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Synthesis and catalytic applications of hierarchical mesoporous $AlPO_4$/$ZnAlPO_4$ for direct hydroxylation of benzene to phenol using hydrogen peroxide†

Peta Sreenivasulu, Devaki Nandan, Manoj Kumar and Nagabhatla Viswanadham*

Amorphous hierarchical mesoporous $AlPO_4$ and $ZnAlPO_4$ materials have been successfully synthesized for the first time by a simple physical mixing method, where tetrapropyl ammonium bromide acts as both a template and structure directing agent. The materials exhibited excellent catalytic activity for the production of phenol from benzene (99% conversion with 85% selectivity).

The synthesis of mesoporous aluminophosphate materials has received great attention due to their wide range of potential applications in catalysis and adsorption.[1,2] The surfactant templating method is most popular for the synthesis of lamellar or hexagonal mesoporous $AlPO_4$.[3] However, the main drawback of this method lies in the structural collapse of the material upon removal of the surfactant by calcination.[4,5] Another drawback is obtaining porous $AlPO_4$ with an adjustable P/Al ratio close to or above 1 : 1,[3a,6,7] which limits the acidic property of the material required for catalytic applications.[8,9] The acidity and catalytic properties of $AlPO_4$ materials are also controlled by introducing a heteroatom into the structure of $AlPO_4$. Divalent metal ions such as Mg^{2+}, Mn^{2+}, Zn^{2+}, and Co^{2+} *etc.* are incorporated into $AlPO_4$ to substitute a small amount of framework negative charges,[10] and the materials possess additional features, due to well-separated active-site centers, allowing them to act as efficient solid catalysts for many reactions.[11] It is interesting to study the possibility of synthesizing $AlPO_4$ and $MAlPO_4$ materials that are structurally stable even after the removal of the structure directing agent, and which possess the desired acidity and catalytic properties which are suitable for various catalytic applications.

Porosity is another important feature of the materials that plays a vital role in facilitating molecular level interactions of reactants in the active sites and governs their suitability for various applications. Recently, hierarchical porous materials have been observed to exhibit superior catalytic and adsorption[12] properties due to the presence of multiple sizes of pore channels and their inter-connectivity, making them suitable for the free accessibility of the reactant molecules, and their facile diffusion which is responsible for the activity and stability of the materials for catalytic applications. The hierarchically porous aluminophosphate materials are also synthesized by using small amines and bulky organosilane surfactants.[13] However, most of the synthesis methods are time consuming and involve multiple steps. Hence, the synthesis of amorphous hierarchically porous $AlPO_4$/$ZnAlPO_4$ materials through a simple one-step method using a single organic template is attempted in the present study. The resultant materials with hierarchical porosity are applied to the industrially important reaction of benzene to phenol in a single-step direct hydroxylation using hydrogen peroxide.

Phenol is one of the most important industrial chemicals that is used in dyes, resins and pharmaceuticals *etc.* The industrial process produces 90% of phenol through a three step reaction system.[14] The direct conversion of benzene to phenol is potentially an area of great interest and is still regarded as one of the 10 most difficult challenges in catalysis,[15] as the phenol selectivity is limited due to the higher oxidation reactivity of phenol when compared to benzene.[16] The direct hydroxylation of benzene to phenol is being investigated using different oxidizing agents such as N_2O,[17] H_2O_2,[18] $NH_3 + O_2$,[19] air + CO,[20] molecular O_2 (ref. 21) and a mixture of $H_2 + O_2$.[22] However, the gas phase hydroxylation has some major drawbacks due to rapid deactivation of the catalyst by coke deposition.[23] Transition metal doped $AlPO_4$ is known for its selective oxidation of hydrocarbons,[24] but it gives a benzene conversion of only 28% in the presence of oxidants such as molecular O_2, N_2O and H_2O_2 (ESI Table S2†).

Herein we report a simple physical mixing method for the synthesis of hierarchical mesoporous $AlPO_4$ and $ZnAlPO_4$ materials by using a single organic template, TPABr. The

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Catalysis and Conversion Processes Division, CSIR-Indian Institute of Petroleum, Dehradun-248005, India. E-mail: nvish@iip.res.in; Fax: +91-135-2525702; Tel: +91-135-2525856

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material exhibited excellent catalytic activity in the direct hydroxylation of benzene for the selective production of phenol. To the best of our knowledge, the present study is the first of its kind in terms of (1) the synthesis of hierarchical mesoporous $ZnAlPO_4$ and $AlPO_4$, (2) a simple solvent-free synthesis method using a single organic template, TPABr, by adopting physical mixing, and (3) showing promising catalytic activity of $ZnAlPO_4$, achieving 85% selectivity for phenol at as high as 99% benzene conversion.

In a typical synthesis method, the amorphous mesoporous $ZnAlPO_4$ materials were synthesized by admixing 4 g of tetramethyl ammonium hydroxide pentahydrate 25 wt% in methanol (TMAHP), 6 g of aluminum isopropoxide, 4 g of tetrapropyl ammonium bromide (TPABr), 3.2 g of ammonium dihydrophosphate and 0.97 g of zinc nitrate to obtain a paste, followed by treatment of the resultant mixture at 150 °C in an oven for 24 h. At the end of the treatment, the compound was washed with an ample amount of ethanol and calcined at 500 °C for 5 h. The zinc samples are denoted by ZAC and the aluminium sample denoted by APC. Before calcination the samples are denoted by ZAS and APS and after reaction the samples are denoted by ZAU and APU.

The presence of Zn, Al, P and O in the synthesized, calcined and used samples was confirmed by energy-dispersive X-ray spectroscopy (EDX) analysis (ESI Fig. S1†). The wide angle X-ray diffraction (XRD) patterns of as-synthesized $AlPO_4$ and $ZnAlPO_4$ show that both samples are crystalline in nature (Fig. 1A), but are both converted to an amorphous material upon calcination (Fig. 1B). This may be due to the removal of the structure-governing organic template during the high temperature calcination.

The scanning electron microscopy (SEM) images (Fig. S2†) indicate that the materials possess layer-like structures, while the transmission electron microscopy (TEM) images (Fig. 2) reveal a sponge-like structure with uniformly distributed pores. The materials retained the textural properties even after the reaction (Fig. 2E and F), which supports the reaction stability of the material. Such a porous material is expected to exhibit high surface area and porosity. The low-angle XRD patterns (ESI Fig. S3†) of the synthesized and calcined samples of $AlPO_4$ and $ZnAlPO_4$ also reveal the presence of mesopores in these materials.[25] The porosity of the APC and ZAC samples measured by N_2 adsorption–desorption measurements (Fig. 3A) further confirms the presence of mesopores with a wide range of pore sizes. The adsorption–desorption isotherm also represents mixed types of isotherms (a combination of type I, II and IV). A steep increase occurs in the curve at a relative pressure of 0.01, indicating the filling of the micropores, something that is commonly observed for larger mesopores and provides direct evidence for the presence of worm-like mesopores in these samples. The isotherm indicates the occurrence of well-defined capillary condensation at a relative pressure (P/P_o) of 0.01–1.0. The BJH pore size distribution curve of APC and ZAC (Fig. 3B) reveals the presence of micropores as well as mesopores with various pore diameters. The mesopores are distributed from a 2–100 nm pore diameter with the major population of pores having a diameter of 10–50 nm (Fig. 3B), revealing the hierarchical nature of the mesopores. The formation of the pores with

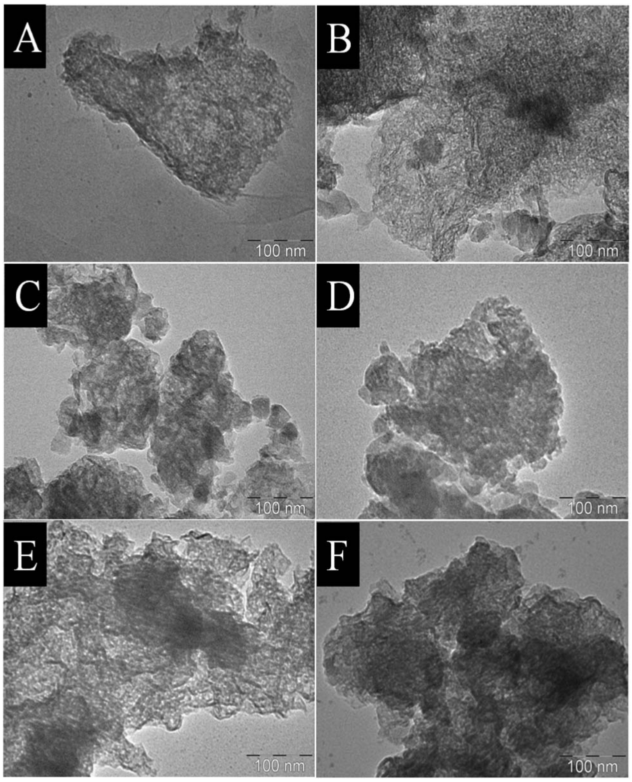

Fig. 2 (A, C and E) TEM images of as-synthesized, calcined and used $AlPO_4$ materials respectively, and (B, D and F) TEM images of as-synthesized, calcined and used $ZnAlPO_4$ materials respectively.

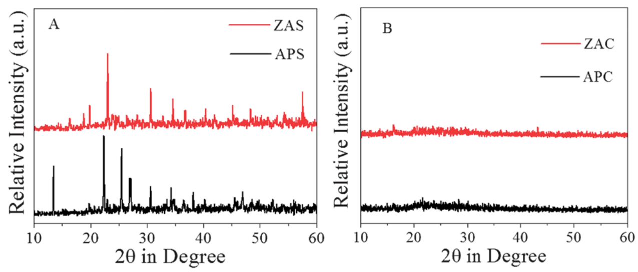

Fig. 1 Wide angle XRD patterns of $AlPO_4$ and $ZnAlPO_4$ materials (A) before and (B) after calcination.

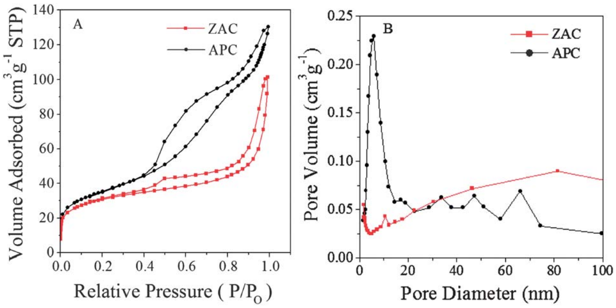

Fig. 3 (A) N_2 adsorption–desorption isotherms, and (B) BJH pore size distribution, of $AlPO_4$ and $ZnAlPO_4$ materials.

different pore diameters obtained in the present study may be due to the heterogeneous distribution and aggregate size of the template which occur in the physical mixing method, where the calcination of the corresponding materials expels the template to form pores of different sizes. In spite of similarities in the hierarchical porous nature, there is a distinct difference in the loop configuration and pore size distribution patterns of $AlPO_4$ and $ZnAlPO_4$ which may be due to the difference in the removal patterns of the organic template from these materials during the calcination. This is also reflected in the difference in the BET surface area (126.7 m^2 g^{-1} and 109.6 m^2 g^{-1}) and pore volume (0.23 cm^3 g^{-1} and 0.16 cm^3 g^{-1}) of the $AlPO_4$ and $ZnAlPO_4$ samples respectively (ESI Table S1†). The $AlPO_4$ and $ZnAlPO_4$ materials exhibiting hierarchical porosity after calcination at 500 °C confirms the high temperature thermal stability, while retaining its porosity. This is a novel property and has not been reported so far.

The Fourier transform infrared spectroscopy (FT-IR) spectra (ESI Fig. S4†) of the samples show a broad band at 3540 cm^{-1}, which is related to the presence of the surface hydroxyl groups associated with phosphorus that is perturbed by a hydrogen bridge bond from a surface hydroxyl band. The other two bands at 1110 cm^{-1} and 468 cm^{-1} may be due to triply degenerate P–O stretching vibrations and triply degenerate O–P–O bending vibrations of tetrahedral PO_4^{3-} respectively.[26] The acidity patterns measured by temperature-programmed desorption (TPD) (ESI Fig. S5†) indicate the presence of two NH_3 desorption peaks in both samples; one broad peak centered at 150 °C and the other at around 400 °C, representing the weak and strong acid sites respectively. However, the high temperature desorption peak is shifted to the higher temperature side in the ZAC sample, indicating the creation of strong acid sites by the Zn.

The $AlPO_4$ and $ZnAlPO_4$ possessing high surface area, hierarchical mesoporosity and strong acidity are expected to exhibit promising catalytic activity and in the present study are explored in the selective hydroxylation of benzene (Table 1). The $AlPO_4$ sample exhibits a lower benzene conversion of around 13%, with 100% selectivity to phenol. It is interesting to see that the conversion increases to 99% in the case of the $ZnAlPO_4$ sample. However, a small amount (15%) of 1,4 benzoquinone by-product (product B) is obtained along with the phenol (product A) (85%) in this case. The acidity patterns of NH_3–TPD (ESI Fig. S5†) suggest the increased acidity as the reason for the enhanced reaction performance of $ZnAlPO_4$ when compared to the corresponding $AlPO_4$ catalyst synthesized by a similar method. Such a high enhancement in catalyst performance of $AlPO_4$ in the presence of Zn clearly shows the vital role of Zn in the benzene hydroxylation reaction. However, both the catalysts exhibited a common phenomenon of high phenol selectivity and reusability, which may be due to the facile diffusion facilitated by the hierarchical mesopores of the catalysts. To the best of our knowledge, this is the highest conversion of benzene ever reported for this reaction on $AlPO_4$/$ZnAlPO_4$ materials and proves the role of Zn in selective hydroxylation reactions. Further, the $ZnAlPO_4$ of the present study exhibited superior performance to that of the reported catalysts in the literature (ESI Table S2†). Moreover, the 100% selectivity to phenol obtained on the $AlPO_4$ catalyst reveals the selective hydroxylation ability of the catalyst for benzene hydroxylation without encouraging further hydroxylation of phenol. A reference experiment was also conducted in the absence of the catalyst, using only H_2O_2, in which no reaction was observed, which confirms the catalytic role of the $AlPO_4$/$ZnAlPO_4$ materials.

Table 1 Performance of catalysts in benzene hydroxylation

Catalyst	Conversion	Product selectivity (%) A	B
Benzene hydroxylation			
$AlPO_4$	13	100	—
$AlPO_4$ (reused)	11	100	—
$ZnAlPO_4$	99	85	15
$ZnAlPO_4$ (reused)	85	88	12

In summary, the present study provides a simple and novel method for the synthesis of hierarchical mesoporous $ZnAlPO_4$ through a solvent-free, single organic template method. The material exhibited promising benzene conversion for the efficient production of phenol by the selective hydroxylation of benzene. Furthermore, the material shows its reusability with an excellent catalytic performance even after three reaction cycles (Table 1). The subject opens up a new property of the metal $AlPO_4$ materials as suitable catalysts for selective oxidation reactions, and has scope in the improvement of the catalytic activity through the optimization of the synthesis procedure of $ZnAlPO_4$ for expansion of its applications to other selective hydroxylation reactions.

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