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Synthesis of Amorphous Hierarchical Mesoporous $ZnAlPO_4$ and its Catalytic Applications for Benzene to Aniline Reaction

Sreenivasulu Peta* & Sadhana Singh

Faculty of Chemical Sciences, Institute of Natural Sciences, Shri Ramswaroop Memorial University, Barabanki, 222 503, U.P, India

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This paper reports a distinctive property of hierarchical mesoporous $ZnAlPO_4$ for benzene to aniline reaction, with 99% selectivity using aqueous ammonia as amine source in presence of hydrogen peroxide at mild reaction conditions (70°C and atmospheric pressure). The catalyst is synthesized by a simple, solvent-free mixing method, which significantly improves properties such as acidity and porosity of the material is gained by increasing the temperature of the physical mixture from room temperature (25ºC) to 100ºC. Detailed characterization analysis by FT-IR, SEM, TEM, XRD, TPD, XPS, and N_2 adsorption–desorption studies of the material helped in understanding the direct amination activity of the material.

Keywords: Aluminophosphates, Amination, Aqueous ammonia, Molecular sieves, Zeolite materials

Introduction

Synthesis of mesoporous materials has been gaining importance lately for their catalytic applications. These materials have space available for the free-accessibility of reactants, for the creation of bulky reaction intermediates and the facile diffusion of the molecules without any mass-transport restrictions.[1–6] First discovered by Wilson *et al.* in 1982,(7) Porous aluminophosphates ($AlPO_4$) constitute an important group of zeolite materials and have versatile applications in adsorption, separation, sensoring, and catalysis. The importance of these materials is further enhanced by the successful introduction of a variety of metal/transition ions such as heteroatoms to isomorphously substitute the Al or P atoms in the $AlPO_4$ so as to create $MAlPO_4$ molecular sieves (M = metal). $MAlPO_4$ have improved properties suitable for the designing of catalysts with excellent redox properties.[8–11] However, synthesis of $AlPO_4$ and $MAlPO_4$ materials involve complicated procedure and obtaining the material possessing pores and good thermal stability is difficult.[12–16] Materials consist of ordered mesoporous aluminophosphates are typically accumulated at hydrothermal and solvo-thermal synthesis conditions,[17–21] which consumes lot of energy and liquid wastage. The creation of hierarchical pores in the materials has been observed to enhance the catalytic applications[22–24] of the materials. This happens due to the enhanced accessibility of the reactants to the active sites for their free diffusion. Thus, synthesis of hierarchically porous aluminophosphate by a simple method, exhibiting active sites and good thermal stability suitable for catalytic applications are still a great challenge. We have reported production of high temperature stable and hierarchically porous $AlPO_4$/$ZnAlPO_4$ by using a simple physical mixing method from a mixture of starting materials.[25]

This unique approach saves energy and controls liquid wastage in the synthesis, yet effective for the production of high quality materials possessing various pores containing mesopores and micropores from a solitary template. This work inspired us to study the role of synthesis parameters, such as treatment temperature of the chemical ingredients in physical mixture on the properties of the synthesised material and to explore its catalytic application which resulted in discovery of the effective amination properties of $ZnAlPO_4$ to convert benzene to aniline with 99% selectivity.

Aniline is an important chemical commodity for polymer and drug industries. Aniline can be produced from benzene by establishing Carbon and Nitrogen bond formation. This can be attained in three ways: 1) reduction of nitro group,[26] 2) through hydroxyl amine or acylamide intermediate[27–32] and 3) instantaneous

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*Author for Correspondence
E-mail: sreenivas.chm@srmu.ac.in.

bracing of the ammonia N-H bond and benzene C-H bond.[33–35] The industrial production of aniline is done by first method in which, nitration of benzene by nitric acid treatment, go after by its reduction using a reducing agent. However, this process has a lot of disadvantages such as, low production yields, harsh operation conditions, formation of huge quantity of side-products, environmental pollution and long time consuming reaction process. The second method involves production of Aniline from halo benzene compounds, Ar–X (X = Cl, Br, etc.) with acyl amide intermediate, or through the amination of benzene with hydroxylamine (NH_2OH). However, this method also involves potential risks due to the requirement of handling the poisonous and explosive NH_2OH. Hence, the direct introduction of an amino group to benzene is attractive in terms of atom economy, low price and direct use of raw material, which falls under the third mentioned method of production of Aniline. However, the complexity involved in the activation of the inert aromatic benzene C-H bond and the N–H bond (107 $kcal \cdot mol^{-1}$) in ammonia makes the process challenging.[36–38] Liquid or solid acid catalyst was used for aniline synthesis from benzene, but most of cases its shown low selectivity toward aniline. Due to less conversion of benzene and low selectivity to aniline in amination of benzene reaction, so it has not been accepted in industry.

In an effort to build up a new catalyst system, we have synthesized hierarchical mesoporous $ZnAlPO_4$ materials by an easy method which exhibited excellent property for the production of 99% aniline (selectivity) in single step amination of benzene using ammonia in presence of hydrogen peroxide. Adding an oxidant such as H_2O_2 into the amination system is observed to promote the reaction by shifting the reaction equilibrium. The method involves simple, solvent-free, single-organic-template-assisted process that yields hierarchical mesoporous acidic material, suitable for the adsorption and activation of ammonia. So far, the $MAlPO_4$ materials have been reported to catalyze various oxidation, hydroxylation and dehydration reactions. However, to the best of our knowledge, they have not been observed to exhibit activity in the direct amination of aryl group through instantaneous commencement of N-H and C-H bonds which is being reported for the first time through the present study. This study is the first of its kind to observe the synthesis of MAlPO4 by easier method for selective production of aniline (99%) from benzene through direct amination reaction and that reports the novel properties of the materials. The aim of the present study is to build a novel catalyst which could be produced by a simple method and use this materials for the amination of benzene to aniline reaction. Further the hierarchical mesoorous $ZnAlPO_4$ materials obtained in the present synthesis method are observed to be stable, even after removing the structure directing agent and have desired acidity suitable for direct amination of benzene.

Experimental Section

Material Synthesis

Ammonium di-hydrogen phosphate, Aluminum isopropoxide, tetramethyl ammonium hydroxide pentahydrate, zinc nitrate nonahydrate and tetra propyl ammonium bromide reagents have been used in this work.

The characteristic synthesis method involves the mixing of 3.2 g of ammonium dihydrophosphate, 6 g of aluminum iso-propoxide, 4 g of tetramethyl ammonium hydroxide pentahydrate (25 wt%), 4 g of tetra propyl ammonium bromide and 0.97 g of zinc nitrate to obtain a semi-solid form, followed by thermal treatment by the action of follow-on mixture at room temperature or 100°C or 150°C in an oven for 24 hours. To end the treatment, the compound is washed with sufficient quantity of ethanol and calcined at 500°C for 5 hours. The samples obtained at the three synthesis temperatures as mentioned, namely, room temperature, 100°C, 150°C are denoted as ZA-R, ZA-100 and ZA-150, respectively. Similar method is adopted for the synthesis of three $AlPO_4$ samples with the only difference being the exclusion of zinc nitrate in the initial synthesis mixture and the materials obtained at various treatment temperatures have been denoted by AlPO-R, AlPO-100 and AlPO-150.

Results and Discussion

Properties of Aluminium Phosphate and Zinc Aluminium Phosphate Materials

Elemental composition of $AlPO_4$ and $ZnAlPO_4$ samples synthesized via. the "Physical mixing" route has been investigated by EDX analysis, in which the existence of P, Al and O in the three $AlPO_4$ samples and, Zn, P, Al and O in the $ZnAlPO_4$ samples has been found (Supplementary Information Fig. S1). The wide angle XRD patterns of all the $AlPO_4$/ $ZnAlPO_4$ materials suggested the amorphous nature

(Supplementary Information Fig. S2- A and B, respectively). Both materials transformed to a non-crystalline form upon calcination. This is due to the exclusion of the organic template during the high temperature calcination. Further, FT-IR spectra (Supplementary Information Fig. S3) of all these samples show the band at 1110 cm^{-1} due to P-O stretching vibrations of tetrahedral PO_4^{-3} (39,40) and broad band at 3540 cm^{-1} related to the presence of the surface hydroxyl groups. All materials possessed layered structure in SEM images (Supplementary Information Fig. S4), while the porous nature of the materials was observed in TEM images (Fig. 1). The N_2 adsorption-desorption studies (Fig. 2 - a & b), where the presence wide range of mesopores have been observed. The adsorption-desorption isotherm represents the existence of mixed type of isotherms (combination of type I, II and IV) of well-defined capillary condensation at relative pressure (P/Po) of 0.01–0.99. A common trend observed in both $AlPO_4$ and $ZnAlPO_4$ samples is the appearance of well-opened adsorption-desorption loop in 100°C treated physical mixing samples (AlPO-100 and ZA-100) when compared to those of room temperature prepared and 150°C treated materials.

The pore size allocation curves of the samples (Fig. 3 a & b) also expose the attendance of mesopores with various pore diameters. However, keen observation of the curves indicate significant difference in the mesopore distribution, where the room-temperature treated $AlPO_4$ / $ZnAlPO_4$ samples

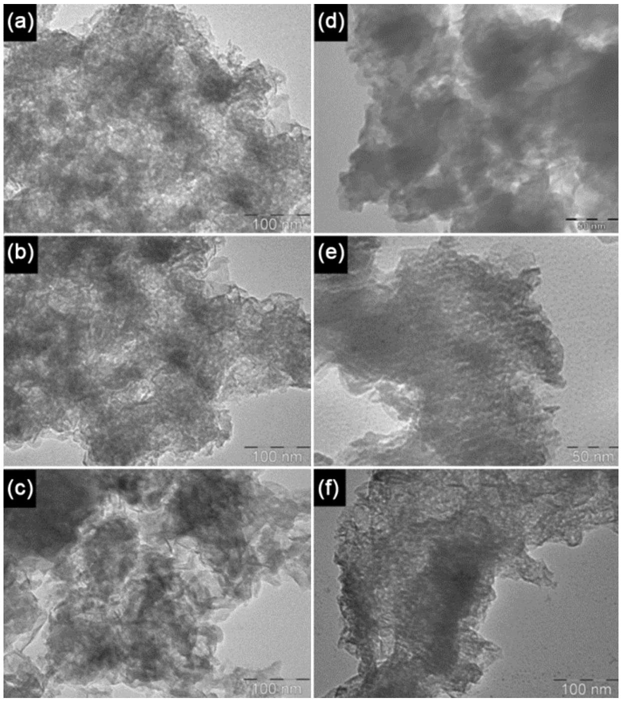


Fig. 1 — TEM images: (a) APO-R, (b) AlPO-100, (c) AlPO-150, (d) ZA-R, (e) ZA-100 (d) ZA-150

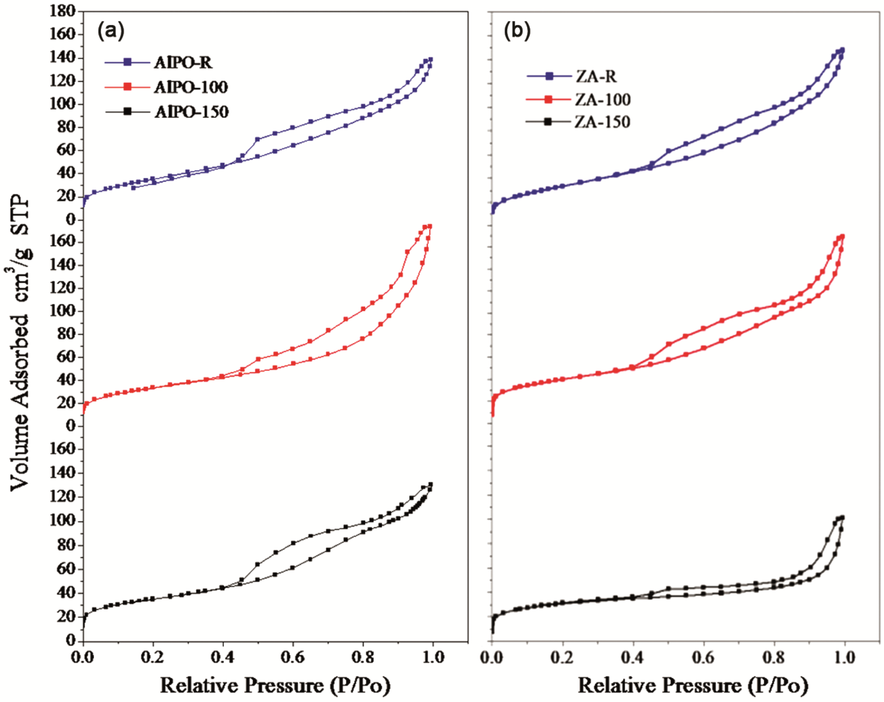


Fig. 2 — N_2 adsorption-desoption isotherm: (a) $AlPO_4$ and (b) $ZnAlPO_4$

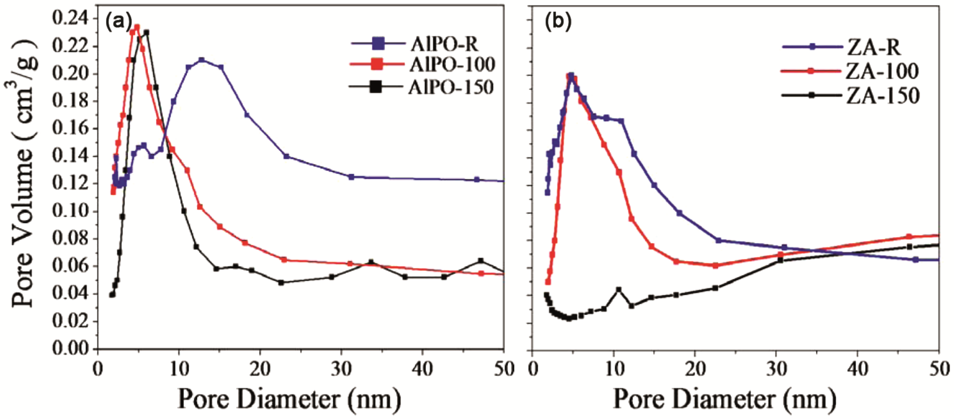


Fig. 3 — BJH pore size distribution: (a) $AlPO_4$ and (b) $ZnAlPO_4$

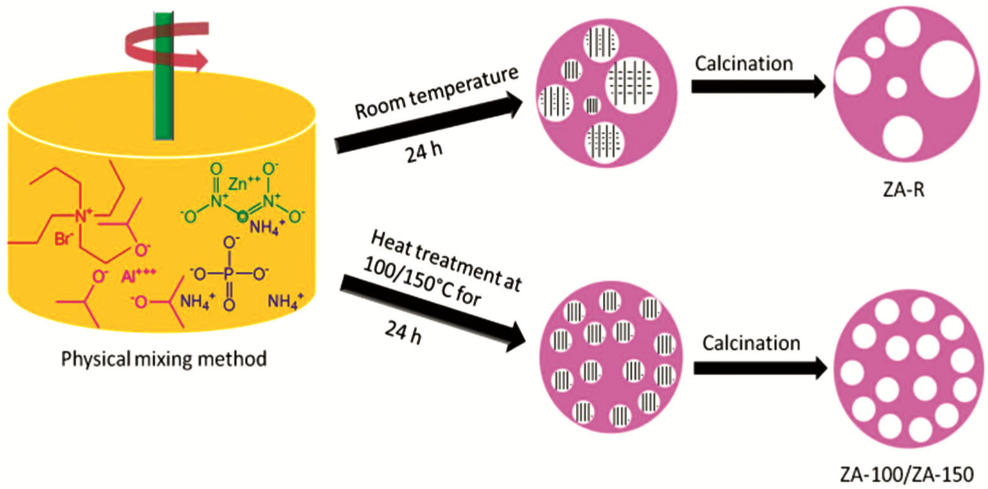
Table 1 — Textual properties of $AlPO_4$/$ZnAlPO_4$ materials

Samples	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Micro pore volume (cm^3/g)	Meso pore volume (cm^3/g)
AlPO-R	129.78	0.27	0.05	0.22
AlPO-100	122.07	0.32	0.05	0.27
AlPO-150	126.7	0.23	0.05	0.18
ZA-R	125.74	0.28	0.05	0.23
ZA-100	143.11	0.28	0.06	0.22
ZA-150	109.4	0.16	0.04	0.12

(AlPO-R and ZA-R) resemble broader range of pores with pore maximum of 5–6 nm and 15 nm, while those of 100°C and 150°C samples exhibit the presence of ordered mesopores (~5–6 nm). This phenomenon is more distinct in case of $AlPO_4$ when compared to $ZnAlPO_4$ materials. Surprisingly, the ZA-150 samples exhibited drastic decrease in mesopores (ZA-150 in Fig. 3b) that is also reflected in the loop configuration of the same sample (Fig. 2b). The pores volume decreases from ZA-100 to ZA-150 due to some pores collapsing at higher temperature. The optimum pore volume is observed at ZA-100 material. The textural parameters of three $AlPO_4$ and three $ZnAlPO_4$ samples are summarized in Table 1 and Supporting Information in Table S1. Overall, all the samples exhibited the existence of hierarchical mesopores, but distribution of the pores varied to considerable extent depending on the treatment temperature of the physical mixture.

Plausible Mechanism for Differences in Mesopore Formation in Various $AlPO_4$ and $ZnAlPO_4$ Samples

The formation of the $AlPO_4$/$ZnAlPO_4$ porous materials with various porosity patterns by treating the physical mixture at different temperatures can be understood from the scheme 1. In the room temperature treated sample, the mixture of starting materials of $Al(O^iPr)_3$, NH_4 H_2PO_4, $TMAOH.5H_2O$ and TPABr is not able to disperse the chemical species uniformly. Hence, the chemical ingredients of the physical mixture in this condition is expected to exhibit heterogeneous distribution, and the resultant material after calcinations yields the formation of $AlPO_4$/$ZnAlPO_4$ with heterogeneous pore size distribution as observed in AlPO-R and ZA-R samples. However, increasing the temperature of the physical mixture from room temperature to 100°C /150°C results in decomposition of the stating materials (melting points of the raw materials starts from 100°C) to give active chemical species and facilitates the interaction among them to give homogeneously distributed chemical mixture. Calcination treatment of such mixture, thus, yields the mesoporous $AlPO_4$/$ZnAlPO_4$ with homogenous pore size distribution (ordered mesopores), as in the case of AlPO-100, AlPO-150, ZA-100 and ZA-150. Irrespective of the initial treatment temperature, all the samples exhibited amorphous nature as confirmed by wide-angle XRD (Supplementary Information Fig. 2). The heterogeneous distribution of pores in the samples can be ascribed to the existence of two forms of organic template in the synthesis mixture; mono-dispersed species and aggregated micelles of different sizes responsible for the formation of micro pores and the mesopores of different sizes upon calcination at 500°C for 5 hours. As proposed in Scheme 1, the



Scheme 1 — Effect of synthesis temperature on porosity patterns of materials

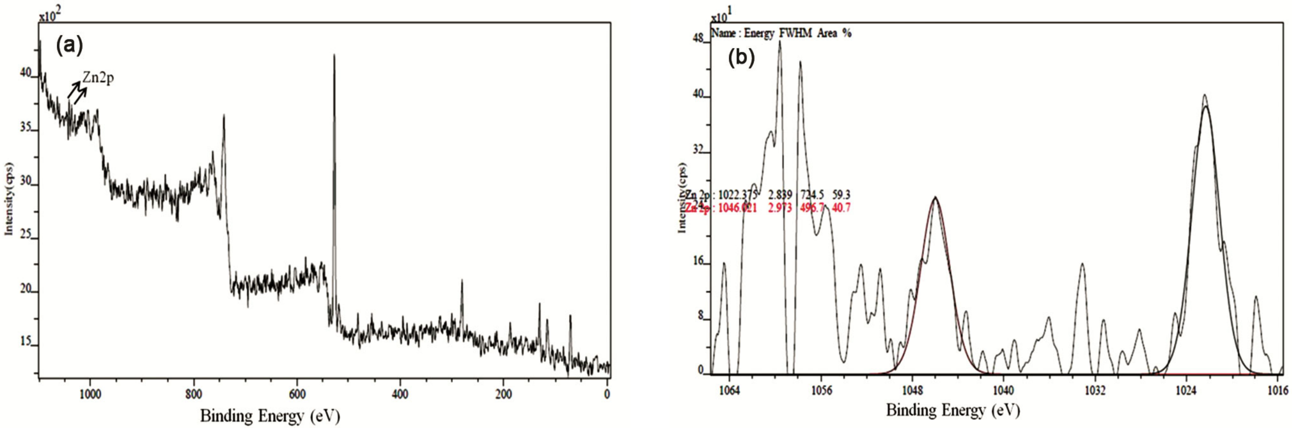


Fig. 4 — XPS spectra of ZA-100 sample: (a) XPS survey spectra and (b) XPS spectra of Zn2p

synthesis mixture possessing heterogeneous distribution of organic template aggregates (as in case of ZA-R sample) creates a broad range of mesopores while that of ZA-100/150 exhibits the much ordered (narrow range) mesopores (Fig. 3). This phenomenon is much prominent in case of pure $AlPO_4$ samples when compared to those of $ZnAlPO_4$ which can be ascribed to the positive role of Zn in the initial synthetic mixture, to facilitate better interaction and distribution of the organic template. Thus, $ZnAlPO_4$ obtained in this study exhibits a novel property, Zn interacting with Al and P species during synthesis treatment of physical mixture. Existence of such interaction of Zn species is indeed supported by high resolution XPS spectra of the $ZnAlPO_4$ samples (Fig. 4). This indicates that the presence of $Zn_{2p3/2}$ peaks with the bond energy of 1022.4 eV in the $ZnAlPO_4$ samples which is more than that of pure ZnO (1020.8 eV), but comparable with that of the support interacted Zn species (2023.6 eV). This reveals the presence of strong interaction of Zn with the Al and P species in the $ZnAlPO_4$. This interaction suggests the existence of a Zn species possessing higher tendency to draw electrons from near-by atomic environment as compared to pure ZnO.[41,42] The change in electronic environment around Zn species in $ZnAlPO_4$ is also expected to alter the acidic properties of the material (decrease in electron density around O-H group results in increase of acidity). For this the catalysts were characterized by NH_3-TPD (Fig. 5) which shows the presences of two desorption peaks (NH_3) in all the three $ZnAlPO_4$ samples. Wide peak centered at 150°C (peak I; Fig. 5b) and other at 400°C (peak II; Fig. 5b) demonstrating both weak and strong interaction of ammonia with catalyst respectively. In other words, the $ZnAlPO_4$ samples

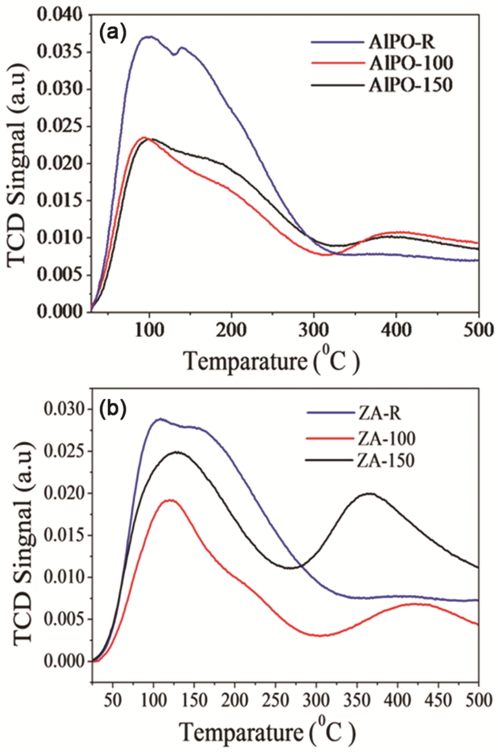


Fig. 5 — NH_3-TPD of A) $AlPO_4$ and B) $ZnAlPO_4$ samples

possess both weak and strong acidity; while strong acidity is absent in all the three $AlPO_4$ samples. This observation is in accordance with the electron drag properties of the chemically interacted Zn in $ZnAlPO_4$. The acidity patterns of the $ZnAlPO_4$ samples vary depending on the treatment temperature of the physical mixture. Where the low temperature desorption peaks (peak I) of all three samples are comparable, while that of high temperature peak (peak II) differs; peak II is absent in ZA-R while it is present in both ZA-100 and ZA-150 samples. This can be attributed to the inefficient chemical contact of the Zn present in the physical mixture at room temperature treatment. Further, the absence of strong acidity in ZA-R (in spite of the presence of Zn) suggests the need of proper interaction of Zn with AlPO in the sample, which is facilitated only in the samples treated at higher synthesis temperature treatments (ZA-100 and ZA-150). The ammonia desorption patterns in TPD also provides the information related to the ammonia adsorption ability of the samples, which is necessary for activation of ammonia (N-H bond), a prime requirement for direct amination reaction. Among the three $ZnAlPO_4$ samples, ZA-100 exhibited high surface area, high porosity (Table 1) and strong acidity (Fig. 5) and is expected to exhibit higher ammonia adsorption capacity required for the benzene amination reaction.

Overall, the $AlPO_4$/$ZnAlPO_4$ materials synthesized during this study possess hierarchical pore range from micro to macro pore region. Presented synthesis method of hierarchically porous $AlPO_4$ and $ZnAlPO_4$ under the ''physical mixing'' way exhibits the following evident features. 1) This process is very easy and desired properties involve only squeezing of raw material compared to the long critical hydrothermal route. 2) This process significantly reduces the production of pollutants by completely avoiding the use of solvents. 3) This process produces a high yield of porous solid material and 4) This process saves energy as it is conducted at room temperature or at lower temperature (100ºC), compared to the hydrothermal synthesis which involves relatively high temperatures. The medium-strong acid sites with Cu-O-Si were helpful for aniline synthesis reaction from benzene.[43] $ZnAlPO_4$ materials synthesized by ''physical mixing'' in the present study are of great importance in industrial processes, strong-medium acid sites provided active sites for the effective chemical adsorption of NH_3/Benzene and Zinc incorporated Al–O–P which offered active sites for the activation of the NH_3 (N–H bond). Therefore, the $ZnAlPO_4$ materials synthesized by ''physical mixing'' in the study are of huge significance in industrial processes and were discovered here for the direct amination reaction.

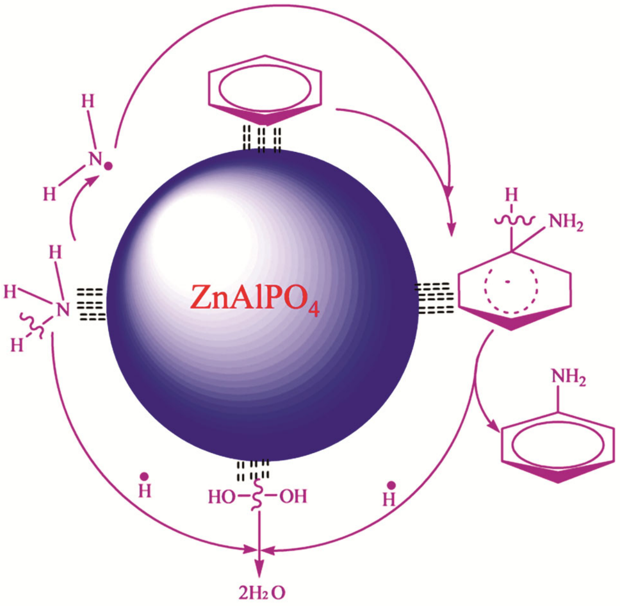
Benzene Amination Reaction

Amination reaction was carried out in a round bottom flask at stirring and reflux condition with continuous cold water flow. In a typical reaction study, catalyst (0.25 g), benzene (5 mL) and $NH_3 \bullet H_2O$ (25–28 wt%, 5 mL) were mixed methodically in a round bottom flask. The mixture was heated at 70°C for 2 hours with continuous stirring, during which 3 mL of H_2O_2 (30 wt%) is added drop wise to the reaction mixture so as to decrease the possible unproductive decomposition of H_2O_2 and to avoid the likely formation of over oxidation products such as phenol. Liquid mixture was separated from the catalyst by filtration, the product was analyzed and quantified by GC. The product is analyzed and also quantified using Varian-CP-3800-DHA model equipped with CP-SIL PONACB column.

The direct production of benzene to aniline requires a catalyst possessing strong ammonia adsorption capacity, which was indeed exhibited by all the three $AlPO_4$ and the three $ZnAlPO_4$ samples. The $ZnAlPO_4$ and $AlPO_4$ having high surface area, strong acidity and hierarchical mesoporosity can predictably show potential catalytic activity and in this study have been explored in the amination reaction of benzene. $ZnAlPO_4$ samples produced aniline with 99% selectivity, but in spite of having ammonia adsorption capacity the $AlPO_4$ samples could not exhibit any amination activity (Table 2). As shown in Scheme 2, the first step of adsorption of ammonia and benzene need to be followed by the instantaneous activation of C-H bond of benzene and N–H bond of ammonia so as to produce aniline. Thus, the obvious reason for absence of such catalytic activity of $AlPO_4$ samples can be explained by the absence of active sites required for the NH_3 adsorption and activation. If not provided sufficient sites for the efficient chemical adsorption of NH_3 and benzene nor active sites for the activation of N–H bond of NH_3 to proceed the benzene amination reaction is difficulty. This observation clearly emphasizes the essential role of Zn in $ZnAlPO_4$ samples for direct amination reaction and the catalytic activity of $ZnAlPO_4$ samples seems to be operating in bi-functional manner; by the efficient adsorption of reactants and by the activation of the C-H and N-H bonds.

Table 2 — Performance of catalysts benzene amination reaction

Catalyst	Conversion (%)	Products Selectivity (%)
ZA-R	2.40	99
ZA-150	3.20	99
ZA-100	5.50	99
ZA100(Reused)	5.30	99
$AlPO_4$	No reaction	



Scheme 2 — Proposed mechanism for benzene amination reaction

A plausible mechanism for the formation of aniline is given in scheme-2, where the adsorption of basic ammonia and electron-rich benzene on the acidic $ZnAlPO_4$ initiates the reaction to proceed through the sequential steps of formation of NH_2 species, its migration to benzene for the formation of aniline. The hydrogen species evolved from aqueous ammonia and benzene will be utilized by hydrogen peroxide to form water molecules. Here, hydrogen peroxide acts as hydrogen acceptor to facilitate the forward reaction. The reaction doesn't proceed in the absence of hydrogen peroxide.

Generally, phenol and dihydroxybenzenes (DHB) are obtained as by-products in these reaction conditions due to over adsorption of H_2O_2 on active site of these materials.[36–38] However, the 99% selectivity to aniline and trace amount of nitro benzene obtained in this study reveals the selective amination ability of the $ZnAlPO_4$ catalysts. The absence of nitro benzene and phenol in the product suggests the selective amination property of the catalysts which it displays by controlling the oxidation reaction of benzene/aniline. Moreover, the 99% selectivity to aniline exhibited by all the three $ZnAlPO_4$ catalysts indicate that the nature of active sites are same on all these catalysts, (irrespective of the difference in treatment temperature of the physical mixture during their synthesis) though the extent of benzene conversion vary depending on the acidic property of the catalysts. Though aniline selectivity is high, the lower conversion of benzene observed on the samples may be due to desorption of most of the ammonia (before its activation) adsorbed on the catalysts at higher reaction temperature (70°C) as applied in this study. Among the three $ZnAlPO_4$ samples, ZA-R exhibited poor strong acidity along with broad mesopore distribution, while ZA-150 exhibited blockage of mesopores (Fig. 3b) and lower pore volume. The ZA-100 sample possessing more strong acidity and more pore volume is supposed to exhibit higher ammonia adsorption and N-H bond activation as compared to ZA-R and ZA-150, as observed in the reaction performances of these catalysts where the conversions on ZA-R and ZA-150 are 2.40% and 3.20% respectively, against 5.50% conversion on ZA-100. Though the conversion of benzene obtained in the present study is not high, the excellent product selectivity exhibited by $ZnAlPO_4$

samples provides a promising catalytic property useful for industrial applications. Further, the aniline selectivity and benzene conversion observed on ZA-100 in the present study are better than those reported in the literature (Supporting Information Table S2). The catalyst ZA-100 was also observed as suitable for its reusability even after three reaction cycles (Table 2). $ZnAlPO_4$ catalysts exhibited a high selectivity of Aniline, which is due to the superficial diffusion facilitated by the hierarchical pores of the catalysts, without encouraging hydroxylation of benzene and control over oxidation.

Overall, the present study demonstrates that the $ZnAlPO_4$ material synthesized by a simple method has capability to concurrently activate N-H bond of aqueous ammonia and C–H bond of benzene in mild reaction conditions (70°C, atmospheric pressure) to facilitate industrially challenging amination of benzene for aniline synthesis. However, further studies in catalyst development are required for the achievement of higher benzene conversions and perhaps the development of low-temperature (ambient temperature) active catalyst may give efficient ammonia adsorption/activation properties suitable for this reaction.

Conclusions

Hierarchically porous $AlPO_4$ and $ZnAlPO_4$ possessing high thermal stability can be obtained by simple, energy saving, environment friendly, solvent-free physical mixing method. The $ZnAlPO_4$ sample synthesized at optimum synthesis conditions exhibits more ordered mesopores and strong acidity to activate liquid ammonia for direct amination of benzene at moderate reaction temperature of 70ºC and atmospheric pressure to yield high selectivity of aniline. This new property of $MAlPO_4$ materials, suitable for direct amination of benzene, has been reported for the first time. Moreover, such a high selectivity to aniline possessed by this material reveal the scope for catalyst development for industrial applications. The physical mixing method adopted in material synthesis has more advantages compared to that of hydrothermal synthesis route in terms of saving energy, effort, convenience of procedure and a high product yield, which are potentially significant for the industrial production of porous materials in the future.

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Conflict of Interest

Authors declare no conflict of interest.

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