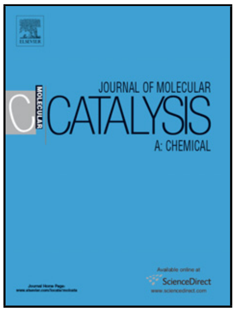

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Solvent-free oxidation of cyclohexane over covalently anchored transition-metal salicylaldimine complexes to α-zirconium phosphate using *tert*-butylhydroperoxide

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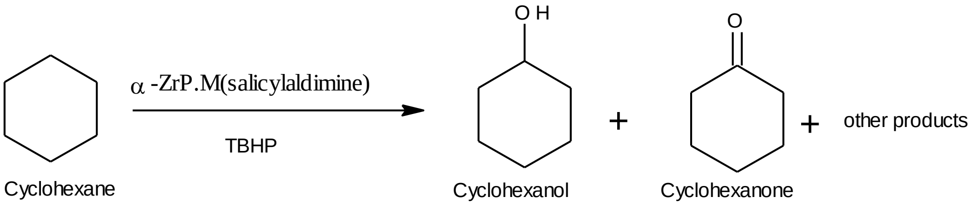
Graphical abstract

A heterogeneous catalytic system, α-ZrP.Co(salicylaldimine)/TBHP gave maximum 14.18% conversion and 92.33% selectivity for KA-oil in oxidation of cyclohexane. The catalyst can be reused for four cycles.



Research Highlights

- New heterogeneous catalysts, α-ZrP.M(salicylaldimine) prepared by covalent bonding.
- Liquid phase oxidation of cyclohexane was studied using α-ZrP.M(salicylaldimine)/TBHP system.
- α-ZrP.Co(salicylaldimine) gave maximum 14.18% conversion with 92.33% selectivity (KA-oil).
- α-ZrP.Co(salicylaldimine) exhibit the excellent reusability.

ABSTRACT

Heterogeneous catalysts were prepared by covalent bonding of transition-metal salicylaldimine complex to α-zirconium phosphate, abbreviated as {α-ZrP.M(salicylaldimine) where M = Co, Mn and Cu}. The resulting compounds were characterized by BET surface area, TGA analysis, X-ray diffraction, Scanning electron micrograph, Energy dispersive X-ray analysis, Fourier transform infrared and Atomic absorption spectroscopy. The catalytic activity of α-ZrP.M(salicylaldimine) was studied for the liquid phase oxidation of cyclohexane using *tert*-butylhydroperoxide as an oxidant under solvent free condition. In the oxidation reaction, cyclohexane was oxidized to cyclohexanol, cyclohexanone and some unidentified products. It was found that the reactivity of α-ZrP.M(salicylaldimine) catalyst for the oxidation reaction decreased in the order □-ZrP.Co(salicylaldimine) □ □-ZrP.Mn(salicylaldimine) □ □-ZrP.Cu(salicylaldimine). A maximum conversion of cyclohexane (14.18%) and selectivity of cyclohexanol (4.99%), cyclohexanone (87.34%) and some other products (7.67%) was observed for catalyst, □-ZrP.Co(salicylaldimine) after 6 hours at 353 K. The catalyst, □-ZrP.Co(salicylaldimine) was reused for four cycles without significant loss of catalytic activity.

Keywords: α-Zirconium phosphate, salicylaldimine complex, *tert*-butylhydroperoxide, cyclohexane oxidation.

1. INTRODUCTION

Selective oxidation of alkanes is an important topic in view of the economical and ecological use of natural raw materials. However, catalytic oxidation of unactivated alkanes to valuable oxygen-containing molecules is important, because desired products sequentially convert into useful products [1-3]. More than 20% of all industrial organic materials are obtained by catalytic oxidation. Oxidative transformations of functional groups are basic to organic chemistry, oxidation being extensively used in the laboratory synthesis of fine organic chemicals as well as in the manufacturing of large-volume petrochemicals [4-10]. The majority of the processes employed industrially involved catalysis by metal complexes and increasing variety of catalytic processes are being developed for laboratory-scale synthesis [1]. The liquid-phase oxidation of cyclohexane is one of the industrially important process for making cyclohexanol, cyclohexanone, and adipic acid. Adipic acid is extensively used in the man-made fiber industry along with hexamethylenediamine for manufacturing of nylon-6 and nylon-66 polymers. In current industrial process, cyclohexane is oxidized at temperature range of 150 -170ºC and pressure of 115-175 psi in the presence of homogeneous cobalt salt, where very less (~4%) conversion with (85%) selectivity of the products. The amount of unreacted cyclohexane and less separation of cyclohexanol and cyclohexanone from cyclohexane and catalyst presents a major problem [11]. Keeping this in mind, various new catalytic systems using cobalt catalyst with molecular oxygen [12-15], *tert*-butyl hydroperoxide (TBHP) [16-18] and Hydrogen peroxide (H_2O_2) [19] were developed for the oxidation of cyclohexane which works under milder conditions compared to the industrial process. However, heterogeneous catalysts offer merits of high catalytic activity, stability, easy separation and reusability. Considerable researches have been devoted to find efficient heterogeneous catalysts for the selective oxidation of cyclohexane using various supports such as alumina [20], silica [21], polymers [22], zeolites [23], MCM-41 [24], AlPO-5 [25] etc. Despite extensive interest in development of new methods for oxidation of cyclohexane, there is still scope for the development of simple, efficient, inexpensive, widely applicable, reusable and environmentally benign catalysts and procedures capable of promoting the oxidation of cyclohexane.

Keeping this in mind, as a part of our ongoing research towards the development of efficient homogeneous and heterogeneous catalysts for oxidation of olefins [26-31], crystalline □-zirconium phosphate, $Zr(HPO_4)_2.H_2O$, a cation exchanger, has a structure of zeolite type cages and has been extensively studied for its intercalation chemistry, ion exchange properties and catalytic properties [32-36]. In the present paper, we are reporting in situ synthesis of heterogeneous catalysts, covalently anchored transition-metal salicylaldimine complexes to α-zirconium phosphate, abbreviated as {α-ZrP.M(salicylaldimine) where M = Co, Mn and Cu} and their catalytic behavior for oxidation of cyclohexane using *tert*-butyl hydroperoxide (TBHP) as an oxidant. For present work, we have chosen three transition metals viz. Co, Mn and Cu, because manganese is used in many oxidations reactions with cobalt, especially in commercial oxidation of cyclohexane. Copper was chosen for this study due to its activity in enzymatic oxidative transformations.

2. EXPERIMENTAL

2.1. Materials

Zirconium oxychloride ($ZrOCl_2.8H_2O$), phosphoric acid, hydrofluoric acid, metals chloride, metals acetate, salicylaldehyde, 3-aminopropyltriehtoxysilane, *tert*-butyl hydroperoxide (70%) and cyclohexane were of reagent grade purchased from E. Merck. Cyclohexane was checked by gas chromatography (GC) to ensure that no oxidation products were present in the substrate. A stock solution of TBHP in cyclohexane (70% in cyclohexane) was prepared by extraction of 50 ml of commercial TBHP (70% in water) into 15 ml of cyclohexane. Phase separation was promoted by saturation of the aqueous layer with NaCl [16]. The organic layer was dried over $MgSO_4$, filtered, and stored at 5 ºC. The molar ratio of cyclohexane to TBHP in this solution was 1:2.18. The reference sample of catalytic products was prepared by the standard procedure [37].

2.2. Instrumentation

Powder X-ray diffraction (XRD) measurements were carried out on a Rigaku diffractometer in the 2θ range of 5°- 40° using CuKα radiation ($\lambda = 1.5418$ Å) at a scanning speed of 2º/min with step size 0.02°. AAS (Atomic Absorption Spectrophotometer, Shimadzu AA-6800 was used for estimation of Metals. Energy dispersive X-ray (EDX) and scanning electron micrographs (SEM) were performed using a JEOL JSM 6100 electron microscope, operating at 20 kV. The Fourier transform infrared (FTIR) spectra were recorded on Perkin Elmer model 1750 FTIR in KBr. The N_2 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. Elemental analysis was performed using a model FLASH EA 1112 series. Thermal analysis measurements were performed using Perkin-Elmer USA model dimond TGA at a heating rate of 10°C/min. The electronic spectra were recorded on Shimadzu UV-1800 Pharma Spectrophotometer. X-ray photoelectron spectroscopy (XPS) studies were carried out on a VSW, UK make X-ray photoelectron spectrometer at a base pressure better than 3×10^{-9} Torr. Al Kα radiation (1486.6 eV) was employed for analysis, with source operated at an emission current of 10 mA and an anode voltage of 10 kV. A concentric hemispherical energy analyzer with 40 eV pass energy, giving an overall resolution of 1 eV, was used. Au $4f_{7/2}$ at 84.7 eV served as an external reference. To correct the shift in binding energies of core levels due to the charging effect, the graphitic C 1s peak at 284.6 eV was used as an internal reference. Analytical gas chromatography was carried out on a Shimadzu Gas Chromatograph GC-14B with dual flame ionization detector (FID) and attached with Shimadzu printer having SE-30 ss column at 393 K. The oxidation products were identified by GC–MS (Hewlett Packard, GCD-1800A) with an electron ionization detector using (Perkin-Elmer Clasus 500 column; 30m×60 mm).

2.3. Preparation of catalyst

2.3.1. Preparation of □-zirconium phosphate

α-Zirconium phosphate (abbreviated α-ZrP) was prepared by reported HF method [38]. A sample of 10 g zirconium oxychloride ($ZrOCl_2.8H_2O$) was mixed with 100 ml 3M H_3PO_4 in a round bottom flask. Then 19 ml of HF solution (5 M) were added to reach a molar ratio of $F^-/Zr^{4+}= 2$. The mixture was refluxed for 24 h at 100°C. After the reaction, the product was washed with distilled water until the pH of the supernatant liquid became 5, then it was dried at 110 °C for 24 h. Finally the structure of α-ZrP was confirmed by powder XRD.

2.3.2. Preparation of Ligand (salicylaldimine)

Salicylaldimine ligand was synthesized by the condensation of 3-aminopropyltriethoxysilane (1mol), and salicyaldehyde (1 mol) in ethanol (40 ml), the solution instantly became yellow due to imines formation [39], the elemental percentage of CHN are following: Anal. Found: C, 58.8%; H, 8.1%; N, 4.3%. Calc. for $C_{16}H_{27}NO_4Si$: C, 59.1%; H, 8.3%; N, 4.2%.

2.3.3. Preparation of neat M(salicylaldimine) complex {Where M= Co, Mn and Cu}

The salicylaldimine ligand was synthesized by adding 3-aminopropyltriethoxysilane (1 mol), and salicyaldehyde (1 mol) in ethanol (40 ml), the solution instantly became yellow due to imines formation then added metals chloride (0.5 mol) to the solution and mixture was stirred for 30 min at room temperature. The precipitate of M(salicylaldimine) complexes was filtered off, washed with petroleum ether and dried. The complexes formed were characterized by elemental analysis and FTIR spectroscopy. In Co(salicylaldimine) complexes, the elemental percentage of CHN is following: Anal. Found: C, 53.7%; H, 8.0%; N, 3.8%. Calc. for $C_{32}H_{54}N_2O_8Si_2Co$: C, 53.86%; H, 8.14%; N, 3.93%.

2.3.4. Preparation of α-zirconium phosphate M(salicylaldimine) complex

The metal salicylaldimine complexes were synthesized by insitu method, 3-aminoproplytriethoxysilane (1 mol) was added to 40 ml ethanolic solution of salicyaldehyde (1 mol), the solution instantly became yellow due to imines formation then ethanolic solution of metals chloride (0.5 mol) was added to the mixture and stirred for 30 min at room temperature. After 30 min, α-ZrP (1 g) was added and mixture was further stirred overnight at room temperature. The final product was washed with distilled water and ethanol. Finally the product was soxhlet extracted using methanol followed by dichloromethane and diethyl-ether until the washing was colourless. The solid was dried in an oven at 110°C for 12 h. In ZrP.Co(salicylaldimine) complexes, the elemental percentage of CHN is following: Anal. Found: C, 35.17%; H, 3.01%; N, 4.01%. Calc. for $C_{20}H_{22}N_2O_{10}Si_2CoZrP_2$: C, 35.82%; H, 3.28%; N, 4.18%. Further, the catalysts were characterized by FTIR, XRD, BET surface area analysis, SEM, EDX, TGA and Atomic absorption spectroscopy.

2.4. General procedure for catalytic oxidation of cyclohexane

The catalytic oxidation of cyclohexane was carried out using {□-ZrP.M(salicylaldimine)} catalysts in a three-necked round bottom flask (100 ml) equipped with a refluxed condenser. In a typical experiment, the flask was loaded with catalyst (0.05 g) and 5 ml mixture of cyclohexane (17.86 mmol %) and TBHP (38.89 mmol %). An additional amount of cyclohexane (1.59 mmol %) was added to maintain 1:2 molar ratio of cyclohexane to TBHP. The mixture was stirred at the desired temperature for 6 h. After completion of the reaction, the contents of the flask was cooled in an ice-bath and the catalyst was filtered out. The liquid layer was analyzed quantitatively by GC using XE-60 ss column at 70ºC. The products were identified by GC-MS. The GC-MS analysis revealed that the products formed in the reaction were cyclohexanol, cyclohexanone and some unidentified products. Selectivity was calculated with respect to the converted cyclohexane. Turn over number (TON) was calculated according to the following formula [40]:

Turn over number = mmol of products/ mmol of catalyst

3. RESULT AND DISCUSSION

3.1. Characterization of the catalyst

The heterogeneous catalyst, α-ZrP.M(salicyladimine) was prepared by covalent bonding of M(salicyladimine) complex to α-zirconium phosphate. Scheme 1 shows the synthetic route for formation of α-ZrP.M(salicylaldimine). The chemical composition and physical data of all compounds are given in Table 1. The metal contents of a catalyst before and after catalytic reaction were determined by atomic absorption analysis. The formation of □-ZrP.M(salicylaldimine) was confirmed by EDX analysis. The EDX measurements results of □-

ZrP and □-ZrP.M(salicylaldimine) are incorporated in Table 2. The presence of metals ions, nitrogen and silicon indicates in □-ZrP.M(salicylaldimine) confirms the presence of M(salicylaldimine) on □-ZrP.

The Scanning electron microscopy was used to study the morphology of the catalysts. The SEM images of □-ZrP and □-ZrP.Co(salicylaldimine) are shown in Fig. 1. The SEM image of {□-ZrP (Fig. 1 (A)} revealed the presence of plates like structure round edges of the sheets indicate that its crystallinity was not very high [41, 29]. The SEM images of {□-ZrP.Co(salicylaldimine) Fig. 1 (B)} are less ordered than that of □-ZrP, and aggregated to form both sheets and spheres of different shapes and sizes which indicates the presence of homogeneous complex on the surface.

The powder XRD patterns of α-ZrP, □-ZrP.Co(salicylaldimine), α-ZrP.Mn(salicylaldimine) and □-ZrP.Cu(salicylaldimine) catalysts are shown in Fig. 2. The d-spacing of the most intense reflection corresponding to the (002) plane of α-ZrP was 7.56 Å which was virtually constant in the α-ZrP.M(salicylaldimine) catalysts this indicates that metal complexes were not present in interlayer of α-ZrP. Furthermore, XRD reveals that the support retains their crystallinity and structure after covalent bonding with covalently bonded of the metal complex.

The results of BET surface area, pore volume and pore size of all the catalysts and support are incorporated in Table 1. The surface area of support, α-ZrP is 5.21m^2/g. The surface area of catalysts, □-ZrP.M(salicylaldimine) ranges from 5.15- 5.18 m^2/g, which was slightly lower than that of the supports whereas the pore size and pore volume of the catalysts are comparable with native support. This indicates that catalysts do not have a significant impact on the surface area of the supports. Similar observation is also reported in the case of silica immobilized salicylaldimine Cu(II) and Co(II) complexes [42].

The FTIR spectra of all compounds were recorded in the 4000 cm^{-1} to 400 cm^{-1} range. The FTIR vibrations of free ligand, neat M(salicylaldimine) complexes, α-ZrP.M(salicylaldimine) and α-ZrP are given in Table 3, The spectrum of the free ligand shows bands at 1627 and 1280 cm^{-1} due to C=N and C-O stretching frequency respectively. These bands are shifted to lower frequency upon coordination in metal complexes. The Si-O vibration of ligand was observed in the range 1192 cm^{-1} was also shifted to lower frequency in metal complexes due to coordination. These data are in good agreement with reported data [43] In spectrum of α-ZrP Fig. 3 (D), the bands at 3539 cm^{-1} is assigned due to the presence of external water in addition to the strongly hydrogen-bonded OH or extremely strongly coordinated H_2O [44, 45]. The band at 1619 cm−1 is due to the bending vibrations of –OH of water associated $PO4^{3-}$ group which supports the presence of water of crystallization in the lamellar solid [44, 45]. The bands appearing at 1044 cm^{-1} is due to symmetrical stretching vibration of PO_4^{3-} and at 597 cm^{-1} is due to stretching vibration of Zr-O. In the spectrum of covalently bonded heterogeneous catalyst, α-ZrP.Co(salicylaldimine) Fig. 3 (C), the band positions of PO_4^{3-} was shifted to lower frequencies while that of Zr–O was shifted to higher frequencies due to presence of Co-O interaction. The C=N stretching frequency of the imines group metal complexes was much weaker and shifted to higher frequency 1619- 1630 cm^{-1} in α-ZrP.M(salicylaldimine). The Si-O vibration of metal complexes was slightly merged with of PO_4^{3-} stretching vibration of α-ZrP in α-ZrP.M(salicylaldimine). Fig. 3 shows comparison of FTIR spectra of free ligand, Co(salicylaldimine), α-ZrP.Co(salicylaldimine) and α-ZrP which provides evidence of coordination of the metal complexes on α-ZrP.

A typical electronic spectra of ligand and Co(salicylaldimine) complex in methanol are shown in Fig. 4. The electronic spectrum of the free ligand exhibit three bands at 216, 251 and

320 nm, these are due to φ→ φ, π→ π* and n→ π* transitions, respectively. The band at 251 nm is assigned due to π-π* transition of phenyl ring, this energy is raised by □19 nm in the complexes. The band at 320 nm is assignable to n → π* transition of the (C=N) moiety in the salicylaldimine ligand. This band is shifted to higher energies 373 nm in Co(salicylaldimine) complex due to ligand to metal charge transfer (LMCT) transition, which indicates the coordination of phenolate oxygen of ligand to an empty d orbital of metal ions. An additional weak and broad band at 570 nm in metal complexes is due to the d–d transition as reported in the literature [46].

Thermal behavior of α-ZrP and α-ZrP.Co(salicylaldimine) were studied by TGA analysis. The TGA-curve of α-ZrP and α-ZrP.Co(salicylaldimine) are shown in Fig. 5. The TGA-curve of the α-ZrP showed first weight loss between 115-220°C which corresponds to the loss of 1 mol of water. Further weight loss was observed between 410-645°C which is due to the loss of another 1 mol of water molecule. The TGA-curve of the α-ZrP.Co(salicylaldimine) complex shows weight loss in the temperature range of 120-600°C which is due to loss of 1 mol of water molecule followed by desorption of the imine group in the complex.

The X-ray photoelectron spectroscopy (XPS) is used to study the chemical state of elements, particularly the non-equivalence of atoms resulting from difference in formal oxidation state, ionic environment and lattice sites in a compound. A change in the chemical and oxidation state of an element can cause small change in its binding energy and this has been used for assignment of the oxidation states of elements in oxide cathodes. The binding energy (B.E.) of core levels of Zr 3d, P 2p, O 1s, N 1s, $Co2p_{3/2}$, $Mn2p_{3/2}$ and $Cu2p_{3/2}$ of α-ZrP.M(salicylaldimine) are given in Table 4.

A typical survey scan of α-ZrP.Co(salicylaldimine), Fig. 6, shows the peaks corresponding to Co2p, Si2p, N1s, Zr3d, P2p and O1s. The carbon peak was also scanned for the compensation of charging effect. The presence of peaks of Co2p, Si2p, N1s along with Zr3d, P2p and O1s in α-ZrP.Co(salicylaldimine) confirms the presences of these elements in the α-ZrP.Co(salicylaldimine). In survey scan Co $2p_{3/2}$ peak appears at binding energy 784.12 eV, which is always associated with satellite peak at 787.01 eV [47]. This clearly indicates the presence of cobalt in +2 oxidation state in α-ZrP.Co(salicylaldimine) which is in good agreement with the earlier reported results [48, 49]. The survey scans of α-ZrP, α-ZrP.Mn(salicylaldimine) and α-ZrP.Cu(salicylaldimine) are given as Fig. S. In survey scan of α-ZrP, the binding energies of core levels $Zr3d_{5/2}$ (181.71 eV), $P2p_{3/2}$ (130.87eV) and O1s (530.09 eV) showed slight variations form earlier reported values for α-ZrP due to change in the chemical environment [50-52]. In the survey scan of α-ZrP.Mn(salicylaldimine) Mn $2p_{3/2}$ peak appears at binding energy 638.33 eV , which is in good agreement with those reported for Mn(Salen) complex immobilized on MCM-41 [53] as well as on organic laponite surface [54]. This confirms that the oxidation state of Mn is 3+ in α-ZrP.Mn(Salen). In the survey scan of α-ZrP.Cu(salicylaldimine) Cu $2p_{3/2}$ peak appears at binding energy 935.05 eV, This confirms the presence of Cu^{+2} oxidation state of copper, which are in good agreement with those reported for copper Schiff base complex immobilized on activated carbon [55, 56]. These results indicates that all the M(salicylaldimine) were successfully covalently anchored onto α-ZrP.

3.2. Catalytic oxidation of cyclohexane

The solvent free oxidation of cyclohexane catalyzed by α-ZrP.M(salicylaldimine) using tert-butylhydroperoxide as an oxidant was investigated. We have also tested support, α-ZrP and homogeneous M(salicylaldimine) complexes for the oxidation of cyclohexane under similar experimental conditions . The results are given in Table 5. It was observed that either no catalyst (as in case of blank reaction) or support was used as catalyst, the oxidation reaction did not proceed. This shows support is catalytically inactive. The homogeneous M(salicylaldimine) catalyst as well as heterogeneous catalysts, α-ZrP.M(salicylaldimine), oxidized cyclohexane to cyclohexanol, cyclohexanone and some other products. The major product is cyclohexanone. It was observed that the homogeneous complexes, M(salicylaldimine), are partially soluble in cyclohexane, therefore the homogeneous complexes does not show high catalytic activity, whereas heterogeneous catalysts, α-ZrP.M(salicylaldimine) show high catalytic activity. The consumption of TBHP was determined iodometrically after each catalytic reaction. The amount of dry TBHP consumed and the efficiency of dry TBHP were calculated according to the reported procedure [29, 57] as follows:

$$\text{TBHP consumed (\%)} = \left\{1 - \frac{\text{remaining TBHP}}{\text{initial TBHP}}\right\} \times 100$$

$$\text{TBHP efficiency (\%)} = \frac{\text{mmol of products}}{\text{mmol of TBHP consumed}} \times 100$$

The selectivity of the products is a measure of the reactivity of the catalyst {α-ZrP.M(salicylaldimine)}. The percentage-conversion of the substrate and the percentage-selectivity of the products in the oxidation reaction are calculated as [28].

Substrate conversion (%) = [substrate converted (Moles) / substrate used (Moles)] ×100

Product selectivity (%) = [Product formed (Moles) / substrate converted (Moles)] ×100

The catalytic oxidation of cyclohexane catalyzed by α-ZrP.M(salicylaldimine)/TBHP system can be explain by Scheme 2.

All the three heterogeneous catalysts were found to be active in the oxidation of cyclohexane with varying conversion (Table 5). It is observed that the conversion of cyclohexane was varied from 4.69-14.18 %, whereas the selectivity of cyclohexanol and cyclohexanone (KA- oil) varied from 92.33-98.85%. A maximum conversion 14.18% was obtained with α-ZrP.Co(salicylaldimine), however the selectivity of KA-oil was 92.33%. In case of α-ZrP.Mn(salicylaldimine) and α-ZrP.Cu(salicylaldimine), conversion of cyclohexane is lesser in comparison with α-ZrP.Co(salicylaldimine), while the selectivity of KA-oil is more. The order of catalytic activity of the α-ZrP.M(salicylaldimine) catalysts on the basis of cyclohexane conversion is as follows:

α-ZrP.Co(salicylaldimine) > α-ZrP.Mn(salicylaldimine) > α-ZrP.Cu(salicylaldimine).

It is observed that α-ZrP.Co(salicylaldimine) exhibits better activity than other metals complexes (viz. Mn and Cu). Therefore, we have carried out optimization of cyclohexane oxidation using α-ZrP.Co(salicylaldimine) as a catalyst.

In order to optimize cyclohexane oxidation to obtain maximum conversion, various parameters viz. effects of various solvents, oxidants, concentration of TBHP, amount of catalyst and reaction temperature were studied in detail.

3.2.1. Effect of various solvents

The effect of various solvents, viz. acetonitrile, acetone and dichloromethane (polar aprotic solvents) on the oxidation of cyclohexane, catalyzed by α-ZrP.Co(salicylaldimine) was studied to develop an efficient catalytic system. In each case, the reaction was carried out by taking solvent (5 ml) at 353 K in an oil bath. The results are given in Table 5. It was observed that when solvents were used in the reaction, the cyclohexane conversion decreases in the following order: no solvent (14.18%) > acetonitrile (9.77%) > acetone (8.43%) > dichloromethane (8.32%). It can be seen that the selectivity of KA-oil is high with a dipolar aprotic solvent in the following order; acetonitrile (82.80%) > acetone (79.45%) > dichloromethane (77.37%). Thus, dipole moment of the solvents probably is an essential factor in oxidation reaction. Oxidation of cyclohexane under solvent free condition gave higher catalytic activity and selectivity of the products in comparison with the presence of solvent (like polar aprotic) [25, 28]. It is well known that the use of solvent leads to many environmental problems. Therefore, activation of cyclohexane under solvent free mild reaction conditions is favorable and environmental friendly for developing new catalytic system. Thus, oxidation of cyclohexane under solvent free condition gave maximum conversion of cyclohexane (14.18%) at 353 K in 6 h of reaction time.

3.2.2. Effect of various oxidants

The effect of various oxidants, viz. 30% H_2O_2, 70% TBHP and TBHP on the oxidation of cyclohexane, catalyzed by □-ZrP.Co(salicylaldimine) was studied under solvent free conditions to develop an efficient catalytic system. The results are given in Table 5. In each case, the reaction was carried out by taking oxidant and cyclohexane in 1:2 molar ratio at 353 K in an oil bath for 6 h. It was observed that, in case of 30% H_2O_2, leaching of the catalyst occurred after 15 minutes and no products formed during this time. In case of 70% TBHP, leaching of catalyst was also observed after 6 h with negligible conversion of cyclohexane (0.59%), while TBHP (70% in cyclohexane) effectively oxidized cyclohexane to cyclohexanol, cyclohexanone and some other products. The major product was cyclohexanone. The conversion of cyclohexane was 14.18% and the selectivity of products followed the order: cyclohexanone (87.34%) > cyclohexanol (4.99%) > other products (7.67%). Thus the best oxidant for our catalytic system is TBHP (70% in cyclohexane).

3.2.3. Effect of TBHP concentration

To study the effect of TBHP concentration on the oxidation of cyclohexane, the three different molar ratio of cyclohexane to TBHP (1:1, 1:2 and 1:2.18) were considered at 353 K in an oil bath for 6 h. The conversion of cyclohexane as a function of time is plotted in Fig. 7 at different molar ratio of cyclohexane to TBHP. It is evident from the Fig. 7 that the conversion of cyclohexane increases sharply from 6.39% to14.18% with increasing molar ratio of cyclohexane to TBHP from 1:1 to 1:2. Further increase in molar ratio to 1:2.18 the conversion increases to 14.28%. It was observed that higher concentration of oxidant showed little increase in conversion. Similar observation is reported in case of TS-1/ionic liquid /TBHP system [59]. The results of the conversion of cyclohexane, TBHP efficiency, TBHP consumption and product selectivity are presented in Table 6. The selectivity of KA-oil decreased from 99-90.89%with increasing molar ratio of cyclohexane to TBHP from 1:1 to 1:2.18. It was also observed that the TBHP consumption decreases, while TBHP efficiency increases with increase in cyclohexane to TBHP molar ratio from 1:1 to 1:2.18. It was observed that higher concentration of oxidant showed little increase in conversion and selectivity of the products. At all molar ratio of cyclohexane to TBHP, cyclohexanone was the major product. Therefore, we have considered 1:2 molar ratio of cyclohexane to TBHP as optimum.

3.2.4. Effect of amount of catalyst

To study the effect of amount of catalyst for the oxidation of cyclohexane, the amount of □-ZrP.Co(salicylaldimine) was varied from 0.025, 0.050 and 0.075 g, while keeping the other parameters are fixed. The results of the conversion of cyclohexane, selectivity of products, efficiency and consumption of TBHP at different concentrations of catalyst are summarized in Table 6. In Fig. 8 the conversion of cyclohexane is plotted against time at different amount of catalyst. It is evident from Fig. 8 that conversion increases with increasing catalyst amount from 0.025 g to 0.05 g. Further increase in catalyst amount, 0.075 g conversion of cyclohexane increased to 14.25%. Only little increase in conversion (0.07%) was observed at higher catalyst amount. Similar observation is reported for Co_3O_4-I/O_2 system [60].The selectivity of KA-oil decreased from 98.15-91.66% upon increasing amount of catalyst from 0.025-0.075 g. It was also observed that the TBHP consumption decreases, while TBHP efficiency increases with increase in amount of catalyst from 0.025-0.075 g. The conversion and selectivity of KA-oil almost remain same at 0.05 g and 0.075 g of catalyst. Therefore, less amount of catalyst, □-ZrP.Co(salicylaldimine), 0.05g was considered optimum.

3.2.5. Effect of temperature

To study the effect of temperature for the oxidation of cyclohexane, the temperature was varied from 343 K, 353 K and 363 K, while keeping the other parameters fixed. The results of the conversion of cyclohexane, efficiency and consumption of TBHP and selectivity of the products are summarized in Table 6. In Fig. 9 the conversion of cyclohexane is plotted against time at different temperature. It is evident from Fig. 9, the conversion of cyclohexane increases from 11.11% to 14.18% with increasing reaction temperature from 343 K to 353 K. Further increase in temperature to 363 K the conversion of cyclohexane increases only little (14.20%), it remains almost same as 353 K. This is due to decomposition of TBHP at higher temperature which result in lower conversion of cyclohexane. Similar type of observation is reported by many researchers [29, 59]. It is found that when the temperature increased from 343-363 K, the efficiency of TBHP decreased while its consumption increased which also confirmed the thermal decomposition of TBHP at higher temperatures. The selectivity of KA-oil decreased from 98.49-91.55% with increasing temperature from 343-363 K. Cyclohexanone was the major product in the oxidation of cyclohexane. Thus the maximum conversion (14.18%) was obtained at 353 K in 6 h of reaction time.

Thus the optimum condition for obtaining maximum conversion of cyclohexane are 1:2 molar ratio of cyclohexane to TBHP, 0.05 g catalyst and 353 K temperature. In Table 7, our catalyst is being compared with the literature catalysts. The catalyst and applied method in this paper has the advantages in terms of heterogeneous nature, high reusability, high conversions and selectivity of the catalyst.

3.2.6. Absorption spectral studies

The methanolic solution of homogeneous {Co(salicylaldimine)}complex was treated with 70% TBHP at room temperature and the reaction was monitored by electronic absorption spectroscopy. The UV-visible spectrum of Co(salicylaldimine) shows a soret band at 315 nm, strong absorption band at 390 nm and a weak broad band at 580 nm. Fig. 10 shows the spectral changes upon drop wise addition of TBHP to 10^{-4} M methanolic solution of Co(salicylaldimine). It is evident in Fig. 10 that the intensity of band at 315, 390 and 580 nm increases continuously. At the same time the band at 315 nm marginally shifts towards longer wavelength along with broadening and increasing in band maximum. A significant change is observed at the 390 nm band, which was shifted to 388 nm along with a gain in intensity. A weak broad band appearing at 580 nm due to d–d transition also shows increase in intensity.

We observed sharp spectral changes upon drop wise addition of TBHP to methanolic solution of Co(salicylaldimine) complex at room temperature {Fig. 10 (b)}.After addition of TBHP when cyclohexane was added to this solution, intensity of all bands get decreased {Fig. 10 (c)}. This sharp spectral changes confirms the formation of Co(III) alkylperoxy intermediates.

Finally, cobalt(III) alkylperoxy transfer oxygen to the substrate (cyclohexane) to give oxidized products such as cyclohexanol and cyclohexanone. The formation of cobalt(III) alkylperoxy intermediates involves a one-electron oxidation of the metal, while the decomposition of cobalt(III) alkylperoxy complexes mainly brings back the initial cobalt(II) compound. The proposed mechanism is similar as proposed by Hermans et al. [61] and Saussine et al. [62] Scheme 3.

3.2.7. Recyclability and heterogeneity of the catalyst

To examine the recyclability of the catalyst, the used □-ZrP.Co(salicyaldimine} was recovered from the reaction media and reused. For recycling, after the first use, the catalyst was separated from the reaction mixture by filtration and washed sequentially with methanol and dichloromethane before being dried at 110°C for overnight and then subjected to further catalytic reaction under similar conditions. The catalyst, {□-ZrP.Co(salicylaldimine)} was recycled for the four cycles. The conversion and selectivity of products obtained with spent catalyst were similar to those obtained with the fresh catalyst up to the second cycle (Table 8). Then conversion dropped gradually. The regenerated catalyst was further characterized by AAS, XRD, BET surface area and FTIR analysis after fourth cycle (data are given in corresponding tables). No significant changes in metal content, composition and morphology were observed in regenerated catalyst after fourth cycle. This suggests that the catalyst was stable during catalytic reaction and suitable for recycling. Only small loss in metal content was observed after fourth cycle was observed. However, metal-leaching is observed in several catalytic systems on the basis of the conversion [63, 25].

The stability of the catalyst during oxidation of cyclohexane was tested by hot filtration technique. The catalyst was filtered out after 1h of reaction at 353 K in order to avoid re-adsorption of leached cobalt onto the catalyst surface. The filtrate collected after 1 hour of first cycle was placed again into the reaction flask and the reaction was continued for next 6 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 cobalt, which was estimated using atomic absorption spectroscopy. It suggested that no cobalt-leaching occurred during the catalytic reaction. This observation indicates that the catalyst is heterogeneous in nature.

4. Conclusions

The □-ZrP.Co(salicylaldimine) was synthesized by insitu method and characterized by Atomic absorption spectroscopy, SEM, EDX, XRD, BET surface area, FTIR, UV-visible spectroscopy and TGA analysis. The catalytic activity of □-ZrP.Co(salicylaldimine) with TBHP as an oxidant for oxidation of cyclohexane was studied. The catalyst, □-ZrP.Co(salicylaldimine) was found to be have potential catalytic activity for oxidation of cyclohexane. Reaction conditions have been optimized considering various parameters viz. effects of various solvents, oxidants, cyclohexane to TBHP molar ratio, catalyst amount and reaction temperature to get maximum conversion of cyclohexane. The maximum conversion of cyclohexane was 14.18%. The major oxidation products follow the order: cyclohexanone (87.34%) □ cyclohexanol (4.99%) □ other products (7.67%). The catalyst, □-ZrP.Co(salicylaldimine) was found to be stable enough for oxidation of cyclohexane, it can be recycled for four times.

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References

[1] R. A. Sheldon, J. K. Kochi, Metal-Catalyzed oxidation of organic compounds, Academic Press, New York. (1981) 34-68.

[2] C. L. Hill, Activation and Functionalization of Alkanes, Wiley, New York. (1989).

[3] U. Schuchardt, D. Cardoso, R. Serchelic, R. Pereira, R. S. Da, Cruz., M. C. Guerreiro, D. Mandelli, E. V. Spinacé, V. Pires, App. Catal. A: Gen. 211 (2001) 1-17.

[4] M. Bre´geault, Dalton Trans (2003), 3289-3302.

[5] K.C. Gupta , A. K. Sutar, Coordin. Chem. Reviews 252 (2008) 1420-1450.

[6] C. S. Marvel, W. M. Sperry, Org. Synth. 1 (1941) 95.

[7] I. C. Chisem, K. Martin, M. T. Shieh, J. Chisem, J. H. Clark, R. Jachuck, D. J. Macquarrie, J. Rafelt, C. Ramshaw, K. Scott, Org. Process Res. Dev. 1 (1997) 365-369.

[8] D. Habibia, A.R. Faraji, M. Arshadib, H. Veisi, A. Gil, J. Mol. Catal. A: Chem. 382 (2014) 41- 54.

[9] G. S. Mishra , S. Sinha, Catal. Lett. 125 (2008) 139-144.

[10] X. Duan, W. Liu, L. Yue, W. Fu, M. N. Ha, J. Li, G. Lua, Daltan Trans (2015) 1-9 .

[11] K. U. Ingold, Aldrichim. Acta. 22 (1989) 69-73.

[12] R. Anand, M. S. Hamdy, P. Gkourgkoulas, Th. Maschmeyer, J. C. Jansen, U. Hanefeld, Catal. Today. 117 (2006) 279- 283.

[13] C. Chen, L. Zhou, Q. Zhang, H. Ma, H. Miao, J. Xu, Nanotechnology 18 (2007) 1-5.

[14] H.X. Yuan, Q. H. Xia, H. J. Zhan, X. H. Lu. K. X. Su, Appl. Catal. A: Gen. 304 (2006) 178-184.

[15] R. Raja, P. Ratnasamy, Catalysis Letters 48 (1997) 1-10.

[16] M. S. Hamdy, A. Ramanathan,T. Maschmeyer,U. Hanefeld, J.C. Jansen, Chem. Eur. J. 12 (2006) 1782- 1789.

[17] J. Y. Wang , F. Y. Zhao, R. J. Liu, Y. Q. Hua,, J. Mol. Catal. A: Chem. 279 (2008) 153-158.

[18] R. Ananda, M.S. Hamdya, U. Hanefelda, T. Maschmeyera,b, Catal. Lett. 95 (2004) 3-4.

[19] C. Jin, W. Fan, Y. Jia, B. Fan, J. Ma, R. Li, J. Mol. Catal. A: Chem. 249 (2006) 23-30.

[20] A. Ebadi, N. Safari, M. H. Peyrovi, Appl. Catal. A: Gen. 321(2007) 135-139.

[21] A. P. Singh, N. Torita, S. Shylesh, N. Iwasa, M. Arai, Catal. Lett. 132 (2009) 492- 499.

[22] K. C. Gupta, A. K. Sutar, C. C. Linb, Coor. Chem. Rev. 253 (2009) 1926-1946.

[23] B. Fan, H. Li, W. Fan, C. Jin, R. Li, Appl. Catal. A: Gen. 340 (2008) 67-75.

[24] A. Sakthivel, P. Selvam, J. Catal. 211 (2002) 134-143.

[25] R. Zhao, Y. Wang, Y. Guo, X. Liu, Z. Zhang, Y. Wang, W. Zhan, G. Lu. Green Chem. 8 (2006) 459-466.

[26] D. D. Agarwal, R. Jain, R. P. Bhatnagar, S. Shrivastava, J. Mol. Catal. 59 (1990) 385-395.

[27] D. D. Agarwal, R. Jain, R. P. Bhatnagar, S. Shrivastava, J. Chem. Soc. Perkins Trans-II, (1990) 989-992.

[28] S. Khare, R. Chokhare, J. Mol. Catal. A: Chem. 353 (2012) 138-147.

[29] S. Khare, R. Chokhare, J. Mol. Catal. A: Chem. 344 (2011) 83-92.

[30] S. Khare, S. Shrivastava, J. Ind. Chem. Soc. 83 (2006) 813-818.

[31] S. Khare, S. Shrivastava, J. Mol. Catal. A: Chem. 217 (2004) 51-58.

[32] A. Clearfield, J. A, Stynes, J. Inorg. Nucl. Chem. 26 (1964) 117-129.

[33] A. Clearfield., Ed. Inorganic Ion Exchange Materials; CRC Press: Boca Raton, FL, (1982) 16-38.

[34] A. Clearfield, W. M. Warmuth, R. Schollhorn, E. K. Dordrecht. In Progress in Intercalation Research. (1994) 240-263.

[35] Z. G. Sun, Z. M. Liu, Y. Yang, Catal. Today. 94 (2004) 639-643.

[36] A. R. Hajipour, H. Karimi, Chin. J. Catal.35 (2014) 1982-1989.

[37] D. Swern, Organic Peroxide, Wiley Interscience, New York., Vol. II (1971) p. 357.

[38] L. Sun, W. J. Boo, H. J. Sue, A. Clearfield, New J. Chem. 31 (2007) 39-43.

[39] I. C. Chisem, J. Rafelt, M. T. Shieh, J. Chisen, J. H. Clark, R. Jachuck, D. Macquarrie, C. Ramshaw, K. Scott, Chem. Commun. (1998) 1949-1950.

[40] E. Tordin, M. List, U. Monkowius, S. Schindler, G. Knör, Inorg. Chimi. Acta. 402 (2013) 90–96.

[41] L. Sun, W. J. Boo, R. L. Browning, H. J. Sue, A. Clearfield, Chem. Mater. 17 (2005) 5606-5609.

[42] N. Mlumbazo, S. F. Malpolie, J. Mol. Catal. A: Chem. 312 (2009) 70-77.

[43] S. Ray, S. F. Mapolie, J. Darkwa, J. Mol. Catal. A: Chem. 267 (2007) 143-148.

[44] K. G. Varshney, A. H. Pandith, U. Gupta, Langmuir, 14 (1998) 7353-7358.

[45] K. Parida, D. P. Das, J. Photochem. Photobiol. A: Chem. 163(2004) 561-567.

[46] S. I. Mostafaa, S. Ikedab, B. Ohtanic, J. Mol. Catal. A: Chem. 225 (2005) 181-188.

[47] G. Fierro, M. A. Eberhardt, M. Houalla, D. M. Hercules, W. K. Hall , J. Phys. Chem. 100 (1996) 8468-8477.

[48] S. S. Bhoware, S. Shylesh, K.R. Kamble, A.P. Singh, J. Mol. Catal. A: Chem. 255 (2006) 123–130.

[49] A. I. Molina, J. M. Robles, E. R. Castellon, B. Pawelec, J.L.G. Fierro, A. J. Lopez, Appl. Catal. A: Gen. 286 (2005) 239–248.

[50] L. Lisi, G. Ruoppolo, M.P. Casaletto, P. Galli, M.A. Massucci, P. Patrono, F. Pinzari, J. Mol. Catal. A: Chem. 232 (2005) 127-134.

[51] F. J. Pérez-Reina, P. Olivera-Pastor, P. Maireles-Torres, E. Rodríguez-Castellón, A. Jiménez-López, Langmuir, 14 (1998) 4017-4024.

[52] E. Paparazzo, E. Severini, A. Jimènez-López, P. Maireles-Torres, P. Olivera-Pastor, E. Rodríguez-Castellón, A. G. Tomlinson, J. Mater. Chem. 2 (1992) 1175-1178.

[53] P. Oliveriava, A. Machado, A. M. Romas, I. M. Fonseca, F. M. B. Fernandes, A. M. B. Do Rago, J. Vital, Micro. Meso. Mater, 120 (2009) 432-440.

[54] I. K. Biernacka, A. R. Silva, A. P. Carvalho, J. Pires, C. Freire, Langmuir, 21 (2005) 10825-10834.

[55] A. R. Silva, M. M. A. Freitas, C. Freire, B. de Castro, J. L. Figueiredo, Langmuir, 18 (2002) 8017-8024.

[56] R. Hernández-Huesca, J. Santamaría-González, P. Braos-Garc´ıa, P. Maireles-Torres, E. Rodr´ıguez-Castellón, A. Jiménez-López_Applied Catalysis B: Environmental 29 (2001) 1–11

[57] M. A. Uguina, J. A. Delgade, J. Carretero, D. Gomez-Diaz, G. Rodrigez, Ind. Eng. Chem. Res. 48 (2009) 4671-4680.

[58] I. R. Ammoumraoui, A. C.Braham, L. P. Roy, C. Kappenstein, Bull. Mater. Sci. 34 (2011) 1127-1135.

[59] W. Jianying, Z. Hua, Z. Xiangjing, L. Runjing, H. Yongqi, Chin. J. Chem. Eng. 16 (2008) 373-375.

[60] X. H. Lu, H. X. Yuan, J. L. Zhang, A. A. Zhou, Q. H. Xia, Ind. J. Chem. 51 (2012) 420-427.

[61] N. Turrà, U. Neuenschwander, A. Baiker, J. Peeters,I. Hermans, Chem. Eur. J. 16 (2010) 13226-13235.

[62] L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fischer, R. Weiss, J. Am. Chem. Soc.107 (1985) 3534-3540.

[63] A. F. Masters, J. K. Beattie, A. L. Roa, Catal. Lett. 75 (2001) 3-4.

List of figure captions:

Fig. 1. SEM image of (A) α-ZrP and (B) □-ZrP.Co(salicylaldimine).

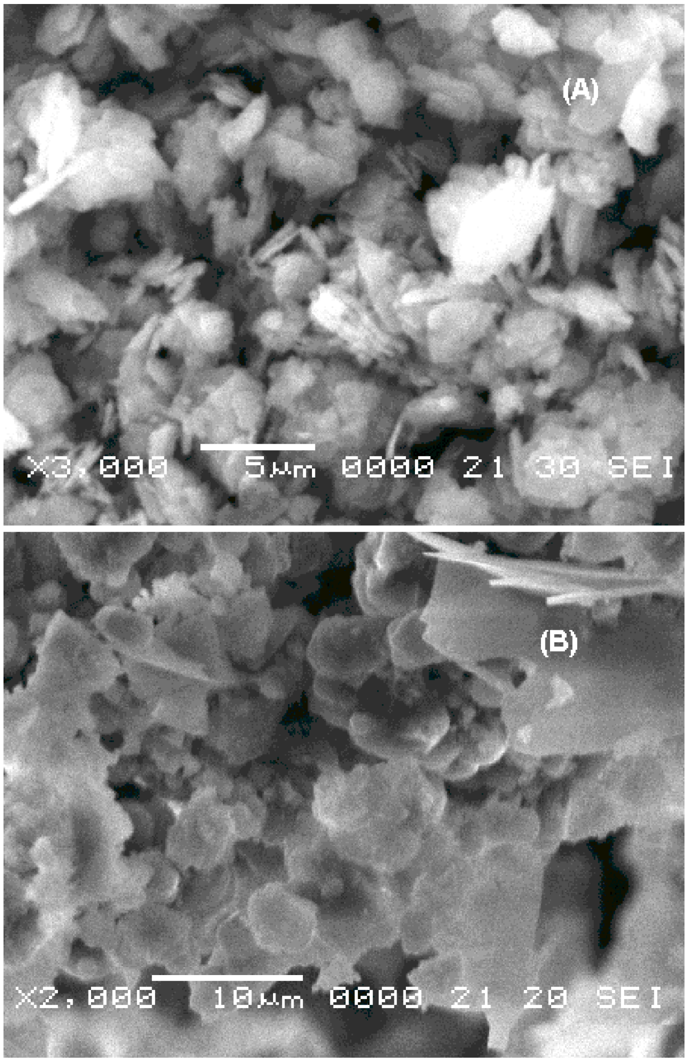

Fig. 2. XRD pattern of (A) α-ZrP, (B) □-ZrP.Co(salicylaldimine),

(C) □-ZrP.Mn(salicylaldimine) and (D) □- ZrP.Cu(salicylaldimine).

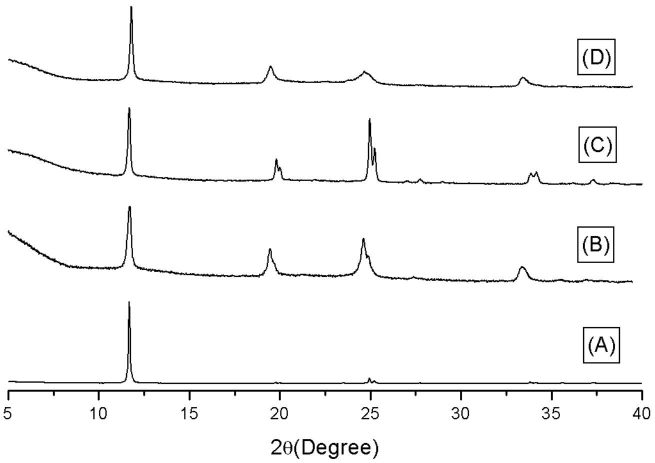

Fig. 3. FTIR Spectrum of (A) Free ligand (B) Co(salicylaldimine), (C) □-ZrP.Co(salicylaldimine) and (D) α-ZrP.

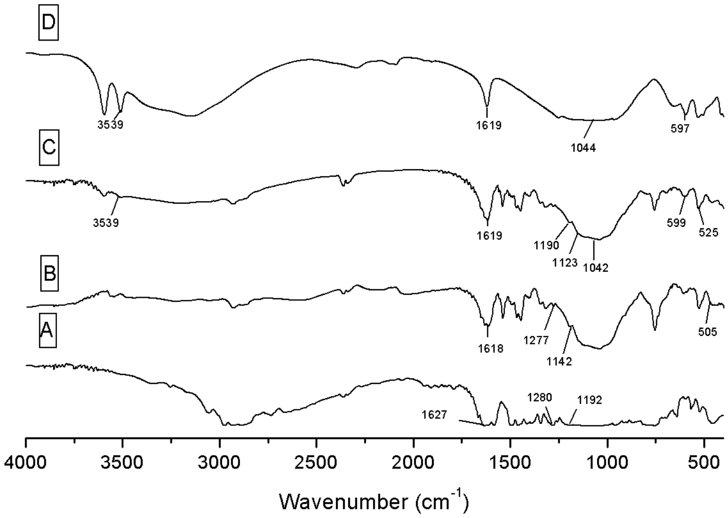

Fig. 4. UV-visible spectrum of (A) and (B) Ligand-salicylaldimine10^{-5} and 10^{-4} M solution in methanol and (C) Co(salicylaldimine) complex in methanol.

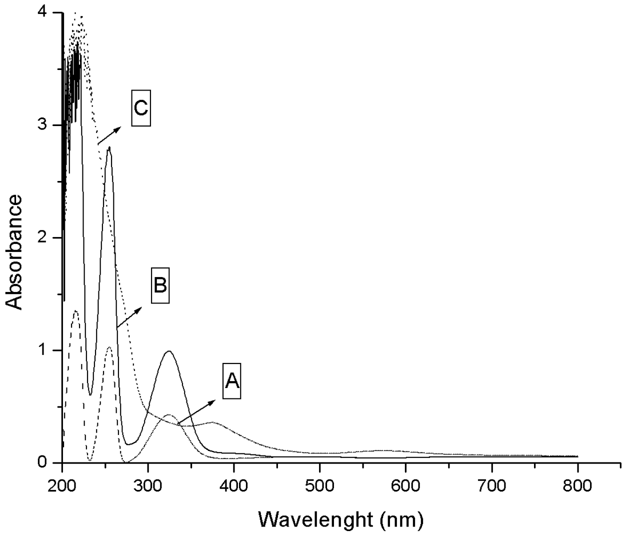

Fig. 5. TGA curves of (A) α-ZrP and (B) □-ZrP.Co(salicylaldimine).

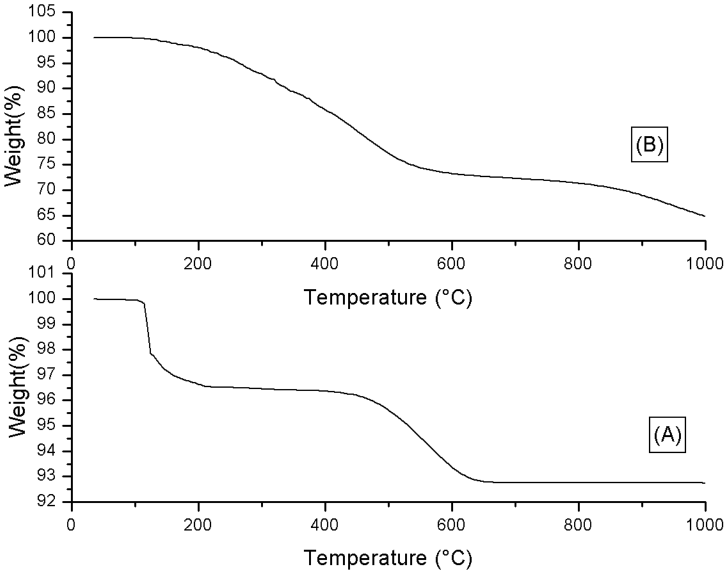

Fig. 6. XPS spectrum; A survey scan of □-ZrP.Co(salicylaldimine).

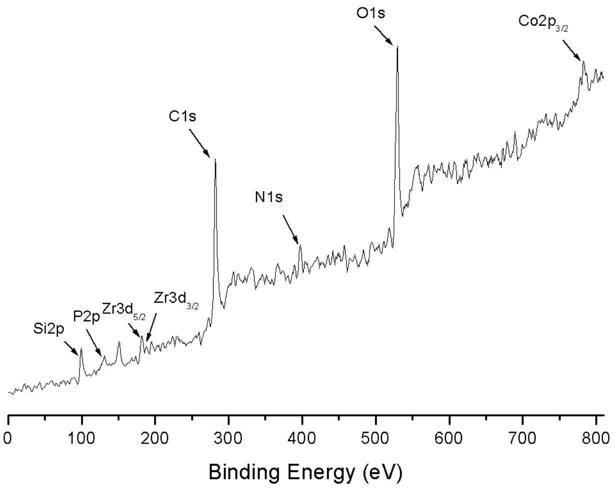

Fig. 7. Effect of oxidant on the oxidation of cyclohexane catalyzed by

□-ZrP.Co(salicylaldimine).

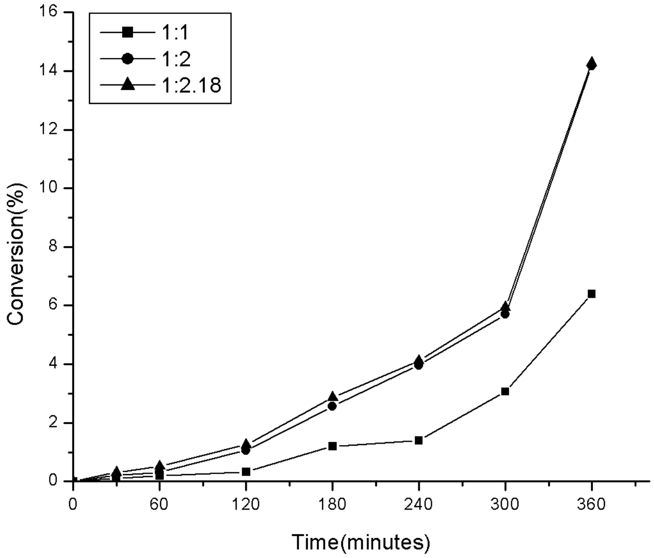

Fig. 8. Effect of amount of catalyst on the oxidation of cyclohexane catalyzed by

□-ZrP.Co(salicylaldimine).

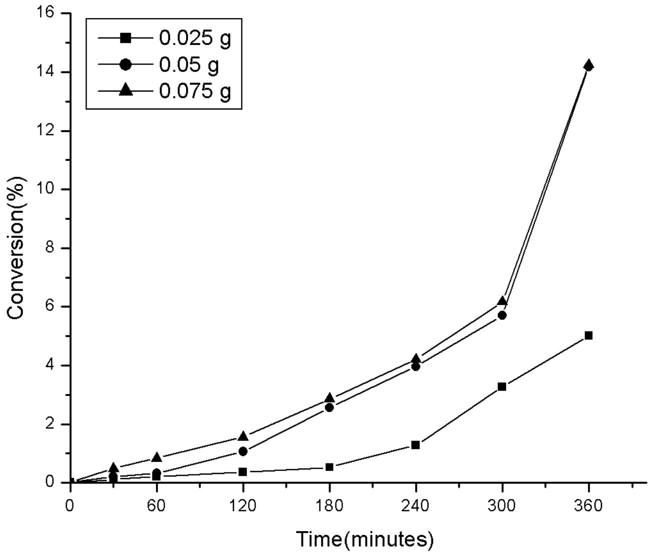

Fig. 9. Effect of temperature on the oxidation of cyclohexane catalyzed by

□-ZrP.Co(salicylaldimine).

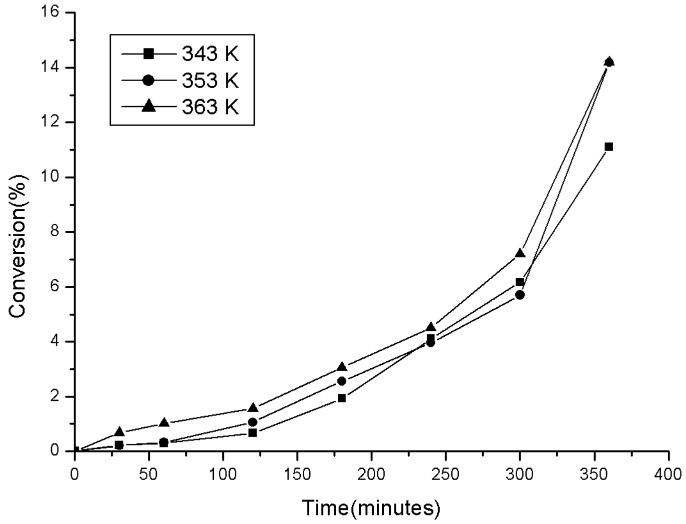

Fig. 10. Titration of Co(salicylaldimine) with 70 % TBHP; the spectra were recorded after the successive addition of one drop portion of TBHP to 10 ml of 10^{-4} M solution of Co(salicylaldimine) in methanol (a) Pure Co(salicylaldimine) in methanol, (b) after addition of 20 drops of TBHP, and (c) after addition of 20 drops of TBHP, 0.1 ml cyclohexane was added.

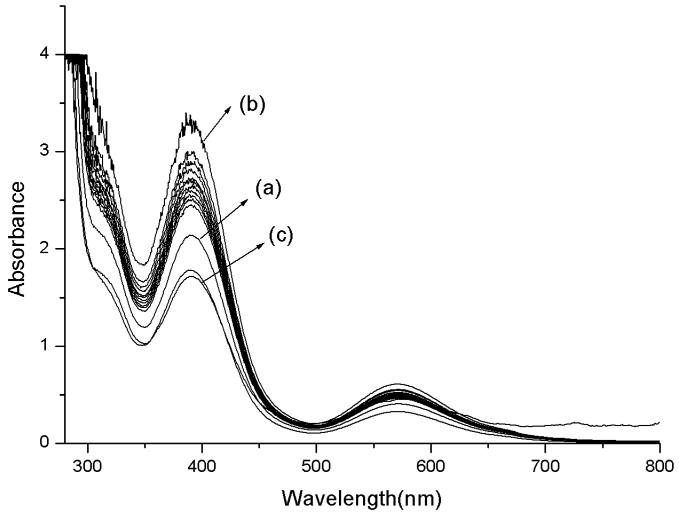

Table.1. Chemical composition and physical data of α-ZrP.M(salicylaldimine)

Catalyst*	Colour	Metal contents (ppm)	BET Surface area (m^2/g)	Pore volume (cm^3g^{-1})	Pore size (Å)
α-ZrP	White	-	5.21	0.026	8.79
α-ZrP. Co(salicylaldimine)[b]	Green	130.53	5.16	0.023	8.72
α-ZrP. Co(salicylaldimine)[a]	Brown	129.09	5.14	0.018	8.45
α-ZrP. Mn(salicylaldimine)	Green	124.49	5.18	0.015	8.56
α-ZrP. Cu(salicylaldimine)	Green	145.38	5.15	0.016	8.51

* a: After catalysis(fourth run); b: Before catalysis.

Table 2. EDX measurements for elemental composition

Catalyst*	Atomic % of Elements					
	Zr	P	O	Si	N	Metal content
□-ZrP	7.61	11.89	80.50	-	-	-
□-ZrP. Co(salicylaldimine)^b	6.15	8.37	73.03	6.64	3.13	2.68
□-ZrP. Co(salicylaldimine)^a	5.28	7.94	70.25	5.51	8.90	2.12
□-ZrP. Mn(salicylaldimine)	6.80	10.21	71.39	6.62	3.41	
□-ZrP. Cu(salicylaldimine)	6.56	9.84	71.93	6.21	3.12	

* a: After catalytic reaction (fourth run); b: Before catalytic reaction.

Table 3. FTIR Vibrations of compounds

Catalyst*	IR group vibrations (wavenumber in cm^{-1})					
	PO^{4-}	Zr-O	C=N	Si-O	C-O	M-O (M= metal)
□-ZrP	1044	597	-	-	-	-
Ligand (salicylaldimine)	-	-	1627	1192	1280	-
Co(salicylaldimine)	-	-	1618	1142	1277	505
□-ZrP. Co(salicylaldimine)[b]	1042	599	1619	1123	1190	525
□-ZrP. Co(salicylaldimine)[a]	1041	608	1619	1117	1193	530
Mn(salicylaldimine)	-	-	1614	1148	1190	504
□-ZrP. Mn(salicylaldimine)	1040	596	1630	1129	1244	531
Cu(salicylaldimine)	-	-	1620	1144	1196	502

□-ZrP. Cu(salicylaldimine)	1033	596	1627	1059	1242	530

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* a: After catalysis (fourth run); b: Before catalysis.

Table.4. Binding Energies of □-ZrP and α-ZrP.M(salicylaldimine)

Core levels	Binding Energies (eV)			
	□-ZrP	□-ZrP.Co(salicylaldimine)	□-ZrP.Mn(salicylaldimine)	□-ZrP.Cu(salicylaldimine)
$Zr3d_{5/2}$	181.38	181.71	181.67	183.69
P2p	130.87	130.87	130.64	132.2
C1s	281.56	283.32	281.71	281.68
O1s	527.56	530.09	530.25	530.01
N1s	-	397.02	398.72	396.70
Si2p	-	99.45	99.55	99.81
$Co2p_{3/2}$	-	784.12	-	-
$Mn2p_{3/2}$	-	-	638.33	-

$Cu2p_{3/2}$	-	-	-	935.05

Table 5. Effect of oxidants, solvents support, homogeneous and heterogeneous catalysts on the oxidation of cyclohexane.

Catalysts	Time	Oxidant/Solvent	Cyclohexane conversion (%)	Product selectivity (%)		TON
				(ol + none = KA-oil)	other products	
α- ZrP.Co(Salicylaldimine)	1	H_2O_2/ solvent free	-	-	-	-
α- ZrP.Co(Salicylaldimine)	6	TBHP (70 %)/ solvent free	0.59	90.40	9.60	23.78
α- ZrP.Co(Salicylaldimine)	6	*TBHP/ solvent free	14.18	92.33	7.67	176.68
α- ZrP.Co(Salicylaldimine)	6	Acetonitrile/*TBHP	9.77	82.80	17.20	139.34
α- ZrP.Co(Salicylaldimine)	6	Acetone/*TBHP	8.43	79.45	20.55	120.38
α- ZrP.Co(Salicylaldimine)	6	Dichloromethane/*TBHP	8.32	77.37	22.63	120.13
α- ZrP	6	*TBHP/ solvent free	-	-	-	-
Co(Salicylaldimine)	6	*TBHP/ solvent free	9.17	99.89	0.1	137.92
Mn(Salicylaldimine)	6	*TBHP/ solvent free	3.26	97.87	2.13	60.76
α- ZrP.Mn(Salicylaldimine)	6	*TBHP/ solvent free	4.80	98.15	1.85	72.10
Cu(Salicylaldimine)	6	*TBHP solvent free	4.35	98.25	1.75	70.79
α- ZrP.Cu(Salicylaldimine)	6	*TBHP/ solvent free	4.69	98.85	1.15	71.78

*70% TBHP in cyclohexane; KA-oil: cyclohexanone (K): cyclohexanol (A).

Table.6. Effect of cyclohexane:oxidant molar ratio, catalyst amount and temperature on the oxidation of cyclohexane catalyzed by α-ZrP.Co(salicylaldimine)/TBHP.

Cyclohexane: Oxidant (molar ratio)	Catalyst amount (mg)	Temperature (K)	Cyclohexane conversion (%)	TBHP consumption (%)	TBHP efficiency (%)	Product selectivity (%)		TON
						(KA-oil)	other products	
1:1	0.050	353	6.39	93.61	6.82	99.00	1.00	80.47
1:2	0.050	353	14.18	85.82	32.88	92.33	7.67	176.68
1:2.18	0.050	353	14.28	83.00	36.31	90.89	9.11	178.02
1:2	0.025	353	5.01	94.99	7.90	98.15	1.85	62.09
1:2	0.075	353	14.25	85.67	33.25	91.66	7.34	178.33
1:2	0.050	343	11.11	88.89	24.87	98.49	1.51	140.35
1:2	0.050	363	14.20	85.80	32.93	91.55	7.45	177.02

*70% TBHP in cyclohexane; KA-oil: cyclohexanone (K): cyclohexanol (A).

Table. 7. Comparison of literature catalysts and our catalyst system for oxidation of cyclohexane.

Entry	Catalyst(amount)	T(K)/Solvent	Oxidant	Time (h)	Conversion (%)	Selectivity* (%)	Reference
1	Co-TUD-1 (0.1 mmol)	343 K/ solvent free	TBHP	18 h	10.3	90.52	[16]
2	CoZSM-5 (0.15 g)	363 K/ [emim]BF4	TBHP	12 h	14.2	99.0	[17]
3	Co-TUD-1 (0.1 mmol)	343 K/ solvent free	TBHP	6 h	5.54	4.35	[18]
4	CoPh-HMS (0.12 g)	388 K/solvent free	O_2	6 h	6.7	80.5	[13]
5	Co-HMS (0.12 g)	388 K/solvent free	O_2,	6 h	4.8	76.9	[13]
6	Co-ZSM-5(200 mg)	373 K/ solvent free	O_2,	4 h.	7.22	90.7	[14]
7	CoAlPO-11 (200 mg)	403 K/solvent free	O_2	2 h	5.5	83.2	[15]
8	Co–$[H_4]$salen/Y (0.1 g)	333K/ Acetonitrile	H_2O_2	2 h	3.8	100	[19]
9	ZrP.Co(salicylaldimine)	353K/ solvent free	TBHP	6 h	14.18	92.33	Present work

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* selectivity % = (ol +none = KA-oil)

Table.8. Recycling experiment

No. of cycle	Cyclohexane conversion (%)	Product selectivity (%)			Selectivity (%) (ol + none = KA-oil)	TON	Metal contents (ppm)
		Cyclohexanol	cyclohexanone	other products			
Fresh	14.18	4.99	87.34	7.67	92.33	176.68	130.53
1	14.18	4.89	87.44	7.67	92.33	176.68	130.53
2	14.10	4.69	87.56	7.75	92.25	130.37	130.13
3	13.97	4.61	87.39	8.80	92.00	81.43	129.95
4	13.45	4.58	87.31	8.11	91.89	81.03	129.09