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Synthesis of Hierarchical Mesoporous KAlPO for Benzene Hydroxylation

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***Abstract*—** An amorphous hierarchical mesoporous KAlPO material was synthesized by a simple method. This compound showed catalytic activity for benzene (48% conversion) to phenol (100% selectivity) reaction.

***Keywords*—** Catalysis, Mesoporous, Hydroxylation and Phenol

I. INTRODUCTION

Meso-structured materials of aluminophosphates alumina-silica and aluminosilicates, transition metal oxides materials have many applications in catalysis which are generally made-up using surfactant micelles in solvent media [1-5]. Among these aluminophosphate materials have a mesoporous aluminophosphates and metal substituted aluminophosphates were observed to exhibit inferior thermal stability and porosity compared to mesoporous silica, which limits their applications for catalysis and adsorption. Huge range of possible applications in catalysis and adsorption, due to which they have attained a great attention for their synthesis [6,7]. The relative concentration of P and Al in these materials influences the creation of acid sites, mesoporosity and thermal stability [8]. The Several studies came in to light to solve this problem and the synthesis of stable mesoporous aluminophosphates have been effectively synthesized under various conditions [9-13]. Most these studies use costly organic templates and surfactants such as long chain cationic surfactant [11[a]] alky aminetemplate[11], biorganic additives[12,14] and black copolymer[13].

Hierarchical porous materials are exhibits various greater adsorption and catalytic applications [15] properties due to the presence of different range of pores and their inner-connectivity suitable for free convenience of the molecules to the active sites and for the facile transmission of the product molecules within the pores of the materials.

II. RELATED WORK

Hierarchically AlPO materials were synthesized by using bulky organo-silane/small amines [16]. But, most of the syntheses methods are involve multiple steps and time consuming. Hence, the synthesis of hierarchically porous KAlPO has been attempted by adopting a simple method using simple organic template and the material is exposed for benzene hydroxylation reaction.

Phenol is one of the significant chemicals required for the as intermediate for the production of various pharmaceutical and drugs applications. Industrially most of phenol is being produced using multi steps process [17]. However the yield of phenol obtained in this process is very low due to the formation of the process are more energy consuming and several side products. Various environmental problems also involved due to the corrosive nature of H_2SO_4 used in the said process. One step synthesis of phenol from benzene is an interest challenges in catalysis [18]. Various oxidizing agents are used in form of gases combination for hydroxylation of benzene reaction [19-24]. But have some major problem are observed like deactivation of catalyst and low selectivity of phenol [25]. Thus the face up to in catalyst development lies in controlling the reaction at the phenol formation level. Metal alumino phosphates (MeAlPO) having reasonable acidity have been tried to increase the selectivity of phenol through control the reactivity at the phenol formation stage, However this has also resulted in lower conversion levels of benzene. Previously, the various Metal aluminophosphate catalysts are reported to give the low benzene conversion in presence of oxidants like molecular H_2O_2, O_2, and N_2O (Table 1). Herein we synthesized hierarchical mesoporous KAlPO which act as an efficient catalyst to give as high as 100% phenol selectivity at 48% benzene conversion.

III. METHODOLOGY

Material synthesis was similar like our previous reports[26], Here we made the Potassium AlPO, Mesoporous KAlPO materials were synthesized by mixing of 6 g of aluminum iso-propaoxide, 5 g of tertamethyl ammoniumhydroxide pentahydrate 25 wt% in methanol, 4.2 g of ammonium dihydrophosphate, 5 g of TPABr and 0.09 g of potassium chloride. Grinding for 10 min the material turned to the form of wet paste. The resultant paste is heated in an oven at 150 ℃ for 24 h and calcined at 500 ℃ for 5 h. which is named as KAlPO.

IV. RESULTS AND DISCUSSION

K, Al, P and O are present in the synthesized sample was confirmed from EDX analysis (Figure 1). The SEM images (Figure 2a) of the material indicate the layered like structure, while the TEM picture (Figure 2c) reveal that structure with regularly distributed pores. The materials after the reaction also exhibited similar textural properties (Figure 2b and d). The BET measurements of the sample certainly confirmed pore volume of 0.59 cm^3/g and along with the surface area of 271 m^2/g (Table 2). Low-angle XRD patterns of the KAlPO sample (Figure 3) disclose the presence of larger meso-porosity in the synthesized material [27]. Porosity of sample was measured by N_2 relative pressure of 0.01 indicates (Figure 4a) the satisfying of the micropores that is commonly observed for larger mesopores.

The isotherm shows the occurrence of well-defined capillary condensation at relative pressure (P/Po) of 0.01–1.0. The BJH pore size distribution curve (Figure 4b) discloses the presence of micro as well as mesopores with various pore diameters. The data shown in Table 2 tells that greater part of the pore volume (~97%) is due to the mesopores with the corresponding meso pore volume and mesopore surface area of 0.575 cm^3/g and 222.8 m^2/g respectively. Major population of pores having the diameter of 10-50 nm (Figure 4b), detailed distribution of the pores (Table 2) indicates the presence of pores with wide range of pore diameters from <2nm to >50nm that revealing the hierarchical nature of the mesopores. In synthesis process TPABr existed aggregated micelles, after calcinations aggregated TPABr created different pore size range. Wide angle XRD patterns (Figure 5) of the sample reveals that the material is amorphous in nature. The sample also exhibited acidity measured by TPD (Figure 6), where, two NH_3 desorption peaks; one broad peak centered at 150 ℃ and the other around 400 ℃ representing presence of both weak and strong acid sites, were observed.

The KAlPO material is anticipated to exhibit catalytic activity by grace of its hierarchical mesoporosity, strong acidity and high surface area which is explored for the selective hydroxylation of benzene in the present study. The reaction products obtained 100% selectivity to phenol at as high as 48% conversion of benzene (48% yields). Selective oxidation reactions are reported on MeAlPO materials for conversion of benzene and selectivity of phenol is very low. The conversion of benzene obtained on KAlPO may be due to high electropositive nature of potassium that can attract H_2O_2 reactant and facilitate its decomposition to generate hydroxyl species required for benzene hydroxylation reaction to yield phenol. The hierarchical pores seem to play role in facile diffusion of the reactant and product molecule that is responsible for higher phenol selectivity and reusability of the catalyst (Table 1). The performance of KAlPO catalyst of the present study is shown better than that of the AlPO/MeAlPO and other catalysts reported in the literature (Table 3).

V. CONCLUSION AND FUTUR SCOPE

In Conclusion, this study given a prominent method for the synthesis of KAlPO through physical mixing method. This material showed catalytic activity for benzene hydroxylation reaction and the shows its recyclability with an excellent catalytic performance even after three reaction cycles (Table 1). The subject opens up a scope in optimization of the synthesis procedure of KAlPO and expansion of its catalytic applications.

Table 1. Catalytic activity of KAlPO in Benzene oxidation.

Catalyst	Benzene Conversion(%)	Phenol Selectivity(%)	Reference
KAlPO	48	100	This work
KAlPO(Reused)	47	100	This work
CuAlPO-5	12.6	47.4	28
FeAlPO	13.4	95.6	29
Pd -VPI-5	----	72	30
CuAlPO	28	100	31

Table 2. Surface area and pore size distribution of KAlPO.

BET Surface area (m^2/g)	Micro Surface area (m^2/g)	Meso Surface area (m^2/g)	Total Pore Volume (cm^3/g)	Micro PoreVol ume (cm^3/g)	Meso Pore Volume (cm^3/g)
270.7	47.9	222.8	0.595	0.020	0.575
Pore size distribution (% Volume in pore Diameter)					
<2nm	2-10nm	10-20nm	20-50nm	>50	
18	25	30	19	8	

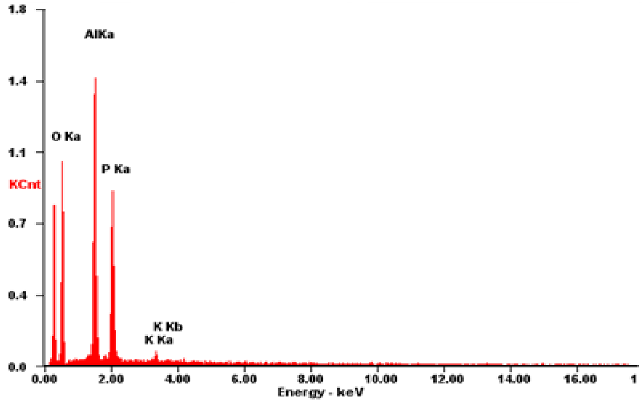

Figure 1 EDX spectra of the KAlPO.

Table 3. Various catalytic systems used for hydroxylation of Benzene with H_2O_2

S. No	Catalyst	Temparature (^0C)	Time (hr)	Benzene Conversion (%)	Selectivity(%)		Ref
					Phenol	Others	
1	PMoV2 @SiO2	60	6	21.6	100	0	32
2	[Dmim]2.5PMoV2	70	4	26.5	100	0	33
3	HPMoV[ethanol]/MCM-41-NH2	70	9	19.8	97.3	2.7	34
4	[Fe(BMPA)Cl3]	25	24	29.7	100	0	35
5	CuPc	Room temperature	15	13.9	>98.0	2.0	36
6	FZP5.0	60	6	3.0	99	1.0	37
7	Cu0.10Ce0.90O2-δ	70	6	43.0	100	0	38
8	CuAlPO-5	70	9	12.6	47.4	52.6	39
9	FeAlPO[a]	380	----	13.4	95.6	4.6	40
10	Pd-VPI-5[b]	130	4	----	72	28	41
11	CuAlPO	60	3	28	100	0	42
12	KAlPO	70	4	48	100	0	This work
13	KAlPO (Reused)	70	4	47	100	0	This work
[a] N_2O Oxidizing Agent [b] O_2 Oxidizing Agent and remaining all catalsyt system used H_2O_2 oxidizing agent							

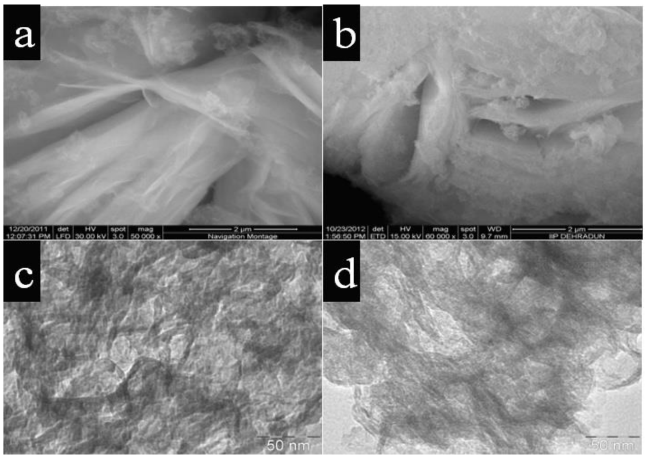

Figure 2 a and b are the SEM images of KAlPO before and after reaction, while c and d represent the before and after the reaction

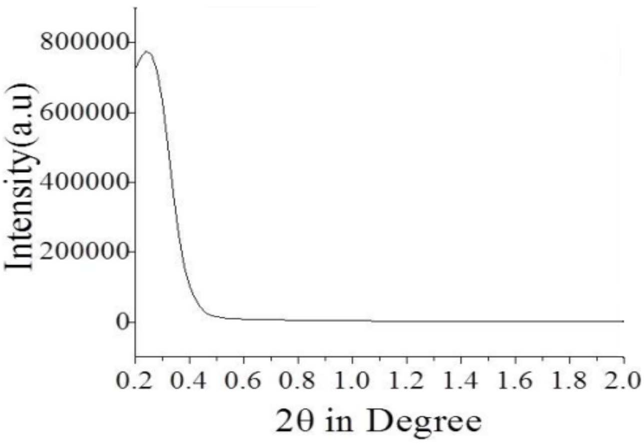

Figure 3. Low angle XRD patterns of KAlPO.

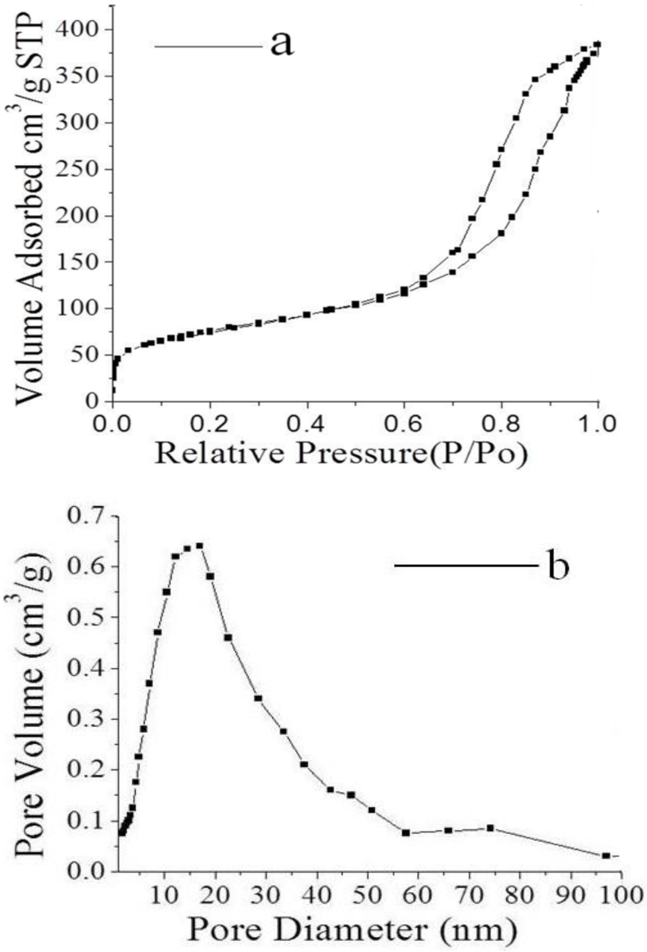

Figure 4 a and b are adorption- desoption isotherm and pore size distirbution of KAlPO respectively.

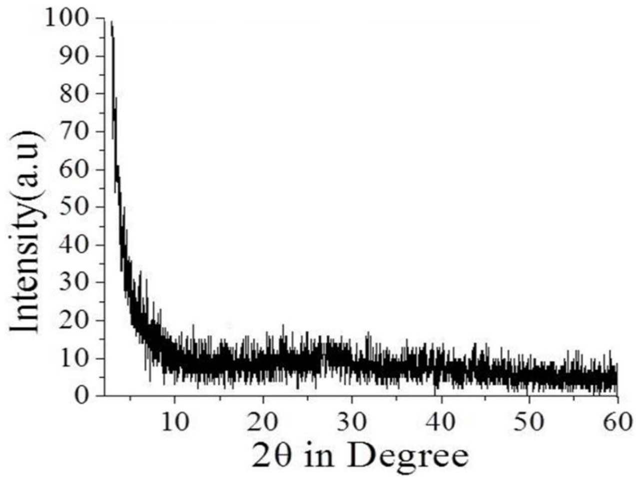

Figure 5 Wide angle XRD patterns of KAlPO4.

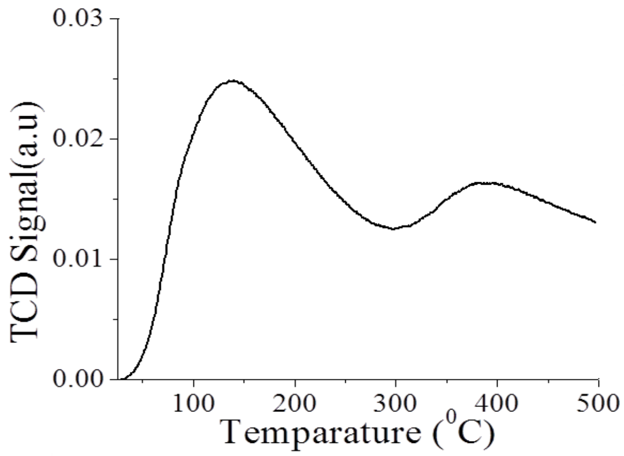

Figure 6 TPD patterns of KAlPO.

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