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Investigation of active sites using solid state ^{27}Al and ^{31}P MAS NMR in ceramic amorphous aluminophosphate materials prepared from different potassium salts of phosphate for the synthesis of diphenyl urea derivatives

N. Harish [a], N. Kathyayini [b], Bindhu Baby [c], N. Nagaraju [a,*]

[a] Catalysis Research Laboratory, Department of Chemistry, St. Joseph's College PG and Research Centre, 36, Langford Road, Shantinagar, Bengaluru, 560 027, Karnataka, India
[b] CIIRC, Jothy Institute of Technology, Tataguni, Off Kanakapura Road, Bengaluru, 560082, Karnataka, India
[c] Bishop Chulaparambil Memorial College (B.C.M), Kottayam, Kumily Road, Kottayam, 686001, Kerala, India

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ABSTRACT

Ceramic amorphous aluminophosphate (CAmAlP) catalysts were prepared by precipitation method using different phosphate salts of potassium such as KH_2PO_4, $K_4P_2O_7$ and K_2HPO_4 as well as H_3PO_4. The prepared materials were characterized by PXRD, FT-IR, XPS, SEM, BET Surface area, NH_3-TPD, ^{27}Al NMR and ^{31}P NMR analytical methods. The catalytic activity of the materials was checked in the synthesis of diphenyl urea (DPU) from aniline and diethyl carbonate, under refluxing conditions. Further, the general application of the catalysts was tested using various substituted anilines. The recyclability of the catalysts was also studied. Uncertainties in percentage yields were calculated to check the reproducible surface properties. The P-XRD, BET Surface area and NH_3-TPD results indicated that the materials were amorphous with mesoporous texture, surface areas and acidities in the range 200–260 m^2/g and 0.4–0.7 mmol/g respectively. ^{27}Al NMR studies revealed that Al is present in three different coordination states such as tetrahedral, pentagonal and octahedral. The relative percentages of these Al sites depends on the type of the potassium precursor phosphate salt used. Both tetrahedral and pentagonal Al sites in conjunction with each other represented catalytically active sites. An increase in the pentagonal sites contributed to additional increments to the catalytic activity of CAmAlP. The catalyst prepared from KH_2PO_4 was found to be the best and demonstrated 96% DPU yield.

1. Introduction

Ceramic materials like crystalline aluminophosphates (ALPOs), silicoaluminophophates (SAPOs), metalalumimophosphates (MAPOs), transition metal phosphates, phosphate ion impregnated metal oxides and mixed metal oxides are well known for their catalytic activity in a number of organic transformations [1–7]. Some of these materials have a well-established long-range 3D network structure of the constituent species, and a few show only short-range order, hence amorphous [8]. Synthesis of ceramic materials with ordered structure involves the use of toxic organic templates whereas the amorphous materials are obtained by straightforward and environmentally benign synthesis procedures. One of the properties of these materials that needs to be addressed, in its development for a particular synthetic application is the nature of the catalytically active centers. Though the nature of catalytically active centers in ceramic crystalline metalaluminophosphate materials is known at present to some extent of clarity, however, in the case of ceramic amorphous metalphosphates, it is still a subject of debate and challenge, because of the low reproducibility met in the preparation of amorphous materials. Both theoretical and experimental methods have been applied to evaluate the kind of active centers present in these aluminophosphate materials. The former methods demand an ordered structure of the material and hence application of such methods for amorphous materials is not only limited but complicated. Experimental methods seem to be more appropriate. Thus, by selecting appropriate types of organic reactions and correlating the catalytic activity in these reactions supported by their surface and bulk properties it is very interesting to establish the nature of active sites.

Earlier, we have investigated the catalytic activity of ceramic amorphous aluminophosphates (CAmAlP), transition metal phosphates

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* Corresponding author.
E-mail address: nagarajun@yahoo.com (N. Nagaraju).

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as well as those modified with different transition metal cations and other anions [9,10]. We have reported the effect of several pre and post-synthesis modifications, such as different sources of phosphate ions, different pH conditions of precipitation, and various combinations of metal ions on the catalytic activity of metal phosphates. In general, the prepared aluminophosphates were found to be effective, economical and eco-friendly heterogeneous catalytic materials for the synthesis of diphenyl urea via a condensation reaction between aniline and diethyl carbonate [11]. Further it was understood clearly that their catalytic activity significantly depends on the synthesis modifications.

Researchers from references [12,13] have prepared CAmAlP using different sodium and ammonium salts of phosphate and studied the effect of phosphate precursor on the catalytic activity and the nature of active centers. In reference to these, we have investigated the nature of active centers using ^{27}Al and ^{31}P MAS NMR studies in CAmAlP, prepared by different potassium salts of phosphate as precursors.

The reasons for selecting different potassium salts for the preparation of aluminium phosphates are as follows, it is well known from the literature that the alkali metals (K & Na) have promoted the catalytic activity of zirconium phosphate in the ethylene oxidation reaction [14,15]. It was also demonstrated that the diameter of the crystallites has more significant effect on the chemical properties than the structural variation. The degree of coordination of surface atoms is a function of crystallite sizes, the later could be altered with the different counter ions of the precursor salt used for the preparation of the catalyst [16]. This has prompted us to investigate the impact of size of the alkali metal (here the larger potassium ion) on the catalytic activity of CAmAlP. The catalytic activity of thus prepared Aluminophosphates was investigated in the synthesis of DPU.

Diphenyl urea and its derivatives are important class of organic compounds which are very useful in many biological applications as fertilizers, antioxidants, resin precursors, medicines (breast cancer inhibitors and anti-tuberculosis agents) and also as intermediates for the synthesis of carbamates [17–20]. DPU and its derivatives are commercially synthesized by phosgene method which involves anilines and phosgene ($COCl_2$) which give rise to the isocyanate: a toxic biproduct [21]. Diphenyl ureas were synthesized homogenously and heterogenously, the methods are throughly discussed in Ref. [22], involved the elaborate reaction conditions, toxic reagents and environmentally unfriendly processes. In realisation, with respect to the problems associated with the existing methods, right catalysts for the synthesis of diphenyl ureas was very necessary and therefore we herewith made an attempt to synthesize using CAmAlP prepared using different potassium phosphate precursors.

2. Experimental

2.1. Materials used

Laboratory Grade Aluminium Nitrate [$Al(NO_3)_3.9H_2O$] obtained from LOBA Chemicals, H_3PO_4, KH_2PO_4, K_2HPO_4, $K_4P_2O_7$, Liquor NH_3, aniline and diethyl carbonate were all obtained from SD fine chemicals and are used as they were obtained from these commercial sources.

2.2. Preparation of ceramic amorphous aluminium phosphate

Calculated amounts of aluminium nitrate and potassium salt of Phosphate/H_3PO_4 (Al:P:: 3:1), as indicated in Table 1, were mixed with 500 ml of hot water. The pH of the mixture was adjusted to 8 by dropwise addition of liquor ammonia solution. The obtained white precipitate was kept aside undisturbed overnight. The precipitate was then separated by filtration and washed with hot distilled water (80 °C). The precipitate was initially dried at 120 °C for 10 h in a hot air oven to eliminate any physisorbed volatile impurities associated with it. The amounts of the products obtained have been introduced in Table 1. The material thus obtained was ground into a fine powder, calcined at 700 °C, cooled and, stored in a desiccator until further use.

Table 1

Different phosphate sources, the amounts of Al and P salts used in the synthesis of Ceramic amorphous Aluminophosphate catalysts.

Sl No	Phosphate source	Amount of phosphate source (g)	Amount of Al $(NO_3)_3.9H_2O$ (g)	Weight of products obtained (g)	Catalyst Abbreviation
1	H_3PO_4	4.9 (2.9 ml)	56.27	14.8	AlP(H_3PO_4)
2	KH_2PO_4	6.8	56.27	17.9	AlP(KH_2PO_4)
3	$K_4P_2O_7$	8.25	56.27	14.2	AlP($K_4P_2O_7$)
4	K_2HPO_4	8.70	56.27	15.8	AlP(K_2HPO_4)

2.3. Characterization of catalysts

The synthesized materials were characterized for their surface and bulk properties by the following analytical techniques. Powder X-ray patterns were obtained by Pan AnalyticalX'pert pro X-ray diffractometer using Cu-Kα radiation of $\lambda = 0.154$ nm in a 2θ range of 5° to 70° at 40 kV. Infra-red spectra were recorded using Nicolet IR200 FT-IR spectrophotometer by KBr pellet technique. Surface acidity of the samples was measured by TPD–NH_3 desorption method on Mayura analytical instrument. The surface area, pore volume and pore diameter were analyzed by Nova1000 Quanta Chrome gas sorption instrument. ^{27}Al and ^{31}P solid-state MAS NMR were recorded on Bruker AV 700 (υAl = 182.43 MHz) spectrometer which is equipped with a 16.4 T magnet using a 2.5 mm probe head at a spinning frequency of 32 kHz. The chemical shifts of ^{27}Al and ^{31}P NMR are referred to 1 M $Al(NO_3)_3$ and H_3PO_4 respectively. All the quantitative ^{27}Al MAS NMR spectra were recorded by direct polarization technique using a pulse width of 0.28μs and 2000 scans were acquired for all the samples. The ^{31}P MAS NMR spectra were recorded using a pulse width of 1 μs and 32 scans were acquired for all the samples. The experimental MAS NMR spectra were fitted using the DMFIT [23] to find out the relative percentage population of the different sites. XPS spectra were recorded using K-α™ + X-ray photoelectron spectrometer (with C1s peak of binding energy at 284.9eV). Surface morphology of the samples were studied by the SEM technique and was obtained from Ultra 55 instrument with the latest Gemini technology. The powdered samples were spread on the carbon tape, excess sample was blown off and further it was made conductive by gold sputtering and was analyzed.

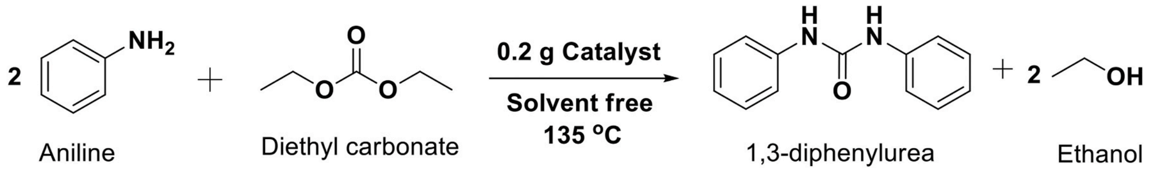
2.4. Catalytic activity studies

The catalytic activity of the prepared aluminophosphates were tested in the condensation reaction between aniline and diethyl carbonate to yield diphenyl urea (Scheme 1).

In a typical DPU synthesis reaction 10 ml of reaction mixture containing 1:1 mol ratio of Aniline and diethyl carbonate were taken in a RB flask attached with a water cooled condenser and containing 0.2 g of the catalyst. The temperature of the RB flask was maintained between 130 and 135 °C. Initially within half an hour a solid product started forming on the inner side walls of the RB flask. The reaction was left for completion for two and half hours. The contents of the flask was treated with hot ethanol to dissolve the organic solid product, then filtered to separate the catalyst and the filtrate was subjected to rota evaporation to isolate the solid product. The purity of the product was checked by TLC and GC methods. Further the catalytic activity studies were conducted using other substituted anilines to check the applicability of the catalyst to synthesize other substituted DPUs.

3. Results and discussion

Initially the basic physicochemical characteristics of the prepared catalysts such as, crystallinity, surface morphology, types of chemical



Scheme 1. Condensation reaction between aniline and diethyl carbonate.

bonds, surface chemical composition, surface area and porosity, relevant to catalytic materials are evaluated and the results are discussed below.

3.1. Powder XRD results

The XRD patterns (Fig. 1) of all the four prepared catalysts samples were recorded in Bragg's reflection 2θ range from 5° to 70°. The catalytic materials exhibited only a broad intense peak centered in a 2θ range of 15° to 30°.This indicated that the particles associated with the catalysts do not possess any long-range order but are only microcrystalline in nature, i.e., they are basically amorphous materials [22]. Henceforth, in the following discussions at times the abbreviation CAmAlP (Ceramic amorphous aluminophosphates) is used to represent the catalysts.

3.2. Infrared spectroscopy results

From IR studies the presence of the characteristic chemical bonds such as O–H, Al–O–H, P–O–H and P–O and P –O– P pertaining to the prepared catalysts could be ascertained. Infrared spectra of the catalysts are given in Fig-2. The broad peak between 3000 and 4000 cm^{-1} and a low-intensity peak at 1640 cm^{-1} are due to the O–H bond stretching and bending vibrations respectively of chemically adsorbed water molecules [24]. The broad peak centered in between 1140 and 1110 cm^{-1} is attributed to the stretching vibrations of tetrahedral P–O bonds [25]. This peak supports the presence of tetrahedral phosphorous associated with tetrahedral aluminium which are interconnected by non-bridging oxygens. The broad peak in the range 700–980 cm^{-1} is attributed to a mixture of both symmetric and asymmetric vibrations of P–O–P bonds [26].

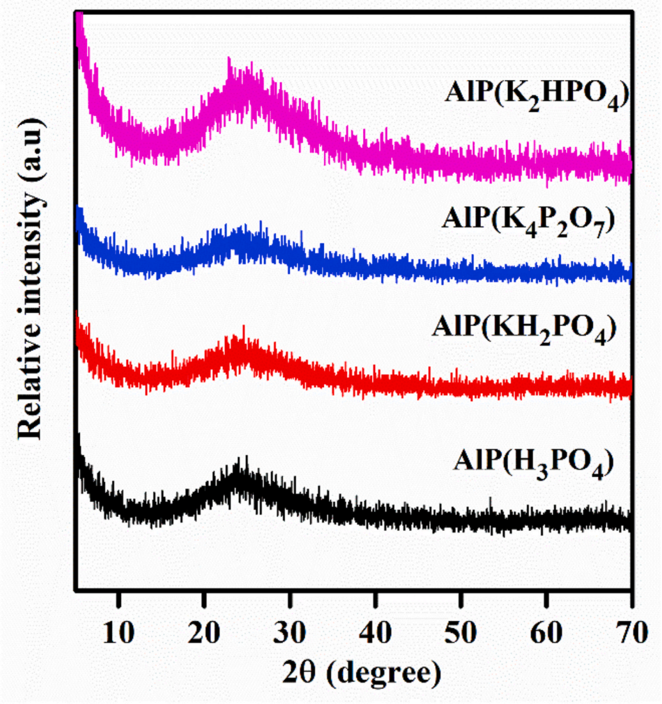


Fig. 1. Powder XRD patterns of CAmAlP catalysts prepared from different phosphate precursors.

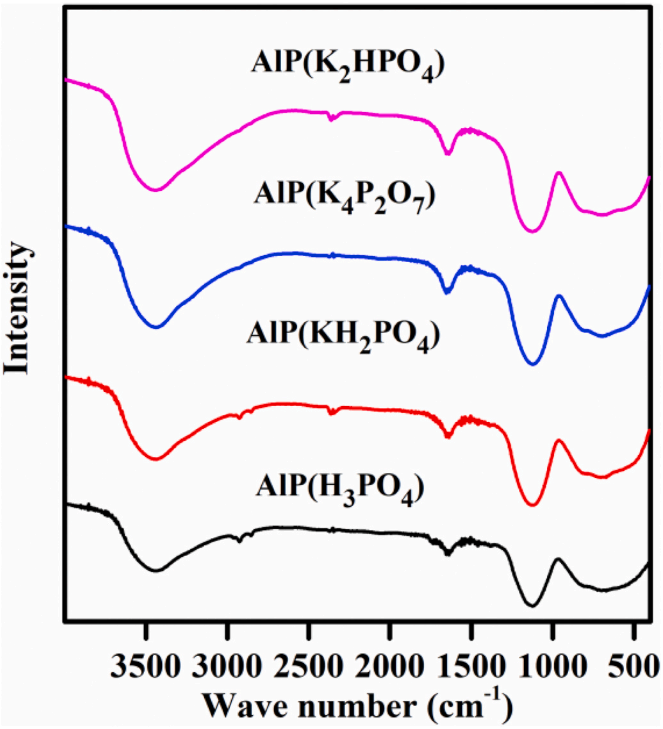


Fig. 2. Infrared spectra of samples prepared from different phosphate precursors.

3.3. XPS studies

Surface composition of Al, P and O and their binding energies in the prepared catalysts were determined by XPS. The XPS spectra of Al2p, P2p3, P2p1 and O1s are shown in the fig-3. Table 2 depicts the quantitative results surface elemental composition with respect to their specific binding energies.

The binding energies of Al,P and O were respectively found to be 75, 135 and 532eV which are in accordance with the values reported [26, 27]. The P peak positioned at 134–135 eV indicates phosphorous is connected to O. The Binding energies between 528 and 536eV in O1s spectra were attributed to the presence oxygen of alumina, free OH and H_2O [28]. The O1s graph also indicated that there are bridging, asymmetric and non bridging oxygens. Bridging and non-bridging are found at higher and lower binding energies respectively under the peak. Asymmetrically bridging oxygens are found at intermediate binding energy between bridging and non-bridging oxygens.

There is a slight shift of peak in the sample which is prepared from KH_2PO_4 as phosphate source might be attributed to the slight increase in the percentage of bridging oxygens. Non-bridging oxygens shown at lower binding energies under the peak are specifically from PO^- (shown in IR graph at 1140-1110 cm^{-1}) which combines with Al ions to form

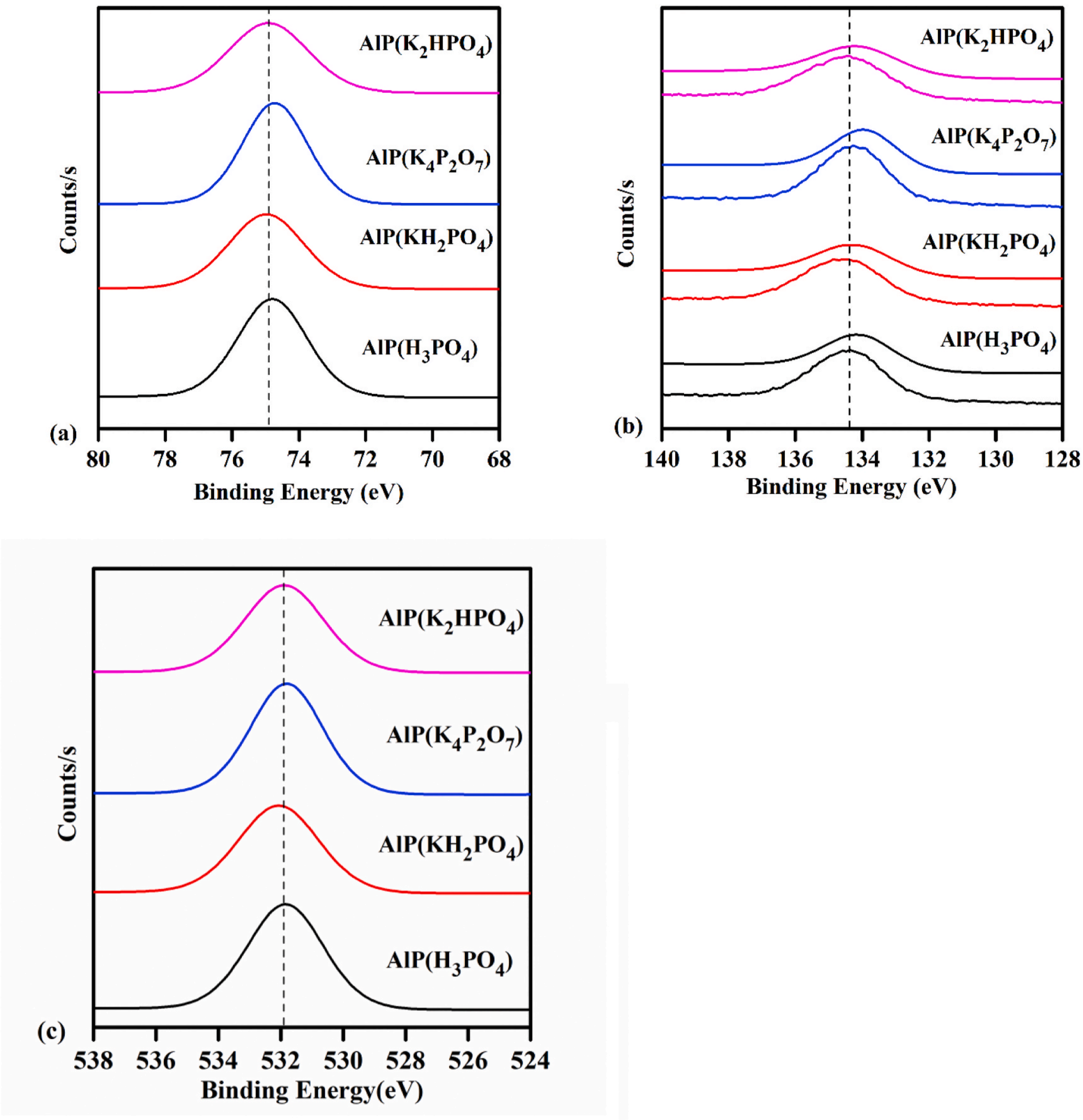


Fig. 3. XPS of CAmAlPs prepared from different phosphate precursors (a) Al2p scans (b) P2p1 scans (down ones on each curve) and P2p3 scans (top ones on each curve) (c) O1s scans.

Table 2
XPS Peak positions and fractions of Al, P and O in XPS spectra of all the samples prepared by different phosphate sources.

Catalyst (source)		O-1s	Al-2p	P-2p
AlP(H_3PO_4)	%	**62.5**	**28.5**	**9.0**
	Binding energy	531.9	74.8	134.0
AlP(KH_2PO_4)	%	**63.5**	**26.4**	**10.0**
	Binding energy	532.0	75.0	134.0
AlP($K_4P_2O_7$)	%	**62.5**	**27.3**	**10.2**
	Binding energy	531.8	74.7	134.0
AlP(K_2HPO_4)	%	**62.5**	**27.0**	**10.5**
	Binding energy	532.0	75	134.0

tetrahedral Al$(OP)_4$ species which is proved by NMR studies [26].

3.4. Scanning electron micrographs (SEM)

The SEM images (Fig-4) showed the presence of particles with heterogeneous sizes and shapes and hence no particular morphology could be assigned. The heterogeneity is attributed to the presence of an intimate composite of $AlPO_4$ and alumina [22]. Due to the difference in the solubility products of aluminium hydroxide and aluminium phosphate, and the former being lower than the later, $Al(OH)_3$ get precipitated initially and then $AlPO_4$.

3.5. BET surface area results

Surface area, pore volume and pore diameter of the CAmAlPs were obtained by nitrogen adsorption-desorption studies. The BJH isotherms of nitrogen adsorption-desorption are given in fig-5. In these isotherms the hysteresis loops appeared at higher partial pressures ($P/P_o > 0.6$) and hence represent type IV isotherms [29]. and this is attributed to an intrinsic mesoporosity in the samples [30]. The surface areas of the samples were in the range 200–300 m^2/g (Table 3), which is neither high nor too low for a catalytic material. When the surface area values of the catalysts prepared using different phosphate sources, were compared with each other, very little variation was noticed. However, the catalyst prepared using KH_2PO_4 as the phosphate source had the highest surface area. It is a known fact that as the surface area increases the number of active sites on the surface also will increase. The surface areas of the prepared catalysts were found to be in the increasing order

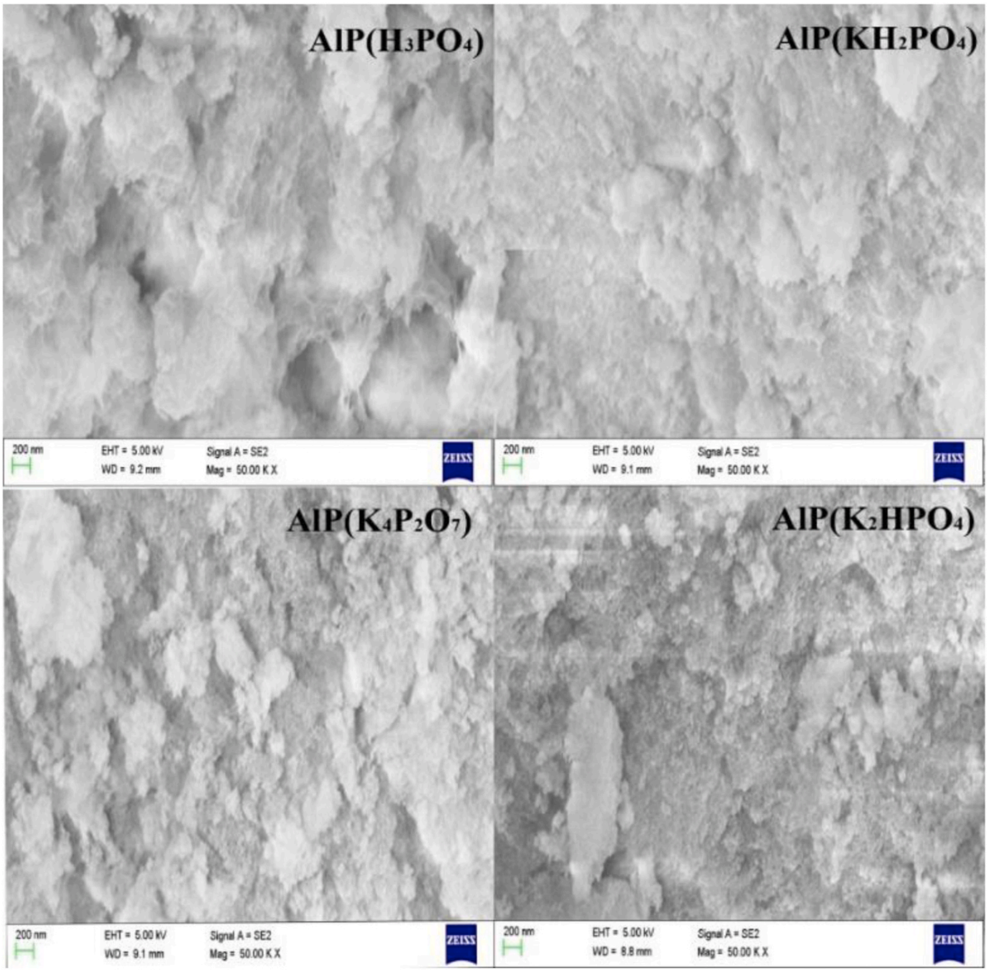


Fig. 4. Scanning electron micrographs of Ceramic aluminophosphates prepared from different phosphate precursors.

AlP(KH_2PO_4) >AlP(H_3PO_4) > AlP(K_2HPO_4) >AlP($K_4P_2O_7$)

The pore volumes of the catalysts were in the range 0.7–1.0 cm^3/g and was found to increase in the same order as that of their surface area.

3.6. TPD ammonia results

TPD ammonia studies were carried out to evaluate the acidic strength and acid sites concentration of the prepared catalysts. The quantity of ammonia gas adsorbed gives the total acidity. TPD profiles indicating the quantity of ammonia desorbed from the surface of the catalysts in the temperature range from 50 °C to 700 °C are given in Fig. 6. The striking feature of all these curves is that most of the adsorbed ammonia is desorbed in the lower temperature range i.e. 100 – 250 °C, indicating the presence of only acid sites with moderate strength [31]. The acid sites concentration was calculated from the area under the desorption peak and were found to be in the range 0.30–0.65 mmol/g (table- 3). The acidity of these catalysts may be attributed to the protons associated with the surface – OH groups bonded to Al and P atoms (bronsted acidity) as well as to the incompletely coordinated Al species (Lewis acidity) [32]. Very subtle difference in the acid sites concentration was observed among the four catalysts and the variation of their acidities was in the following increasing order, which is the same as that of their surface area. AlP(KH_2PO_4) >AlP(H_3PO_4) > AlP(K_2HPO_4) >AlP ($K_4P_2O_7$).

The difference in the total acidity of the catalysts may be attributed to the difference in the nature of the degree of different types of coordination of Al. The higher acidity of the catalyst prepared from KH_2PO_4 is thus due to the presence of tetrahedral alumina and the higher concentration of pentacoordinated Al species as well as the associated tetrahedral phosphate groups.

3.7. ^{27}Al and ^{31}P MAS NMR results

In a pursuit to find the relationship between the chemical environment of the Al and P sites in aluminophosphates prepared from various potassium phosphate precursors, and their catalytic activity, all the prepared samples were characterized by recording ^{27}Al and ^{31}P MAS NMR spectra (Fig. 7a and b).

^{27}Al MAS NMR spectra showed 3 different distinct peaks with the chemical shift values in the range 75 to −25 ppm. The chemical shift values representing different types of Al species and their relative percentages are shown in Table 4.

The coordination of Al pertaining to each of these peaks was assigned as per the related literature reported [33–37]. Accordingly, the peak between 65 and 40 ppm represents tetrahedral AlO_4 units (T_d-AlO_4) of alumina. Alumina is obtained from the precipitated aluminum hydroxide along with aluminium phosphate during its preparation. The peak in the range 35 to 25 ppm is due to the tetrahedrally coordinated $Al(OP)_4$ species. The peaks in between 15 and −10 ppm represent penta and hexa coordinated Al sites. A few references [34,38] states that the chemical shift values of Hexa coordination are lower than the pentagonal coordination peaks in aluminophosphates. The composition of these penta and hexa coordinated species is $Al(OP)_x$ (OH)y.

The peak representing T_d-AlO_4 was found to be dominant in all the four AlP catalysts, as observed by the area under the peak. The presence

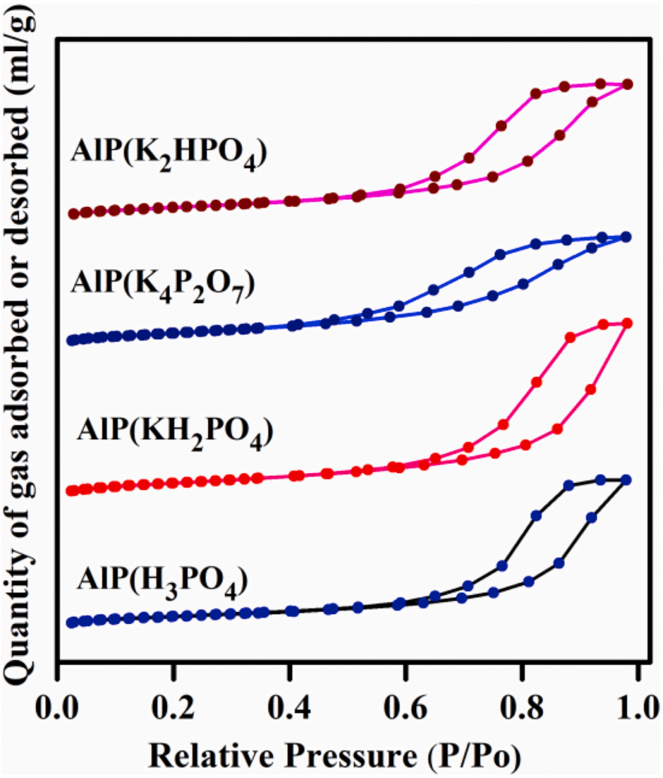


Fig. 5. BJH isotherms for the samples of Ceramic Aluminophosphates prepared from different phosphate precursors.

and coexistence of 3 differently coordinated Al species was further confirmed using MQMAS (3QMAS) NMR studies, the detailed explanation is reported in our earlier work [13]. It is said that alumina (T_d-AlO_4) is present in only tetrahedral coordination [39], however in our samples the addition of hydroxyl ions resulted in the penta and hexa coordinated Al sites which had unbalanced charges and these along with T_d-AlO_4 represent the potential catalytically active sites on the surface of CAmAlPs the materials. These results further confirm that a mixture of alumina and aluminophosphate is formed during precipitation.

T_d-$Al(OP)_4$ is formed by Al which is tetrahedrally coordinated to phosphate. This species is charge neutral and non-acidic. It is found that the catalyst prepared from KH_2PO_4 as phosphate precursor had lowest percentage of these species. This inturn has increased the concentration of pentacoordinated Al species.

Penta coordinated Al species could be in distorted trigonal bipyramidal geometry with D_3h symmetry [40,41]. The axial bonds of pentacoordinated Al species are less stable and hence energetically potential active sites for catalytic activity [42–44]. These Pentacoordinated Al sites were observed in AlP catalysts prepared from H_3PO_4 and KH_2PO_4 as phosphate sources and their percentage was found to be more in the later case (29%) than in the former (20%). The more stable octahedral Al species are formed only in the catalysts prepared from $K_4P_2O_7$ and K_2HPO_4 as phosphate sources with 22 and 14% respectively. Further, is to be noted that NH_3 -TPD studies, as discussed later in the text, also indicated the surface acidity of the catalysts {AlP(H_3PO_4) and AlP (KH_2PO_4)}, associated with pentacoordinated Al species is higher than those {AlP($K_4P_2O_7$) and AlP(K_2HPO_4)} with octahedral species.

^{31}P NMR spectra of all the samples exhibited a broad peak with the chemical shift values in the range −5 to −35 ppm attributed to tetrahedral phosphate species [45]. According to the reported literature [39,46,47] chemical shift values in this range represent three different tetrahedral phosphate species, such as (a) phosphate species attached to AlO_6 (octahedral) units in the range −7.8 to −16.2 ppm (b) phosphate species coordinated to $AlPO_5$(pentagonal) units in the range −8.2 to −15.7 ppm and (c) phosphate groups associated with AlO_4 (tetrahedral) units in the range −11.5–5.9 ppm. All the mentioned chemical shifts are noticed in the ^{31}P NMR spectra of the prepared catalysts, but covered under a broad peak (Fig. 7b). However, due to the poor resolution of the peaks, they were not deconvoluted, as it may lead to wrong interpretation.

The following points may be further be noted from the results presented in Table 4:

a. Aluminium in the catalyst is present in three differently coordinated environments – tetrahedral, pentagonal and octahedral.
b. Tetrahedrally coordinated Al sites are present in all the samples, as AlO_4 and $Al(OP)_4$ units irrespective of the nature of the potassium precursor salt used for their preparation. The relative percentage of AlO_4 and $Al(OP)_4$ units varies with the nature of the precursor.
    1. AlO_4 increases in the order $K_2HPO_4 = H_3PO_4 > KH_2PO_4 > K_4P_2O_7$
    2. $AlOP_4$ increases in the order $K_4P_2O_7 > K_2HPO_4 > H_3PO_4 > KH_2PO_4$
c. The hexa and penta coordinated units have composition Al(OP)x (OH)y. The octahedral units are formed only when $P_2O_7^{4-}$ and HPO_4^{-2}

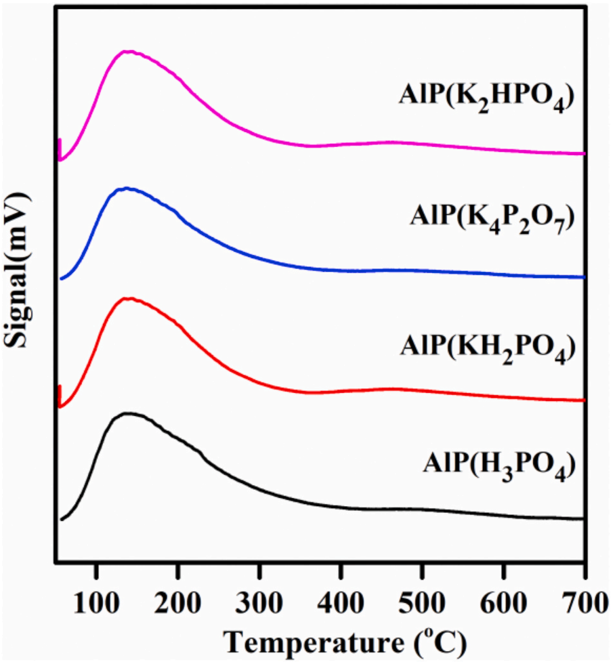


Fig. 6. Ammonia Desorption curves of all the samples prepared from different phosphate precursors.

Table 3
Surface properties of Ceramic amorphous aluminophosphate materials prepared from different phosphate sources.

Sl no	Catalyst (Phosphate source)	Surface area m^2/g	Total pore volume (cc/g)	Average pore diameter (Å)	No of active sites	Acidity mmol/g	Nature
1	AlP(H_3PO_4)	252	0.94	106.5	2.52×10^{13}	0.58	Amorphous
2	AlP(KH_2PO_4)	267	0.96	105.8	2.67×10^{13}	0.63	Amorphous
3	AlP($K_4P_2O_7$)	210	0.70	110.4	2.10×10^{13}	0.38	Amorphous
4	AlP(K_2HPO_4)	237	0.79	108.6	2.37×10^{13}	0.42	Amorphous

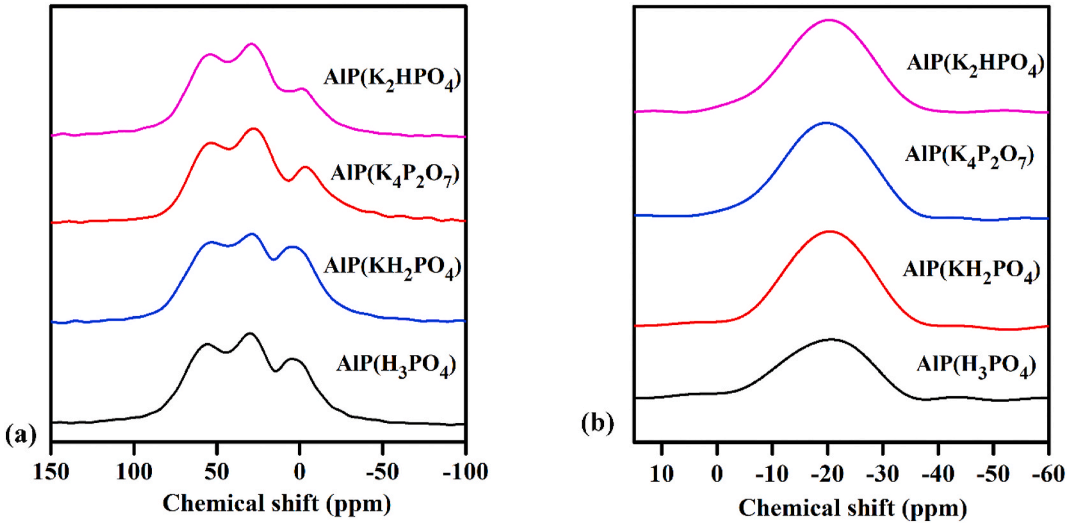


Fig. 7. (a) ^{27}Al NMR and (b) ^{31}P NMR Spectra of aluminophosphates samples prepared from different potassium phosphate precursors.

Table 4
^{27}Al and^{31}P MAS NMR results of catalysts prepared from different phosphate precursors.

Sl NO	Catalyst	^{27}Al NMR								^{31}P NMR	
		T_d-AlO_4		T_d-$Al(OP)_4$		penta coordinated $Al(OP)_x$ $(OH)_y$		Hexa coordinated $Al(OP)_x$ $(OH)_y$		T_d-PO_4	
		∂ iso (ppm)	T_d %	∂ iso (ppm)	T_d %	∂ iso (ppm)	penta %	∂ iso (ppm)	octa %	∂iso (ppm)	T_d % PO_4
1	AlP(H_3PO_4)	58.7	59.5	30.7	20.5	3.2	20.0			−20.68	100
2	AlP(KH_2PO_4)	56.6	54.0	29.8	17.0	3.3	29.0			−20.66	100
3	AlP($K_4P_2O_7$)	56.8	49.6	28.3	28.4			−3.7	22.0	−19.50	100
4	AlP(K_2HPO_4)	57.3	61.5	29.2	24.8			−0.7	14.0	−19.77	100

were used as the precursor salts and pentagonal sites with $H_3PO_4 >$ and $H_2PO_4^{-1}$

d. Phosphorous in the catalyst is only tetrahedrally coordinated possibly with only oxygen atoms which are in turn are coordinated Al sites.
e. TPD-NH_3 surface acidity measurement studies revealed the fact that the catalyst obtained from KH_2PO_4 precursor had higher acidity than the other catalyst, which is attributed to the presence of pentagonal Al species.

Both T_d and pentagonal Al sites in conjunction with each other represent catalytically active sites however an increase in the pentagonal sites contribute to an additional increment to the catalytic activity of CAmAlPs.

3.8. Catalytic activity studies

The catalytic activity of the CAmAlPs prepared in this work was evaluated in an acid-catalyzed reaction i.e. between aniline and dimethyl carbonate, under refluxing conditions. The % conversion of aniline, % yield of Diphenyl urea and the other products formed are presented in Table 5. It is noticed at the outset that all the catalysts showed activity in catalyzing the organic reaction. Further, when the reaction was conducted without any catalyst or a solid base, such as CaO, it did not yield any expected product. The fact that the reaction did occur in the presence of all the CAmAlPs, their acidic nature is confirmed, as determined by NH_3-TPD studies. The % conversions of aniline was almost 100% and the % yield of the expected major product of the reaction i.e., Diphenyl urea (DPU) was in the range of 58–96%. The purity of the product though was found to be good, the % of byproducts formed varied with the type of precursor potassium salt used for the preparation of CAmAlPs catalysts. The difference in the percentage yields of the main, as well as the byproducts further indicated that the concentration and strength and of the surface acidic active sites are different. This difference in the active sites is mainly due to the variation in the precursor potassium salts used in the preparation of the catalytic CAmAlPs.

Table 5
Mole percentage yields and selectivities for condensation reaction between aniline and dimethyl carbonate.

Sl NO	Catalyst	Condensation reaction between Aniline and Diethyl carbonate		
		mol % Aniline conversion	mol % DPU	mol % of other products
1	AlP(H_3PO_4)	100	90	10
2	AlP (KH_2PO_4)	98	96	2
3	AlP ($K_4P_2O_7$)	90	58	32
4	AlP (K_2HPO_4)	100	86	14

The yield of the product has a close relevance with the number of catalytically active acid sites, which in turn related to the surface area of the catalysts, whereas the purity of the product or the formation of byproducts depend on the nature and strength of the acid sites (Table 3). In the present investigation as described under the characterization sections that the surface area and acid sites concentrations of CAmAlPs are in the following increasing order; AlP(KH_2PO_4) >AlP(H_3PO_4) > AlP (K_2HPO_4) >AlP($K_4P_2O_7$), and the catalytic activity also vary in the same order. This order of catalytic activity has a good correlation with the total number of tetrahedral (T_d-AlO_4) and pentagonal Al species. It may be stated that the Brønsted and Lewis acid sites associated with these Al sites are the potential catalytic sites in the prepared CAmAlPs. The catalysts, AlP(KH_2PO_4) and AlP(H_3PO_4) which exhibited higher percentage of these Al sites also showed higher catalytic activity. Further it is also to be noted that as T_d-Al(OP)$_4$ increases the total conversion to DPU decreases. This is due to its charge neutral non-acidic nature. Thus the catalyst AlP(KH_2PO_4) which has less amount of T_d-Al(OP)$_4$ showed higher conversion to DPU. The presence of these T_d-AlO_4, T_d-Al(OP)$_4$ and pentagonal Al sites are confirmed by ^{27}Al MAS-NMR studies.

Sodium and ammonium salts of phosphates and H_3PO_4 as phosphate source in the synthesis of CAmAlPs were studied recently [13] and reported that the catalyst prepared from H_3PO_4 showed better catalytic activity towards the synthesis of DPU, than the ones prepared from sodium ammonium sources of phosphates. In the present studies, where potassium salts are used in the preparation of catalysts, higher yields and selectivity of DPU were noticed. This is attributed to the generation of larger number of active sites due to higher surface areas and pore volumes of the catalysts. Further the catalyst which is prepared from KH_2PO_4 as phosphate source was found to be the best. The higher surface areas and pore volume of the catalyst may be due to the following reasons. The catalysts prepared from sodium sources of phosphates showed the presence of sodium on their surfaces which would block the pores. In the present catalysts where potassium phosphates as sources were devoid of potassium on the surface which has led to the higher surface areas and pore volumes and therefore the higher catalytic activities compared to catalysts where sodium sources used. The higher acidity is due to presence of higher percentage of pentacoordinated Al species. Al NMR studies showed the catalyst prepared from KH_2PO_4 as phosphate source showed highest percentage of pentacoordinated Al sites, which in turn showed higher acidity and hence catalytic activity as compared to sodium sources.

Further the catalyst obtained from $K_4P_2O_7$ as phosphate source, was devoid of pentacoordinated Al sites, showed least catalytic activity similar to catalysts prepared from sodium sources. These comparative studies helped us to prove that the catalysts prepared from KH_2PO_4 as phosphate source was the best catalyst for the preparation of DPU compared to all other sodium, ammonium and potassium sources. The general application of AlP(KH_2PO_4) as a catalyst for the preparation of other substituted DPUs was investigated, by conducting reactions under the same conditions as that between aniline and diethyl carbonate, using differently substituted anilines and diethyl carbonate. The results are presented in Table – 6.

The selected catalyst showed good catalytic activity and selectivity towards the formation of other urea derivatives. In general, it was observed that the presence of electron donating groups on the aromatic ring gave rise to higher yields of the expected product compared to electron withdrawing groups which are present. Presence of electron donating groups on the aromatic ring of aniline makes the nitrogen atom electron rich and can attack partially positive carbonyl carbon in the carbonate readily. Particularly electron donating group at para position give rise to high conversion and selectivity towards Diphenyl Ureas. Presence of electron withdrawing group like –NO_2 on anilines makes N of –NH_2 as slightly electron deficient to attack partially positive carbonyl carbon thereby decreasing the yield of DPU derivative. In addition to these electronic effects, position of substituents on the aromatic ring also has also played a significant role towards the percentage yield of ureas. When compared to reactants with substituents at ortho positions, reactants with substituents at para positions gave higher yield and selectivity towards ureas. Substituents at ortho positions on aromatic rings are sterically repelled by the lone pair of electrons from the nitrogen atom, resulting in a decrease in yield. Substituents at para position experienced lesser steric hindrance compared to the substituents at ortho positions. As a result, the reactants p-toludine, p-chloroaniline, and p-nitroaniline provided the highest yields and selectivities for their respective ureas.

As indicated by PXRD analysis, the prepared catalysts are amorphous and are associated with inherent heterogeneity in composition and structure due to the lack of long range order. In such materials, it is difficult to maintain the same surface properties when prepared at different batches, as their surface properties are sensitive to the method and conditions of synthesis. We have made an attempt to see this effect on the catalytic activity of CAmAlPs. Hence, three sets of the same catalysts were prepared, at different times maintaining the same synthesis conditions every time. We have checked the Catalytic activities of thus prepared materials were determined in the synthesis of DPU. The uncertainties in the percentage yield obtained for each set of catalysts were calculated using the following equations [48]. The results are presented in Table 7. The calculated in the percentage yield were used to evaluate whether the surface properties of the catalysts are reproducible or not.

$$S = \sqrt{\frac{\sum_{i=1}^{N}\left(x_i - \frac{1}{N}\left(\sum_{i=1}^{N} x_i\right)\right)^2}{N-1}}$$

Equation 1: formula to calculate standard deviation

S = standard deviation, x_i = value of the measurement, N = number of degrees of freedom (number of replicate measurements) and $\sum_{i=1}^{N} X_i$. = sum of the degrees of freedom (sum of replicate measurements).

The Confidence interval was calculated using the formula.

$$u = \overline{X} \pm \frac{ts}{\sqrt{N}}$$

Equation 2: formula to calculate uncertainty error

Where μ is the confidence interval, $\overline{x}$ = mean of replicate measurements N= Number of replicate measurements t = value for confidence level probability (at 95% class interval the t value was found to be 4.30) The formulas were reproduced from reference [48] The uncertainties of percentage yields are mentioned in detail in the table no 7.

The uncertainties were high for the catalyst which was prepared by $K_4P_2O_7$ as phosphate source and we cannot say it is highly not a suitable catalyst for the above mentioned reaction. We did not obtain the preferred products due to the difference in selectivity and all along there is a much larger difference in uncertainty compared to others which make it less suitable. Lesser uncertainty results were obtained from the catalysts AlP(H_3PO_4) and (AlP)KH_2PO_4 making them more selective with good yields. These lesser uncertainty values says this catalyst is best suitable for above mentioned reaction. This is also best attributed to beneficial reproducible surface properties compared to the catalysts (AlP)$K_4P_2O_7$ and (AlP)K_2HPO_4.

4. Conclusions

Aluminophosphate samples prepared from different phosphate salts of potassium were found, from ^{27}Al and ^{31}P MAS NMR studies, to be associated with three types i.e. Tetrahedral, pentagonal and octahedral Al sites. The relative concentrations of these sites depend on the type of phosphate salt of potassium. Thus ^{27}Al NMR investigations of CAmAlP supplemented in the correlation of catalytic activity and the nature of coordination of Al species in the catalysts. The materials were found to be good catalysts in the reaction between aniline (and its derivatives) and dimethyl carbonate in the synthesis of diphenyl urea, with up to 96% yield of the expected product. Pentagonal Al sites in conjunction with T_d sites showed a beneficial effect on catalytic activity. Catalysts prepared from KH_2PO_4 as phosphate sources showed better catalytic activities compared to other phosphates sources used. The uncertainties in the percentage yield of the product were minimum.

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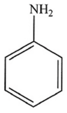
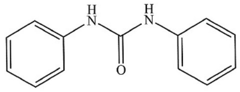
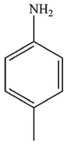
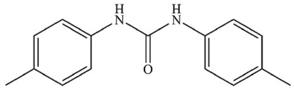
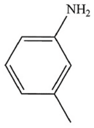
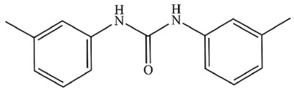
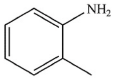
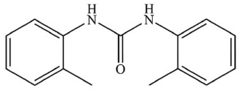
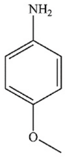
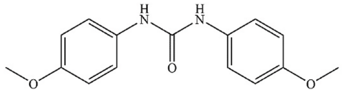
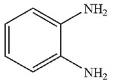
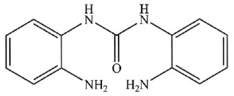
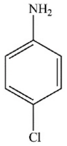
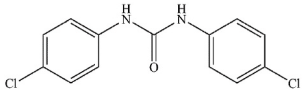
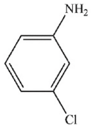
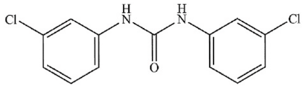
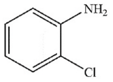
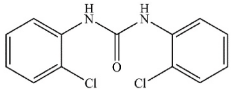
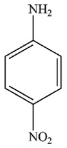
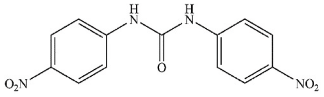
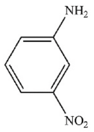
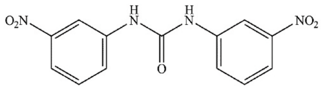
Table 6
Generality studies for Condensation reaction with different anilines using CAmAlPs catalysts prepared using KH2PO4 as phosphate source.

Sl NO	Amines	% of amine conversion	Products (Ureas)	mol % yield of Ureas	mol % of other products
1	 Aniline	98	 1,3-di-phenylurea	96	2
2	 p-Toludine	100	 1,3-di-p-tolylurea	100	0
3	 m-Toludine	88	 1,3-di-m-tolylurea	71	17
4	 o-Toludine	80	 1,3-di-o-tolylurea	57	23
5	 p-Anisidine	91	 1,3-bis(4-methoxyphenyl)urea	72	19
6	 o-Phenylenediamine	79	 1,3-bis(2-aminophenyl)urea	64	15
7	 p-Chloroaniline	92	 1,3-bis(4-chlorophenyl)urea	82	10
8	 m-Chloroaniline	73	 1,3-bis(3-chlorophenyl)urea	62	11
9	 o-Chloroaniline	62	 1,3-bis(2-chlorophenyl)urea	56	8
10	 p-Nitroaniline	70	 1,3-bis(4-nitrophenyl)urea	54	16
11	 m-Nitroaniline	81	 1,3-bis(3-nitrophenyl)urea	68	13

(*continued on next page*)

Table 6 (*continued*)

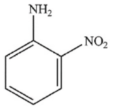
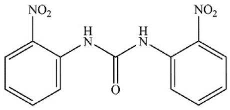
Sl NO	Amines	% of amine conversion	Products (Ureas)	mol % yield of Ureas	mol % of other products
12	 o-Nitroaniline	58	 1,3-bis(2-nitrophenyl)urea	42	16

Table 7
The estimated uncertainties in the product yield from three different sets of each catalyst prepared in the Condensation reaction between aniline and diethyl carbonate. (A,B and C represent three different sets of catalysts prepared and the respective mol % yields of the product DPU obtained).

Sl. No	Catalysts	A	B	C	Avg mol % DPU	Uncertainty estimate
1	AlP(H_3PO_4)	90	90	89	89.66	89.66 ± 1.43
2	AlP (KH_2PO_4)	96	97	96	96.33	96.33 ± 1.43
3	AlP($K_4P_2O_7$)	58	55	64	58.66	59 ± 11.37
4	AlP (K_2HPO_4)	86	84	83	84.33	84.33 ± 3.79

agencies in the public, commercial, or not-for-profit sectors.

Credit author statement

Mr Harish N : Conceptualization, Methodology, Software, Investigation, writing- original draft preparation, Reviewing and editing , formal analysis.

Dr. H. Kathyayini : Visualization, Resources, supervision.

Dr. Bindhu Baby : software, Data Curation and Validation.

Dr.N.Nagaraju : Supervision, project administration, Reviewing and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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