

비정질 인산알루미늄 철의 표면 성질 및 촉매 특성: 함유된 철의 양에 의한 효과

A. V. Vijayasankar, C. U. Aniz[†], and N. Nagaraju*

Department of Chemistry, Catalysis Research Laboratory, St. Joseph's College Research Centre, 36. Lalbagh Road, Shanthi Nagar, Bangalore 560027, India

[†]R & D Division, Sud-Chemie India (P) LTD, Binanipuram, Cochin 683 502, India
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Surface Properties and the Catalytic Activity of Amorphous Iron Aluminophosphates: Effect of Fe Loading

A. V. Vijayasankar, C. U. Aniz[†], and N. Nagaraju*

Department of Chemistry, Catalysis Research Laboratory, St. Joseph's College Research Centre, 36. Lalbagh Road, Shanthi Nagar, Bangalore 560027, India *E-mail: nagarajun@yahoo.co.in

[†]R & D Division, Sud-Chemie India (P) LTD, Binanipuram, Cochin 683 502, India
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요약. 다양한 철 원소의 조성을 갖는 인산알루미늄 철을 합성하여 표면 성질과 벌크 성질을 조사하였다. 벤질 알코올과 디에틸 말론산의 transesterification 반응에 의해 촉매 특성을 결정 하였다. 에틸 벤질 말론산과 디벤질 말론산을 유일한 생성물로 얻었다. 철 성분이 0.025 몰 퍼센트인 FeAIP의 경우에 특이한 촉매 특성과 조직상의 특성이 나타난다. 디에스터의 형성은 중간 정도 크기의 산성 자리에서 이루어진다. 물질 안에 수화된 알루미늄과 polycondensed 인산이 존재할 경우에는 에스터교환 반응에서 인산 알루미늄 철의 촉매 특성이 감소하게 된다.

주제어: 비정질 인산알루미늄, 에스터교환반응, 벤질 말론산, 함유된 철의 양

ABSTRACT. Iron aluminophosphates (FeAIP) with different percentage of iron were synthesized and characterized for their surface and bulk properties. The catalytic activity was determined in the transesterification of diethyl malonate with benzyl alcohol. Benzyl ethylmalonate and dibenzyl malonate were obtained as the only products. FeAIP with 0.025 mole % of iron was found to be distinctly different in its textural and catalytic properties. Formation of diester was found to be favored by the acid sites of intermediate strength. The presence of hydrated alumina and the polycondensed phosphates in the materials reduced the catalytic activity of iron aluminophosphates in transesterification reaction.

Keywords: Amorphous aluminophosphates, Transesterification, Benzyl malonates, Iron loading

INTRODUCTION

Iron compounds catalyse several organic reactions¹ amorphous transition metal aluminophosphates have also been found effective catalysts in several organic transformations.²⁻⁶ Recently we have observed iron aluminophosphate exhibited distinctly different catalytic activity compared to other transition metal phosphates. The catalytic activity, selectivity and yield of the products were found to depend on the method of preparation of the catalysts as well as on the nature of the transition metal. These observations prompted us to further work on iron aluminophosphates to find out the role of iron and phosphate species and also understand the scientific basis for the catalytic activity of these materials in the transesterification reaction between diethyl malonate and benzyl alcohol. To the best of

our knowledge such studies have not been reported in the literature.

EXPERIMENTAL SECTION

Preparation of Catalysts

Aluminophosphate (AIP) and iron phosphate (FeP): Pure Aluminophosphate (AIP) samples with three different mole ratios (Al and P = 0.95:1, 1:1 and 1:0.95) were prepared by co precipitation method. Aluminum nitrate (Al(NO₃)₃·9H₂O) and 85 % of H₃PO₄ were mixed in the desired molar ratio in 500 mL of deionised water and heated to 60 ~ 70°C to get a homogeneous solution. To this hot solution 28% liquor ammonia was added drop wise from a micro burette. Aluminium phosphate gel thus obtained was separated by filtration, washed

and dried at 120 °C in a hot air oven for 12 hours. The solids thus prepared were powdered and further calcined at 550 °C for 5 hours in a muffle furnace. A sample of iron phosphate (FeP) was also prepared by a similar method by taking ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in the place of aluminum nitrate.

Iron aluminophosphates (FeAIP): Iron aluminophosphates with 0.01, 0.025, 0.05 and 0.1 molar concentration of iron were also prepared by co precipitation technique as described above using a mixture of Aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and 85% of H_3PO_4 with Al : P ratio of 0.95 : 1.

Characterization of catalysts

BET specific surface area of the materials was determined using NOVA 1000 Quantachrome high speed gas sorption analyser using liquid nitrogen as the adsorbent. The samples prior to their BET analysis were degassed at 120 °C for 2 hours then the usual adsorption-desorption procedure was followed to obtain the data on specific surface area, pore diameter and pore volume. The PXRD diffraction patterns were obtained with Xpert Pro Philips diffractometer equipped with a Ni filtered $\text{Cu-K}\alpha$ radiation with $\lambda = 1.5418 \text{ \AA}$ using a graphite crystal monochromator in 2θ range $5 \sim 80^\circ$ FTIR spectra were recorded using Nicolet IR 200 instrument by KBr pellet technique. The acid strength of the catalysts was evaluated by Temperature Programmed Desorption of NH_3 gas using Puls Chemisorb 2705 from Micrometrics. SEM studies were carried out in a JEOL JED-2300 analysis station apparatus.

Catalytic activity studies

Transesterification of diethyl malonate with benzyl alcohol was carried out in liquid phase under refluxing conditions. After a predetermined period the reaction mixture was cooled and the solid catalyst was separated by centrifugation. The components in the filtrate were analyzed by gas chromatography using 10% carbowax column and further by GC-MS.

RESULTS AND DISCUSSION

The composition and surface properties of the catalysts are given in *Table 1*. In the case of iron aluminophosphates (FeAIP) the numbers given in the brackets correspond to the mole % of iron in the respective sample.

Surface area

The BET surface area of AIP, iron phosphate (FeP) and FeAIP calcined to 550 °C was in the following increasing order, $\text{FeP} < \text{AIP} < \text{FeAIP}$. An increase in the mole% of Phosphorus in AIP and Fe in FeAIP decreased the surface area of the respective samples. At the outset these changes in surface area qualitatively indicate the effect of phosphorous and iron on the textural properties of AIPs and FeAIPs.

The decrease in surface area with increase in phosphorous content in AIP may be attributed to the formation of poly condensed phosphates,⁷ whereas the decrease in the surface area of FeAIP with increase in iron loading due to the iron pyrophosphate.⁸ It is worth noting that FeAIP samples containing 0.025 mole% of iron exhibited highest surface area. This may be attributed to the reduced possibility of poly condensed phosphates formation due to the utilisation of all the phosphate ions in the formation of FeP and AIP in the presence of phosphate as the limiting reagent.

Total surface acidity (NH_3 -TPD)

Surface acidity of the calcined AIP, FeP and FeAIP in terms of mg of NH_3 /g of catalyst are presented in *Table 1*. The values are calculated from the following standard method. The area of the peak obtained from the graph of temperature Vs desorption of NH_3 gives the amount of ammonia desorbed from each sample. The TPD- NH_3 profile for FeAIP is given in *Fig. 1* The AIP samples showed lower acidity than FeAIP samples. Further among the different AIP samples the one which had lowest mole% of P showed highest surface acidity. In the case of FeAIP samples total acidity increased with an increase in iron

Table 1. Composition & surface properties of catalysts

Abbreviation of the catalyst	Al : P mole ratio	Amount of Fe (mol)	Total acidity ^a	Surface area m^2/g	Average Pore diameter (A°)
AIP-1	0.95 : 1	-	12.0	78.63	54.813
AIP-2	1 : 1	-	11.0	98.37	63.759
AIP-3	1 : 0.95	-	2.2	109.70	57.914
FeP	0 : 1	0.025	3.1	3.2	-
Fe(0.012)AIP	0.95 : 1	0.012	13.2	159.13	189.156
Fe(0.025)AIP	0.95 : 1	0.025	16.3	181.48	79.46
Fe(0.050)AIP	0.95 : 1	0.050	13.4	139.86	98.519
Fe(0.100)AIP	0.95 : 1	0.100	11.5	128.53	59.679

^amg of NH_3 per gm of catalyst.

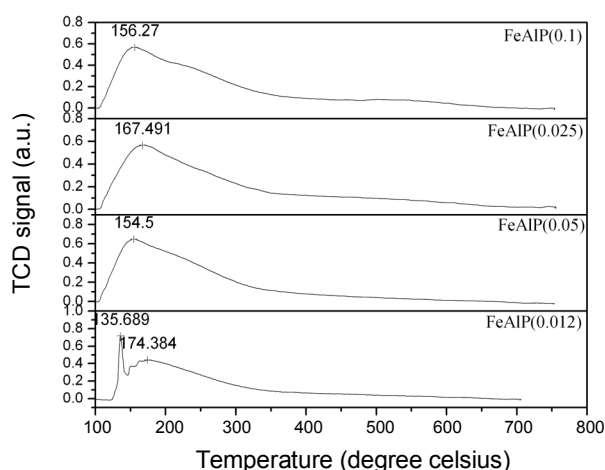


Fig. 1. NH_3 -TPD profile for FeAlP samples.

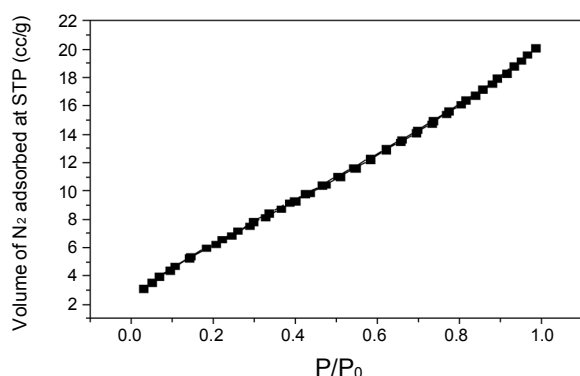


Fig. 2. Adsorption-desorption isotherm of AIP-1.

content from 0.012 to 0.025 mole%. Loading iron beyond 0.025 mole%, the acid strength decreased, this may be attributed to the formation of poly phosphate. It is supported by the fact that this effect was not observed when the iron content is < 0.025 mole%.

Adsorption-desorption isotherms

These studies were useful in identifying the nature of the pore structure of the catalysts. The isotherm of AIP-1 (Fig. 2) was a straight line. This indicated an unclear nature of pores in the material. The adsorption-desorption isotherms of FeAlP samples calcined at 550°C for 5 h are given in Fig. 3. The shapes of these isotherms are of the type-IV and hysteresis loops H1 type, characteristic of mesoporous materials.⁹ It is to be noted that the starting point of the hysteresis loop is displaced towards higher relative pressures on increasing iron loading indicating a decrease in pore volume. FeAlP is thus found to have mesoporous structure. Campello and co-workers have also made similar kind of observations with metal aluminophosphates and attributed this behaviour to continuous restructuring of the porous texture resulting in a variation of

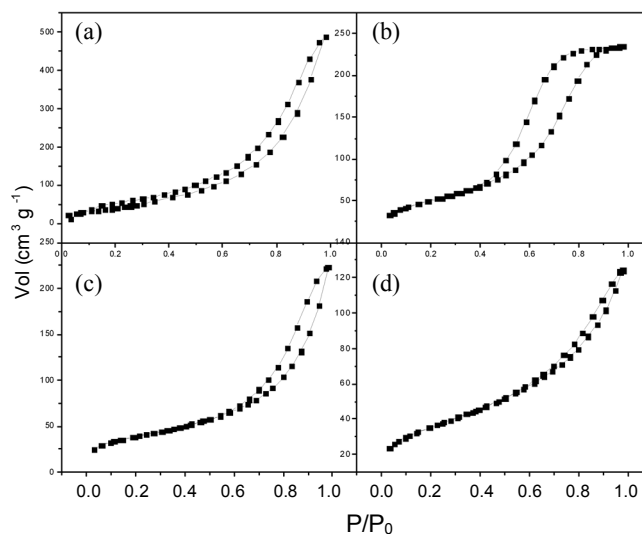


Fig. 3. Adsorption-desorption isotherms of FAIP samples. (a) Fe(0.012)AIP (b) Fe(0.025)AIP (c) Fe(0.050)AIP (d) Fe(0.100)AIP.

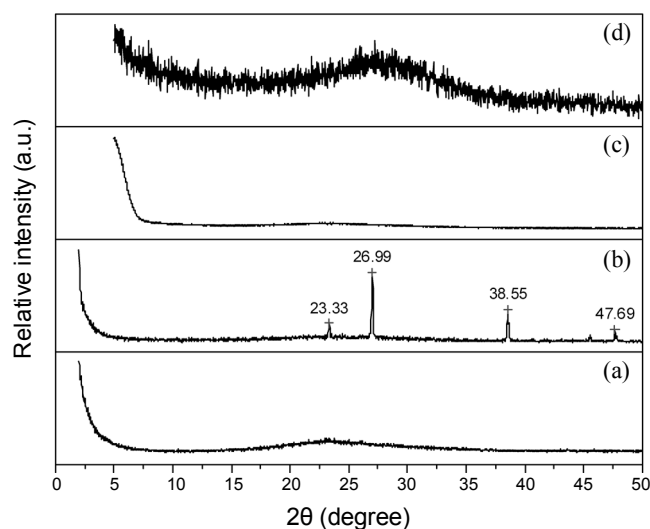


Fig. 4. PXRD patterns of FAIP samples with different iron loading, (a) Fe(0.012)AIP (b) Fe(0.025)AIP (c) Fe(0.050)AIP (d) Fe(0.100)AIP samples calcined at 550°C .

the mesopore diameter and pore volume due to the different iron content in the material.¹⁰

Powder X ray diffraction

The PXRD patterns of both calcined and uncalcined AIP, FeP (not given) and FeAlP samples except the one containing 0.025% of iron exhibited only a broad peak in the 2θ range of $20^\circ \sim 30^\circ$ (Fig. 4). This indicated an amorphous nature and small particle size of the materials. However, FeAlP sample containing 0.025 mole % of iron exhibited sharp diffraction peaks at $2\theta = 23.3, 26.99, 38.5$ corresponding to FePO_4 .¹¹

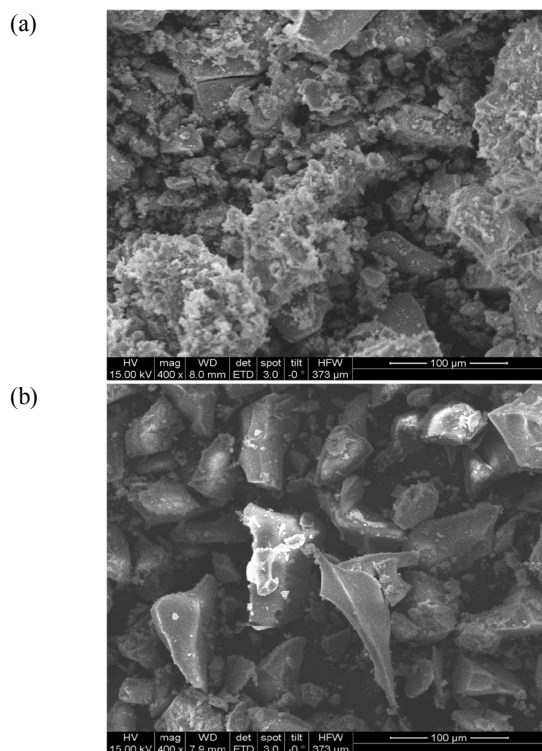


Fig. 5. (a) SEM picture of AIP-1 (b) SEM picture of Fe(0.025)AIP.

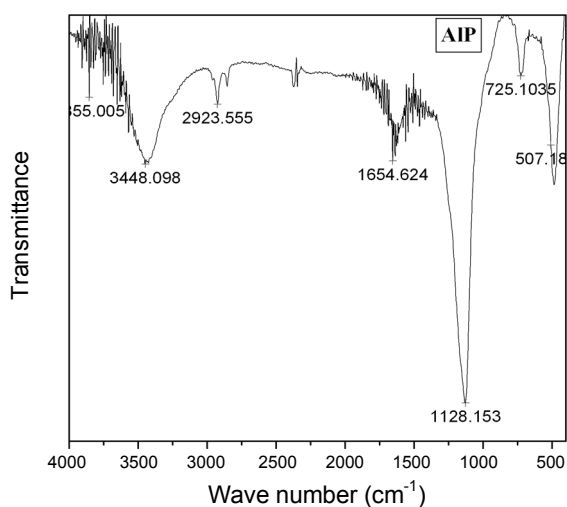


Fig. 6. FTIR spectra of AIP-1 sample.

SEM

SEM observation showed a very widely varied distribution in morphology, texture and particle sizes for all the samples. SEM micrographs of AIP and FeAIP samples are shown in Fig. 5a and 5b respectively.

FTIR

The FTIR absorption spectra of AIP, FeP & FeAIP samples are given in the Fig. 6-8 respectively. It is to be noted that all

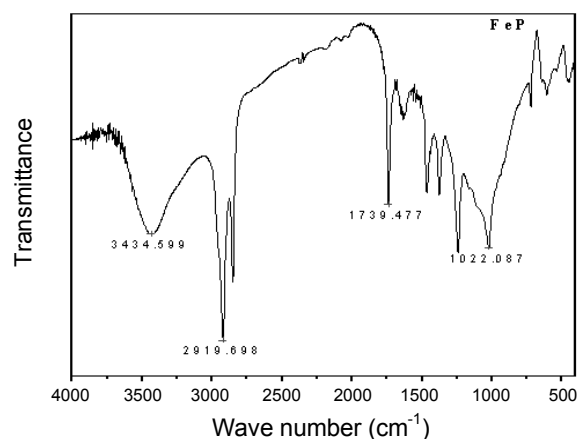


Fig. 7. FTIR spectra of FeP sample.

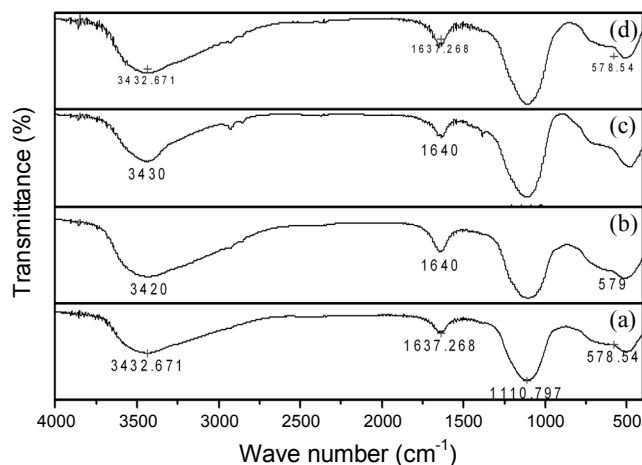


Fig. 8. FTIR spectra of FAIP samples with different iron loading (a) Fe(0.012)AIP (b) Fe(0.025)AIP (c) Fe(0.050)AIP (d) Fe(0.100)AIP samples.

the samples exhibited characteristic absorption peaks due to the asymmetric vibrations of phosphate in the range of $1100 \sim 1128 \text{ cm}^{-1}$. The IR spectra also exhibited shoulder peaks at 725 and 507 cm^{-1} which are respectively assigned to the symmetric stretching mode of P-O-P and bending mode of O-P-O bonds in pyrophosphate. The absorption bands in the range $3430 \sim 3448 \text{ cm}^{-1}$ are due to the surface hydroxyl groups.^{12,13} Thus FTIR analysis indicated the formation of pyrophosphate.

Hence, analysis of the materials for their acidity, crystallinity and adsorption-desorption properties clearly indicated that FeAIP containing 0.025 mole % of Fe had distinctly different textural properties.

NMR

The ^{27}Al -NMR investigations on FeAIP containing 0.025 mole% of iron and calcined at $550 \text{ }^\circ\text{C}$ for 5 h exhibited two signals, a broad peak at 38.1 and short one at -13.5 ppm assigned to four and six coordinated Al species respectively

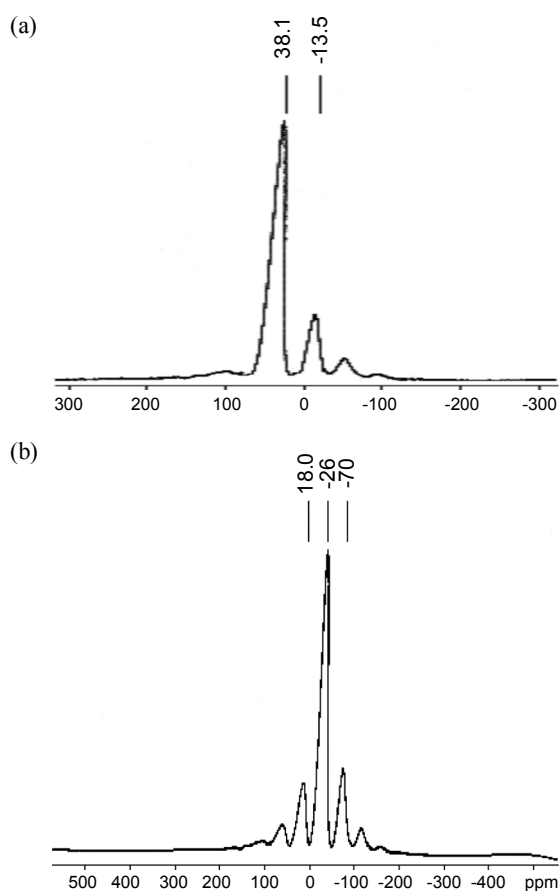


Fig. 9. (a) ^{27}Al -MAS NMR of Fe(0.025)AIP sample. (b) ^{31}P -MAS NMR of Fe(0.025)AIP sample.

(Fig. 9a). This defines the sharing of oxygen atoms with four tetrahedra of phosphorus [$\text{Al}(\text{OP})_4$]. It was also proposed that six coordination of Al species resulted from the coordination with not only PO_4 units but also water molecules.¹⁴⁻¹⁶ The ^{31}P NMR spectra exhibited one broad signal at -26.6 ppm which support the presence of $\text{P}(\text{-OAl})_4$ units with the P-O-Al bonds in a tetrahedral coordination environment (Fig. 9b). A. Sayari *et al.*¹⁷ and Z. Luan *et al.*¹⁸ have assigned the value in the region -19.0 to -30.0 ppm are due to full condensation of phosphorous species. These facts clearly support limited poly condensation of PO_4 . The ^1H NMR showed a single signal at -5 ppm indicating the presence of highly shielded environment of proton.

Catalytic activity

Transesterification of diethyl malonate (DEM) with benzyl alcohol (BA) was found to be effective in the presence of all the metal phosphates used. The major products were found to be only benzylethyl malonate (BEM) and dibenzyl malonates (DBM). However the yield and selectivity of the products were significantly influenced by the composition and the surface acidity of the catalyst.

Table 2. Catalytic activity of the AIP, FeP & FeAIP in transesterification reaction of DEM with BA

Sl. No	Catalyst	Selectivity of BEM (%)	Selectivity of DBM (%)	Total transester yield (%)
1	AIP-1	100	-	32.24
2	AIP-2	100	-	23.34
3	AIP-3	100	-	6.10
4	FeP	100	-	4.00
5	Fe(0.012)AIP	74.1	25.8	32.94
6	Fe(0.025)AIP	49.3	50.6	79.00
7	Fe(0.05)AIP	65.0	34.9	37.20
8	Fe(0.1)AIP	72.7	27.2	29.40

Reaction conditions: amount of catalyst = 0.1g, DEM : BA = 1 : 3, time = 4 h

Aluminium phosphates (with different Al/P ratios) and Iron phosphate exhibited 100% selectivity for BEM (Table 2 entries 1-4). The total surface acidity of these samples was also found to be in the same order. NH_3 -TPD studies on these samples revealed that these materials had only weak acid sites. From this it may be inferred that the selectivity towards the formation of BEM is associated with the weak acid sites.

The lower catalytic activity of the sample with higher concentration of Al (Al/P > 1) may be attributed to the basic $\text{Al}(\text{OH})_3$ that was precipitated along with the AlPO_4 . Low catalytic activity of iron phosphate indicated the presence of such acid sites in very low concentration.

The catalytic activity of FeAIP samples is given in the Table 2 in terms of the selectivity and percentage yield towards transester products. It is interesting to note that the presence of Fe in aluminophosphate resulted in the formation of the diester, dibenzyl malonate (DBM). The optimum amount of Fe for the formation of diester was found to be 0.025 mole % of Fe. Further the catalytic activity was also found to depend on the iron loading. The catalytic activity of various FeAIP's is in the order Fe(0.025)AIP > Fe(0.012)AIP > Fe(0.05)AIP > Fe(0.1)AIP.

It is reported earlier that acidity of catalysts was one of the surface properties that favour the formation of a diester.¹⁹ This aspect is further confirmed by our observation based on the NH_3 -TPD studies that iron containing catalysts possessed higher acidity compared to AIP and FeP. The catalyst, Fe(0.025)AIP which exhibited stronger acidity among the other FeAIP's also exhibited greater diester formation activity. The stronger acidity of this sample may be due to the generation of Lewis acid sites by the Fe species present in association with aluminium species. It is also noteworthy that this sample had acid sites of intermediate strength as evidenced by TPD- NH_3 adsorption studies. This observation further makes it clear that the intermediate strength acid sites are catalytically active in the formation of dibenzyl esters where as the weaker acid sites are

active for the mono benzylester. Thus it may be inferred from these studies that iron loading in iron aluminophosphate influence the surface acidity by altering its textural properties. This aspect may thus be taken as a guiding principle to alter the surface properties of iron aluminophosphate to direct its catalytic activity to increase the selectivity either towards the monoester or diester in the transesterification between DEM and BA.

CONCLUSION

The textural properties of the FeAlP catalyst are influenced by the amount of iron loading. The presence of iron reduces the crystallinity and the particle size of the pure aluminophosphate. The acid strength of the pure aluminophosphate increases with incorporation of iron. The catalytic activity depends on the amount of iron present in the catalyst. The mole ratio of Al:Fe:P is 0.95:0.025:1 in FeAlP is most suitable for the synthesis of mono and dibenzyl substituted malonates. The high surface area, surface acidity and mesoporous nature of Fe-(0.025)AlP were responsible for its better catalytic activity. The presence of acid sites of intermediate strength favored the formation of the dibenzyl substituted esters. The formation of hydrated alumina and polycondensed phosphates in the catalysts reduced the catalytic activity of the material. Thus the amount of iron present in catalyst can be used as a controlling measure for determining the surface properties and catalytic properties of the amorphous iron aluminophosphates.

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