be less, particularly in reactions that need weak acidity.

Bautista et al. observed the formation of α-crystobalite phase in $AlPO_4$ samples when they are heated to temperatures of 1273 K [15]. In the ^{27}Al MAS NMR spectra reported by them, they have shown that the ratio Al_0/Al_t intensities decreased with increase in the calcination temperature i.e. with the increase in the crystallinity of the $AlPO_4$ sample. In the present study also similar observations have been made where it is found that the Al_0/Al_t ratio (as seen in Fig. 4A) in the crystalline AP-IV sample is much lower compared to the AP-III amorphous one. Thus it seems that the octahedral sites play a key role in determining the activity of the catalyst. The crystalline phases as evidenced from the XRD results seem to be less or inactive for the dehydration of methanol to DME.

3.2. Activity results

Fig. 5 represents the activity of the catalysts towards the dehydration of methanol. Over AP-I, the rate of production of DME is very low below 498 K and beyond this temperature it started increasing continuously. Over AP-II catalyst, the rate of production of DME against temperature shows altogether a different trend compared to that on AP-I up to 498 K, it started increasing and thereafter decreased with rise in temperature. The methanol dehydration ability of AP-III is similar to that of AP-I and

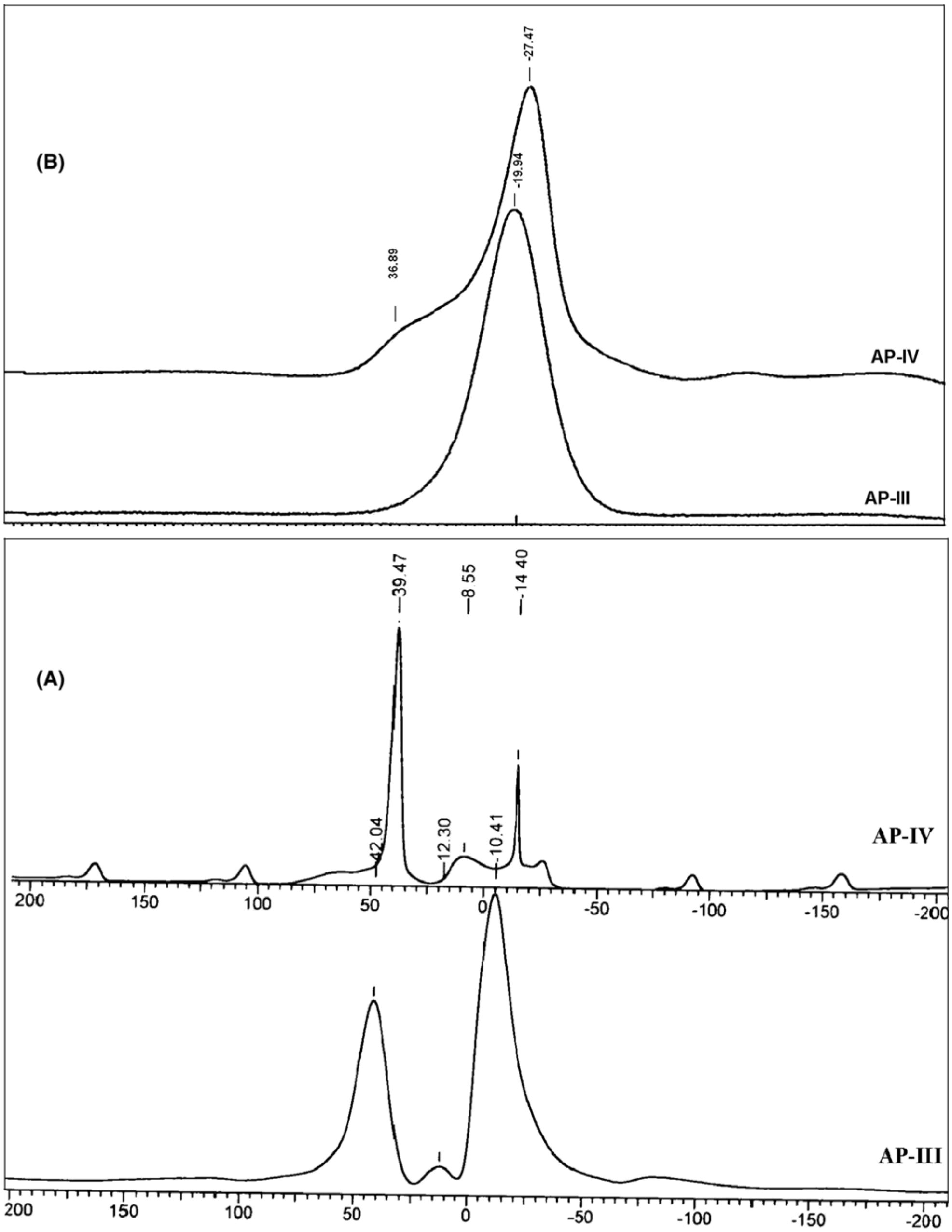

Fig. 4. (A) ^{27}Al MAS NMR spectra of AP-III and AP-IV fresh catalysts; (B) ^{31}P MAS NMR spectra of AP-III and AP-IV fresh catalysts.

the activity on AP-II and AP-IV is very low. From the Fig. 5, it is clear that AP-II has poor thermal stability and AP-IV shows low activity. The AP-I and AP-III catalysts seem to possess more number of medium strength sites with higher over all acidity compared to AP-II and AP-IV catalysts. The variation in the population of acidic sites in all these catalysts which is a result of the different preparation methods adopted can be correlated to their activity patterns as observed in Fig. 5 with AP-I and AP-III showing better and longer activity compared to AP-II and AP-IV.

Most of the researchers claimed acid sites of weak or intermediate strength to be responsible for the selective formation of DME and strong acid sites to be responsible for the formation of hydrocarbons. However, there are certain authors, who differed in their opinions about the nature of the acidic centers particularly the involvement of Lewis or Bronsted sites; those are active for formation of DME and hydrocarbons. It is observed from our results that DME formation needs acidic sites of medium strength, since the catalysts under study show 100% selectivity to DME, in comparison to that reported over γ-Al_2O_3 alone. γ-Al_2O_3 with weak sites is found to be inefficient in catalyzing the dehydration of methanol to DME and other catalysts viz., HZSM-5 with strong acidic sites form hydrocarbons thus being responsible for the poisoning of the catalyst (by coking) leading to the deactivation of the catalysts [4,7]. Thus it may be opined that

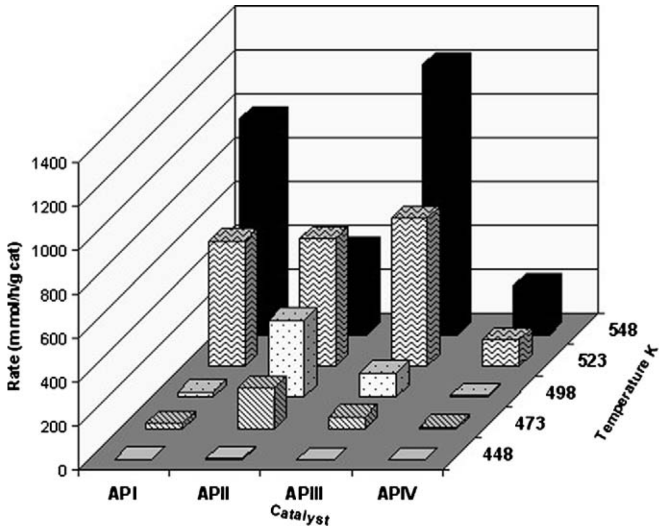

Fig. 5. Rate of conversion of methanol dehydration to DME on aluminum phosphate catalysts.

medium strength acidic sites are the active centers for the selective formation of DME and are effective for the long-term reaction.

The transformation of amorphous $AlPO_4$ to crystalline $AlPO_4$ (as observed from XRD and ^{31}P MAS NMR studies) may probably be attributed to lower activity of these catalysts compared to AP-I and AP-III and also a further loss in activity observed for AP-II at higher temperature of 548 K. Thus it may be supposed that these crystalline phases (α-crystobalite and berlinite) are inactive for the dehydration reaction and only amorphous $AlPO_4$ seems to be active in catalyzing the dehydration of methanol to DME. Hence, it is clearly seen that the method of preparation has a great effect on the catalytic activity of $AlPO_4$. In turn the morphology of $AlPO_4$, which varies with the method adopted in its preparation, appears to play a key role in determining the dehydration activity of $AlPO_4$. From the methanol dehydration reaction to DME over phosphate-based catalysts, it is clear that a steady increase in the yield of DME is obtained over AP-III catalyst as seen from the Fig. 5 and has been chosen as a promising methanol dehydration catalyst.

4. Conclusions

Synthesis of phosphate ion doped alumina is sensitive to the method of preparation; particularly it depends on the mode of introduction of phosphate ion. Introduction of phosphate ion prior to the hydrolysis of aluminum salt by ammonia is always a better way of preparing a suitable methanol dehydration catalyst. This catalyst may not be effective for coke deposition because of the presence of acid sites with moderate strength.

Introduction of phosphate ion after the hydrolysis of aluminum precursor yields a compound with low acidity. Such catalyst is not suitable to dehydrate methanol into DME.

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