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Room temperature synthesis of ZnAlPO₄ nanoparticles and their catalytic applications[†]

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Here, we report a simple method for the synthesis of $ZnAIPO_4$ nanoparticles possessing stable structures even after the removal of the structure directing agent. The material can act as an efficient bi-functional catalyst for the alkylation of acetophenone with benzyl alcohol.

The synthesis of the aluminophosphate (AlPO₄) class of molecular sieves has been paid immense attention since its first discovery by Wilson in 1982.¹ Due to its exceptional hydrophilic properties and heat transformation ability, the zeotype AlPO₄ material has been successfully used in closed solar cooling systems. However, the neutral framework charge obtained by the presence of Al³⁺ and P⁵⁺ make this material non-acidic and this limits its applications in catalysis. This limitation has been successfully overcome by the introduction of a divalent heteroatom, such as Mg, Co and Zn, into the framework of the AlPO4 to create a negative charge in the framework responsible for acidity. The quantity of the heteroatom in the framework is directly related to the concentration of acidic sites. This has resulted in the synthesis of a wide variety of metal aluminophosphates (MAIPO₄s),² that exhibit the characteristics of zeolites and also show novel physicochemical properties suitable for acid-catalyzed reactions, magnetism, photoluminescence and ion-exchange applications.³⁻⁴ However, the introduction of high numbers of heteroatoms into the framework of AlPO₄ leads to its structural instability, which increases as the number of heteroatoms increases.⁵

AlPO₄ and MAlPO₄ materials are commonly synthesized under hydrothermal conditions using structure directing agents (SDAs) that are specific for each type of material. Many heteroatomcontaining aluminophosphates are unstable after the removal of SDAs which greatly limits their applications in catalysis and adsorption. Recently, research has been undertaken to synthesize

E-mail: nvish@iip.res.in; Fax: 91-135-2525702; Tel: 91-135-2525856 ^bCSIR-Indian Institute of Chemical Technology, Hyderabad, India. thermally stable MAIPO₄ materials by using novel SDAs, where the protonated organic SDA and H₂O played a charge-balancing role as per the host–guest charge density matching principle proposed by Stucky *et al.*⁶ In some cases, fluoride ions were also employed as structure directing agents along with organic amines to facilitate the formation of some special cage structures, such as a double 4-ring and to compensate the changes in the framework.^{7,8}

The control of molecular sieve synthesis on the nanoscale is gaining importance due to their high surface area and improved accessibility to active sites, because the small crystal size results in the presence of a shorter path length in the nanoaggregates, when compared to those in the corresponding microscale materials. Furthermore, the pore channels in the nanosystem also facilitate the facile diffusion of the reactants and products required for the efficient conversion of reactants with improved catalyst life; the most important property desired by both academia and industry.9 Several efforts have been made in recent years to obtain nanoparticles of the desired size, morphology and crystallinity through the optimization of the synthetic procedure, where a special emphasis was given to the stabilization of the nanoparticles in suspension and to decrease the production price.^{10,11} A typical synthesis of nanosized materials involved the use of excess organic additives and different solvents (water, methanol, ethanol, etc.). The crystal size was reduced in most cases by increasing the concentration of the organic template significantly, replacing the water with other solvents, decreasing the synthesis temperature and extending the crystallization process.¹² Unfortunately, these conditions made the synthesis of the nanocrystalline material complicated and economically non-viable, due to the large consumption of the expensive organic template and the increased consumption of energy.13

The α -alkylation of ketones is an industrially important reaction, where a transition metal based catalyst is used in the presence of a strong base such as KOH and a hydrogen trapping reagent such as an olefin.^{14–16} Since Zn is known for its dehydrogenation activity and MAIPO₄s have good catalytic applications, attempts have been made in the present study to apply a ZnAIPO₄ material for this reaction. Here, for the first time,

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we report a novel method for the room temperature synthesis of a nanosized $ZnAlPO_4$ material possessing a stable structure, using tetrapropylammonium bromide (TPABr) and fluoride as template and co-template. The material retained its structural identity even after the removal of the template by calcination, which makes the present material useful for high temperature applications. The novelty of the present work lies in (1) the first synthesis of a nanosized $ZnAlPO_4$ material, (2) the economical and room temperature synthesis of the nanomaterial and (3) its potential catalytic application for an α -alkylation reaction.

A typical synthetic method involves the dispersion of aluminum nitrate and zinc nitrate powders in a solution of ammonium orthophosphate with vigorous stirring at room temperature, followed by the sequential addition of tetrapropy-lammonium bromide and hydrofluoric acid, and leaving the resultant mixture stirring for one hour to obtain a homogeneous gel with an overall molar composition of $0.1Al_2O_3: 0.011Zn: 0.35P_2O_5: 0.0016SDA: 0.1HF: 3H_2O.$

The crystallization was carried out at room temperature by adding a few drops of ammonia and the white crystals obtained were filtered and washed with copious amount of de-ionized water and dried at room temperature overnight, followed by calcination for 5 h at 500 °C. The samples obtained before and after calcination were denoted as ZAP and ZAPC, respectively.

The X-ray diffraction patterns of the ZnAlPO₄ samples (Fig. 1) indicate the formation of a crystalline material with some ANA zeotype¹⁷ structure (ZAP), which upon calcination yielded a prominent phase of ANA along with an enhancement in the intensity of the peaks (ZAPC) (Fig.S1, ESI†). This may be due to the presence of impurity phases and the template in the assynthesized sample (ZAP) which were decomposed during calcination to give the pure crystalline structure (ZAPC). This synthesis of an ANA zeotype of ZnAlPO₄ is the first of its kind to be reported. The structural stability of the ZnAlPO₄ sample was confirmed by TGA-DTA analysis (Fig. S2, ESI†), where the sample showed a weight loss at 80–150 °C, related to the desorption of physically/chemically sorbed water and a high temperature weight loss, at up to 450 °C, related to the decomposition of the organic template and HF.¹⁸ There was no peak observed above 450 °C in



Fig. 1 Wide angle XRD patterns of the ZnAIPO₄ samples.

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Fig. 2 FTIR spectra of the ZnAIPO₄ samples.

the DTA analysis, indicating no further weight loss, suggesting the structural stability of the ANA crystalline phase of the ZnAlPO₄.

The structural identity of all the ZnAlPO₄ samples was confirmed by FTIR spectroscopy (Fig. 2 and Fig. S3, ESI[†]), where the samples, before and after calcination exhibited the characteristic vibrational bands associated with the $[PO_4]^{3-}$ unit (1127, 504 cm⁻¹) and pseudo-lattice Al (748 cm⁻¹).¹⁹ Furthermore, the two bands obtained at 1009 and 990 cm⁻¹ should be caused by the incorporation of Zn into the framework and were assigned to the vibrations of Zn–O–P.^{20,21} The additional bands observed in the samples before calcination (which disappeared after calcination) are related to the stretching vibrations of the SDA. The EDX analysis (Fig. S4, ESI[†]) also confirmed the presence of zinc, alumina and phosphorous species in the samples.

The structural morphology of the ZnAlPO₄ samples before and after calcination are shown in Fig. 3a and 3b; the sample synthesized at room temperature (ZAP) exhibited a spherical morphology, and well-defined spheres of 5 μ m size were obtained after calcination (ZAPC). The internal structure of the materials



Fig. 3 SEM and TEM images of the $ZnAIPO_4$ samples; (a) and (b) represent the SEM images of ZAP and ZAPC, while (c) and (d) represent the TEM images of ZAP and ZAPC.

Table 1 Catalytic performance of the ZnAIPO₄ (ZAPC) sample

		Selectivity (%)		
Catalyst	Acetophenone conversion	P1	P2	Р3
$ZAPC^{a}$ $ZAPC^{b}$	100 98	26 20	40 60	34 20
^{<i>a</i>} Fresh cat	alyst. ^b Used catalyst.			

was measured by TEM (Fig. 3c and 3d), where, the samples ZAP and ZAPC exhibited spherical particle aggregates of 30-40 nm size. The ANA zeotype (ZAPC) exhibited the highest acidity (Fig. S5, ESI[†]) and catalytic activity towards the alkylation of acetophenone with benzyl alcohol, where the conversion of acetophenone was observed to be almost 100% with the selectivity of three products, namely benzaldehyde (P1), 1-hydroxy-1,3-diphenylpropane (P2) and 1,3-diphenylpropane (P3) in 26%, 40% and 34%, respectively (Table 1). Used catalyst gave the maximum quantity of 1-hydroxy-1,3-diphenylpropane (P2) compared to the other products P1 and P3 (the maximum reaction was to stop at the hydrogenation product), which may be due to the maximum number of Zn active sites being present, compared to the acidic proton active sites (the maximum product P2 is the alcohol compared to the dehydrogenation product). This can be explained by a bi-functional mechanism facilitated by the presence of Zn and the acidic proton on the catalyst, where the formation of benzaldehyde occurred through the dehydrogenation of benzyl alcohol on the Zn sites, followed by the reaction of the resultant benzaldehyde with acetophenone to form an alkylation product, in the presence of the acidic sites (Fig. 4). Here, the hydrogen evolved from benzyl alcohol could be utilized in the hydrogenation steps of the alkylation intermediates, to form products P2 and P3, whose derivatives have potential pharmaceutical and therapeutic applications.²² The effective conversion of benzyl alcohol observed in the reaction demonstrated the effective dehydrogenation activity of the Zn sites and the catalyst exhibited a comparable activity after



Fig. 4 Scheme for reaction pathways.

three reaction cycles. These results indicated a better performance of the ZAPC catalyst, when compared with previously reported results (ESI[†] Table 1). A reference experiment conducted in the absence of the catalyst, using only acetophenone and benzyl alcohol, ascertained that no reaction occurred and confirmed the catalytic role of the ZnAlPO₄. At this stage, the role of the ANA phase of the material in catalysis is not clear. However, the nanometer particles obtained in the present study may be responsible for the catalytic activity of the ZnAlPO₄. In general, ANA zeolites, as well as ZnAlPO₄ materials obtained in the micrometer range^{23,24} and the nano level material of the ANA phase obtained in the present method, are important for material applications.

In summary, the present study describes a novel method for the synthesis of ANA zeotype nanostructures of a ZnAlPO₄ material with high thermal stability. The synthesis of ZnAlPO₄ possessing an ANA zeotype obtained by just the room temperature mixing of chemical ingredients is reported for the first time and provides an effective synthetic method using a simple organic template, TPABr, with a short synthesis time. Moreover, the material retained its structure even after the removal of the organic template through calcination, that further revealed the suitability of these materials for high temperature applications. The ANA zeotype material also exhibited an excellent catalytic activity in the conversion of benzyl alcohol with considerable selectivity towards the alkylated products of acetophenone through a bi-functional reaction network facilitated by the presence of the dehydrogenation functional Zn in combination with acidic protons. These findings open up an opportunity to explore the potential of this class of materials for various high temperature applications.

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