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Article

Amorphous metal-aluminophosphate catalysts for aldol condensation of *n*-heptanal and benzaldehyde to jasminaldehyde

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ABSTRACT

Amorphous aluminophosphate (AIP) and metal-aluminophosphates (MAIPs, where M = 2.5 mol% Cu, Zn, Cr, Fe, Ce, or Zr) were prepared by coprecipitation method. Their surface properties and catalytic activity for the synthesis of jasminaldehyde through the aldol condensation of *n*-heptanal and benzaldehyde were investigated. The nitrogen adsorption-desorption isotherms showed that the microporosity exhibited by the aluminophosphate was changed to a mesoporous and macroporous structure which depended on the metal incorporated, with a concomitant change in the surface area. Temperature-programmed desorption of NH₃ and CO₂ revealed that the materials possessed both acidic and basic sites. The acidic strength of the material was either increased or decreased depending on the nature of the metal. The basicity was increased compared to AIP. All the materials were X-ray amorphous and powder X-ray diffraction studies indicated the absence of metal oxide phases. The Fourier transform infrared analysis confirmed the presence of phosphate groups and also the absence of any M-O moieties in the materials. The selected organic reaction occurred only in the presence of the AIP and MAIPs. The selectivity for the jasminaldehyde product was up to 75% with a yield of 65%. The best conversion of *n*-heptanal with a high selectivity to jasminaldehyde was obtained with FeAIP as the catalyst, and this material was characterized to have less weak acid sites and more basic sites.

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1. Introduction

Amorphous aluminophosphate (AIP) and metal-aluminophosphates (MAIPs) have gained significant importance in catalysis owing to their flexible textural properties, surface acidity, and thermal stability [1–3]. The structural and acidic properties of amorphous AIP can be fine-tuned by controlling the preparation conditions and also by adding selected transition metals during the synthesis. The addition of a transition metal during synthesis can lead to the formation of Lewis and Brönsted acid sites along with basic sites [4]. These acidic and basic sites along with redox properties suggest the possibility

to design unique bifunctional catalysts. In recent years, many reports have been published on the catalytic application of amorphous AIP and MAIPs in a wide range of organic transformations including dehydrogenation [5], cracking [6], transesterification [7], and alkylation [8], and as supports for other catalytic systems such as oxides [9].

Jasminaldehyde (α -pentylcinnamaldehyde) is a well-known flavor and fragrance and also an important pharmaceutical intermediate. It is synthesized by the aldol reaction of *n*-heptanal and benzaldehyde catalyzed by sodium or potassium hydroxide in stoichiometric amounts [10]. The reaction is catalyzed by both acids and bases (Scheme 1). The use of a

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Scheme 1. Condensation reaction of *n*-heptanal and benzaldehyde to form jasminaldehyde.

caustic liquid as the catalyst is not eco-friendly due to environmental pollution and also has many other drawbacks such as separation difficulties, corrosion of reactor lining and difficult reagent handling. These drawbacks and difficulties can be overcome by the use of fine-tuned solid catalysts with good efficiency. There have been reports on the use of solid catalysts such as Mg–Al mixed oxide [11], magnesium organo-silicates [12] and silica-alumina [13] for this reaction. Climent et al. [14] reported the superior activity of solid acid molecular sieves in aldol and Knoevenagel condensation reactions, and found that MCM-41 was a better catalyst than microporous aluminosilicates. Sudheesh et al. [15] investigated the application of a biopolymer chitosan as a solid catalyst for the condensation of heptanal and benzaldehyde at 140 °C. Corma's group [16] studied the catalytic activity of various basic solids and compared their activity with that of amorphous AIP and ammonia-treated AIP for the aldol condensation of *n*-heptanal and benzaldehyde. They reported the high activity of amorphous AIP characterized by the presence of weak acidic sites along with very weak basic sites. In their investigation, the catalyst was prepared by the Lindblad method [17] in which ammonium phosphate was used as the phosphorous source instead of phosphoric acid. In this method, the authors generated basic sites on AIP by using ammonia. However, some of the catalytically active acid sites may also be lost. As aldol condensation is catalyzed by both acidic and basic materials, it would be interesting to evaluate the catalytic influence of these sites on aldol condensation, and this was selected for the present study.

In the present work, we prepared AIP and MAIPs using phosphoric acid as a phosphorous source and ammonium hydroxide as precipitating agent. Precipitation was carried at ice temperature to obtain particles with a smaller size and high surface area, by Von Weimarn precipitation under relatively super saturated conditions [18]. These materials were tested for their catalytic activity in the synthesis of jasminaldehyde by the condensation of *n*-heptanal and benzaldehyde under reflux conditions. An attempt was made to evaluate the structure-activity relationship of these catalysts.

2. Experimental

2.1. Material preparation

The pure and metal-loaded AIPs were prepared by an earlier reported co-precipitation method [3] from the corresponding metal salts using 85% of H₃PO₄ as the phosphorous source and 28% ammonia solution as the precipitating agent. All the materials were prepared at ice temperature and with the

dropwise addition of the ammonia solution for 20 min in order to obtain particles with high surface areas. For example, pure AIP was prepared by mixing Al(NO₃)₃·9H₂O and 85% of H₃PO₄ in the desired molar ratio in 500 mL of de-ionized water at ice temperature to get a homogeneous solution. To the above clear solution, 28% liquid ammonia was added dropwise from a burette until the pH reached 7.5. The AIP gel thus obtained was filtered, washed thoroughly with distilled water and dried at 120 °C in an air oven for 10 h. The dried samples were powdered and further calcined at 350 °C for 5 h.

The MAIPs were prepared by mixing Al(NO₃)₃·9H₂O and the metal salt in 500 mL of de-ionized water followed by 85% of H₃PO₄ in the desired molar ratio at ice temperature to get a homogeneous solution. To the above clear solution, 28% liquid ammonia was added dropwise from a burette until the pH reached 7.5. The resulting precipitate was processed in a similar procedure to that used for the AIP preparation. In the preparation of the MAIPs, the metal precursors used were the nitrates of Cu, Zn, Cr, and Fe, and ceric ammonium nitrate and zirconyl oxychloride for Ce and Zr. The phosphorous to total metal molar ratio was kept 1:1 in all the catalysts with 2.5 mol% of the metal.

2.2. Material characterization

N₂ adsorption-desorption isotherms were determined using a Micromeritics Tristar 3000 instrument. In a typical measurement, 0.2 g of the material (40–60 mesh) was degassed at 250 °C for 2 h in N₂ flow. After cooling to room temperature, the catalyst was loaded in the instrument for adsorption study using N₂ as adsorbate. The X-ray diffraction (XRD) patterns of the materials were analyzed using a Rigaku instrument (Japan) with Cu K α radiation. Fourier transform infrared (FT-IR) spectra were recorded using a Thermo-Scientific Nicolet IR-380 instrument and the KBr pellet technique. Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were performed on a pulse Chemisorb instrument (Micromeritics). In a typical experiment, 0.15 g of sieved particles (40–60 mesh) was pretreated at 250 °C for 1 h in He flow, cooled to room temperature and then 5% NH₃/N₂ gas was passed through the bed for 30 min. After purging with He for 10 min to remove excess ammonia present on the surface, NH₃-TPD was performed in the temperature range of 35–800 °C at a heating rate of 10 °C/min. The TCD signals were measured after reaching 100 °C and a waiting time of 15 min to remove physisorbed ammonia. The CO₂-TPD experiments were carried out on the same instrument with a similar procedure as described above using CO₂ as the adsorbate.

2.3. Catalytic activity test

The catalytic condensation of *n*-heptanal and benzaldehyde was performed in a three necked round bottom (RB) flask. A reflux condenser was fitted to one of the necks and the other two were used for purging with inert gas and sampling. Calculated amounts of *n*-heptanal, benzaldehyde and the catalyst were placed in the RB flask, purged with N₂ and heated in an oil bath at a predetermined temperature. The reaction mixture was agitated using a magnetic stirrer. After a fixed time, the reaction mixture was cooled, ethanol added and the catalyst was separated by filtration. The reaction mixture was analyzed using a Thermo-Scientific GC (Chemito 8610) with a 5% SE-30 packed column of length 8 ft (240 cm) and diameter of 1–8 inch (2.5–20 cm). The reaction products were also analyzed using GC-MS.

3. Results and discussion

3.1. Surface and bulk properties

3.1.1. Surface area and porosity

The surface areas of the samples determined by the BET method are given in Table 1. All the materials were found to possess a high surface area in the range from 152 to 188 m²/g. While there was not much change in the surface area with divalent Cu- and ZnAIPs, a substantial decrease was observed with the trivalent and tetravalent metal-loaded samples except for CrAIP. A substantial decline in the surface area was observed in the case of FeAIP and ZrAIP. From Table 1, it can be noted that the average pore diameter and total pore volume were increased significantly with hetero-metal incorporation in the AIP. This indicated a change in the type of pores from micropores to meso- and to macropores in some cases. An interesting observation was that due to metal loading of the pure AIP, the total pore volume was increased from 0.5 to a maximum of 1.05 ml/g. The maximum pore volume and pore diameter were achieved with the FeAIP and ZrAIP samples. In Fig. 1, the pore volume versus pore diameter is plotted for pure AIP, and all the MAIPs. In AIP, CuAIP, and ZnAIP, the pore size distributions (PSDs) were comparatively narrow with a mesoporous structure while in the case of CrAIP, FeAIP, CeAIP, and ZrAIP, significant amounts of macropores were also present along with the mesopores.

Table 1
MAIPs and their surface and acidic-basic properties.

Sample	Metal content* (wt%)	Surface area (m ² /g)	Pore volume (ml/g)	Pore diameter (nm)	Total acidity (mmol/g)	Total basicity (10 ⁻⁶ mmol/g)
AIP	—	181	0.50	10.9	0.101	2.6
CuAIP	1.93	188	0.74	15.5	0.117	9.6
ZnAIP	2.32	177	0.68	14.8	0.107	9
CrAIP	2.18	181	0.90	19.6	0.124	30
FeAIP	2.15	153	1.03	26.4	0.043	13
CeAIP	1.96	172	0.85	19.5	0.055	29
ZrAIP	2.25	152	1.05	27.1	0.053	55

* Analyzed by ICP-AES.

Fig. 1. Pore size distributions of AIP and MAIPs.

AIP, CuAIP, and ZnAIP exhibited Type V isotherms and H4 hysteresis loops with limiting adsorption. The CrAIP, FeAIP, CeAIP, and ZrAIP exhibited Type V isotherms with H3 type hysteresis loop which did not exhibit any limiting adsorption at high p/p_0 values (Fig. 2). The hysteresis can be attributed to capillary condensation taking place in a narrow range of tubu-

Fig. 2. N₂ adsorption-desorption isotherms of AIP and MAIPs.

lar pores, confirming the large number of pores [19]. The H4 type hysteresis isotherm of AIP, CuAIP, and ZnAIP revealed the presence of more microporous structure with very narrow slit-like pores, which is complimentary to the surface area results. The H4 type hysteresis in the high valent MAIPs revealed widened pores with aggregates of plate-like particles. The comparatively low pressure hysteresis loops in the former case also pointed to a dominant amount of micropores. In the metal-loaded samples, the relative pressure at which hysteresis was observed was shifted to higher p/p_0 when compared to AIP.

3.1.2. Powder XRD results

XRD patterns of AIP and MAIPs catalysts are shown in Fig. 3. Amorphous AIP is characterized by a broad peak at $2\theta = 20^\circ$ – 40° , which indicates the tetrahedral structure [20]. All the calcined materials were found to be amorphous and showed a similar pattern with a broad peak at $2\theta = 25^\circ$. The intensity of this peak was reduced with metal loading and further broadening of the peak was observed, indicating a decrease in particle size. The amorphous nature persisted even after high temperature drying which was shown by the XRD figures of high temperature-dried (850 °C) samples that showed no metal oxide peaks.

3.1.3. FT-IR results

The FT-IR spectra of AIP and MAIPs are shown in Fig. 4. All the phosphates showed a nearly similar spectrum in the OH stretching vibration region (3600–3000 cm^{-1}) with a broad band centered at 3500 cm^{-1} , which was attributed to surface hydroxyl groups associated with the metal, aluminum, and phosphorous atoms [21]. The weak absorption bands around 1640 cm^{-1} indicated the presence of adsorbed water molecules. All the samples exhibited the characteristic absorption peaks of the asymmetric vibrations of phosphate in the range of 1100–1140 cm^{-1} . The IR spectra also exhibited shoulder peaks at 725 and 507 cm^{-1} which were respectively assigned to the symmetric stretching mode of P–O–P and bending mode of O–P–O bonds [22].

Fig. 3. XRD patterns of AIP and MAIPs.

Fig. 4. FT-IR spectra of AIP and MAIPs.

3.1.4. NH_3 -TPD results

The acidic properties of the materials were evaluated by NH_3 -TPD studies. It was found that the acidity depended on the type of metals incorporated in the AIP (Fig. 5 and Table 1). While the acidity of CuAIP, ZnAIP, and CrAIP were higher than that of the pure AIP, the acidity of FeAIP, CeAIP, and ZrAIP were lower. The number of acidic sites in the divalent MAIPs was higher than in the trivalent and tetravalent MAIPs. The higher acidity of CuAIP and ZnAIP may be due to the formation of more Brönsted acidic sites. The anion vacancies formed by the substitution of trivalent Al or P by the divalent metals may lead to the abstraction of proton during the sol-gel transition, which in turn may result in the Brönsted acid sites. The CuAIP material was slightly more acidic than ZnAIP, and CuAIP was the most acidic catalyst of all the MAIPs in this work. The lower acidity of trivalent CrAIP and FeAIP may be due to maintaining electro-neutrality by the substitution of Al^{3+} or by the formation of fewer Brönsted acidic sites due to the substitution of the P^{5+} . FeAIP was less acidic than CrAIP, which may be due to the suc-

Fig. 5. NH_3 -TPD profiles of AIP and MAIPs.

successful incorporation of Fe into the AIP while the increased acidity of the latter was due to the existence of unsubstituted Cr^{3+} and formation of Cr^{6+} by oxidation during calcination of the precipitate. This can also be explained in terms of the difficulty of Cr to occupy the tetrahedral structure. The number of weak acidic sites further decreased in the tetravalent MAIPs, CeAIP and ZrAIP, which may be due to fewer Brönsted sites created due to decreased anion vacancies. On the substitution of Al by the tetravalent metals Ce and Zr, the excess positive charge may lead to the formation of weak Lewis acidic sites rather than strong Brönsted acid sites. The order of acidity of the MAIPs was $\text{CrAIP} > \text{CuAIP} > \text{ZnAIP} > \text{AIP} > \text{FeAIP} = \text{CeAIP} = \text{ZrAIP}$.

3.1.5. CO_2 -TPD results

The CO_2 -TPD studies revealed the formation of weak and medium strength basic sites, and that the basicity of all the MAIPs was stronger than pure AIP irrespective of the valence of the metal (Fig. 6 and Table 1). In CrAIP, some strong basic sites were also formed. The total basicity of AIP, CuAIP, and ZnAIP were lower than that of CrAIP, FeAIP, CeAIP, and ZrAIP. The order of basicity was $\text{ZrAIP} > \text{CeAIP} > \text{FeAIP} > \text{CrAIP} > \text{ZnAIP} = \text{CuAIP} > \text{AIP}$.

3.2. Catalytic activity studies

The catalytic activity of the AIP and MAIPs was investigated for the synthesis of jasminaldehyde through the condensation of *n*-heptanal with benzaldehyde (Table 2). All the catalysts exhibited activity with more than 30% jasminaldehyde selectivity and 20% *n*-heptanal conversion. The byproduct formed was 2-*n*-pentyl-2-*n*-nonenal, which was formed by the self condensation of *n*-heptanal. The selectivity towards jasminaldehyde as well as the *n*-heptanal conversion gradually increased with reaction time and doubled from 2 to 4 h. A higher (75%) *n*-heptanal conversion was achieved using 2.5% FeAIP. The surface area and porosity of the MAIPs did not have any direct correlation with the catalytic performance since all the materials prepared in this work have high surface area and

Table 2

Catalytic performance in the condensation of heptanal with benzaldehyde to jasminaldehyde (JA).

Catalyst	2-h reaction			4-h reaction		
	<i>n</i> -Heptanal conversion (%)	Selectivity (%)		<i>n</i> -Heptanal conversion (%)	Selectivity (%)	
		PNA ^a	JA		PNA ^a	JA
AIP	41	40	60	46	45	55
CuAIP	31	54	46	50	59	41
ZnAIP	35	61	39	52	64	36
CrAIP	31	50	50	39	47	53
FeAIP	59	66	34	75	29	71
CeAIP	47	54	46	65	37	63
ZrAIP	51	60	40	67	35	65

Reaction conditions: heptanal to benzaldehyde molar ratio = 1:5, 140 °C, catalyst 10 wt%, atmospheric pressure.

^a 2-*n*-pentyl 2-*n*-nonenaldehyde.

porosity. The trend in catalytic activity was explained based on the change in the strength and concentration of acid/base sites as result of the incorporating metals into AIP.

With the incorporation of the divalent metals Cu and Zn, the activity was increased slightly but the selectivity towards jasminaldehyde decreased. The higher conversion may be due to the created basic sites and the lower selectivity due to the increased acidity. Of the trivalent MAIPs, CrAIP which was a higher acidity than AIP gave the lowest heptanal conversion and selectivity to jasminaldehyde. Interestingly, a very high conversion of heptanal and selectivity to jasminaldehyde were obtained with FeAIP, CeAIP, and ZrAIP, in which acidity was significantly decreased and they possessed a higher basicity than pure AIP. Thus FeAIP in which the acidity was decreased significantly and with more basic sites was the highest heptanal conversion at 4 h reaction time with the highest selectivity to jasminaldehyde. In general, the MAIPs with more weak acidic sites than AIP gave an inferior catalytic performance in aldol condensation and those with less acidity than AIP gave a superior performance.

The performance with respect to both the activity and selectivity was improved by the loading of Fe, Ce, and Zr metals in the AIP. The basic sites are believed to help to abstract the proton from *n*-heptanal to form the corresponding enolate ion and the acidic sites to activate the benzaldehyde which does not have a α -hydrogen atom. The carbonyl group of activated benzaldehyde is then attacked by the enolate ions to form the condensation products [11]. Corma's group [16] also reported the importance of the tuned acidic-basic sites of amorphous AIP. The authors have tried to boost the basic strength of AIP by the modification of the surface by ammonia treatment, and found that increased basic sites did not favor the aldol condensation, but rather that an optimized acidity was required for a high conversion of heptanal and benzaldehyde and higher selectivity to jasminaldehyde. From the above observations, it was clear that the superior activity and selectivity with FeAIP as catalyst was due to the optimum level of weak acidic and basic sites, which supports the combined acid-base mechanism. Further optimization of the reaction conditions were carried out using this catalyst.

Fig. 6. CO_2 -TPD profiles of AIP and MAIPs.

Table 3

Effect of FeAlP catalyst amount on the performance.

$m(\text{catalyst})/m(\text{heptanal})$ (%)	Heptanal conversion (%)	JA selectivity (%)
0	4	23
5	36	45
10	75	71
15	80	60
20	88	49

FeAlP as catalyst, heptanal to benzaldehyde molar ratio 1:5, 140 °C, 4 h.

3.2.1. Effect of the catalyst amount

The effect of catalyst amount on the conversion of *n*-heptanal and selectivity to jasminaldehyde was studied by varying the amount of FeAlP catalyst from 5% to 20% with respect to the amount of *n*-heptanal (Table 3). The maximum selectivity of 71% with a conversion of 75% was observed using 10% catalyst. Further increase in catalyst amount to 20% improved the conversion to 88% but the selectivity to jasminaldehyde decreased to 49%, which is not desirable. The decrease in the selectivity to jasminaldehyde with more catalyst was due to the self condensation of 1-heptanal to 2-pentyl-non-2-enal due to the increase in the number of weak acid sites, which lead to the activation of the carbonyl group of heptanal rather than proton abstraction. The reaction carried out without any catalyst resulted in negligible conversion. Further optimization studies were carried out with 10% FeAlP catalyst as it exhibited high activity.

3.2.2. Effect of reaction temperature

The effect of reaction temperature on the condensation of heptanal and benzaldehyde over FeAlP was investigated by varying the temperature from 80 to 150 °C using the FeAlP catalyst. The heptanal conversion increased from 9.3% to 81% accompanied by an increase in selectivity to jasminaldehyde on increasing the reaction temperature (Table 4). The selectivity towards jasminaldehyde decreased with the increase of temperature beyond 140 °C. However, the tendency to undergo self condensation of heptanol decreased with an increase of reaction temperature up to 140 °C. It was concluded that 140 °C is the optimum temperature with the FeAlP catalyst.

3.2.3. Effect of molar ratio of *n*-heptanal to benzaldehyde

The molar ratio of heptanal to benzaldehyde played an important role in the selectivity of the desired product, jasminaldehyde. The molar ratio did not play a significant role in heptanal conversion (Table 5). The selectivity to jasminalde-

Table 4

Effect of reaction temperature on the condensation of heptanal with benzaldehyde to jasminaldehyde over FeAlP.

Temperature (°C)	Heptanal conversion (%)	JA selectivity (%)
80	9.3	36
100	22	47
120	47	54
140	75	71
150	81	52

Heptanal to benzaldehyde molar ratio 1:5, catalyst 10 wt%, 4 h.

Table 5

Effect of heptanal to benzaldehyde molar ratio on the condensation of heptanal with benzaldehyde to jasminaldehyde over FeAlP.

Heptanal to benzaldehyde molar ratio	JA selectivity (%)
1:1	22
1:2	30
1:3	47
1:4	56
1:5	71
1:7	69
1:10	74

140 °C, catalyst 10 wt%, 4 h.

hyde increased with an increase in the molar ratio of the heptanal-benzaldehyde. As the concentration of 1-heptanal was decreased on increasing the benzaldehyde to 1-heptanal mole ratio, the self-condensation of 1-heptanal seems to be suppressed significantly. A ratio of 1:5 was the best for satisfactory catalyst performance. There was not much increase in the jasminaldehyde selectivity with further increase in the molar ratio after 1:5.

3.2.4. Reusability of the catalyst

The reusability of the FeAlP catalyst was tested by five recycles. It was found that the conversion and selectivity of the catalysts remained almost the same in all experiments. The slight change in activity may be due to physical loss of the catalyst during separation. The catalyst in the reaction mixture after each experiment was separated by filtration and stirred in acetone for 15 min, washed thoroughly to remove the organics and the sample was dried slowly to 250 °C. The observations are given in Fig. 7.

4. Conclusions

Amorphous AlP, and MAIPs of Cu, Zn, Cr, Fe, Ce, and Zr were synthesized by the coprecipitation method without using a surfactant. The samples were characterized for their surface, bulk, and acid-base properties. By incorporating a suitable metal in AlP, the surface area, porosity and acidic-basic proper-

Fig. 7. Reusability of the FeAlP in the aldol condensation of *n*-heptanal with benzaldehyde.

Graphical Abstract

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Amorphous metal-aluminophosphate catalysts for aldol condensation of *n*-heptanal and benzaldehyde to jasminaldehyde

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Amorphous aluminophosphate and metal-aluminophosphates (metal = Cu, Zn, Cr, Fe, Ce, and Zr) were investigated for their surface and bulk properties, and as catalyst for the synthesis of jasminaldehyde through aldol condensation of *n*-heptanal and benzaldehyde without a solvent.

ties were significantly altered. The porosity and acid-base behaviour depended on the type of metals used. These materials were used as catalyst for the synthesis of the industrially important fine chemical jasminaldehyde through the condensation of *n*-heptanal and benzaldehyde. The high catalytic activity of FeAlP was attributed to the cooperative role of optimum amounts of acidic and basic sites of weaker strength. A higher molar ratio of benzaldehyde suppressed the self-condensation of *n*-heptanal, which improved the selectivity to jasminaldehyde. The optimum temperature for high selectivity and conversion was 140 °C. An increase in catalyst amount played an important role in selectivity but not in the conversion of *n*-heptanal.

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