Catalytic liquid phase oxidation of cyclohexane with tert-butylhydroperoxide over transition metal exchanged α-zirconium phosphate

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Transition metal exchanged α-zirconium phosphate, α-ZrP.M (where, M = Mn(II), Cu(II) and Fe(III)) has been prepared by ion exchange method and characterized by X-ray diffraction, scanning electron micrographs, energy dispersive X-ray analysis, Fourier transform infrared and atomic absorption spectroscopy. The catalytic activity of α-ZrP.M is tested for the oxidation of the cyclohexane in liquid phase with tert-butylhydroperoxide as an oxidant. In the oxidation reaction, cyclohexane is oxidized to cyclohexanol and cyclohexanone. The order of reactivity of α-ZrP.M for the oxidation of cyclohexane to cyclohexanone and cyclohexanol is: α-ZrP.Mn(II) > α-ZrP.Cu(II) > α-ZrP.Fe(III). A maximum of 6.12% conversion and 100% selectivity for KA oil (cyclohexanone (K) + cyclohexanol (A)) for oxidation of cyclohexane is observed with the α-ZrP.Mn(II)/TBHP system after 5 h of reaction. Influence of various reaction parameters, viz. concentrations of oxidant and catalyst, reaction temperature, etc., has been studied. The catalyst, α-ZrP.Mn(II), can be recycled three times under similar reaction conditions.

Keywords: Catalysts, Heterogeneous catalysts, Oxidation, Liquid phase oxidation, Cyclohexane, tert-Butylhydroperoxide, Transition metals, α-Zirconium phosphate

Functionalization of hydrocarbons by selective oxidation is a very useful reaction and has been studied comprehensively over the past years. Among hydrocarbon oxidations, the selective oxidation of cyclohexane occupies an important place in both laboratory and industry because of its oxidized products such as cyclohexanol and cyclohexanone, which are important intermediates in the production of adipic acid and caprolactam. In the current industrial process, cyclohexane is oxidized at the temperature range of 150–170 °C and pressure of 115–175 psi in the presence of homogeneous cobalt salt, where the conversion is very poor (~4%) and the process is environmentally hazardous. Various new catalytic systems have been developed for the oxidation of cyclohexane which work under milder conditions as compared to the industrial process. However, heterogeneous catalysts offer merits of high catalytic activity, stability, easy separation and reusability. Considerable research has been devoted to finding efficient heterogeneous catalysts for the selective oxidation of cyclohexane using various supports such as alumina, silica, polymers, zeolites, MCM-41, etc. However, either leaching or low selectivity was the main problem during their application as catalysts. The ion-exchange method of catalyst immobilization on layered compounds is simpler as compared to the procedures required for attachment of complexes to polymers. Cation exchange polymer-supported catalysts have also been developed, but the thermo-oxidative instability of the polymer under reaction conditions and the poor mechanical properties of the organic support are the main drawbacks of these systems. In this regard also, the ion-exchange method of catalyst immobilization on layered compounds is better since it comprises temperature- and solvent-stable inorganic layered exchangers of known structure as support. Crystalline α-zirconium phosphate, Zr(HPO$_2$)$_2$·2H$_2$O abbreviated as {α-ZrH$_2$P}, a cation exchanger, has a zeolite type cage structure and has been extensively studied for its intercalation chemistry, ion exchange properties, catalytic properties and proton conductivity. Various transition-metal ions, viz. Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) are substituted on α-zirconium phosphate for catalytic epoxidation of propylene. Hajipour et al. have reported the catalytic activity of copper zirconium phosphate (ZPCu) and iron zirconium phosphate (ZPFe) in the selective oxidation of alcohols to their corresponding products such as cyclohexanol and cyclohexanone.
ketones or aldehydes, using H₂O₂ as an oxidant. In previous studies, we have reported the use of Fe(Salen) and Cu(Salen) intercalated in α-zirconium phosphate as an active and reusable catalyst for the oxidation of cyclohexene with dry tert-butylhydroperoxide as oxidant. In continuation, herein we report the synthesis of transition metal exchanged α-zirconium phosphate abbreviated as α-ZrP.M (where M = Mn(II), Cu(II) and Fe(III)) by ion exchange method. Its catalytic behavior was studied for the liquid-phase oxidation of cyclohexene using tert-butylhydroperoxide (TBHP) under solvent-free condition.

Materials and Methods

All chemicals viz., manganese acetate, copper acetate, ferric chloride, zirconium oxychloride (ZrOCl₂.8H₂O), phosphoric acid, hydrofluoric acid, and cyclohexane, were reagent grade chemicals (E. Merck). Cyclohexane was checked by gas chromatography (G.C.) to ensure the absence of any oxidation product in the substrate. Commercial grade TBHP (70%) in H₂O was purchased from E. Merck. Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku diffractometer in the 2θ range of 5°–40° using Cu-Kα radiation (λ = 1.5418 Å). Scanning electron microscopy and energy dispersive X-ray analysis were performed using a JEOL JSM 6100 electron microscope, operating at 20 kV. The Fourier transform infrared spectra were recorded in KBr on Perkin Elmer (model 1750) instrument. Atomic absorption spectrometer (Shimadzu AA-6800) was used for metal estimation. The N₂ adsorption data, measured at 77 K by volumetric adsorption set-up (Micromeritics ASAP-2010, USA), were used to determine BET surface area, pore volume and pore size. Analytical gas chromatography was carried out at 393 K on a Shimadzu gas chromatograph (GC-14B) fitted with aXE-60 ss column and a dual flame ionization detector (FID) and attached to a Shimadzu printer. The products were identified by GC–MS (Perkin-Elmer Clasus 500 column; 30 m x 60 mm).

Preparation of heterogeneous catalysts (α-ZrP.M: where M = Mn, Cu and Fe)

The α-zirconium phosphate, abbreviated as α-ZrH₂P was used as support and was prepared by direct precipitation method reported in literature. The α-ZrP.Mn(II) was prepared by ion exchange procedure. Hydrogen ions of α-ZrH₂P were exchanged with Mn(II) ions from a Mn(CH₃COO)₂.4H₂O solution. Stock solution of Mn(CH₃COO)₂.4H₂O (0.1 N) was prepared and 100 mL of Mn(CH₃COO)₂.4H₂O solution per g of α-ZrH₂P was refluxed for 24 h at 373 K. It was then filtered hot through a sintered glass crucible. The clear filtrate was allowed to cool to 298 K and analyzed for metal ion content by atomic absorption analysis. The solid obtained was washed with distilled water and dried at 383 K for 24 h. Similar procedures were used for the preparation of α-ZrP.Cu(II) and α-ZrP.Fe(III) using stock solutions of copper acetate (0.1 N) and ferric chloride (0.1 N) respectively.

Catalytic oxidation of cyclohexane

The liquid phase catalytic oxidation of cyclohexane was carried out using the catalyst, α-ZrP.M, in a three-necked round-bottom flask (100 mL) under solvent-free condition with tert-butylhydroperoxide (TBHP). A stock solution of TBHP in cyclohexane was used, which was prepared by extraction of commercial grade TBHP (E. Merck, 70% in water) into an equal volume of cyclohexane. Phase separation was promoted by saturating the aqueous layer with solid NaCl. The organic layer was dried over anhydrous MgSO₄, filtered and stored at 5 °C. In a typical experiment, the three-necked round bottom flask (100 mL) was loaded with cyclohexane (23 mmol), TBHP (23 mmol, 41% TBHP in cyclohexane), dodecane (internal standard, 0.1 mL) and the catalyst (0.05 g), and heated at 3

Results and Discussion

Characterization of heterogeneous catalysts

The heterogeneous catalysts α-ZrP.M, where M = Mn(II), Cu(II) and Fe(III), were prepared by exchanging surface protons (hydrogen ions) from α-ZrH₂P with the corresponding transition-metal ion. Scheme 1 represents the various stages of synthesis of the heterogeneous catalyst, α-ZrP.M. The colour of α-ZrH₂P was white due to the absence of any metal ions. The colour of α-ZrP.Mn(II)₆, α-ZrP.Cu(II) and
α-ZrP,Fe(III) was found to be pink, blue and yellow respectively due to the presence of manganese (27.55%), copper (20.54%) and iron (23.03%) which were determined by atomic absorption analysis.

The surface areas of α-ZrH₂P, α-ZrP,Mn(II)b, α-ZrP,Mn(II)a, α-ZrP,Cu(II) and α-ZrP,Fe(III) were determined by BET surface area analysis. The ion exchange of the metal ions led to an increase in surface area of α-ZrH₂P from 13.58 m²/g to 20.65, 21.19 and 18.56 m²/g in the case of Mn(II), Cu(II) and Fe(III) respectively. This is due to an increase in the number of extra-framework cations due to replacement of hydrogen ions with bivalent and trivalent cations.

The pore volume of α-ZrH₂P is 0.04 Å, which increased to 0.05 Å in the case of Mn(II) and Fe(III) ions, while it remained the same in the case of Cu(II) ions. However, the pore sizes of α-ZrP,Mn(II)b and ZrP,Cu(II) decreased to 94.43 Å and 83.35 Å from 116.69 Å, while the pore size in α-ZrP,Fe(III) remained almost the same.

The XRD patterns of α-ZrH₂P, α-ZrP,Mn(II)b, α-ZrP,Mn(II)a, α-ZrP,Cu(II) and α-ZrP,Fe(III) are shown in Fig. 1. The d-spacings correspond to the (002) plane, and are 7.40, 8.60, 8.19, 9.50 and 7.46 Å respectively. The XRD patterns of α-ZrP indicate that a well-crystallized material is obtained, which is in agreement with published data. On the other hand α-ZrP,Mn(II)b, α-ZrP,Cu(II) and α-ZrP,Fe(III) present broad reflections indicating their low crystallinity. This low crystallinity may be due to the exchange of hydrogen ions by manganese, copper and iron ions. Similar observations have been reported earlier.

EDX analysis is useful in the determination of elemental composition. The EDX spectra of α-ZrH₂P, α-ZrP,Mn(II), α-ZrP,Cu(II) and α-ZrP,Fe(III) are shown in Fig. 2. The support, α-ZrH₂P, contains oxygen (81.47%), zirconium (7.09%) and phosphorous (11.44%). The α-ZrP,Mn(II) contains oxygen (78.81%), zirconium (5.36%), phosphorous (10.65%) and manganese (5.18%). The α-ZrP,Cu(II) contains oxygen (79.8%), zirconium (5.48%), phosphorous (8.44%) and copper (6.21%). The α-ZrP,Fe(III) contains oxygen (80.05%), zirconium (5.76%), phosphorous (10.30%) and iron (3.81%). The presence of manganese, copper and iron in α-ZrP,Mn(II), α-ZrP,Cu(II) and α-ZrP,Fe(III) respectively confirms the formation of the complexes. The SEM images of α-ZrH₂P, α-ZrP,Mn(II), α-ZrP,Cu(II) and α-ZrP,Fe(III) are shown in Fig. 3. The SEM image of α-ZrH₂P clearly shows a plate-like structure. The round edges of the sheets indicate that its crystallinity was not very high. The SEM images of α-ZrP,Mn(II), α-ZrP,Cu(II) and α-ZrP,Fe(III) are less ordered than that of α-ZrH₂P; the heterocatalysts aggregate to form both sheets and spheres of different shapes and sizes.

In the FTIR spectrum of α-ZrH₂P, the bands at 3500 and 1625 cm⁻¹ are due to external water in addition to the strongly hydrogen-bonded OH or extremely strongly coordinated H₂O. (Supplementary Data, Fig. S1). The bands at 1044 and 597 cm⁻¹ are due to symmetrical mode of P = O bond and stretching vibration of Zr-O. In α-ZrP,Mn(II)b, α-ZrP,Mn(II)a, α-ZrP,Cu(II) and α-ZrP,Fe(III), the band position of PO₄²⁻ shifted to lower frequencies, i.e., 991, 990, 991 and 991 cm⁻¹ respectively, while the band of Zr-O was shifted to higher frequencies, i.e., 637, 630, 637, and 602 cm⁻¹ respectively, due to the exchange of hydrogen with Mn(II), Cu(II) and Fe(III) ions.

Catalytic activity
Oxidation of cyclohexane

The oxidation of cyclohexane using α-ZrP,M and TBHP as an oxidant were investigated under solvent-free conditions. The reaction was also carried out in the

![Scheme 1](image)

**Fig. 1** — XRD pattern of (1) α-ZrH₂P, (2) α-ZrP,Mn(II)b, (3) α-ZrP,Mn(II)a, (4) α-ZrP,Cu(II)b, and (5) α-ZrP,Fe(III)b.

[b: before catalytic reaction and a: after catalytic reaction].
Fig. 2 — EDX spectra of $\alpha$-ZrH$_2$P, $\alpha$-ZrP.Mn(II), $\alpha$-ZrP.Cu(II) and $\alpha$-ZrP.Fe(III).

Fig. 3 — SEM image of (a) $\alpha$-ZrH$_2$P, (b) $\alpha$-ZrP.Mn(II), (c) $\alpha$-ZrP.Cu(II) and (d) $\alpha$-ZrP.Fe(III).
presence of the support, α-ZrH₂P, as well as the metal salts, (Mn(CH₃COO)₂·4H₂O, Cu(CH₃COO)₂·H₂O and FeCl₃·6H₂O. The reaction without catalyst (blank reaction) was also tested for the oxidation of cyclohexane under similar reaction conditions. The results are incorporated in Table 1. It was observed that in the absence of any catalyst (as in the case of blank reaction) as well as with α-ZrH₂P catalyst, the oxidation reaction did not proceed. The metal salts, Mn(CH₃COO)₂·4H₂O, Cu(CH₃COO)₂·H₂O and FeCl₃·6H₂O, as well as the three heterogeneous catalysts, α-ZrP·M {M = Mn(II), Cu(II) and Fe(III)}, were active for the oxidation of cyclohexane. The activity of the heterogeneous catalysts showed that the ion exchange of Mn(II), Cu(II) and Fe(III) converted the non-catalyst, α-ZrH₂P, into an active catalyst for the oxidation of cyclohexane. In the cases of both, homogeneous and heterogeneous catalysts, cyclohexane was oxidized to cyclohexanol (A) and cyclohexanone (K). The conversion of cyclohexane was higher with Mn(CH₃COO)₂·4H₂O (6.95%) and Cu(CH₃COO)₂·H₂O (5.81%) as compared to that with α-ZrP·Mn(II) (6.12%) and α-ZrP·Cu(II) (3.10%). However, recovery of the catalyst was not possible in the case of Mn(CH₃COO)₂·4H₂O and Cu(CH₃COO)₂·H₂O. FeCl₃·6H₂O (1.2%) in homogeneous reaction gave lower conversion due to poor solubility in cyclohexane whereas α-ZrP·Fe(II) gave slightly higher conversion (1.6%). The cyclohexane conversion and the amounts of the products, cyclohexanol and cyclohexanone, were calculated using the internal standard method and the consumption of TBHP was determined iodometrically at the end of the reaction (after 5 h) by testing the organic phase. Selectivity was calculated with respect to the converted cyclohexane.

The percentage-conversion of the substrate and the percentage-selectivity of the products and turnover number (TON) in the oxidation reaction were calculated as:

Substrate conversion (%) = (substrate converted (moles)/substrate used (moles)) ×100

Product selectivity (%) = (Product formed (moles)/substrate converted (moles)) ×100

TON = Converted substrate (moles)/amount of metal ions in the added catalyst (moles)

The catalytic oxidation of cyclohexane, catalyzed by α-ZrP·M/TBHP system can be explained by Scheme 2.

Scheme 2 represents the formation of cyclohexanol and cyclohexanone, which were well reported in literature. The reactivity of the three catalysts in the oxidation reaction decreased in the following order: α-ZrP·Mn(II) > α-ZrP·Cu(II) > α-ZrP·Fe(III).

It was observed that the conversion of cyclohexane was maximum (6.12 %) in the case of α-ZrP·Mn(II), (Table 1), while the selectivity of cyclohexanol and cyclohexanone was 50% each. Hence, α-ZrP·Mn(II) is the best catalyst for the oxidation of cyclohexane in the present experimental conditions.

Therefore, catalytic activity of α-ZrP·Mn(II) was examined in detail for obtaining maximum conversion of cyclohexane.

We have also studied oxidation of cyclohexane catalysed by α-ZrP·Mn(II) with other oxidants such as

![Scheme 2](image-url)

**Scheme 2**

Where M = Mn(II), Cu(II) and Fe(II)

We have also studied oxidation of cyclohexane catalysed by α-ZrP·Mn(II) with other oxidants such as

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cyclohexane conv. (%)</th>
<th>Product selectivity (%)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cyclohexanol (A)</td>
<td>Cyclohexanone (K)</td>
</tr>
<tr>
<td>α-ZrH₂P</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn(CH₃COO)₂·4H₂O</td>
<td>6.95</td>
<td>61</td>
<td>39</td>
</tr>
<tr>
<td>α-ZrP·Mn(II)</td>
<td>6.12</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Cu(CH₃COO)₂·H₂O</td>
<td>5.81</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>α-ZrP·Cu(II)</td>
<td>3.10</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>FeCl₃·6H₂O</td>
<td>1.20</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>α-ZrP·Fe(III)</td>
<td>1.60</td>
<td>61</td>
<td>39</td>
</tr>
</tbody>
</table>

*Mixture of cyclohexanone (K) and cyclohexanol (A) is commercially known as KA oil.
H₂O₂ and dioxygen under similar reaction conditions. In the of 30% H₂O₂ leaching of the catalyst was observed after 15 minutes. With dioxygen, only traces of the products were observed. Thus, the best oxidant for our catalytic system is TBHP in cyclohexane, which gave 6.12% of cyclohexane conversion.

Optimum conditions

In order to optimize the reaction conditions for the maximum oxidation of cyclohexane catalysed by α-ZrP.Mn(II)/TBHP system, the effects of various parameters such as amount of oxidant, catalyst and reaction temperature were studied in detail.

The amount of TBHP was varied to study its effect on the oxidation of cyclohexane. Three different cyclohexane/TBHP molar ratios, viz., 1:0.5, 1:1 and 1:2, were considered, keeping other parameters fixed as cyclohexane (23 mmol), catalyst (0.05 g) and dodecane (internal standard, 0.1 mL). The reaction mixture was heated at 343 K in an oil bath for 5 h in solvent-free condition. The results are presented in Table 2. It was observed that when cyclohexane/TBHP molar ratio increases from 1:0.5 to 1:1 the conversion sharply increases from 3.71% to 6.12%. On further increase in cyclohexane/TBHP ratio to 1:2, the conversion slightly decreased to 6.08%, while the selectivity remained almost the same at high TBHP/cyclohexane ratio. No favorable change in either conversion or product selectivity was noticed by increasing TBHP/cyclohexane ratio from 1:1 to 1:2. This could be presumably due to the limitation of oxidizing agent and non-productive decomposition of TBHP at high concentration. This indicates that higher TBHP/cyclohexane molar ratio is not an essential condition to maximize the oxidation of cyclohexane. Thus, 1:1, TBHP/cyclohexane molar ratio was found to be the best for obtaining maximum oxidation of cyclohexane (6.12%) in 5 h.

The effect of the amount of catalyst on the oxidation of cyclohexane was studied by varying the amount of catalyst, α-ZrP.Mn(II) from 0.025-0.075 g, keeping the other parameters fixed as cyclohexane (23 mmol), TBHP (23 mmol) and dodecane (0.1 mL). The reaction mixture was heated at 343 K in an oil bath for 5 h in solvent-free condition. The results are incorporated in Table 2. The conversion increases from 3.00% to 6.12% on increasing the amount of catalyst from 0.025 g to 0.05 g. On further increase in the amount of the catalyst to 0.075 g, the conversion of cyclohexane remains almost the same (6.14%)³⁵. Therefore, 0.05 g of the catalyst, α-ZrP.Mn(II), was considered optimum to obtain maximum conversion of cyclohexane (6.12%) in 5 h reaction time.

Temperature plays an important role in catalytic reaction hence, to study the effect of temperature on the oxidation of cyclohexane, the temperature was varied as 333 K, 343 K, 353 K and 363 K keeping other parameters fixed (Table 2). It was found that when the temperature was increased from 333 K to 343 K, the conversion of cyclohexane increased from 3.87% to 6.12% at 343 K and then decreased to 3.00% at 353 K. Further increase in temperature led to fast decomposition of TBHP, which resulted in lower conversion of cyclohexane.³² ⁴⁶ Cyclohexanone was the major product in the oxidation of cyclohexane. Hence, the maximum conversion (6.12%) was obtained at 353 K in 5 h of reaction time.

In summary, the optimum condition for obtaining maximum conversion of cyclohexane are 1:2 molar ratio of cyclohexane/TBHP, 0.05 g catalyst and 353 K temperature under solvent-free condition in 5 h reaction time.

**Table 2 — Effect of various parameters on the oxidation of cyclohexane catalyzed by α-ZrP.Mn(II)/TBHP after 5 h of reaction**

<table>
<thead>
<tr>
<th>Cyclohexane/TBHP (molar ratio)</th>
<th>Catalyst amt. (mg)</th>
<th>Temp. (K)</th>
<th>Conv. (%)</th>
<th>Product selectivity* (%)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.05</td>
<td>50</td>
<td>343</td>
<td>3.71</td>
<td>59/41</td>
<td>17.22</td>
</tr>
<tr>
<td>1:1</td>
<td>50</td>
<td>343</td>
<td>6.12</td>
<td>50/50</td>
<td>31.28</td>
</tr>
<tr>
<td>1:2</td>
<td>50</td>
<td>343</td>
<td>6.08</td>
<td>51/49</td>
<td>31.21</td>
</tr>
<tr>
<td>1:1</td>
<td>25</td>
<td>343</td>
<td>3.00</td>
<td>60/40</td>
<td>10.44</td>
</tr>
<tr>
<td>1:1</td>
<td>75</td>
<td>343</td>
<td>6.14</td>
<td>58/42</td>
<td>31.38</td>
</tr>
<tr>
<td>1:1</td>
<td>50</td>
<td>333</td>
<td>3.87</td>
<td>47/53</td>
<td>14.79</td>
</tr>
<tr>
<td>1:1</td>
<td>50</td>
<td>353</td>
<td>3.00</td>
<td>49/51</td>
<td>14.57</td>
</tr>
</tbody>
</table>

*Mixture of cyclohexanone (K) and cyclohexanol (A) is commercially known as KA oil.
Recyclability and stability of the catalyst
To check the reusability of α-ZrP.Mn(II), after the first run, the catalyst was filtered and washed with methanol followed by dichloromethane and dried at 383 K and then reused for the next catalytic run under similar reaction conditions. The fresh catalyst gave 6.12% conversion of cyclohexane while conversion of cyclohexane remained almost same in the first run (6.11%) then dropped to 5.48% and 4.36% after second and third runs respectively. The metal contents were reduced from 27.55% to 22.35% from first to third run. The reduction in the metal contents suggests that metal-leaching has occurred, which was also observed in the several catalytic systems 11, 13, 15. The recycled catalyst was further characterized by XRD, FTIR and AAS.

The heterogeneity of the catalyst during oxidation of cyclohexane was tested by hot filtration experiment (Fig. 4). The catalyst was filtered out after 1 h of reaction at 353 K in order to avoid re-adsorption of leached manganese onto the catalyst surface. The filtrate collected after 1 h of the first cycle was placed again into the reaction flask and the reaction was continued for the next 5 h. The gas chromatographic analysis showed no further increase in conversion of cyclohexane. The solution did not exhibit any colour due to the absence of manganese, which was estimated using atomic absorption spectroscopy. This suggests that manganese leaching did not occur during the catalytic reaction. These observations indicate that the catalyst is heterogeneous in nature.

Conclusions
α-ZrP.M has been synthesized by ion exchange method and characterized by BET surface area, XRD, EDX, SEM, FTIR, and AAS. The catalytic activity of α-ZrP.Mn(II) with TBHP was studied for the oxidation of cyclohexane under solvent-free condition. The reaction conditions were optimized with respect to various parameters to obtain maximum conversion of cyclohexane. A maximum conversion for the oxidation of cyclohexane was 6.12% after 5 h of reaction under the optimized conditions. The selectivity of the mixture (cyclohexanol + cyclohexanone) was 50% each. Results of the recycling experiment suggest that the catalyst, α-ZrP.Mn(II) was stable and suitable for recycling up to three cycles for oxidation of cyclohexane. The α-ZrP.Mn(II)/TBHP catalyst system showed efficient catalytic activity under solvent-free and milder reaction condition as compared to the commercial catalyst.

Supplementary Data
Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/jica/IJCA_57A(03)427-434 _SupplData.pdf.

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