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COMMUNICATION

Synthesis of orderly nanoporous aluminophosphate and zirconium phosphate materials and their catalytic applications†Peta Sreenivasulu,^{ab} Nagabhatla Viswanadham^{ab*} Trymbkesh Sharma^b and B. Sreedhar^c⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

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Amorphous aluminophosphate (AP) and zirconium phosphate (ZP) materials possessing ordered nanoporosity have been successfully synthesized by a hydrothermal method using P123 block copolymer as structure directing agent. The materials exhibited excellent catalytic activity towards selective alkylation of phenol with cyclohexanol, where AP shows as high as 100% selectivity to produce industrially important O-alkylation product, while the corresponding ZP selectively produces C-alkylation product (93% selectivity).

Porosity is an important feature of the materials that plays a vital role in facilitating molecular level interactions of reactants with the active sites and governs their suitability for various applications. Nano pores, referring to the pores of nanometer range, are recently gaining importance due to their suitability for accommodating bulky molecular transformations. Porous materials should have a narrow pore size distribution which is critical for size-specific applications and a readily tunable pore size allowing flexibility for host-guest interactions and the materials should possess high thermal, chemical and mechanical stabilities, with high surface area and large pore volumes.¹ The materials should also have appropriate particle size and morphology.

The ordered framework structures of crystalline aluminosilicate and aluminophosphate materials possessing the uniform (narrow) pore size distribution have been successfully applied for size-specific adsorption, molecular sieving, host-guest chemistry and shape-selective catalysis.²⁻⁶ However, the pore size in such crystalline materials (zeolites) is limited to ~1.5 nm thus excludes size specific processes involving large molecules such as heavy oil conversion in petroleum refining, macromolecule transformations in drug and fine chemical applications, separation processes and for support applications to host large molecules. Further, the narrow pores in such materials also cause severe mass transfer limitations. Here, the amorphous materials provide alternate solution for creation of large size pores (nano pores > 2nm) but, obtaining ordered nano pores in amorphous materials is critical yet important in catalysis and organic synthesis.

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†Electronic supplementary information (ESI) available: Experimental details, wide angle XRD, EDX, SEM images, IR spectra, etc.

Metal phosphates are one of such important materials need to be addressed for the creation of nano pores as the applications of many open-framework and layered metal phosphates with varied compositions and properties have been constrained by the lack of large surface areas and the dominance of small pores or interlayer spaces.⁷⁻¹⁰ Two synthesis approaches are reported in the literature for these materials. The first approach involves the direct synthesis of nano porous metal phosphates via surfactant templating¹¹⁻¹⁹ but the material obtained in this method suffers from lower surface area and pore volume essential for catalytic applications. The second approach involves the dispersion of metal phosphate guest on nano porous silica host (possessing large surface areas and ordered nanopores).²⁰⁻²² However, it is difficult to finely control the guest-host interaction to obtain homogenous composition and structure via wetness impregnation in this method. Though the synthesis of zirconium phosphates by using P123 block copolymer has been reported, most of the methods involve complicated procedures and longer synthesis time required to obtain the material.^{23, 24} These deficiencies prompted us to develop methodologies for the synthesis of metal phosphates with large surface areas and large pores which were successfully explored for the industrially important alkylation of phenol with cyclohexanol. Further, the nature of metal (Al or Zr) is observed to influence the selective alkylation at oxygen or carbon atom of the phenol group to produce the desired product.

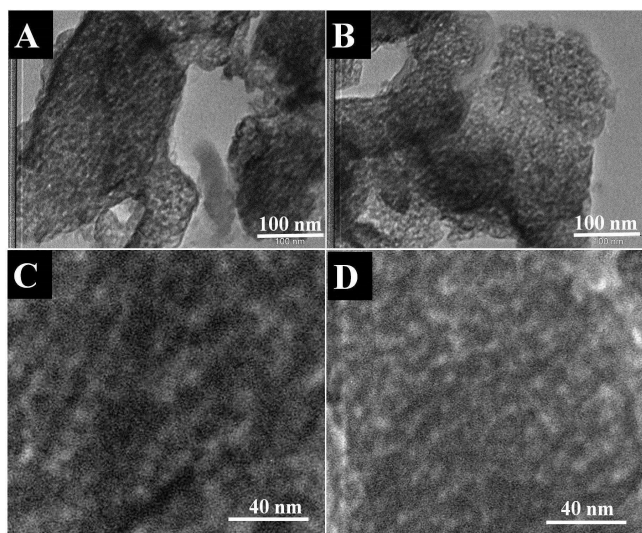
Herein we report a simple method for the synthesis of zirconium phosphate and aluminophosphate materials by using P123 block copolymer as an organic template. The typical synthesis method involves the admixing of 6.102 g of P123, 2.12 g of 1N HCl, 12.21 g of ammoniumdihydrogenphosphate, 75 g of methanol followed by its stirring at 60 °C for 2 hr until the formation of a clear solution (mixture A). Similarly 28.26 g of zirconium acetylacetonate and 75 g of methanol were admixed and heated at 45 °C under stirring for obtaining clear solution (mixture B). Now, mixture A is added slowly to mixture B with a continuous stirring (for 30 minutes) to form a precipitate. The resultant mixture was treated inside the Teflon-lined autoclave at 150 °C for 24 h. At the end of the treatment, the compound was washed and collected by filtration, dried and calcined at 500 °C for 5 hr. The same procedure is followed for the synthesis of aluminophosphate with the only difference being the use of aluminoisopropoxide in place of zirconium acetylacetonate. The resultant materials are denoted as ZP (zirconium phosphate) and AP (aluminophosphate) respectively.

The presence of Al, Zr, P and O samples was confirmed from EDX analysis (ESI Fig S1). Both AP and ZP sample exhibited similar weight loss patterns in TGA (ESI Fig S2), where major weight loss of ~17-26 wt% related to the degradation of P123-
 5 polymer was observed. The minor weight losses of 1.8-4.3 wt% was also observed at higher temperature range of 400-500°C in these samples, which indicates the continuous dehydrogenation and carbonization processes of the polymer species. These results indicate that the copolymer templates can be decomposed by
 10 calcination at 500°C for 5 h under N₂.²⁵

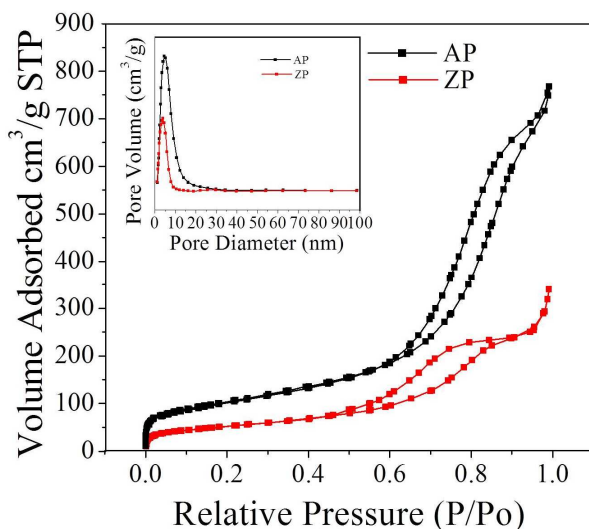
The low-angle XRD patterns (ESI Fig S3) of AP and ZP samples reveal the presence of mesopores in these materials.²⁶ The wide angle XRD of AP and ZP shows that both the sample are amorphous in nature (ESI Fig S4). The SEM (ESI Fig S5) and
 15 TEM images (Fig1) reveal the porous nature of the samples. The enlarged portion given in Fig 1 C and D indicates the uniformly distributed pores. Such a porous material is expected to exhibit high surface area and porosity. The porosity of the AP and ZP samples measured by N₂ adsorption-desorption measurements
 20 (Fig 2) further confirms the presence of mesopores. The adsorption-desorption isotherm also represent mixed type of isotherms (combination of type I, II and IV). The isotherm indicates the occurrence of well-defined capillary condensation at relative pressure (P/Po) of 0.5-1.0. The BJH pore size distribution
 25 curve of AP and ZP samples (Fig 2, inset) reveals the presence of mesopores. However, the shape of isotherms is different for two samples this may be due to the difference in interaction of the

30 **Table 1:** Textual properties of AP and ZP samples

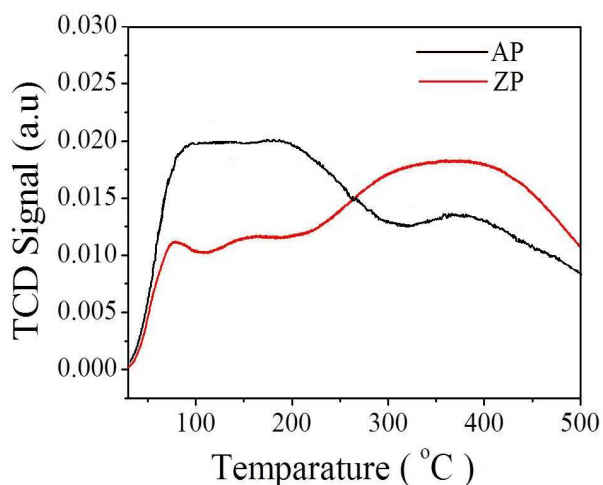
Samples	BET Surface Area(m ² /g)	Total Pore Volume(cm ³ /g)	Mean Pore Diameter (nm)
AP	370	1.17	12.68
ZP	188	0.51	10.92



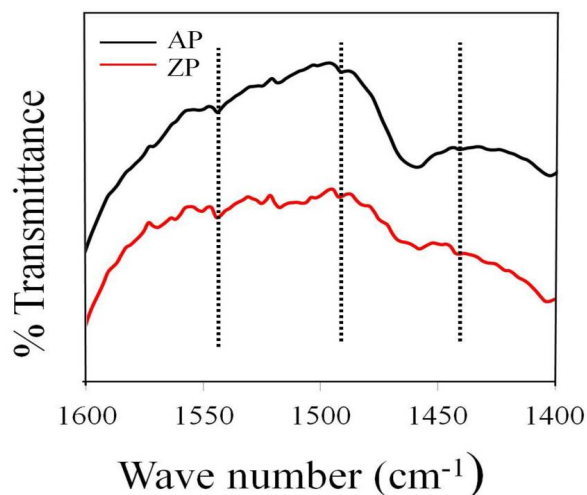
35 **Fig.1.** A, C and B, D are TEM images of AP, and ZP samples respectively



40 **Fig. 2.** N₂ adsorption-desorption isotherm, and BJH pore size distribution of AP and ZP materials (inset)



45 **Fig.3.** TPD spectra of the AP and ZP samples.



50 **Fig.4:** Pyridine FT-IR XRD of the AP and ZP samples

Table-2: Performance of catalysts in phenol alkylation reaction

Entry	Catalyst	Temperature (°C)	Time (h)	Cyclohexanol Conversion (%)	Product Selectivity (%)	
					O-Alkylation	C-Alkylation
1	AP	50	4	48	100	----
2		100	4	56	100	----
3		150	4	68	100	----
4		175	4	66	100	----
5		150	1	39	100	----
6		150	2	47	100	----
7		150	3	53	100	----
8		150	6	69	100	----
1	ZP	50	4	82	12	88
2		100	4	87	9	91
3		150	4	100	7	93
4		175	4	99	6	94
5		150	1	62	20	80
6		150	2	73	14	86
7		150	3	87	11	89
8		150	6	99	6	94

phenol= 1 mole, cyclohexanol=1 mole, Catalyst= 0.5 g.

chemical ingredients and the distribution of organic template with the Al and Zr. This is also reflected in the difference in BET surface area (370 m²/g and 180 m²/g) and pore volume (1.17 cm³/g and 0.51 cm³/g) of AP and ZP samples (Table 1). Relatively lower surface area and pore volume observed in ZP can be ascribed to the involvement of heavy metal Zr and higher density of the material. Both the samples exhibited similar BJH pore size distribution patterns with majority of pores having the diameter of 5 nm (peak maxima in Fig 3) revealing the formation of ordered nano size pores in these two amorphous materials.

The acidity patterns measured by TPD (Fig 3) indicates the presence of two NH₃ desorption peaks in both the samples; one broad peak centered at 150 °C and the other around 400 °C representing the weak and strong acid sites respectively. The intensity of strong acidity peak is relatively higher in case of ZP which indicates the creation of strong acid sites by the interaction of Zr with P in this material. The nature of acidity is further characterized by Pyridine FT-IR spectroscopy (Fig. 4). Usually, the IR bands appear at 1540–1548 cm⁻¹ and 1445–1460 cm⁻¹ relate with Brønsted (B) and Lewis (L) acid sites respectively. The IR patterns given in Fig 4 clearly indicate the presence of both Brønsted and Lewis acid sites in both AP and ZP samples, However, higher intensity of both Brønsted (at ~1540) and Lewis (~1445) acid sites was observed in the sample ZP when compared to those in AP. A band at ~1490 related to the combination of both Brønsted and Lewis acid sites is also observed in both the samples.²⁷

Catalytic alkylation of substituted phenols with cyclohexanol is one of the most important industrial organic reactions.²⁸ These reactions yield both O- and C-alkylated products having commercial utility. The O-alkylated products are promising perfumery compounds,²⁹ whereas the C-alkylated products are used as important intermediates in the preparation of dyestuffs, drugs, printing inks, wire enamels, rubber chemicals, petroleum additives, polymer additives, resins and so on.³⁰ Hence, the selective production of each alkylated product is quite challenging in these reaction processes. The concept of green chemistry and its applications in synthetic organic chemistry has been emerging as major route for the development of clean

chemical synthesis. Green chemical process for sustainable development always involves considerations such as use of cost-effective catalysts without any additives and employing a solvent-free system.³¹ In alkylation of phenol with cyclohexanol very few catalysts have been used, such as cation-exchange resin KU-2, H-zeolite and other conventional Lewis and Brønsted acid catalysts.³² But these catalysts produce many side products, the process is time consuming and consume large amount of solvent that gets wasted. Hence, the development of environmentally benign catalyst works in solvent-free alkylation yet exhibits efficient activity is a challenging task for modern organic synthesis. The AP and ZP samples possessing nanoporosity along with acidity are expected to exhibit promising catalytic activity towards this reaction. In the present study we have conducted reaction studies on these two nanoporous materials for the selective alkylation of phenol with cyclohexanol (ESI). The influence of the reaction temperature and reaction time was studied to understand the catalyst performance. By varying the reaction temperature from 50 to 150 °C, a gradual improvement in conversion of cyclohexanol (48 to 68 %) and selectivity of O-alkylated product (100%) is observed for the AP sample (Table 2 entries 1 to 3). The ZP sample also exhibited similar trend in conversion of cyclohexanol (82 to 100 %) and selectivity of C-alkylated product (88 to 93%) at constant reaction time of 4h (Table 2 entries 1 to 3). However, further increase in reaction temperature (175°C) did not cause any accountable effect on the conversion values on both the catalysts (Table2, entries 4 for AP and 4 for ZP). By varying the reaction time from 1 to 4 h, a gradual improvement in conversion of cyclohexanol (39 to 68 %) and selectivity of O-Alkylated product (100%) is observed for the AP sample (Table 2 entries 5 to 7 and 3). The ZP sample also exhibited same trend in conversion of cyclohexanol (62 to 100 %) and selectivity of C-alkylated product (80 to 93%) at constant reaction temperature of 150°C (Table 2 entries 5 to 7 and 3). However, further increase in reaction time (6) did not cause any accountable effect on the conversion values on both the catalysts (Table 2, entries 8 for AP and 8 for ZP). Overall, the AP/ZP catalysts of the present study exhibited maximum catalytic activity at 150°C at with in short reaction time of 4h reveals the promising catalytic activity of the samples.

The AP catalyst exhibited as high as 100% selectivity (Table 1) towards O-alkylation product at 68% conversion values. At similar reaction conditions, the ZP exhibited as high as 100% conversion with shifting of selectivity towards C-alkylation (93% selective) from O-alkylation product. Earlier alkylation studies on other types of catalysts such as zeolites indicated that large pore size of catalysts is responsible for ring alkylation whereas narrow pore size favors O-alkylation.^{33,34} Prins et al.³⁵ mentioned that the alkylation mainly occurred in the mesoporous parts of zeolites due to diffusion limitation of bulky molecules in the narrow pores. Moreover, the selectivity towards a particular product was mainly directed by the acidity of the catalyst system used.³⁶ Based on these reports we can deduce that both mesoporosity and external acid sites of catalysts play an important role on activity and selectivity in such chemo-selective alkylation reactions. The higher conversion values and C-alkylation activity of ZP catalyst of the present study can be ascribed to its higher acidity in terms of both Bronsted and Lewis acid sites (since, the porosity of ZP is comparable with AP). The studies, for the first time, indicate the potential applications of these materials for selective O-alkylation (AP) and C-alkylation (ZP) reactions. A reference experiment was also conducted in the absence of the catalyst, using only phenol and cyclohexanol, where no reaction was observed to proceed, which confirms the catalytic role of AP/ZP materials. The AP/ZP materials of the present study exhibited superior performance compared to those reported in the literature (ESI Table 1).

In summary, the present study provides a simple and novel method for the synthesis of ordered nanoporous aluminophosphate and zirconiumphosphate materials possessing promising catalytic activity towards industrially important selective alkylation of phenol for the efficient production of C-alkylation and O-alkylation products. Further, the materials show their reusability with an excellent catalytic performance even after five reaction cycles (ESI Table 2). The subject opens up a new property of the nanoporous aluminophosphate and zirconiumphosphate materials as suitable catalysts for selective alkylation reactions and has scope in improvement of the catalytic activity through the optimization of the synthesis procedure of nanoporous aluminophosphate and zirconiumphosphate for expansion of their applications to other selective alkylation reactions.

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