A new organic-inorganic hybrid porous iron phosphonate material, HPFP-1 has been synthesized under hydrothermal condition using hexamethylenediamine-N, N, N', N'-tetrakis-(methylphosphonic acid) (HDTMP) as the organophosphorus precursor. Under three different temperatures, the morphology of the material was found to be different. The material synthesized at 453 K shows flake-like particle morphology and the material is highly crystalline. Whereas, the materials synthesized at 443 and 423 K are semi-crystalline and show rod-like and spherical morphological features, respectively. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to understand the change in particle morphology while change in synthesis temperature. Powder XRD analysis suggested the formation of a new tetragonal phase ($a = 11.313 \, \text{Å}; \, c = 15.825 \, \text{Å}$ and unit cell volume $2025.659 \, \text{Å}^3$) in HPFP-1. $N_2$ sorption study suggested the existence of supermicropores and interparticle mesopores in these materials. Elemental and thermal analyses as well as FTIR spectroscopy were employed to verify the composition and framework bonding of the material. HPFP-1 material showed excellent catalytic activity for the synthesis of benzimidazole derivatives under mild liquid phase reaction conditions.
6.1 Introduction

Organic-inorganic hybrid porous materials have attracted widespread attention by merging the mechanical properties of inorganic solid and versatile functionality of innumerable organic groups. Installation of organic functionality into the inorganic framework made it possible to extend the use of these materials in many emerging applications like medicine,\textsuperscript{1} optoelectronics,\textsuperscript{2,3} organocatalysis\textsuperscript{4} etc. Very soft and sustainable synthesis conditions, easily tunable topological and chemical properties are the main advantages of these porous hybrids. To make use of these materials for different applications, well defined and tunable chemical functions can be incorporated into porous structure by choosing proper organic building blocks and conditions, which could suite the formation of self-assembled structure. Cooperative interaction between different functional groups precisely positioned at well defined sequences can greatly influence the rate of a catalytic reaction and by doing so it is possible to mimic the basic principles of natural enzymatic catalysis where electrostatic, hydrogen bonding and covalent interactions among the functional groups at fixed distance influence the reactivity of the catalysts.\textsuperscript{5}

Among the different types of porous materials, metal phosphates hold great importance for their application in catalysis,\textsuperscript{6,7} ion exchange,\textsuperscript{8,9} conductivity,\textsuperscript{10} lithium ion battery\textsuperscript{11} etc. But catalytic activities of these materials are restricted by low surface area, formation of large aggregated particles, small pore size etc. So it is necessary to design suitable metal phosphonate based catalysts having uniform particle size and readily accessible pore apertures. There are reports of different transition metal phosphate nanoparticles\textsuperscript{12-14} with well defined morphology and porosity. Among the transition metals, iron containing catalysts are attracting increasing attention for different chemical transformations due to their high abundance.\textsuperscript{15} Till date more interest has been paid for the synthesis of inorganic
iron phosphate based nanomaterials. But there are very less number of reports of porous organic-inorganic hybrid iron phosphonates. Moreover, the morphology of these materials is also not well defined. Here we report for the first time a facile one-pot synthesis and temperature induced morphology control in a hybrid porous iron phosphonate material. Conversion from semi-crystalline nanoparticles to crystalline flake-like morphology via nanorod-like particles has been achieved very efficiently only by changing the duration and temperature of the reaction. This material shows excellent catalytic activity for the synthesis of 2-arylbenzimidazole from o-phenylenediamine and aromatic aldehydes. The metal center and the organic functional group present in the framework synergistically play role in catalyzing the synthesis of benzimidazole. The benzimidazole derivatives have drawn immense attention because of their medicinal applications as antivirals, antiulcers, antifungals, antihypertensives, anticancers and antihistamines. Apart from these, they are also important intermediates in different organic reactions. Various homogeneous catalytic methods have been reported for the synthesis of benzimidazole derivatives. But the main drawback of these procedures is that the catalysts cannot be reused for repeated cycles. Moreover, these methods suffer from low yield, long reaction time, occurrence of side reactions and harsh reaction conditions. Therefore it is essential to design an economically cheap, reusable and highly selective catalyst for this reaction. There is also report of solid supported homogeneous catalyst for the synthesis of 2-arylbenzimidazole derivatives. But in general the major problem associated with these supported catalysts is leaching of the metal ions from the solid support. Non-uniformity of active catalytic sites throughout the support is also another drawback of these catalysts. These problems can be solved if the entire surface of the material acts as a catalyst. In this report, the iron phosphonate material HPFP-1 have been synthesized and used as the catalyst is free from all these problems. The material has
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further advantage of small particle size because small sized particles eliminate the possibility of compositional difference between surface and the bulk of the material, thus making the catalytically active sites available uniformly throughout the material.

6.2 Experimental Section

6.2.1 Material synthesis

HPFP-1 samples were synthesized by using anhydrous iron(III) chloride (Merck) and 25% aqueous solution of hexamethylenediamine-N, N, N', N'-tetrakis-(methylphosphonic acid) (HDTMP, Fluka). The reagents were used without further purification. In a typical synthesis, FeCl₃ (1.63 g, 10 mmol) was dissolved in distilled water (10 g) and 25% aqueous solution of HDTMP (5 g, 2.54 mmol) was added dropwise. The solution was stirred for 30 minutes and hydrothermally treated in a steel-lined teflon autoclave in three different batches. In one batch, to produce the nanoparticles, the solution was kept at 423 K for 24 h and the sample was labeled as HPFP-1(NP). The second batch of the reaction yielded nano-rod like particles when the solution was treated at 443 K for 24 h and this sample was labeled as HPFP-1(NR). Flake-like sample was obtained when the solution was heated at 453 K for 48 h and the sample was labeled as HPFP-1(F). Finally the products were collected by filtration and dried at room temperature.

6.2.2 Catalysis

6.2.2.1 General experimental procedure for the synthesis of 2-arylbenzimidazole

In a typical synthesis, a mixture of o-phenylenediamine (1 mmol, 108 mg, Loba Chemie) and benzaldehyde (1 mmol, 106 mg, Loba Chemie) was stirred in EtOH (5 ml) in presence of HPFP-1(NP) catalyst (30 mg) in air at room temperature for 5 h (monitored by TLC). After the reaction was over, ethanol was evaporated to dryness. Then the reaction mixture was diluted with dichloromethane (20 mL) followed by washing with
brine (3×2 mL). Organic phase was dried over Na₂SO₄ and evaporated to dryness to leave the crude product, which was crystallized from ethanol to afford pure 2-phenylbenzimidazole. The spectroscopic data (¹H NMR and ¹³C NMR) of this product are in good agreement with those of an authentic sample.

6.2.2.2 Recycling efficiency test of the catalyst

After the completion of the reaction the catalyst was separated by simple filtration technique and the recovered catalyst was washed thoroughly with EtOH and EtOAc respectively to remove the un-reacted diamine and aldehyde. Then the catalyst was dried in the air for overnight and activated at 373 K for 2 h to perform the further reactions under identical conditions.

6.2.2.3 Leaching test

In this technique, the reaction mixture was filtered at room temperature from the suspended catalyst after 2 h of the reaction and with the filtrate the reaction was continued at the same temperature for further 2 h. Iron content in the filtrates after 2 and 4 h reactions are analyzed by using atomic absorption spectroscopy.

6.3 Results and discussion

6.3.1 Material synthesis and characterization

HDTMP (Scheme 6.1) solution was added to an aqueous FeCl₃ solution during the synthesis of the materials. As soon as the ligand solution was added, a light yellow precipitate was obtained. However, because of low pH (~1) of the solution extended cross-linking leading to bulk material was prevented. When the solution was hydrothermally treated at 423 K for 24 h, spherical nanoparticles were obtained. But upon treatment of the solution at 443 K for 24 h, one dimensional growth of the particles occurred leading to nanorods of hybrid iron phosphonate material. Further growth of
these nanorods at little higher temperature 453 K, flake-like morphology of the material was obtained. From FT-IR spectrum of HPFP-1(F) (Figure 6.1 A) it is seen that there is a sharp band at 1085 cm⁻¹, which could be attributed to Fe-O-P stretching vibration. The weak shoulder band at 1000 cm⁻¹ could be due to free P-OH groups present in the material. The two weak bands at 1468 and 1431 cm⁻¹ corresponding to C-H bending and P-C stretching modes of the methylphosphonic acid moiety are also observed. Another two weak bands at 1385 and 1330 cm⁻¹ are attributable to stretching vibrations of P=O and C-N covalent linkages. The small bands in the region 2850-3050 cm⁻¹ correspond to the C-H stretching vibration of methylene carbons of the organo-phosphorus ligand. The broad bands around ~3400 and 1630 cm⁻¹ are due to asymmetric OH stretching and bending vibrations of adsorbed water molecules.

Figure 6.1 A) FTIR spectrum and B) TGA (a)- DTA (b) plots of HPFP-1 (F) material
AAS and CHN elemental analyses of the iron phosphonate material show wt.% of Fe, C, H and N as 26.74, 14.71, 3.51 and 3.39, respectively. This result suggests Fe/C/N molar ratio of 2:5:1 in the hybrid iron phosphonate material and it is in agreement with the calculated C/N molar ratio of 5:1 in the organo-phosphorus ligand. Thermal stability of the material was examined by TG-DTA analysis carried out under N₂ flow and it has been shown in Figure 6.1 B. Sharp weight loss below 423 K is due to loss of moisture adsorbed on the surface of the material. In between 473 K and 1073 K, the material shows ~21% weight loss and it is very close to the cumulative wt.% (21.61) of C, H and N as obtained by CHN analysis. These FT-IR and thermal analysis results semi-quantitatively show that the organo-phosphorus ligand, HDTMP is present in the material and the material can be formulated as Fe₂(HDTMP)ₓH₂O.

6.3.2 Microstructural analysis

In Figure 6.2 FE-SEM and TEM images of HPFP-1 samples are shown to understand the nature of particle morphology of these organic-inorganic hybrid materials. Figure 6.2 a shows that HPFP-1(NP) material is composed of small spherical nanoparticles of 50-70 nm.
Figure 6.3 a) High resolution TEM image and b) corresponding FFT pattern of HPFP-1(F)

Scheme 6.2 Schematic representation for the formation of HPFP-1 materials

nm in diameter. These particles are aggregated throughout the material and it gives rise to inter-particle mesoporosity. From the magnified TEM image shown in Figure 6.2 d, it is seen that there is some randomly distributed worm-hole like micropores present in the material. Rod-like morphology of HPFP-1(NR) is clearly visible from Figure 6.2 b. Due to one dimensional growth of the spherical nanoparticles at higher temperature these nanorods are formed. From both FE-SEM (Figure 6.2 b) and TEM (Figure 6.2 e) images it is seen that the nanorods are of ~500 nm in length and aggregation is also much less compared to the nano particles. When the reaction was carried out at more elevated
temperature, these nanorods are fused together producing flake-like morphology and this is shown in Figure 6.2 d and f. A schematic representation for the formation of these materials is shown in Scheme 6.2. This temperature regulated growth of the nanoparticles leading to different morphologies is a very facile process. There are several reports of inorganic iron phosphate nanoparticles,33 nanorods34 and other morphologies.35 Although, there are reports on change in crystallographic phase and subsequent morphology while changing the synthesis temperature through conventional heating or microwave irradiation,36 till date temperature induced morphology control of hybrid iron phosphonate material is unprecedented. The HPFP-1(F) material also shows good crystallinity. The high resolution TEM image in Figure 6.3 a shows the crystal fringes and the corresponding FFT pattern is shown in Figure 6.3 b. These crystal planes are correlated with the wide angle XRD pattern of the material.

6.3.3 Powder X-ray diffraction

Wide angle powder X-ray diffraction patterns of HPFP-1 samples are shown in Figure 6.4. HPFP-1(F) material shows multiple diffraction peaks in the PXRD pattern. Interestingly, this diffraction pattern does not match with any crystalline phase reported in the JCPDS files. This experimental PXRD pattern was evaluated with the calculated PXRD pattern obtained from Reflex, a software package for crystal structure determination. Lattice parameters and estimated standard deviation (ESD) values were obtained from CELSIZ program. This diffraction pattern has been assigned with a new tetragonal phase, where $a = 11.313$ Å and $c = 15.825$ Å. Unit cell parameters with estimated standard deviations and hkl for different planes are given in Table 6.1. Very small deviations indicate that the calculated values are fitted well with the experimental data. The HPFP-1(NP) material synthesized at 423 K shows only two sharp diffraction peaks corresponding to (001) and (100) planes. In case of the HPFP-1(NR) material the
Figure 6.4 Wide angle powder X-ray diffraction pattern of HPFP-1 materials

Table 6.1 Unit cell parameters of HPFP-1(F)

<table>
<thead>
<tr>
<th>Phase: Tetragonal</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>Deviations</td>
</tr>
<tr>
<td>$a$ = 11.313 Å</td>
<td>0.0226</td>
</tr>
<tr>
<td>$c$ = 15.825 Å</td>
<td>0.0141</td>
</tr>
<tr>
<td>Unit Cell Volume = 2025.659 Å³</td>
<td>ESD = 6.824</td>
</tr>
</tbody>
</table>
The intensity of the (001) diffraction peak becomes stronger compared to the intensity of the (100) plane and it indicates 1-D growth of the particles along c-axis and by this way nanorods are formed. But in the diffraction pattern of HPFP-1(F), (113), (220) and other peaks also become strong and it is due to growth of the particles along all the directions, while supplying more energy at elevated synthesis temperature. This observation matches well with the morphology of the material shown in Figure 6.2 d and f.
6.3.4 \( \text{N}_2 \) adsorption/desorption study

![Graph showing \\( \text{N}_2 \) adsorption/desorption isotherms for HPFP-1 materials.](image)

**Figure 6.5** \( \text{N}_2 \) adsorption/desorption isotherm of HPFP-1 materials. Volume adsorbed was shifted by 45 and 10 cc g\(^{-1}\) for HPFP-1(NP) and HPFP-1(NR) respectively.

![Graph showing pore size distribution of HPFP-1 materials.](image)

**Figure 6.6** Pore size distribution of HPFP-1 materials following NLDFT method.

The \( \text{N}_2 \) adsorption/desorption isotherms of HPFP-1 materials are shown in Figure 6.5. These isotherms are classified as type II according to IUPAC nomenclature. In the intermediate relative pressure region of 0.05 to 0.3 there is gradual increase in \( \text{N}_2 \) uptake. This could be attributed to multilayer adsorption corresponding to the presence of mesopores in the materials.\(^{38-42}\) From these isotherms it is seen that the materials adsorbed large amount of nitrogen at high \( \text{P}/\text{P}_0 \) value indicating inter-particle porosity. In the desorption branch, all the three isotherms show hysteresis loop which is unusual for type...
II isotherms. The occurrence of the hysteresis loops is due to mesoporosity originating from interparticle void spaces. Pore size distributions of the materials are shown in Figure 6.6. From pore size distribution it is seen that there is mesoporosity in all the three samples. But the materials synthesized at higher temperatures, HPFP-1(NR) and HPFP-1(F) show supermicroporosity along with the mesoporosity. At higher temperatures when the particles grow to form nanorods and nano flakes, cross-linking also increases and supermicroporosity could originates from this framework cross-linking. The HPFP-1(NP) material shows a H1 hysteresis loop which generally occurs due to agglomeration of approximately spherical particles. This observation is supported by the SEM image shown in Figure 1a. But in case of HPFP-1(NR), due to formation of nanorods, the interparticle aggregation is relatively weak and because of this the hysteresis loop is also narrower. The BET surface area of HPFP-1(NP) is also higher than that of HPFP-1(NR). Because of densification at higher temperature, the surface area of HPFP-1(F) is lowest. The adsorption isotherm of HPFP-1(F) shows H3 hysteresis loop which does not show any limiting adsorption at high relative pressure. The desorption branch of this hysteresis does not level off at relative pressure close to saturation vapor pressure. This H3 hysteresis loop is the signature of aggregated plate-like particles having slit-like pores. From the SEM and TEM images of HPFP-1(F), it was shown that the material is composed of plate-like particles. Surface area, pore size and pore volume data are summarized in Table 6.2.

Table 6.2 Physico-chemical properties of HPFP-1 materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Size by NLDFT (nm)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPFP-1(NP)</td>
<td>153.6</td>
<td>4.5</td>
<td>0.35</td>
</tr>
<tr>
<td>HPFP-1(NR)</td>
<td>121.0</td>
<td>3.1, 5.4</td>
<td>0.20</td>
</tr>
<tr>
<td>HPFP-1(F)</td>
<td>58.0</td>
<td>1.6, 5.4</td>
<td>0.08</td>
</tr>
</tbody>
</table>
6.3.5 Benzimidazole Synthesis

The catalytic activity of HPFP-1(NP) catalyst was investigated in one-pot condensation reaction for the synthesis of benzimidazole derivatives via reaction of o-phenylenediamine and aromatic aldehydes containing various electron donating and withdrawing groups. The yields of different products are given in the Table 6.3. The HPFP-1(NP) catalyst shows high reactivity at room temperature and it takes only 2-4 h for the completion of reaction. The elemental iron content of the catalyst was determined by AAS analysis. The Fe content in this HPFP-1 material is 26.74 %. From the table it is clear that the one-pot condensation reaction was consistent for both electrodonating and electrowithdrawing substituents attached with the aromatic ring. A possible mechanism for this reaction has been shown in Scheme 6.3. It is proposed that the Fe center of the catalyst coordinates with the carbonyl oxygen of the aromatic aldehyde similar to the Lewis acid sites and by this way it activates the carbonyl carbon. Since all the reactions give almost equal yield irrespective of the substituents in the benzaldehyde moiety, the interaction between catalyst and the carbonyl oxygen seems to be strong enough to subsidize the effect of the substituents. In the next step the amine groups of o-phenylenediamine get attached to the carbonyl carbon. The tertiary amine groups present in the hybrid framework help to eliminate proton in the subsequent water removal step. So this synergistic effect of Fe center and the tertiary amine groups catalyze the synthesis of benzimidazole derivatives. We were interested to check the role of morphology and surface area of the material in catalytic activity. Since reaction with p-nitrobenzaldehyde showed highest yield when HPFP-1(NP) was used as the catalyst, the same reaction was chosen to check catalytic activity of HPFP-1(NR) and HPFP-1(F). In both the cases the reaction was carried out for 4 h and HPFP-1(NR) gave 44 % yield while HPFP-1(F) gave 30 % yield. Further, it is seen that the yield of the product also decreases with decreasing
Table 6.3 Synthesis of 2-arylbenzimidazole catalyzed by HPFP-1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aromatic aldehyde&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Benzimidazole</th>
<th>Time (h)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Mp&lt;sup&gt;c&lt;/sup&gt;°C (Lit M.P.)</th>
<th>TOF&lt;sup&gt;d&lt;/sup&gt; (h&lt;sup&gt;e&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHO</td>
<td><img src="image1.png" alt="Image" /></td>
<td>3</td>
<td>90</td>
<td>288 (289–291)</td>
<td>211.2</td>
</tr>
<tr>
<td>2</td>
<td>O&lt;sub&gt;2&lt;/sub&gt;N—CHO</td>
<td><img src="image2.png" alt="Image" /></td>
<td>2</td>
<td>92</td>
<td>328 (327)</td>
<td>323.9</td>
</tr>
<tr>
<td>3</td>
<td>Br—CHO</td>
<td><img src="image3.png" alt="Image" /></td>
<td>3</td>
<td>88</td>
<td>298 (299–300)</td>
<td>206.5</td>
</tr>
<tr>
<td>4</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;CO—CHO</td>
<td><img src="image4.png" alt="Image" /></td>
<td>4</td>
<td>90</td>
<td>224 (224–226)</td>
<td>158.4</td>
</tr>
<tr>
<td>5</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CHO</td>
<td><img src="image5.png" alt="Image" /></td>
<td>3</td>
<td>87</td>
<td>332 (330)</td>
<td>204.2</td>
</tr>
<tr>
<td>6&lt;sup&gt;d&lt;/sup&gt;</td>
<td>O&lt;sub&gt;2&lt;/sub&gt;N—CHO</td>
<td><img src="image6.png" alt="Image" /></td>
<td>4</td>
<td>44</td>
<td>328 (327)</td>
<td>77.4</td>
</tr>
<tr>
<td>7&lt;sup&gt;e&lt;/sup&gt;</td>
<td>O&lt;sub&gt;2&lt;/sub&gt;N—CHO</td>
<td><img src="image7.png" alt="Image" /></td>
<td>4</td>
<td>30</td>
<td>328 (327)</td>
<td>52.8</td>
</tr>
<tr>
<td>8&lt;sup&gt;f&lt;/sup&gt;</td>
<td>O&lt;sub&gt;2&lt;/sub&gt;N—CHO</td>
<td><img src="image8.png" alt="Image" /></td>
<td>7</td>
<td>55</td>
<td>-</td>
<td>55.3</td>
</tr>
<tr>
<td>9&lt;sup&gt;g&lt;/sup&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHO</td>
<td><img src="image9.png" alt="Image" /></td>
<td>6</td>
<td>Trace</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: Ar-CHO: 1.0 equiv., o-phenylenediamine: 1.0 equiv., Reaction temperature: 298 K, Catalyst: 30 mg, Ethanol 5 ml; <sup>b</sup>Isolated yield of pure product; <sup>c</sup>Turn over frequency (TOF) = (moles of substrate converted per mole of iron per hour X 10<sup>e</sup>). <sup>d</sup>Reaction was carried out using HPFP-1(NR) as the catalyst. <sup>e</sup>Reaction was carried out using HPFP-1(F) as the catalyst. <sup>f</sup>Reaction was carried out in presence of FeCl<sub>3</sub>. <sup>g</sup>Reaction was carried out in absence of catalyst.
surface area of the catalyst. Again since HPFP-1(NP) is composed of nanosized spherical particles, porous framework is more accessible for this material. Whereas, in HPFP-1(NR) aggregation is much lower and in case of HPFP-1(F) the highly dense plate-like particles hinder the mass transport through the porous channels. The catalytic activity of our hybrid iron phosphonate catalyst was verified by employing the reaction without using any catalyst. When the reaction was carried out in absence of catalyst (Table 6.3, entry 9), for long time no benzimidazole product was obtained. On the other hand, in a control experiment when homogeneous phase FeCl₃ was used as the catalyst under optimized conditions at 298 K only 55% yield of the benzimidazole (Table 6.3, entry 8) was obtained. Singh et al. also reported FeCl₃ catalyzed benzimidazole synthesis at higher temperatures to obtain better yields. But reusability of this homogeneous catalyst is limited and separation from reaction medium is also a serious problem. In Table 6.3 we have summarized the TOFs for the synthesis of benzimidazole catalyzed by HPFP-1(NP) catalyst.

From the recycling efficiency test it is seen that this hybrid iron phosphonate catalyst can be recycled and reused for further four repetitive cycles without any significant loss of catalytic activity which clearly indicates that the catalyst is purely heterogeneous in nature. We have plotted the recycling efficiency of the HPFP-1(NP) catalyst for four consecutive catalytic cycles for the condensation reaction between benzaldehyde and o-phenylenediamine and the result is shown in the Figure 6.7. To test any leaching of the iron into the reaction mixture during the catalytic reactions a controlled experiment was conducted taking the condensation reaction between benzaldehyde and o-phenylenediamine as a representative case. After 2 h the catalyst was removed from the reaction mixture and the mixture was allowed to stir for another 2 h under identical reaction conditions. It was observed that there was almost no increase in product yield.
after 4 h compared to the conversion that took place after 2 h (75.2% and 76.5% yield at 2 and 4 h, respectively) and there were no detectable Fe in the reaction mixture. This result suggests that no leaching of Fe occurred during the course of reaction as otherwise the conversion would have increased considerably and the filtrate would have dissolved Fe. Thus the catalytic pathway described herein over HPFP-1 is purely heterogeneous in nature.
6.4 Conclusion

In this chapter it has been shown that a new organic-inorganic hybrid porous iron phosphonate material can be synthesized in a one-pot hydrothermal reaction condition. Nanoparticle, nanorod and flake like morphology of the material can be obtained just by tuning the synthesis temperature. PXRD results show that the HPFP-1(F) material is crystalline and forms a new tetragonal phase. From N\textsubscript{2} adsorption/desorption experiments it is seen that the materials are porous having the size in the range of supermicroporous and mesoporous regions. Mesopores in the materials originate from interparticle porosity. The material shows very good catalytic activity for the synthesis of benzimidazole derivatives from various substituted aromatic aldehydes and o-phenylenediamine. Simple and convenient catalytic process described herein for the synthesis of benzimidazoles could open new avenues for the hybrid porous metal phosphonates for the synthesis of organic fine chemicals.
BIBLIOGRAPHY


