



Short Communication

## Simple Synthesis of Large pore Mesoporous Iron Substituted Aluminophosphate Molecular Sieves

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Available online at: [www.isca.in](http://www.isca.in)

Received 9<sup>th</sup> August 2013, revised 24<sup>th</sup> August 2013, accepted 16<sup>th</sup> September 2013

### Abstract

Iron containing mesoporous aluminophosphate ( $FeAlPO_4$ ) synthesized by simple synthesis using anionic sodium dodecyl sulphate (SDS) as structure directing agent leads to an active, selective and recyclable catalyst for the esterification reaction. This material was characterized by FT-IR,  $N_2$  adsorption desorption, temperature programmed desorption (TPD) and thermal analysis (TG/DTA). The influence of this synthesis procedure makes the material more stable, reusable and it exhibits uniform large pore diameter (27 nm) with the surface area of  $116m^2/g$ . This material exhibits highly acidic nature and hence the activity of the catalyst  $FeAlPO_4$  was analyzed for esterification of acetic acid and n-butanol in liquid phase and the experimental conditions were determined. The same reaction has been done again to find out the reusability of the catalyst and it is found active with high yield of ester.

**Keywords:** Mesoporous  $FeAlPO_4$ , anionic surfactant, thermal stability, large pore diameter, esterification.

### Introduction

The phosphate and alumina based materials have vast catalytic applications<sup>1-4</sup>. Mesoporous aluminophosphates are a class of materials which possess flexibility in its framework and make the heteroatoms to easily substitute in its structure. This amendments leads to the production of acidic and redox sites<sup>5</sup>. The metal substituted mesoporous materials have shown excellent properties as catalysts. Particularly iron containing mesoporous  $AlPO_4$  have shown excellent catalytic activities<sup>6-8</sup>. Hence, in this study, a new approach has been made to synthesize the iron substituted  $AlPO_4$  by using anionic surfactant as organic templating agent. This new synthesis method makes the material more thermally stable and it creates extremely large pores. These pores provide enough space to carry out the reactions in a right way. Moreover, the metal iron in its  $2^+$  and  $3^+$  oxidation states in the  $AlPO_4$  framework makes the material more acidic. The esterification efficiency of this catalyst was analyzed by esterification of acetic acid and n-butanol.

### Material and Methods

**Experimental:** Mesoporous iron substituted aluminophosphate was prepared by using anionic surfactant SDS as template by simple synthesis method with the following gel composition  $0.8Al_2O_3:1P_2O_5:0.2FeO:0.5SDS:300H_2O$ . Aluminium hydroxide (Merck, GR), Phosphoric acid (Nice chemicals, GR) and Iron (III) chloride (Merck, GR) were chosen as the sources for aluminium, phosphorous and iron respectively. In an aqueous solution of SDS, aluminium hydroxide was added and stirred vigorously. To the above

mixture, aqueous solution of phosphoric acid and iron (III) chloride was added and stirred continuously for 2 h to achieve homogeneous mixture. The resulting gel was heated and dried at  $150^\circ C$  in open air. The resulting solid was thoroughly washed with deionised water. The solid was then filtered, dried and calcined at  $600^\circ C$  for 6 h to remove the organic template.

The mesoporous  $FeAlPO_4$  was characterized by using FT-IR, Nitrogen adsorption desorption measurements, Thermal analysis (TG/DTA) measurements and temperature programmed ammonia desorption analysis.

Esterification reaction was performed in a batch reactor equipped with a reflux condenser and a thermometer. The required amount of n-butanol, acetic acid and 0.5g of calcined  $FeAlPO_4$  catalyst was taken in the reactor and stirred for 2 h. The temperature of the reaction mixture was slowly raised up to  $200^\circ C$  and continues refluxing for 6h. The change in mole ratio of alcohol: acid was also studied to attain high percentage of conversion and selectivity. The reaction products were separated from solid  $FeAlPO_4$  catalyst by filtration and the product was analyzed by gas chromatography (Chemito 1000).

### Results and Discussion

The FT-IR spectrum of calcined mesoporous  $FeAlPO_4$  confirms the complete removal of the surfactant from the material and stability of the material after calcination. The strong band at  $3,464\text{ cm}^{-1}$  is assigned to the hydroxyl group (O-H) vibration of  $H_2O$  molecules and C-H stretching bands at  $2900 - 2800\text{ cm}^{-1}$  in addition to C-H deformation bands around  $1460\text{ cm}^{-1}$  are absent after calcination<sup>9</sup>. The strong band at  $1142\text{ cm}^{-1}$  and bending

mode near  $465\text{cm}^{-1}$  are attributed to the symmetric stretching and bending mode of  $\text{PO}_4^{3-}$ . Thus, it is confirmed from the spectra that there is no collapse in the tetrahedral framework of  $\text{FeAlPO}_4$  after calcination.

Nitrogen adsorption-desorption measurements of  $\text{FeAlPO}_4$  are shown in figure-1. The BET surface area and pore diameter of the  $\text{FeAlPO}_4$  is found to be as  $106\text{m}^2/\text{g}$  and 27 nm. The enhancement in the pore diameter of the material was achieved by the new synthesis method and isomorphous substitution of Fe into the framework of  $\text{AlPO}_4$ . This is attributed to the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations which has larger ionic radii than  $\text{Al}^{3+}$ .

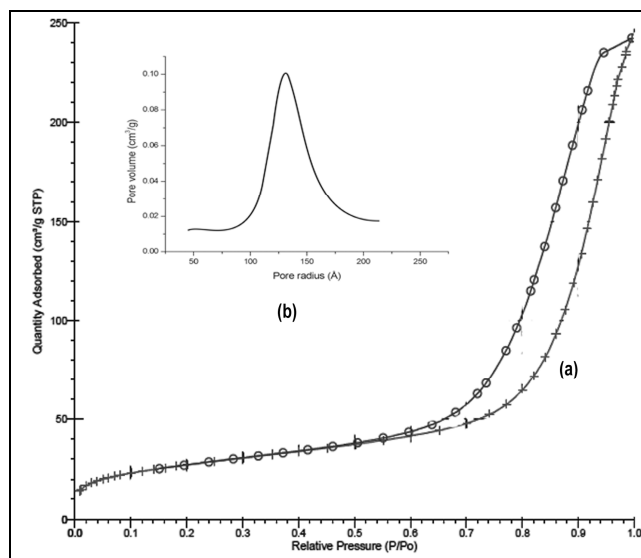


Figure-1

(a)  $\text{N}_2$  adsorption – desorption isotherm of calcined  $\text{FeAlPO}_4$   
(b) Pore size distribution of mesoporous  $\text{FeAlPO}_4$

The thermogravimetric analysis curves of as-synthesized  $\text{FeAlPO}_4$  sample shows mainly three weight loss regions. The initial weight loss between  $90 - 150^\circ\text{C}$  owing to the loss of water physisorbed on the surface of the material. The corresponding second weight loss around  $300^\circ\text{C}$  may be ascribed to the entire decomposition of the anionic template inside the framework. The gradual weight loss between  $500$  and  $600^\circ\text{C}$  is related to loss of water molecules due to the condensation of  $\text{Fe-OH}$ ,  $\text{P-OH}$ ,  $\text{Al-OH}$  groups in the framework<sup>10</sup>. There are no weight losses with the further increase of temperature and the material remains stable up to  $1000^\circ\text{C}$ .

The acidity of  $\text{FeAlPO}_4$  sample was investigated by temperature-programmed ammonia desorption experiment ( $\text{NH}_3$ -TPD) (figure-2). The information on the acid strength distribution in  $\text{FeAlPO}_4$  system can be obtained from TPD spectra. In the TPD curve of mesoporous  $\text{FeAlPO}_4$ , the desorption of ammonia distributes at two different types of temperature. The desorption at  $150^\circ\text{C}$  to  $170^\circ\text{C}$  reveals the presence of medium acid sites (Lewis acid sites  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ) and another desorption around  $250-300^\circ\text{C}$  proved the presence of

strong bronsted acid sites because of the substitution of  $\text{Fe}^{2+}$  in the framework of  $\text{AlPO}_4$  system<sup>11</sup>.

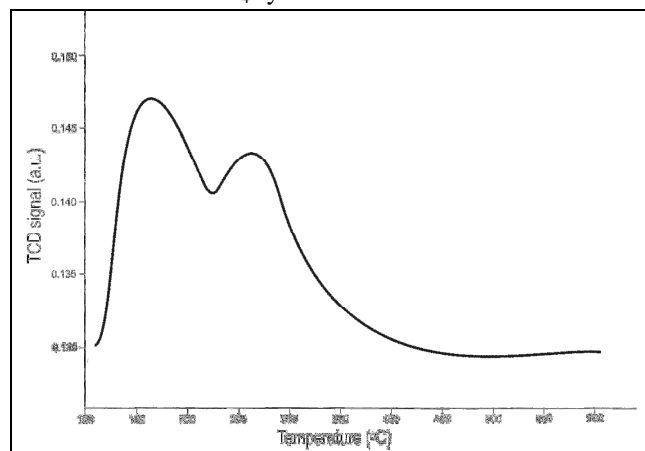


Figure-2

Temperature programmed desorption ( $\text{NH}_3$ -TPD) of calcined  $\text{FeAlPO}_4$

The efficiency of the catalyst was investigated by esterification of acetic acid with n-butanol. Table-1 shows the n-butyl acetate conversion and selectivity percentage of the reaction. The activity of the catalyst ( $\text{FeAlPO}_4$ ) almost remains the same after regeneration. It is shown in table-1 (entry 4)

Table-1

Effect on esterification of n-butanol and acetic acid

S.No	Esterification of n-butanol and acetic acid using $\text{FeAlPO}_4$		
	Mole ratio (acid:alcohol)	Conversion of n-butyl alcohol (%)	Product selectivity of n-butyl acetate (%)
1	1:1	57	97.5
2	2:1	79	99.3
3	3:1	92	99.5
4	3:1	91.2	99.2

Temperature= $200^\circ\text{C}$ , Time=3h, Catalysts dosage=0.5g

## Conclusion

In conclusion, mesoporous  $\text{FeAlPO}_4$  with high thermal stability and large pore diameter was synthesized successfully by simple method. The surface acidity and uniform large pore size distribution of the material enhances the esterification reaction of alcohol and acid. The reusability of the catalyst makes an additional advantage in the reaction side.

## Acknowledgement

The authors are thankful to IIT – Madras and IIT-Bombay for BET surface area analysis, TPD analysis and TG/DTA analysis.

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