

Contents lists available at ScienceDirect

Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

Mesoporous zirconium phosphate catalyzed reactions: Synthesis of industrially important chemicals in solvent-free conditions

Apurba Sinhamahapatra^a, Narottam Sutradhar^a, Biplab Roy^a, Abhijit Tarafdar^b, Hari C. Bajaj^a, Asit Baran Panda^{a,*}

^a Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (Council of Scientific and Industrial Research), G.B. Marg, Bhavnagar 364021, Gujarat, India

^b Department of Chemistry, Indian Institute of Technology, Kharagpur, W.B., India

ARTICLE INFO

Article history: Received 8 April 2010 Received in revised form 4 June 2010 Accepted 9 June 2010 Available online 1 July 2010

Keywords: Solid acid catalyst Zirconium phosphate Mesoporous Industrial chemicals Benzylation reaction

ABSTRACT

Mesoporous zirconium phosphate (m-ZrP) having high specific surface area and narrow pore size distributions is synthesized in basic medium using zirconium carbonate as source of zirconium. The concentration of phosphate in precursor solutions, as well as the calcination temperature, is found to influence the textural properties and acidity of synthesized m-ZrP significantly. Microscopic analysis indicates the presence of worm like pores with spherical morphology. The porous structure has remarkable thermal stability (up to 800 °C). DRIFT and NH₃-TPD analysis suggest the presence of reasonable amount of Lewis and Brönsted acid sites. High catalytic activity of synthesized m-ZrP is observed towards Friedel–Craft (F.C.) benzylation reaction. The effect of acid strength of catalyst, reaction time, temperature and amount of catalyst towards Friedel–Craft benzylation reactions in solvent-free conditions. The catalytic activity of m-ZrP is much higher than that of conventional layered ZrP. The catalysts were separated easily from reaction mixture, regenerated after a simple activation step and reused at least six times without significant loss in catalytic activity.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In the field of catalysis, solid (heterogeneous) acid catalysts are increasingly needed because they are environmentally green with respect to corrosiveness and safe to use, generation of waste, ease of recovery and reusability [1]. These solid acids are safe alternatives to hazardous mineral acids. In the recent past, numbers of solid acids have been developed for different applications [2–10]. However, the reported catalysts have disadvantages like low thermal stability, low surface area, less water tolerance ability and small pores for bulky reactant; their sedimentation property is low and some times large amounts of catalyst are required for high yields [10–13]. Therefore, a solid acid which can overcome all these drawbacks would be of interest.

Zirconium phosphate (ZrP), a well-known layered inorganic material exhibits proton conductivity and ion exchange and adsorption properties [14–17]. ZrP is also an important solid acid catalyst [18–20] with high thermal stability, high water tolerance ability and easy sedimentation [11,21]. However, its use as a solid acid catalyst is limited to dehydration, isomerization and ester

hydrolysis [11,18–20]. Use of layered ZrP as solid acid catalyst for the synthesis of industrially important fine chemicals involving bulky molecules is rare, due to its low surface area and small interlayer distance (0.76 nm) [14], that often limit the reactions of bulkier molecules only to the surface [22,23]. To increase the surface area and interlayer distance, attempts have been made to synthesize its "pillared" derivatives through intercalation of inorganic, organic and organometallic molecules [24,25].

Mesoporous zirconium phosphate (m-ZrP) with uniform pore diameter (>2 nm) is an alternative of layered ZrP and may improve its surface area as well as its catalytic activity towards bulky molecules. Different groups have synthesized surfactant-assisted m-ZrP with surface areas in the range of 200–500 m² g⁻¹ [26–31] using zirconium oxychloride and moisture-sensitive zirconium alkoxide in acidic conditions. Beside these, syntheses of m-ZrP by basic route [32], acid–base pair route [33] and non-template route [34] are also available. However, catalytic use of m-ZrP is rare and limited only to esterification, ester hydrolysis and dehydration of alcohol [26,29,32].

Here, we report the preparation of thermally stable m-ZrP with excellent acidic nature, high surface area $(532 \text{ m}^2 \text{ g}^{-1})$ and narrow pore size distribution (~2.9 nm) by employing *in situ* generated zirconium carbonate complex as zirconium precursor, and cetyltrimethylammonium bromide (CTAB) as surfactant under

^{*} Corresponding author. Tel.: +91 278 2567760x704; fax: +91 278 2567562. *E-mail addresses*: abpanda@csmcri.org, asit012@gmail.com (A.B. Panda).

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2010.06.016

basic condition (pH 9.2). The activity of the synthesized m-ZrP as solid acid catalyst was explored in the Friedel–Craft (F.C.) benzylation of benzene to bi-phenyl methane. Also, 7-hydroxy-4-methyl coumarin, 3,4-dihydropyrimidine, chalcone and flavanone, benzoxanthene and ketal of cyclohexanone were synthesized using the catalyst. All the synthesized compounds and their derivatives are industrially important and have versatile applications either directly or as synthetic intermediates [35–37]. All these reactions were carried out in solvent-free conditions.

2. Experimental

2.1. Materials

Zirconium oxychloride octahydrate (ZrOCl₂•8H₂O), diammonium hydrogen ortho-phosphate [(NH₄)₂HPO₄] and cetyltrimethylammonium bromide (CTAB) were purchased from s. d. Fine chemicals, India; Ammonium carbonate was purchased from Rankem, India and used as such. Water with a resistivity of 18 M Ω cm was used for all the reactions. All the chemicals for organic reactions were purchased from Spectrochem and SRL India.

2.2. Synthesis of m-ZrP

Syntheses of m-ZrP were performed using the optimized amounts of water and CTAB. Only the ratio of phosphate was varied and the molar composition for all the syntheses was 1 Zr^{4+} : 0.25 – 3 PO₄³⁻: 0.25 CTAB: 1000 H₂O. In this paper, the m-ZrPs synthesized with varying amounts of phosphate are named as m-ZrP-*x*, where *x* stands for the molar ratio of phosphate to zirconium (P/Zr) in the precursor solution.

In a typical synthesis of the m-ZrP-2 with $1Zr^{4+}$: 2 PO₄³⁻:0.25 CTAB: 1000 H₂O molar ratio, 8.0 g zirconium oxychloride was dissolved in 100 ml of water. A dilute aqueous solution of ammonium carbonate was added slowly to the zirconium oxychloride solution under continuous stirring. A white precipitate appeared. After complete precipitation, the precipitate was filtered off and washed with water to remove the chloride ions. The chloride free precipitate was re-dissolved in aqueous solution of ammonium carbonate (5 g); a clear solution was obtained and the volume of the solution was make up to 175 ml by water. A fifty ml aqueous solution of 6.55 g di-ammoniumhydrogen orthophosphate was added to the clear solution and the mixture was stirred for 20 min. This clear solution mixture was added at a fixed flow rate $(5 \text{ ml} \text{ min}^{-1})$ to a pre-prepared 225 ml 1% (w/v) aqueous solution of CTAB under constant stirring. It resulted in a white precipitate. The whole reaction mixture was stirred for 12 h at ambient condition, then aged at 80 °C for 2 days and at 90 °C for 1 day in a closed glass reactor. Then, it was aged for another one day in a teflon lined autoclave at 120 °C. After cooling, the reaction mass was filtered, washed thoroughly with distilled water and dried in a hot air oven at 80 °C. The dried samples were calcined at 550 °C for 6 h to get pure mesoporous zirconium phosphate.

2.3. Catalyst characterization

Powder X-ray diffraction patterns were collected in two different 2θ ranges of $1-7^{\circ}$ and $20-80^{\circ}$ with a Philips X'pert X-ray powder diffractometer using Cu K α (λ = 1.54178 Å) radiation.

Nitrogen adsorption/desorption measurements were performed at 77 K using a ASAP 2010 Micromeritics instrument, USA, after degassing of samples under vacuum (10^{-2} Torr) at 250 °C for 3 h. The surface area was determined by the BET equation. Pore size distributions were determined using BJH model of cylindrical pore approximation. An inductively coupled plasma-optical emission spectrophotometer (ICP-OES, Optima 2000 DV, PerkinElmer, Eden Prarie, MN) was used to determine the percentage of the phosphate ion incorporated in the calcined samples.

A scanning electron microscope (SEM) (Leo series 1430 VP) equipped with INCA was used to determine the morphology of samples. The sample powder was supported on aluminium stubs and then coated with gold prior to measurement.

Transmission electronic microscope (TEM) images were collected using a JEOL JEM 2100 microscope. Samples were prepared by mounting ethanol-dispersed samples on lacey carbon formvar coated Cu grids.

³¹ P solid-state NMR was performed using a Bruker AvanceII-500 spectrometer.

The FT-IR spectroscopic measurements and Diffuse reflectance FT-IR (DRIFT) measurements were carried out using a PerkinElmer GX spectrophotometer. The spectra were recorded in the range 400–4000 cm⁻¹ using a KBr technique.

Temperature programmed desorption (TPD) measurements were conducted on a Micromeritics Autochem-II Chemisorption analyzer instrument, and for this 200 mg of sample were placed in a U-shaped sample tube. Samples were pre-treated in helium $(35 \text{ cm}^3 \text{ min}^{-1})$ at $250 \,^{\circ}\text{C}$ for 30 min and then, 1 h at $350 \,^{\circ}\text{C}$ and cooled to $100 \,^{\circ}\text{C}$. Then ammonia (100 Torr) was adsorbed on the samples for 1 h. The physisorbed ammonia was removed by flushing the sample by helium for 1 h. TPD measurements were carried out in the temperature range of $100 \,^{\circ}\text{C}$.

2.4. Catalytic application

All catalytic organic reactions were performed under reflux condition using a pre-heated oil bath under ambient pressure in solvent-free conditions with continuous stirring (500 rpm). Catalytic activity of the synthesized m-ZrPs was studied in Friedel–Craft benzylation reaction. The effect of phosphate loading in m-ZrP on catalytic activity for benzylation of benzene by benzylchloride was studied. The effect of reaction parameters, such as reaction time (1–6 h), reaction temperature (70–140 °C), amount of catalyst (1–5 wt%) and ratio of benzene to benzylchloride (14:1 to 1:1) on the benzylation reaction of benzene were also studied.

In a typical benzylation reaction of benzene by benzylchloride, 7.5 mmol of benzylchloride and 75 mmol of benzene with 2.5 wt% (weight percent) catalyst with respect to benzylchloride was refluxed at 110 °C for 5 h under constant stirring and the final product was analyzed by GC–MS (GC–MS QP 2010, Shimadzu). Benzylations of substituted benzenes such as toluene, xylene, anisole, phenol, chloro benzene or nitro benzene by benzylchloride were also performed in optimized condition. At the end of the reaction, the catalysts were separated from reaction mixtures by centrifuging and regenerated by a simple regeneration step for re use. Each used sample was re-cycled for six times. In a typical procedure for regeneration of the catalyst, 1 g of catalyst was refluxed with 40 ml 30% (w/v) H₂O₂ for 3 h at 80 °C with continuous stirring. Then the catalyst was filtered, washed with distilled water, and dried at 100 °C for 3 h.

Another five different acid catalyzed reactions were also performed using the best m-ZrP catalyst (as identified in benzylation reaction) to check the catalytic efficiency of the synthesized m-ZrP, which includes synthesis of 7-hydroxy-4methyl coumarin by Pechmann condensation reaction using resorcinol and ethylacetoacetate; synthesis of 14-phenyl-14Hdibenzo[a,j]xanthene using benzaldehyde and β -naphthol; synthesis of 3,4-dihydropyrimidin-2(1H)-ones by Biginelli type reaction using ethylacetoacetate, benzaldehyde and urea; synthesis of chalcone and flavanone by Claisen–Schmidt condensation reaction using 2'-hydroxyacetophenone and benzaldehyde; protection of



Fig. 1. N_2 adsorption–desorption isotherm and corresponding pore size distribution curves (inset) of the synthesized mesoporous zirconium phosphate calcined at 550 $^\circ$ C for 6 h.

carbonyl group of cyclohexanone by ethylene glycol through ketal formation. The detailed experimental procedures of these reactions are described in supporting information.

Separately, all the above-mentioned reactions were performed under identical procedure and conditions, using conventional layered ZrP as catalyst. The layered ZrP was synthesized following the method described by Alberti and Costantino [38].

The hydrolysis of ethyl acetate and esterification of acetic acid with ethanol in aqueous solution were performed, following the procedure described by Kamiya et al. [11] using m-ZrP-2, to evaluate the water tolerance capacity of the synthesized m-ZrP.

3. Results and discussion

3.1. Catalyst characterization

m-ZrP was synthesized hydrothermally using zirconium carbonate complex as the source of zirconium in the presence of di-ammonium hydrogen ortho-phosphate and CTAB, with a molar ratio of 1 Zr⁴⁺:0.25–3 PO₄^{3–}:025 CTAB:1000 H₂O. After aging and drying, the as-synthesized samples were calcined at 550 °C to remove the structure-directing reagent (CTAB).

3.1.1. Textural properties

Table 1 summarizes the effects of the amount of phosphate in the precursor solution on textural properties like specific surface area (S_{BET} , $m^2 \, g^{-1}$) and average pore size distribution (D_{ave} , nm) on synthesized m-ZrP. Fig. 1 represents the nitrogen adsorption–desorption isotherms and pore size distribution curve of m-ZrP-2 as typical representative. Nitrogen adsorption–desorption jotherm patterns of all the samples are

Table 1

Textural, structure and composition results of m-ZrP samples calcined at 550 °C.



Fig. 2. Relation of surface area with calcination temperature of m-ZrP-2.

almost identical and correspond to type IV indicating that the synthesized m-ZrPs are mesoporous in nature, except m-ZrP-0.25. Nitrogen adsorption–desorption isotherms patterns of m-ZrP-0.25 is correspond to type II typically pores between the particles. The pore size distribution analysis using BJH method from desorption part of the isotherm of m-ZrP-2 (inset Fig. 1) reveals a very narrow pore size distribution. From the data listed in Table 1, one can conclude that the samples synthesized using phosphate to Zr molar ratio in the range of 0.5–2.5 in the precursor solution do not show any significant variation on surface area (391–407 m² g⁻¹) as well as pore size (Table 1). For the samples synthesized using the molar ratio of phosphate to zirconium beyond the range, i.e., m-ZrP-0.25 and m-ZrP-3, the surface area is low and at the same time the pore size is low for m-ZrP-0.25 and high for m-ZrP-3 (*vide supra*).

The sample m-ZrP-2 was calcined at different temperature (450–800 °C) for 6 h to study the effect of calcination temperature on the specific surface area of the synthesized m-ZrP. Fig. 2 represents the change of surface area with calcination temperature. It shows gradual reduction in specific surface area from $532 \text{ m}^2 \text{ g}^{-1}$ (calcined at $450 \,^{\circ}\text{C}$) to $223 \,\text{m}^2 \text{ g}^{-1}$ (calcined at $800 \,^{\circ}\text{C}$) with increasing calcination temperature. The specific surface area of m-ZrP-2 after calcining at $800 \,^{\circ}\text{C}$ is much higher than that found in the previous report ($132 \,\text{m}^2 \,\text{g}^{-1}$) [34], which suggests that the as-synthesized m-ZrP in the present investigation has high thermal stability.

3.2. Structure and composition analysis

3.2.1. XRD pattern

Wide and small angle powder XRD patterns of calcined m-ZrP samples are shown in Fig. 3. The wide angle powder XRD patterns of calcined samples exhibit two broad peak in 2θ ranges of

| Samples | Reactant ratio of Zr ⁴⁺ :PO ₄ ³⁻ :CTAB:H ₂ O | $S_{\rm BET}{}^{\rm a} ({\rm m}^2{\rm g}^{-1})$ | $D_{\rm ave}{}^{\rm b}$ (nm) | $2\theta^{c}$ | P/Zr ^d |
|------------|--|---|------------------------------|---------------|-------------------|
| m-ZrP-0.25 | 1:0.25:0.25:1000 | 263 | 2.6 | - | 0.22 |
| m-ZrP-0.5 | 1:0.5:0.25:1000 | 398 | 2.9 | 2.25 | 0.42 |
| m-ZrP-1 | 1:1:0.25:1000 | 394 | 2.9 | 2.2 | 0.95 |
| m-ZrP-1.5 | 1:1.5:0.25:1000 | 391 | 2.9 | 2.25 | 1.43 |
| m-ZrP-2 | 1:2:0.25:1000 | 407 | 2.8 | 2.2 | 1.76 |
| m-ZrP-2.5 | 1:2.5:0.25:1000 | 396 | 2.8 | 2.2 | 1.93 |
| m-ZrP-3 | 1:3:0.25:1000 | 261 | 5 | 1.7 | 2.21 |
| | | | | | |

^a BET surface area.

^b Average pore width (4V/A by BET).

^c Low angle peak positions.

^d Determined from the elemental analysis.



Fig. 3. Wide angle (a) and small angle (b) XRD patterns of synthesized m-ZrP.

 $10-40^{\circ}$ and $40-70^{\circ}$ (Fig. 3a) indicating their amorphous nature. Only for the m-ZrP-0.25 was a distinct crystalline peak of zirconia was observed, where the phosphate to zirconia ratio was very low (0.25). In other samples, no individual crystalline peaks of zirconium phosphate and zirconia were observed even after calcining at 800 °C. This again confirms the high thermal stability of synthesized m-ZrP. A single broad peak in small angle region was observed at around 2θ = 2.2–2.3, corresponding to a *d*-value of ~4 to 3.8 nm (Fig. 3b). No significant change in the small angle peak positions was observed on varying phosphate loading in the precursor solution in the range of 0.5–2.5. Lowering of the peak position was observed in samples synthesized taking P/Zr ratio beyond the range. The shifting of low angle XRD peak position towards low angle (i.e., higher *d*-value) was observed in the sample m-ZrP-3. This result also supports the increase of average pore width in BET surface area measurements for m-ZrP-3, whereas, in m-ZrP-0.25 no distinct XRD peak was identified in low angle region. The low angle diffraction peak also signifies the formation of a mesoporous zirconium phosphate phase unlike normal intercalated or layered zirconium hydrogen phosphate [39]. Presence of only one broad peak implies the presence of pores in short range order.

From the ICP data (Table 1), it is evident that, the phosphate incorporation was gradually increased in m-ZrP as the amount of phosphate was increased in the precursor solution. Initially the incorporation of phosphate was linear, and then it started decreasing when the P/Zr molar ratio equals to 1.5.

3.2.2. Morphology

Fig. 4 represents the SEM and TEM micrographs of the synthesized m-ZrP-2 calcined at 550 °C for 6 h, as a typical example. The SEM micrograph (Fig. 4a) shows spherical particles in nature with very smooth surface. The low resolution TEM micrograph (Fig. 4b) indicates that all the spherical particles are attached together and porous. A comparatively more magnified microgram (Fig. 4c) confirms the presence of worm like pore structures. The pores are highly mono-dispersed with an average pore size of ~3 nm, supporting the average pore size data obtained from BET results. SEM and TEM results of all the calcined (450–800 °C) samples show similar uniform morphology.

3.2.3. ³¹P MAS NMR spectroscopy

Solid-state ³¹P MAS NMR spectra of the synthesized m-ZrP samples were performed to evaluate the co-ordination state of the phosphorous atom. Fig. 5 represents the ³¹P MAS NMR spectra of as-synthesized and calcined (550 °C) m-ZrP-2 as typical representative. Peaks at -5.8 and -12.6 ppm in the as-synthesized m-ZrP-2 can be assigned to the tetrahedral phosphates connected with one $[(OH)_3P-OZr]$ zirconium atom and two $[(OH)_2P-(OZr)_2]$ zirconium atom, respectively. The sample calcined at 550 °C (Fig. 5) showed low intense peaks at -6.1 [(OH)₃P-OZr] and -16.2 ppm $[(OH)_2P-(OZr)_2]$ and a high intense peak at -21.3 ppm due to the presence of the tetrahedral phosphates connected with three zirconium atoms[(OH)P-(OZr)₃] [40]. On further increment of calcination temperature of m-ZrP-2 at 650°C, a peak at -24.7 ppm was observed indicating the presence of phosphate with 4 P-O-Zr bonds. Spectra of the samples calcined at 750 and 800 °C showed the presence of an intense peak at -24.7 ppm and a low intense peak at -30.1 ppm, implying the presence of large amount phosphate with 4 P-O-Zr bonds and small amount of P-O-P bonds respectively [40]. The changes in ³¹P NMR peak position are due to changes of the environment of the phosphate group on calcination. It may be possible that the connectivity of phosphorous atom of the synthesized material was increased during calcination and at a very high temperature a certain amount of phosphate was converted to poly phosphate. The as synthesized and calcined (550 °C) samples with different amount of phosphate loading showed almost identical spectra to that of m-ZrP-2, except m-ZrP-3. The spectra of the m-ZrP-3 shows the peaks at -18.5, -24.7 and -30.1 ppm, which can be attributed to the presence of $[(OH)P-(OZr)_3]$, $[P-(OZr)_4]$ and polyphosphate (P–O–P) bonds. The relevant broad resonance peak in ³¹PNMR may be due to amorphous nature of m-ZrP which lacks the atomic resolution that is present in crystalline phosphate.

3.2.4. FTIR spectroscopic analysis

FTIR spectra of as-synthesized and calcined (550°C) m-ZrP-2 (Fig. 6a) show absorption bands at 1000–1100 cm⁻¹ corresponding to P–O stretching vibration and bands at 2361 cm^{-1} due to the (P)–OH stretching vibration [41]. The bands at 3500 and 1650 cm⁻¹ are attributed to the asymmetric OH stretching and bending of water molecule, respectively. Bands at 1471 and 2800-3000 cm⁻¹ that disappear after calcinations are assigned to the C-H stretching of the surfactant. After calcinations in the P-O stretching region $(1000-1100 \text{ cm}^{-1})$, the bands shift towards higher wave numbers by ca. 55-65 cm⁻¹, which indicates that the P-O bonds in the tetrahedra become more covalent. The absence of band at \sim 750 cm⁻¹ suggests the nonexistence of P–O–P (poly phosphate) like groups which would also explain the absence of signal at around -30 ppm in the solid state ³¹P MAS NMR of m-ZrP-2. The FT-IR spectra of m-ZrP-2 calcined at different temperatures and m-ZrP samples synthesized with varying amount of phosphate shows almost identical patterns to that of m-ZrP-2, except for m-ZrP-2 calcined at 800 °C and m-ZrP-3. In these two samples an additional peak at 755 cm⁻¹

A. Sinhamahapatra et al. / Applied Catalysis A: General 385 (2010) 22-30



Fig. 4. SEM (a) and TEM (b and c) micrographs of m-ZrP-2.

is observed, which would again support the result of ³¹P MAS NMR spectra, the presence of a polyphosphate group.

3.3. Determination of acidity of m-ZrP by DRIFT and TPD

For the determination of surface acidity of m-ZrP, FT-IR using pyridine as probe molecule is an important and effective method. Pyridine forms pyridinium ions with protons (Brönsted acid sites) and is coordinated to electron-pair deficient site (Lewis acid centers) [42]. In DRIFT spectra of the pyridine absorbed m-ZrP-2 (Fig. 6b), the strong bands at 1634 and 1541 cm⁻¹ indicating typical pyridinium ion confirming the presence of Brönsted acid sites. This Brönsted acidity arises probably due to the presence of reasonable amount of geminal P (OH) groups [43]. The band at 1450 cm⁻¹



Fig. 5. Solid-state ³¹P MAS NMR spectra of the as synthesized and calcined m-ZrP-2.

is due to the pyridine attached to a Lewis acid centre. The band at 1489 cm⁻¹ is a combination band between two separate bands at 1541 and 1450 cm⁻¹, corresponding to Brönsted and Lewis acid sites, respectively. With an increasing temperature during DRIFT analysis, the intensity of 1450 and 1489 cm⁻¹ bands are decreased, however the intensity of the 1541 cm⁻¹ band remains almost the same, indicating that the Lewis acid sites are weak compared to the Brönsted acid sites (Fig. 6b). It is possible to measure a semi-quantitative ratio of Brönsted and Lewis acid sites present in the catalyst by calculating area under the peak of 1450 cm⁻¹ (exclusively due to pyridine at Lewis acid sites) and 1541 cm⁻¹ (exclusively due to pyridine at Brönsted acid sites) [44]. The ratios of Brönsted and Lewis sites of all the catalyst are presented in Fig. 7. As can be seen in Fig. 7, increase in phosphate loading in m-ZrP samples gradually increases Brönsted acidity up to P to Zr ratio of 2. Brönsted acidity values of m-ZrP-2 and m-ZrP-2.5 (P/Zr ratio 2 and 2.5) are almost the same. Further increase of phosphate content (m-ZrP-3, P/Zr ratio 3) results in a decrease in Brönsted acidity. Moreover, a gradual increase of phosphate (confirmed by ICP results) as well as of P-OH groups causes an increase in Brönsted acid sites. The decrease in the Brönsted acidity in m-ZrP-3 may be due to the formation of polyphosphate, as a single poly-phosphate bond formation occurs by sacrificing two P-OH groups (responsible for Brönsted acidity).

NH₃-TPD was measured to evaluate the total acidity and the strength of acid sites of the synthesized m-ZrP. The characteristic TPD curves of all the samples are very similar. NH₃-TPD curve of m-ZrP-2, calcined at 550 °C (Fig. 8) shows that desorption of ammonia starts significantly at 205 °C, and does not complete even at 900 °C. Further, one distinct peak, centered at 433 °C with a hump at ~326 °C is also observed. The result indicates the presence of significant amount of strong acid sites in the calcined m-ZrP. In addition, Fig. 7 illustrates the total concentration of acid sites of all samples and in particular, shows that the total acidity of the samples



Fig. 6. FT-IR spectra of as synthesized and calcined m-ZrP-2 (a) and DRIFT spectra of pyridine absorbed m-ZrP-2 at various temperature 50-450 °C (b).

increases gradually with increasing phosphate loading. It reaches a maximum in m-ZrP-2, with a P/Zr value of 2 due to enhanced P-OH group concentration. Further addition of phosphate loading decreases the acidic properties, probably because of polyphosphate formation. It is interesting to note that the P-OH groups present



Fig. 7. Contribution of Brönsted and Lewis acid sites in surface acidity as obtained from DRIFT measurements using pyridine as probe. Total acidity obtained from NH₃-TPD.



Fig. 8. NH₃-TPD profile of m-ZrP-2.

on the surface are responsible for the acidity that was measured by TPD analysis. The total acidity also decreased with increasing the calcinations temperature. Initially $(450-550 \,^{\circ}\text{C})$ the decrease in acidity with the increase in calcination temperature was nominal, but at a higher temperature $(800 \,^{\circ}\text{C})$ the total acid strength decreased remarkably; this may be due to the decrease in surface area and polyphosphate formation.

3.4. Formation mechanism

Mesoporous ZrP is synthesized hydrothermally using zirconium carbonate complex, di-ammonium hydrogen ortho-phosphate and CTAB as cationic pore directing agents in basic medium (pH \sim 9.2). As zirconium exhibits very pronounced polyoxo ion chemistry in aqueous solution [45], depending on the reaction conditions, there are various possibilities for preparing mesostructure phosphate composite. The zirconium ions in basic aqueous solution (pH 9.2) exist as negatively charged species (isoelectric point of hydrous zirconium is 6-8 depending upon other ions in the solution) in aqueous solution. In the present studies we have used cationic surfactant CTAB as pore directing agent, analogous to MCM-41 synthesis, the charge interaction between anionic inorganic species (I)and cationic surfactant (S⁺) induces mesostrucrure formation. The phosphate interacts with hydroxyl groups of zirconium. Phosphate ion can form three types of bonds with zirconium (Fig. 9). During surfactant removal through calcination, the pore structure may collapse partially due to self-condensation of -OH groups in hydrated zirconium phosphate. However, the phosphate ions attached to zirconium ion in a cross-linked way (Fig. 9a) are expected to stabilize the pore structure and prevent pore collapsing. The phosphate ions bonded to Zirconium as in Fig. 9b may, however, be unable to stabilize the structure effectively, as they are co-ordinated in an isolated manner. Phosphate ions bonded according to Fig. 9b condense with neighboring phosphate groups or free phosphate groups and formed the bond as seen in Fig. 9c [45].



Fig. 9. Probable structure of phosphate with zirconia.



Scheme 1. Organic reactions performed using synthesized mesoporous ZrP as solid acid catalyst.

When the amount of phosphate is very low (m-ZrP-0.25, P/Zr = 0.25) in comparison to the total zirconium ions, zirconium ions are partially stabilized. On calcination, partial crystallization of non-stabilized zirconium took place, which resulted in the formation of non-structural pores and reduction of structural pore size. So the surface area of m-ZrP-0.25 is less and pores are random. For the presence of random and nonstructural pores, we could not identify any peak in the low angle region. With an increase in the amount of phosphate, particularly for the m-ZrP samples where the P/Zr ratio in the precursor is \geq 0.5, maximum stabilization of zirconium ion takes place. So the samples are amorphous in nature as the maximum zirconium ions are stabilized by phosphate ion even after calcination at 800 °C.

3.5. Catalytic performances

The catalytic performances of the synthesized m-ZrP were screened in the liquid phase F. C. benzylation reaction of aromatic compounds using benzylchloride as benzylating agent in solvent-free condition (Scheme 1).

In the first set of experiments, the benzylation reaction was carried out using 75 mmol of benzene and 7.5 mmol of benzylchloride at 110 °C using 2.25 wt% (with respect to benzylchloride) of synthesized m-ZrP as solid acid catalysts. Fig. 10 represents the respective reaction profiles. As can be seen, all the catalysts with different phosphate loadings show a similar profile and exhibit conversion



Fig. 10. Reaction profile (conversion) obtained for the benzylation of benzene with benzylchloride over the prepared m-ZrP catalyst.

of benzyl chloride ranging from 82 to 94% with 100% selectivity for bi-phenyl methane in 5 h. The conversion of benzylchloride increases gradually with increasing reaction time and becomes steady after a certain time (Fig. 10). Since observed selectivity is 100% for all the catalysts, the conversion can be used as a good indicator of catalytic activity, and consequently the obtained conversions were used to compare the catalytic performances of the different prepared samples. As can be seen in Fig. 10, samples with different amounts of phosphate loading has significant influence in benzylation reaction; conversion increases gradually with increasing amount of phosphate. The conversion reaches \sim 94% in the presence of m-ZrP-2 and m-ZrP-2.5 (P/Zr = 2 and 2.5 respectively). With further increase of phosphate (m-ZrP-3) the conversion decreases. The surface areas of all the catalysts are almost the same except m-ZrP-3, but the acidity increased with phosphate and decreased above P/Zr ratio of 2.5. So, increase in catalytic activity is only due to the increase of acidic nature of the catalyst. Due to its better performance, m-ZrP-2 was used for further studies.

The effects of reaction temperature on catalytic activity and selectivity were examined in the temperature range of 70 and 140 °C in the absence of solvent using m-ZrP-2 as catalyst (Fig. 11). It was found that the conversion of benzylchloride increased gradually with temperature (70–110 °C) having excellent selectivity of



Fig. 11. Effect of reaction temperature on the benzylation of benzene with benzylchloride over the m-ZrP-2.

| Table 2 | 2 |
|---------|---|
|---------|---|

| Friedel-Craft benzylation reaction | of different substituted benze | ne by benzylchloride an | d m-ZrP-2 as solid acid catalyst. |
|------------------------------------|--------------------------------|-------------------------|-----------------------------------|
|------------------------------------|--------------------------------|-------------------------|-----------------------------------|

| Entry | Substrate | Conversion ^a (wt%) | Name of product | Selectivity (%) | | |
|-------|---------------|-------------------------------|-------------------------------|-----------------|------------|----|
| | | | | 0- | <i>m</i> - | р- |
| 1 | Toluene | 94 | Benzylmethyl benzene | 33 | 0 | 67 |
| 2 | Ethyl benzene | 97 | Benzylethyl benzene | 47 | 0 | 53 |
| 3 | o-Xylene | 99 | 4-Benzyl-1,2-dimethyl-benzene | 100 | | |
| 4 | p-Xylene | 88 | 2-Benzyl-1,4-dimethyl-benzene | 100 | | |
| 5 | Anisole | 92 | Benzylmethoxy-benzene | 38 | 0 | 62 |
| 6 | Phenol | 96 | Benzyl phenol | 52 | 0 | 48 |

Reaction conditions: substrate, 70.5 mmol; benzylchloride, 8.7 mmol; catalyst, 2.7 wt%; temperature, 70 °C; time, 5 h.

^a Conversion was calculated with respect to benzylchloride.

bi-phenyl methane formation (100%). Further increase in temperature increases the conversion slightly but decreases the selectivity significantly. A di-benzylated product was observed at higher temperature. At elevated temperature, the rate of reaction became very high and favored the di-benzylated product.

The effect of amount of reactants and catalyst were also studied for the FC reaction. When the benzene/benzyl chloride molar ratios were in the range of 14:1 to 6:1, conversion was ~94% with 100% selectivity. For further decrease in the ratio, the conversion and selectivity decreased slightly. The conversion was 83% with 94% selectivity when the ratio was 1:1. Again, it was found that the conversion gradually decreased as the amount of catalyst decreased from 2.5 wt%. However, the effect on conversion and selectivity was almost negligible as the catalyst amount was increased from 2.5 wt%.

Due to its better catalytic activity for the benzylation of benzene using benzylchloride as benzylation reagent, m-ZrP-2 was used as acid catalyst for a series of benzylation reactions of substituted benzene in optimized conditions. The results are depicted in Table 2. The substituting groups in the benzene ring have great influence on conversion. Substituted benzene rings attached to electron donating groups show relatively high conversion, whereas benzene rings with electron withdrawing groups (-Cl, $-NO_2$ and -CHO) did not participate in the reaction.

Both Lewis acid- as well as Brönsted acid-catalyzed benzylation reaction mechanisms has been reported in the literature [46,47]. We believe that both Lewis and Brönsted acid sites are responsible in the present reaction, as m-ZrP-2 calcined at 650 °C and m-ZrP-0.25 calcined at 550 °C showed almost the same conversion and selectivity values. However, both catalysts have comparable surface area and total acidity, but they varied in ratio of Lewis and Brönsted acid sites. Detailed mechanistic studies are beyond the scope of the present work; still a proposed mechanism is described in the "supporting information".

In order to check the recyclability, we reused the catalyst six times in the benzylation reaction of benzene after regeneration. No significant change in catalytic efficiency was observed compared to fresh catalyst. The efficiency of the catalyst was not affected even



Fig. 12. Re-use of catalyst m-ZrP-2 for F. C. benzylation of benzene with benzylchloride.

after six cycles (Fig. 12). After the sixth cycle, 85 wt% conversion of benzylchloride was observed with 97% selectivity. The catalyst regenerated after each reaction was characterized for its chemical composition by elemental analysis, FT-IR and ³¹P NMR. No significant changes in composition or in environment of phosphate group in zirconium phosphate were observed after regeneration.

The water tolerance ability of the synthesized m-ZrP catalyst was verified by hydrolysis of ethyl acetate and esterification of acetic acid with ethanol, following the procedure described by Kamiya et al. [11]. Very high catalytic activity for both hydrolysis (22%) and esterification (41%) was observed, which are much better than the results reported by Kamiya et al. (8 and 20%, respectively). The difference in activity is most probably due to the differences in surface area as well as in acidity. Here it should be mentioned that the crystalline layered ZrP does not have any catalytic activity for the above mentioned hydrolysis and esterification [48].

Table 3

Catalytic activity of m-ZrP-2 towards different organic reactions.

| Reaction | Product | Reaction conditions | Conversion (wt%) | Selectivity (%) |
|-----------------|---------|---------------------|------------------|-------------------------------------|
| Pechmann | a | 160 °C, 4 h | 94 | 100 |
| Biginelli | b | 130°C, 1 h | 90 | 99 |
| Claisen–Schmidt | c,d | 150 °C, 5 h | 80 | 59 ^c and 41 ^d |
| Protection | e | 50 °C, 5 h | 97 | 99 |
| Benzoxanthene | f | 140°C, 3 h | 94 | 100 |

^a 7-Hydroxy-4-methylcoumarin.

^b 5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one.

^c Flavanone.

^d 2ĭ-Hydroxychalcone.

e 1,4-Dioxaspiro-[4,5]-decane.

^f 14-Phenyl-14H-dibenzo[a,j] xanthene.

Table 4

Comparative chart of catalytic activity of m-ZrP-2 and layered ZrP.

| Catalyst | F.C. benzylation | Peachmann condentation | Claisen-Schmidt condensation | Biginelli |
|-----------------|---|------------------------------------|--|--|
| m-ZrP-2 ZrP* | 96 ^a , 100 ^b 73 ^a , 87 ^b | 94 ^c 69 ^c | 80ª, 41/59 ^b 57ª, 46/56 ^b | 90 ^a , 99 ^b 93 ^a , 51 ^b |
| ZrP | | 61 ^c [22] | | |

^{Zrp*}, layered zirconium phosphate was synthesized following previous report.

^a Convertion.

^b Selectivity.

^c Yield.

As m-ZrP-2 was found to be highly effective for F.C. benzylation reaction, it was further employed in various acid catalyzed reactions such as synthesis of 7-hydroxy-4-methylcoumarin by Pechmann reaction between resorcinol and ethylacetoacetate, synthesis of bezoxanthene (14-phenyl-14H-dibenzo[a,j]xanthenes) using a mixture of benzaldehyde and β -naphthol, Claisen–Schmidt condensation reaction using benzaldehyde and acetophenone, and protection reaction of cyclohexanone through ketal formation using ethylene glycol (Scheme 1). To make all the procedures more acceptable and more environmentally friendly, the reactions were performed in solvent-free condition. The conversion-selectivity for desired compounds of the above mentioned reactions are summarized in Table 3. The catalytic activity of the synthesized m-ZrP-2 is quite remarkable towards these organic transformations. All reactions were also repeated using layered ZrP as solid acid catalyst for comparison. Table 4 represents the comparison of catalytic activity of synthesized m-ZrP-2 and of layered ZrP. In Table 4, it is evident that the catalytic activity with respect to the conversion and selectivity for desired product using synthesized m-ZrP as solid acid catalyst is much superior to that of layered ZrP.

4. Conclusions

m-ZrP, with high surface area and narrow pore size distribution was prepared through a simple, versatile, and economical synthetic procedure. The synthesized m-ZrP exhibits ultra high thermal stability, which is far better than that of ZrP synthesized by previously reported methods. The synthesized m-ZrP shows very strong acidic properties with appreciable amounts of Brönsted acid sites, tunable with phosphate loading. The synthesized m-ZrP is water tolerant. The m-ZrP shows excellent catalytic activity towards benzylation reaction of benzene as well as substituted benzene with benzylchloride. The catalyst results one as high as 94% conversion of benzylchloride with 100% selectivity for di-phenyl methane in benzylation of benzene. The conversion and selectivity are highly dependent on reaction time, temperature, amount of catalyst and ratio of substrate. The catalyst is also highly effective as a solid acid catalyst for a large variety of acid catalyzed reactions involving small as well as bulky molecules in solvent-free conditions. The catalytic activity of the synthesized m-ZrP is much higher than that of layered ZrP. The m-ZrP can be recycled at least six times without significant loss of its catalytic activity.

Acknowledgements

The authors are thankful to DST (SR/S1/IC-11/2008) and CSIR Network project (NWP 010) for funding. The authors are also very much thankful to Dr. H.M. Mody for his valuable advice regarding surface area measurement and analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2010.06.016.

References

- [1] K. Tanabe, W.F. Hoelderich, Appl. Catal. A: Gen. 181 (1999) 399-436.
- [2] R. Srivastava, N. Iwasa, S.I. Fujita, M. Arai, Chem. Eur. J. 14 (2008) 9507-9511.
- [3] N. Narender, K.V.V.K. Mohan, S.J. Kulkarni, I.A.K. Reddy, Catal. Commun. 7 (2006) 583–588.
- [4] B.M. Reddy, M.K. Patil, Chem. Rev. 109 (2009) 2185–2208.
- [5] G.P. Romanelli, D. Bennardi, D.M. Ruiz, G. Baronetti, H.J. Thomas, J.C. Autino, Tetrahedron Lett. 45 (2004) 8935–8939.
- [6] K.G. Yng, R.M. Hua, H. Wang, B.Q. Xu, Chin. Chem. Lett. 16 (2005) 527-530.
- [7] S. Selvakumar, M. Chidambaram, A.P. Singh, Catal. Commun. 8 (2007) 777-783.
- [8] X. Wang, Y.H. Tseng, J.C.C. Chan, S. Cheng, Micropor. Mesopor. Mater. 85 (2005) 241–251.
- [9] K. Mantri, K. Komura, Y. Kubota, Y. Sugi, J. Mol. Catal. A: Chem. 236 (2005) 168–175.
- [10] R. Sabou, W.F. Hoelderich, D. Ramprasad, R. Weinand, J. Catal. 232 (2005) 34-37.
- [11] Y. Kamiya, S. Sakata, Y. Yashinaga, R. Ohnishi, T. Okuhara, Catal. Lett. 94 (2004) 45–47.
- [12] S.X. Song, R.A. Kydd, J. Chem. Soc. Faraday Trans. 94 (1998) 1333–1338.
- [13] S. Palaniappan, R.C. Shekhar, J. Mol. Catal. A: Chem. 209 (2004) 117-124.
- [14] K. Segawa, S. Nakata, S. Asaoka, Mater. Chem. Phys. 17 (1987) 181-200.
- [15] L. Sun, W.J. Boo, H.J. Sue, A. Clearfield, New J. Chem. 31 (2007) 39-43.
- [16] G. Alberti, M. Casciola in proton conductors, in: P. Colomban (Ed.), Cambridge University Press, Cambridge, UK, 1992, p. 238.
- [17] F. Bellezza, A. Cipiciani, U. Costantino, M.E. Negozio, Langmuir 18 (2002) 8737-8742.
- [18] K. Segawa, Y. Kurusu, Y. Nakaiima, M. Kinoshita, J. Catal. 94 (1985) 491-500.
- [19] A. Clearfield, D.S. Thakur, Appl. Catal. 26 (1986) 1-26.
- [20] T. Hattori, H. Hanai, Y. Murakami, J. Catal. 56 (1979) 294–295.
- [21] G. Alberti, M. Casciola, F. Marmottni, R. Vivani, J. Porous Mater. 6 (1999) 299-305.
- [22] R. Joshi, U. Chudasama, J. Sci. Ind. Res. 67 (2008) 1092–1097.
- [23] M.C.C. Costa, R.A.W. Johnstone, D. Whittaker, J. Mol. Catal. A: Chem. 103 (1995) 155–162.
- [24] G. Alberti, S.M. Mascars, R. Vivani, J. Am. Chem. Soc. 120 (1998) 9291-9295.
- [25] G. Alberti, F. Marmottini, S. Cavalaglio, D. Severi, Langmuir 16 (2000) 4165-4170.
- [26] J.J. Jiménez, P.M. Torres, P.O. Pastor, E.R. Castellón, A.J. López, D.J. Jones, J. Roziére, Adv. Mater. 10 (1998) 812–815.
- [27] Z.Y. Yuan, T.Z. Ren, A. Azioune, J.J. Pireaux, B.L. Su, Catal. Today 105 (2005) 647-654.
- [28] J.H. Jung, H.J. Sohn, Micropor. Mesopor. Mater. 106 (2007) 49-55.
- [29] K.N. Rao, A. Sridhar, A.F. Lee, S.J. Tavener, N.A. Young, K. Wilson, Green Chem. 8 (2006) 790–797.
- [30] A. Dong, N. Ren, Y. Tang, Y. Wang, Y. Zhang, W. Hua, Z. Gao, J. Am. Chem. Soc. 125 (2003) 4976–4977.
- [31] Y. Sun, P. Afanasiev, M. Vrinat, G. Coudurier, J. Mater. Chem. 10 (2000) 2320-2324.
- [32] A. Tarafdar, A.B. Panda, N.C. Pradhan, P. Pramanik, Micropor. Mesopor. Mater. 95 (2006) 360–365.
- [33] B. Tian, X. Liu, C. Yu, J. Fan, L. Wang, S. Xie, G.D. Stucky, D. Zhao, Nat. Mater. 2 (2003) 159–163.
- [34] T.Z. Ren, Z.Y. Yuan, B.L. Su, Chem. Commun. (2004) 2730-2731.
- [35] A.E. Braun, A.G. Gonzalez, Nat. Prod. Rep. 14 (1995) 465-475.
- [36] E. Musgrove, C. Rugg, D. Hedley, Cytometry 7 (1986) 347-355.
- [37] C.O. Kappe, Eur J. Med. Chem. 35 (2000) 1043–1052.
- [38] G. Alberti, U. Costantino, J. Colloid Interface Sci. 107 (1985) 256-263.
- [39] C. Trobajo, S.A. Khainakov, A. Espina, J.R. Garca, Chem. Mater. 12 (2000) 1787–1790.
 [40] H. Benhamza, P. Barboux, A. Bouhaouss, F.A. Josien, J. Livage, J. Mater. Chem. 1
- (1991) 681–684. [41] H.N. Kim, S.W. Keller, T.E. Mallouk, J. Schmitt, G. Decher, Chem. Mater. 9 (1997)
- 1414–1421.[42] D.K. Chakrabarty, B. Viswanathan, Heterogeneous Catalysis, New Age International Publishers, India, 2008, p. 213.
- [43] A. Corma, Chem. Rev. 95 (1995) 559–614.
- [44] B. Tyagi, C.D. Chudasama, R.V. Jasra, Appl. Clay Sci. 31 (2006) 16-28.
- [45] P. Wu, Y. Liu, M. He, M. Iwamoto, Chem. Mater. 17 (2005) 3921-3928.
- [46] J.J. Li, Name Reactions, Springer, Berlin, Germany, 2002, p. 128.
- [47] M.H. De la Cruz, J.F.C. Da Silva, E.R. Lachter, Catal. Today 118 (2006) 379-384.
- [48] K. Segawa, A. Sugiyama, Y. Kurusu, Stud. Surf. Sci. Catal. 60 (1991) 73-80.