Catal Lett
DOI 10.1007/s10562-015-1647-8

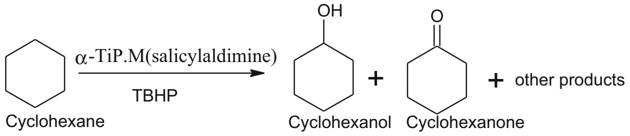
Liquid Phase Solvent-Less Cyclohexane Oxidation Catalyzed by Covalently Anchored Transition-Metal Schiff Base Complex on α-Titanium Phosphate

Savita Khare[1] · **Priti Shrivastava**[1]

Received: 28 August 2015 / Accepted: 29 October 2015
© Springer Science+Business Media New York 2015

Abstract Covalently anchored transition-metal salicylaldimine complexes on α-titanium phosphate {α-TiP.M(salicylaldimine) where M = Co, Cr, Cu and Fe} were synthesized by in situ method and characterized by BET surface area, XRD, SEM, EDX, FTIR, TGA and ICP techniques. Its catalytic activity was tested for the oxidation of cyclohexane under solvent free condition using *tert*-butyl hydroperoxide as an oxidant. The oxidation of cyclohexane gave cyclohexanol, cyclohexanone and some unidentified products. The activity of heterogeneous catalysts in the oxidation reaction decreased in the order of α-TiP.Co(salicylaldimine) > α-TiP.Cr(salicylaldimine) > α-TiP.Cu(salicylaldimine) > α-TiP.Fe(salicylaldimine). The α-TiP.Co(salicylaldimine) gave maximum conversion 14.85 % of cyclohexane with 92.13 % selectivity of KA-oil (cyclohexanol + cyclohexanone) in 6 h. The catalyst, α-TiP.Co(salicylaldimine) was reused for five cycles without significant loss of catalytic activity.

Graphical Abstract A heterogeneous catalytic system, α-TiP.Co(salicylaldimine)/TBHP gave maximum 14.85 % conversion and 92.13 % selectivity for KA-oil in oxidation of cyclohexane. The catalyst can be reused for five cycles.



Keywords Liquid phase · Cyclohexane oxidation · α-Titanium phosphate · Salicylaldimine complex · *tert*-butylhydroperoxide · Solvent free

1 Introduction

The liquid-phase oxidation of cyclohexane is an industrially important process for making cyclohexanol, cyclohexanone. The oxidation products of cyclohexane which is cyclohexanol and cyclohexanone are important intermediates in the production of adipic acid and caprolactam. Caprolactam and adipic acid is extensively used in the man-made fiber industry along with hexamethylenediamine for manufacturing nylon-6 and nylon-66. A mixture of cyclohexanone and cyclohexanol is known as KA-oil. The industrial commercial process involves oxidation of cyclohexane using molecular oxygen at temperature 150 °C under pressure of 175 psi in the presence of homogeneous cobalt salts [1]. This process gave only 4 % conversion of cyclohexane with 85 % selectivity of desired products, cyclohexanol and cyclohexanone. The drawback of this process is that, 96 % of cyclohexane must be separated from products and recycled. Keeping this in mind, many heterogeneous catalysts were developed using various supports such as zeolites, alumina, silica, clay, polymers, carbon tubes and layered compounds [2–14]. Salavati-niasari et al. [2–5], synthesized binuclear transition metal complexes using zeolites Y as a supported for oxidation of hydrocarbons. Singh et al. [6] synthesized chromium-containing periodic mesoporous organosilica and used it as catalyst in the aerial oxidation of cyclohexane. Anisia et al. [7], have prepared a heteronuclear bimetallic macrocyclic iron copper complex, $FeCuL(NO_3)$-$24H_2O$ supported on zirconium pillared montmorillonite. The oxidation of cyclohexane in the presence of this catalyst

---

✉ Savita Khare
kharesavita@rediffmail.com

[1] School of Chemical Sciences, Devi Ahilya University, Takshashila Campus, Khandwa Road, Indore, MP 452001, India

Published online: 04 November 2015

with molecular oxygen as an oxidant at 190 °C, the cyclohexane conversion was 14.2 % and cyclohexanone was formed with 87.4 % selectivity. Gupta et al. [8–10], prepared polymer supported schiff base complexes in oxidation reaction. Karabach et al. [11], synthesized copper(II) coordination polymers from triethanolamine and pyromellitic acid for bioinspired mild peroxidative oxidation of cyclohexane by hydrogen peroxide in acidic medium. An overall yield (based on cyclohexane) of 29 % has been achieved. Heterogeneous catalysts are stable, can be easily separated from reaction zone, gave high catalytic activity and can be reused for several runs without loss of their catalytic activity. The oxidation of cyclohexane was also studied using various oxidants such as molecular oxygen, *tert*-butyl hydroperoxide (TBHP) and hydrogen peroxide (H_2O_2) [15–23]. Transition metal plays an important role in oxidation of cyclohexane; in biological system an enzyme cytochrome P-450 catalyzed this reaction. To mimic this reaction some researchers has been developed heterogenization of various homogeneous transition metal complexes having various ligands. Salvati-Nisari et al. [24, 25], have been encapsulated transition metal (M = Mn(II), Co(II), Ni(II) and Cu(II)) complexes with tetrahydro-salophen (salophen = *N*,*N*-bis-salycilidene)-1,2- phenylenedimine: H_2 [H_4salophen] = 2-({2-[(2hydroxybenzyl)amino]anilino} methyl)phenol) and bis(salicyaldehyde) oxaloyldihydrazone on zeolite-Y. Gua et al. [26], synthesized iron, manganese and cobalt tetraphenylporphyrins to catalyze cyclohexane oxidation with air in the absence of additives and solvents. Parton et al. [27] have been studied cyclohexane oxidation with *tert*-butylhydroperoxide catalyzed by iron phthalocyanine complex homogeneously supported on Y zeolite. Fan et al. [28] and Tembe et al. [29] designed schiff base metal complexes to make these systems more practical using zeolites, Cruz et al. [30], synthesized chromium containing silicates by a simple acid-catalyzed sol–gel process. Carvalho et al. [31], synthesized mesoporous Si-MCM-41, which can be easily organofunctionalised by anchoring [$H_2NC_3H_6$-$Si(OCH_3)_3$] at the surface of the Si-MCM-41 with iron and copper. The use of layered compound as a support for the synthesis of heterogeneous catalysts is effective because their structure is known and they are temperature- and solvent-stable [14]. The α-titanium phosphate is a layered compound with a flexible layer structure and has been studied for its cation exchange, proton transport, intercalation chemistry, and catalytic properties [32–35]. In previous studies we have reported the use of Fe(Salen) and Cu(Salen) intercalated α-zirconium phosphate as an active, and reusable catalyst for the oxidation of cyclohexene [36, 37]. Here with, we are reporting in situ synthesis of heterogeneous catalysts, covalently bonded transition metal salicylaldimine complexes to α-titanium phosphate, abbreviated as {α-TiP.M(salicylaldimine) where M = Co, Cr, Cu and Fe} and their catalytic behavior for oxidation of cyclohexane using *tert*-butyl hydroperoxide (TBHP) as an oxidant.

2 Experimental

2.1 Materials

Titan(IV)-isopropylate (97 %, Aldrich), phosphoric acid, hydrofluoric acid, metals chloride, metals acetate, salicylaldehyde, 3-aminopropyltriehtoxysilane (APTES) and cyclohexane were of reagent grade (E. Merck). Cyclohexane was checked by gas chromatography (GC) to ensure that the absence of any oxidation products in the substrate. A stock solution of TBHP (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 [38]. The organic layer was dried over $MgSO_4$, filtered, and stored at 5 °C. 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 [39].

2.2 Catalysts Preparation

2.2.1 Preparation of α-Titanium Phosphate

α-Titanium phosphate (abbreviated α-TiP) was prepared by reported method [40]. A sample of 10 ml Titan(IV)—isopropylate (97 %), was mixed with 100 ml 3 M H_3PO_4 in a flask to which 57 ml of HF solution (5 M) was added to reach a molar ratio of $F^-/Ti^+= 6$. 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 becomes 5, then it was dried at 110 °C for 24 h. The final product was identified as α-TiP. Finally the structure of α- TiP was confirmed by powder XRD.

2.2.2 Preparation of Ligand (Salicylaldimine)

The salicylaldimine ligand was synthesized by the condensation of 3-aminopropyltriethoxysilane (1 mol), and salicyaldehyde (1 mol) in ethanol (40 ml), the solution instantly became yellow due to imines formation [41], 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 %.

2.2.3 *Preparation of Neat M(salicylaldimine) Complex {Where M = Co, Cr, Cu and Fe}*

The metal salicylaldimine complexes 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 %.

2.2.4 *Preparation of α-Titanium 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 metal chloride (0.5 mol) was added to the mixture and stirred for 30 min at room temperature. After 30 min, α-TiP (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 diethylether until the washing was colourless. The solid was dried in an oven at 110 °C for 12 h. The catalysts were characterized by FTIR, XRD, BET surface area analysis, SEM, EDX, TGA and ICP-AES analysis.

2.3 Catalysts Characterization

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) 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. 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 2°/min with step size 0.02°. 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. The electronic spectra were recorded on Shimadzu UV-1800 Pharma Spectrophotometer. 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; 30 m × 60 mm). Thermal analysis measurements were performed using (Perkin-Elmer USA model diamond TGA) at a heating rate of 10 °C/min.

2.4 Catalytic Performance

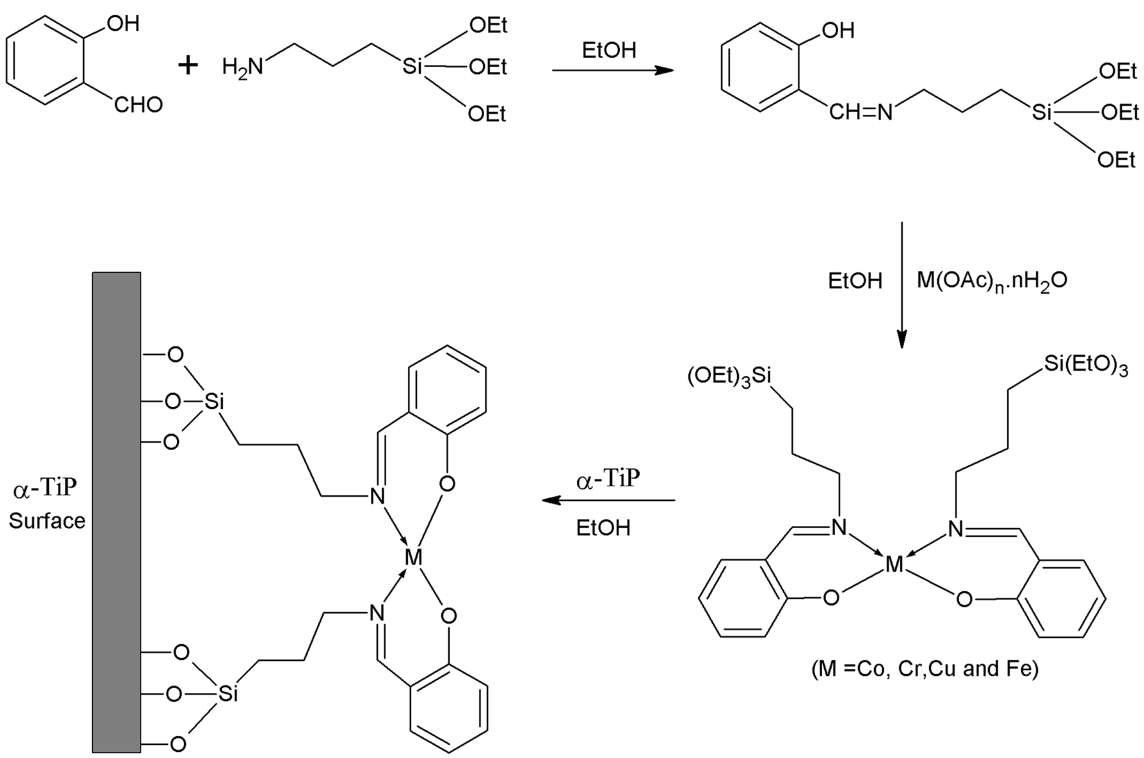
The catalytic oxidation of cyclohexane was carried out using {α-TiP.M(salicylaldimine)} catalysts in a three-necked round bottom flask (100 ml) equipped with a refluxed condenser. In a typical experiment, the flask was loaded with catalyst (0.05 g) and 5 ml mixture of cyclohexane (17.86 mmol%) and TBHP (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 70 °C. The products were identified by GC–MS. The GC–MS analysis revealed that the cyclohexanol, cyclohexanone and some unidentified products are formed in the reaction.

3 Result and Discussion

3.1 Characterization of the Catalyst

3.1.1 *Estimation of Metal Contents*

Covalently anchored catalysts, α-TiP.M(salicylaldimine) were prepared by covalent bonding of M(salicylaldimine) complex to α-titanium phosphate. Scheme 1 shows the synthetic route for formation of α-TiP.M(salicylaldimine). Physical, analytical and surface properties of all compounds are given in Table 1. The colours of α-TiP, α-TiP.Co(salicylaldimine)^b, α-TiP.Co(salicylaldimine)^a (b = before and a = after five catalytic reaction) and α-TiP.M(salicylaldimine) compounds were different due to change in metal content, which was determined by ICP-AES analysis. There were no metals in α-TiP and its colour was white. The colours and metal contents in α-TiP.M(salicylaldimine) depend on the presence of metals loading.



Scheme 1 Synthetic route for formation of α-TiP.M(salicylaldimine)

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

Catalysts	Colour	Metal contents (%)	BET surface area (m^2/g)	Pore volume (cm^3g^{-1})	Pore size (Å)	d-spacing (Å)
α-TiP	White	–	5.46	0.04	23.51	7.56
α-TiP.Co(salicylaldimine)[b]	Green	2.93	5.38	0.03	22.00	7.56
α-TiP.Co(salicylaldimine)[a]	Brown	1.45	4.41	0.02	18.05	7.54
α-TiP.Cr(salicylaldimine)	Brown	2.52	5.32	0.02	20.49	7.56
α-TiP.Cu(salicylaldimine)	Green	2.48	5.34	0.03	22.89	7.56
α-TiP.Fe(salicylaldimine)	Green	2.30	5.25	0.02	21.32	7.56

[a] After catalysis

[b] Before catalysis

3.1.2 EDX and SEM Analysis

The formation of α-TiP.M(salicylaldimine) was confirmed by EDX analysis. The EDX measurements results of α-TiP and α-TiP.M(salicylaldimine) are incorporated in Table 2. The presence of metals ions, nitrogen and silicon in α-TiP.M(salicylaldimine) confirms the presence of M(salicylaldimine) complex on the α-TiP surface. The SEM images, which allow us to monitor how the morphology of the sample evolves during the above commented process, are shown in Fig. 1 {α-TiP, α-TiP.Co(salicylaldimine)[b] and α-TiP.Co(salicylaldimine)[a]}. The SEM image of α-TiP (Fig. 1a) revealed the presence of well-defined hexagonal plates with smooth surface. The SEM images of α-TiP.Co(salicylaldimine) (Fig. 1b) are less ordered than that of α-TiP, contains both sheets and spheres of different shapes and sizes which indicate the presence of homogeneous complex on the surface. The SEM images of α-TiP.Co(salicylaldimine) (Fig. 1c) after five catalytic cycles shows clear change on the surface structure.

3.1.3 XRD Studies

The powder XRD patterns of α-TiP, α-TiP.Co(salicylaldimine)[b,] α-TiP.Co(salicylaldimine)[a] and α-TiP.M(salicylaldimine) catalysts are shown in Fig. 2 and their d-spacing incorporated in Table 1. The XRD pattern of α-TiP shows most intense peak corresponding to the (002)

Table 2 EDX measurements for elemental composition

Catalyst*	Atomic % of elements					
	Ti	P	O	Si	N	Metals
α-TiP	11.14	14.48	74.38	–	–	–
α-TiP. Co(salicylaldimine)[b]	9.83	12.78	65.71	6.94	3.13	1.61
α-TiP. Co(salicylaldimine)[a]	8.42	10.95	65.26	6.04	8.09	1.24
α-TiP. Cr(salicylaldimine)	9.46	12.30	66.68	6.85	3.61	1.10
α-TiP. Cu(salicylaldimine)	9.76	12.70	65.28	6.95	3.61	1.70
α-TiP. Fe(salicylaldimine)	9.57	12.45	66.42	6.83	3.50	1.23

* [a] After catalytic reaction

[b] Before catalytic reaction

plane at 7.56 Å (*d* value), this shows material is crystalline. In all α-TiP.M(salicylaldimine) catalysts the d-spacing is virtually constant which indicates that metal complexes are not present in interlayer of α-TiP. Thus, XRD pattern confirms that the supports essentially retain their crystallinity and structure after covalent bonded of the metal complex.

3.1.4 Surface Area Analysis

The results of BET surface area, pore volume and pore size of all the compounds are incorporated in Table 1. The surface area of α-TiP is 5.46 m^2/g, whereas the surface area of α-TiP.M(salicylaldimine) ranges from 5.25 to 5.38 m^2/g was lower than the supports, which indicates that covalent bonding of M(salicylaldimine) complexes lead to marginal decrease in surface area. Similar observation is also reported for silica immobilized salicylaldimine Cu(II) and Co(II) complexes [42]. The pore size and pore volume of the α-TiP sample were 23.51 nm and 0.04 cm^3/g respectively which was slightly decreases in the α-TiP.M(salicylaldimine). The decrease in pore volume and pore diameter due to the presence of metal ion near the opening of the layered structure, block the access of nitrogen molecules to the whole lamellar structure [43]. The surface area, pore volume and pore size of the α-TiP is retained after covalent bonding of the metal complexes on its surface which indicate the formation of α-TiP.M(salicylaldimine).

3.1.5 FTIR Spectral Studies

The FTIR spectra of all compounds were recorded in the 4000 to 400 cm^{-1} range. FTIR spectral frequencies of free ligand, neat M(salicylaldimine) complexes, α-TiP.M(salicylaldimine) and α-TiP 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 [44]. In the spectrum of α-TiP, the bands at 3400 and 1635 cm^{-1} are assigned due to the presence of external water in addition to the strongly hydrogen-bonded OH or extremely strong coordinated H_2O [45]. A band in the region ~1038 cm^{-1} is attributed to the presence of P=O stretching. A medium intensity band at 1400 cm^{-1} is attributed to the presence of δ(POH). These bands indicate the presence of structural hydroxyl groups/protonic sites in the material. The band at 599 cm^{-1} is due to stretching vibration of Ti–O. In the spectrum of covalently bonded heterogeneous catalyst, α-TiP.Co(salicylaldimine) Fig. 3c, the band positions of PO_4^{3-} was shifted to lower frequencies while that of Ti–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 1619–1622 cm^{-1} in α-TiP.M(salicylaldimine). The Si–O vibration of metal complexes was slightly merged with of PO_4^{3-} stretching vibration of α-TiP in α-TiP.M(salicylaldimine). Figure 3 shows comparison of FTIR spectra of free ligand, Co(salicylaldimine), α-TiP.Co(salicylaldimine) and α-TiP which provides evidence of coordination of the metal complexes on α-TiP.

3.1.6 Electronic Spectral Studies

Typical electronic spectra of ligand and Co(salicylaldimine) complex in methanol are shown in Fig. 4. The probable electronic assignments of ligand and M(salicylaldimine) complexes are given in Table 4. The electronic spectrum of the free ligand exhibit three bands at 216, 251 and 320 nm are assigned as due to φ → φ, π → π* and n → π* transitions, respectively. The band at 251 nm is assigned due to π-π* transition of phenol 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 372–375 nm in metal-complexes due to ligand to metal charge transfer (LMCT) transition, which indicates the coordination of phenolate oxygen of ligand to

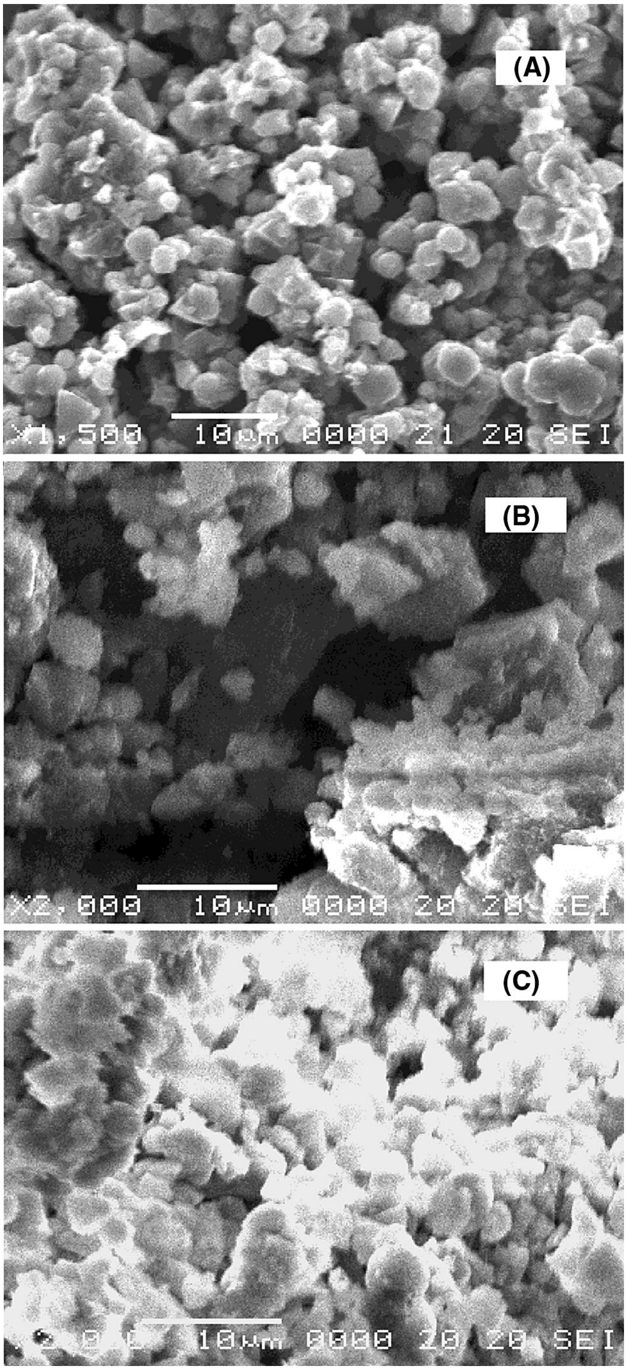


Fig. 1 SEM image of (**a**) α-TiP, (**b**) α-TiP.Co(salicylaldimine), and (**c**) recycled α-TiP.Co(salicylaldimine)

an empty d orbital of metal ions. An additional weak and broad band at 570-572 nm in metal complexes is due to the d–d transition as reported in the literature [46].

3.1.7 TGA Analysis

Thermal behavior of α-TiP and α-TiP.Co(salicylaldimine) were studied by TGA analysis. The TGA-curve of α-TiP and α-TiP.Co(salicylaldimine) are shown in Fig. 5. The TGA-curve of the α-TiP (Fig. 5a) showed first weight loss between 120-248 °C which is attributed to loss of moisture/hydrated water. Second weight loss was observed between 255 and 755 °C which is attributed to the condensation of structural-OH groups. The TGA-curve of the α-TiP.Co(salicylaldimine) (Fig. 5b) complex shows weight loss in the temperature range of 120–135 °C which is attributed to loss of moisture/hydrated water. Second weight loss was observed between 187 and 558 °C which is due to loss of water molecule followed by decomposition of the imine group in the complex.

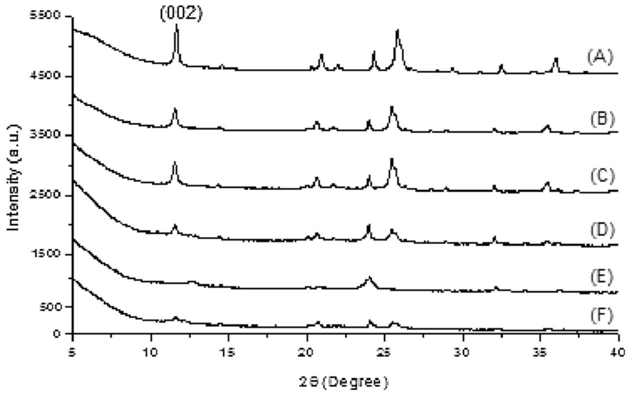


Fig. 2 XRD pattern of (*A*) α-TiP, (*B*) α-TiP.Co(salicylaldimine), (*C*) recycled α-TiP.Co(salicylaldimine), (*D*) α-TiP.Cr(salicylaldimine), (*E*) α-TiP.Cu(salicylaldimine) and (*F*) α-TiP.Fe(salicylaldimine)

3.2 Catalytic Experiments

Catalytic oxidation of cyclohexane was investigated using various α-TiP.M(salicylaldimine) catalysts with TBHP under solvent free condition. Under similar experimental conditions support, α-TiP, homogeneous catalyst, M(salicylaldimine) and reaction without catalyst (blank reaction) were also investigated. The results are incorporated 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-TiP.M(salicylaldimine), oxidized cyclohexane to cyclohexanol, cyclohexanone and some other products. The major products are cyclohexanol and cyclohexanone in all cases. Further, 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-TiP.M(salicylaldimine) showed high catalytic activity. The catalytic oxidation of cyclohexane catalyzed

Table 3 FTIR frequency

Catalysts	IR group frequency (cm^{-1})					
	PO^{4-}	Ti–O	C=N	Si–O	C–O	M–O (M = metal)
α-TiP	1038	599	–	–	–	–
Ligand (salicylaldimine)	–	–	1627	1192	1280	–
Co(salicylaldimine)	–	–	1618	1042	1277	505
α-TiP.Co(salicylaldimine)[b]	1037	611	1619	1040	1297	512
α-TiP.Co(salicylaldimine)[a]	1034	603	1619	1039	1280	510
Cr(salicylaldimine)	–	–	1619	1143	1251	501
α-TiP.Cr(salicylaldimine)	1031	621	1622	1132	1279	517
Cu(salicylaldimine)	–	–	1620	1144	1196	502
α-TiP.Cu(salicylaldimine)	1032	614	1621	1040	1234	513
Fe(salicylaldimine)	–	–	1614	1142	1248	503
α-TiP.Fe(salicylaldimine)	1035	614	1618	1131	1317	522

[a] After catalysis

[b] Before catalysis

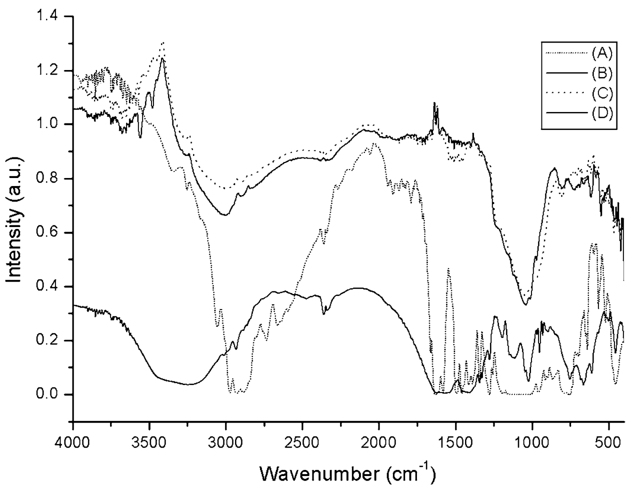


Fig. 3 FTIR spectrum of (*A*) Free ligand, (*B*) Co(salicylaldimine), (*C*) α-TiP.Co(salicylaldimine), and (*D*) α-TiP

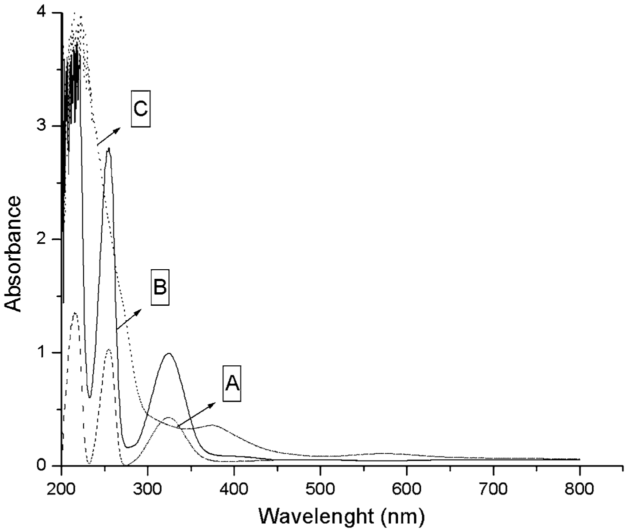


Fig. 4 UV–Vis spectrum of (*A*) and (*B*) Ligand-salicylaldimine 10^{-5} and 10^{-4} M solution in methanol and (*C*) Co(salicylaldimine) complex in methanol

by α-TiP.M(salicylaldimine)/TBHP system can be explain by Scheme 2.

The selectivity of the products is the measure of the reactivity of the catalyst {α-TiP.M(salicylaldimine)}. The percentage-conversion of the substrate and the percentage-selectivity of the products in the oxidation reaction are calculated as [14]. Turn over number (TON) was calculated according to the following formula [47]:

$$\text{Substrate conversion }(\%) = [\text{Substrate converted (moles)} / \text{substrate used (moles)}] \times 100$$

$$\text{Product selectivity }(\%) = [\text{Product formed (moles)} / \text{substrate converted (moles)}] \times 100$$

Turn over number = mmol of products/mmol of catalyst.

The consumption of TBHP was determined iodometrically after each catalytic reaction. The amount of TBHP consumed and the efficiency of TBHP were calculated according to reported formula [37, 48] as follows:

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

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

All the four heterogeneous catalysts, TiP.Fe(salicylaldimine), TiP.Cu(salicylaldimine), TiP.Cr(salicylaldimine) and TiP.Co(salicylaldimine) were studied for

Table 4 UV–Vis data of ligand and complexes in methanol

Compounds	λ_{max} (nm)	Assignment
(salicylaldimine) ligand	216, 251, 320	$\varphi \rightarrow \varphi$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$
Co(salicylaldimine)	225, 269, 372, 570	$\varphi \rightarrow \varphi$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and d–d transition
Cr(salicylaldimine)	218, 268, 371, 571	$\varphi \rightarrow \varphi$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and d–d transition
Cu(salicylaldimine)	220, 267, 372, 572	$\varphi \rightarrow \varphi$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and d–d transition
Fe(salicylaldimine)	221, 268, 373, 572	$\varphi \rightarrow \varphi$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and d–d transition

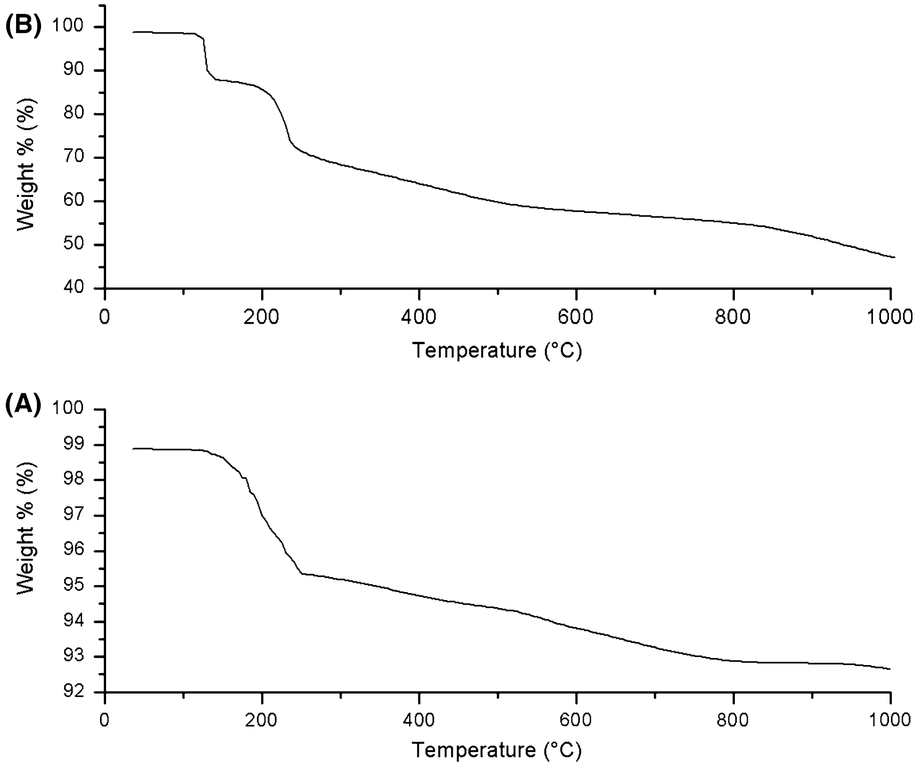


Fig. 5 TGA analysis of (**a**) α-TiP and (**b**) α-TiP.Co(salicylaldimine)

the oxidation of cyclohexane were found to be active as the shown in Table 5. It is observed that the conversion of cyclohexane was varied from 3.59 to 14.85 %, whereas the selectivity of KA-oil (cyclohexanol + cyclohexanone) varied from 92.13 to 98.54 %. A maximum conversion 14.85 % was obtained with α-TiP.Co(salicylaldimine), however the maximum selectivity 98.54 % of KA-oil, was obtained with α-TiP.Cr(salicylaldimine). In the case of α-TiP.Cr(salicylaldimine), TiP.Cu(salicylaldimine) and α-TiP.Fe(salicylaldimine) conversion of cyclohexane is less in comparison with α-TiP.Co(salicylaldimine). Conversion of substrate plays an important role in a catalytic reaction, Therefore the orders of catalytic activity of the α-TiP.M(salicylaldimine) catalysts on the basis of cyclohexane conversion are as follows:

α-TiP.Co(salicylaldimine) > α-TiP.Cr(salicylaldimine) > α-TiP.Cu(salicylaldimine) > α-TiP.Fe(salicylaldimine).

The catalyst, α-TiP.Co(salicylaldimine) shows best activity for the oxidation of cyclohexane in comparison with other catalysts. Therefore, the optimization of reaction conditions for oxidation of cyclohexane to obtain maximum conversion of cyclohexane using various parameters were considered such as, effects of various solvents, oxidants, cyclohexane: TBHP molar ratios, amount of catalyst and the reaction temperature for detail study.

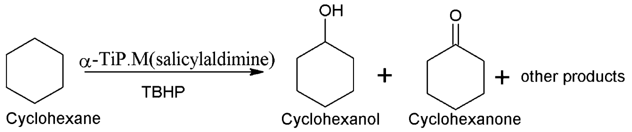
The effect of various oxidants, viz. 30 % H_2O_2, 70 % TBHP and TBHP (70 % in cyclohexane) on the oxidation of cyclohexane, catalyzed by α-TiP.Co(salicylaldimine) was studied to develop an efficient catalytic system and the results are given in Table 6. In each case, the reaction was carried out by taking oxidant and cyclohexane in 1:2 molar ratio at 353 K in an oil bath for 6 h. It was observed that leaching of the catalyst occurred after 15 min in case of 30 % H_2O_2. In case of 70 % TBHP, 3.59 % conversion of

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

Catalysts	Cyclohexane conversion (%)	Product selectivity (%)			Selectivity (%) (ol + none = *KA-oil)	TON
		Cyclohexanol	Cyclohexanone	Other products		
α-TiP	–	–	–	–	–	–
Co(salicylaldimine)	9.17	49.55	50.34	0.1	99.89	137.92
α-TiP.Co(salicylaldimine)	14.85	32.83	59.30	7.87	92.13	184.01
Cr(salicylaldimine)	1.86	35.35	52.88	11.77	88.23	11.44
α-TiP.Cr(salicylaldimine)	5.03	12.58	85.96	1.46	98.54	85.49
Cu(salicylaldimine)	4.35	54.27	43.98	1.75	98.25	70.79
α-TiP.Cu(salicylaldimine)	3.75	51.57	45.34	3.09	96.91	55.63
Fe(salicylaldimine)	1.52	54.57	45.43	–	100	18.96
α-TiP.Fe(salicylaldimine)	3.59	38.53	54.43	7.04	92.96	41.16

* Reaction conditions: catalyst (0.05 g); TBHP (38.89 mmol); cyclohexane (19.45 mmol); Time (6 h); 353 K in oil bath

*KA-oil: cyclohexanone (K): cyclohexanol (A)



Scheme 2 Oxidation of cyclohexane catalyzed by α-TiP.M(salicylaldimine)/TBHP system

cyclohexane was obtained, however, after 1 h the leaching of catalyst was observed. A maximum, 14.85 % conversion of cyclohexane with 92.13 % selectivity of KA-oil was observed with TBHP in cyclohexane. The order of selectivity of products are as follows: cyclohexanone (59.30 %) > cyclohexanol (32.83 %) > other products (7.87 %). Cyclohexanone was the major product. Thus the best oxidant for our catalytic system is TBHP in cyclohexane.

The effect of various solvents, viz. acetonitrile, acetone and dichloromethane on the oxidation of cyclohexane, catalyzed by α-TiP.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 6. It was observed that when solvents were used in the reaction, the cyclohexane conversion decreases in the following order: solvent-less (14.85 %) > acetonitrile (9.45 %) > acetone (8.96 %) > dichloromethane (8.78 %). The selectivity of KA-oil decreased in the following ordered:

$$\text{Solvent-less } (92.13\,\%) > \text{Acetonitrile } (85.79\,\%) > \text{acetone } (79.37\,\%) > \text{dichloromethane } (78.66\,\%).$$

Table 6 Effect of oxidants and solvents on the oxidation of cyclohexane catalyzed by α-TiP.Co(salicylaldimine)/TBHP

Solvents/oxidants	Time (h)	Cyclohexane conversion (%)	Product selectivity (%)			Selectivity (%) (ol + none = *KA-oil)
			Cyclohexanol	Cyclohexanone	Other products	
H_2O_2/no solvent	1	–	–	–	–	–
TBHP (70 %)/no solvent	1	3.95	33.26	58.14	8.60	90.40
*TBHP/no solvent	6	14.85	32.83	59.30	7.87	92.13
Acetonitrile/*TBHP	6	9.45	32.89	52.90	14.21	85.79
Acetone/*TBHP	6	8.96	31.78	46.88	21.34	79.37
Dichloromethane/ *TBHP	6	8.78	30.60	48.77	20.63	78.66

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

The selectivity of KA-oil increases with increasing in dipole moment of polar aprotic solvents. Thus, dipole moment of the solvents probably is an essential factor in oxidation reaction. Similar observations were reported by various authors [49–51]. A maximum 14.85 % conversion of cyclohexane with 92.13 % selectivity of KA-oil (cyclohexanol, 32.83 % + cyclohexanone, 59.30 %) was obtained under solvent-less condition because according to molecular collision theory any reaction takes place when there is effective collision in between molecules of substrate but when we add some solvent in it, the collision between the two substrate decreases as collision between substrate and solvent molecules also takes place which results as lowering of effective collision between two substrate molecules hence rate of reaction decreases. This observation also demonstrates that substrate and solvent molecules are in competition for the active sites of metal center in catalyst. Similar type of observation is reported in the oxidation of ethylbenzene [52]. However, the use of solvent leads to many environmental problems. Therefore, activation of cyclohexane under solvent free reaction conditions is favorable and environmental friendly for developing new catalytic system. Thus, we have chosen solvent free oxidation of cyclohexane which gave maximum (14.85 %) conversion of cyclohexane in 6 h of reaction time.

The three different molar ratio of cyclohexane to TBHP (1:1, 1:2 and 1:2.18) were considered to study the effect of cyclohexane to TBHP molar ratio on the oxidation of cyclohexane at 353 K in an oil bath for 6 h. In Fig. 6, the conversion of cyclohexane as a function of time is plotted. As shown in Fig. 6, when cyclohexane to TBHP molar ratio increases from 1:1 to 1:2, the conversion of cyclohexane increases from 12.67 to 14.85 %. Further increase in cyclohexane to TBHP molar ratio to 1:2.18, the conversion of cyclohexane increased slightly to 14.96 %. The results of the conversion of cyclohexane, TBHP efficiency, consumption, product selectivity and TON are presented in Table 7. The selectivity of KA-oil decreased from 99 to 91.90 % 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 [53–55]. This is probably due to the non-productive decomposition of TBHP at higher concentration. Similar observation is reported in case of TS-1/ionic liquid/TBHP system [56]. At all molar ratio of cyclohexane to TBHP, cyclohexanone was the major product. Moreover, higher concentration of oxidant showed little increases in conversion, we have chosen 1:2 molar ratio of cyclohexane to TBHP best due to economic point of view.

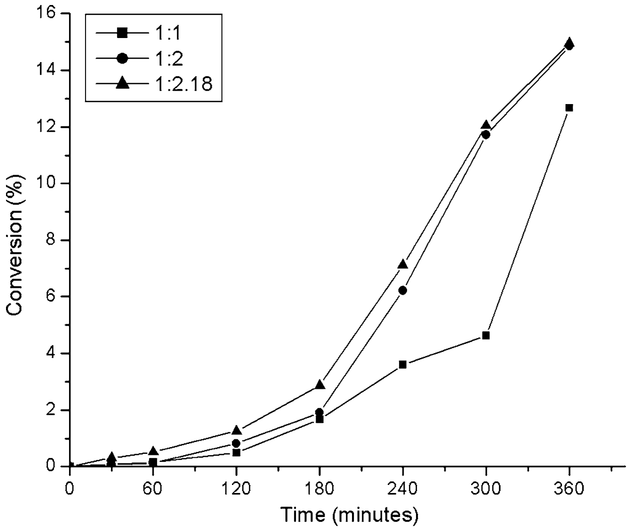


Fig. 6 Effect of oxidant on the oxidation of cyclohexane catalyzed by α-TiP.Co(salicylaldimine)

To study the effect of amount of catalyst on the oxidation of cyclohexane, the amount of α-TiP.Co(salicylaldimine) was varied as 0.025, 0.050 and 0.075 g, while keeping the other parameters fixed. In Fig. 7, the conversion of cyclohexane is plotted against time at different amount of catalyst. It is evident from Fig. 7 that conversion increases sharply from 6.97 to 14.85 % with increasing catalyst amount from 0.025 g to 0.05 g. Further increase in catalyst amount to 0.075 g conversion of cyclohexane also increased to 14.98 %. Only little increase in conversion was observed at higher catalyst amount. Similar results were observed with Co_3O_4-I/O_2 system also [57]. The results of the conversion of cyclohexane, selectivity of products, TON, efficiency and consumption of TBHP at different amount of catalyst are summarized in Table 7. The selectivity of KA-oil decreased from 99.21 to 91.24 % with increasing amount of catalyst from 0.025 to 0.075 g. The reduction of selectivity of KA-oil at higher catalyst amount is due to the increase in the formation of other products. It was also observed that the TBHP consumption decreases, while TBHP efficiency increases with increase in amount of catalyst from 0.025 to 0.075 g. Only little increase in conversion and selectivity of KA-oil was observed at 0.075 g of catalyst. Therefore, less amount of catalyst, α-TiP.Co(salicylaldimine), 0.05 g was considered optimum.

Temperature plays an important role in a catalytic reaction therefore, the effect of temperature on the oxidation of cyclohexane was studied. The temperature of reaction was varied as 343 K, 353 K and 363 K keeping the other parameters fixed. In Fig. 8 the conversion of

Table 7 Effect of cyclohexane: TBHP molar ratio, catalyst amount and temperature for oxidation of cyclohexane catalyzed by α-TiP.Co(salicylaldimine)/TBHP

Cyclohexane/TBHP (molar ratio)	Catalyst amount (g)	Temperature (K)	Conversion (%)	TBHP consumption (%)	TBHP efficiency (%)	Product selectivity (%)^a			KA-oil^b	TON
						ol	None	Others		
1:1	0.050	353	12.67	87.33	14.51	42.00	57.00	1.00	99.00	155.50
1:2	0.050	353	14.85	85.15	17.44	32.83	59.30	7.87	92.13	184.01
1:2.18	0.050	353	14.96	85.05	17.51	32.75	59.15	8.10	91.90	185.23
1:2	0.025	353	6.97	93.03	11.20	46.89	52.32	0.79	99.21	83.49
1:2	0.075	353	14.98	85.02	38.40	32.21	59.03	8.76	91.24	184.19
1:2	0.050	343	11.98	88.02	20.41	49.00	50.10	0.9	99.10	149.84
1:2	0.050	363	14.90	85.09	38.19	32.81	59.12	8.07	91.93	184.09

ol cyclohexanol; *none* cyclohexanone

[a] Reaction conditions: catalyst (0.05 g); oxidant: cyclohexane molar ratio (1:2); 353 K; 6 h; without solvent

[b] KA-oil = cyclohexanol (A) and cyclohexanone (K) mixture

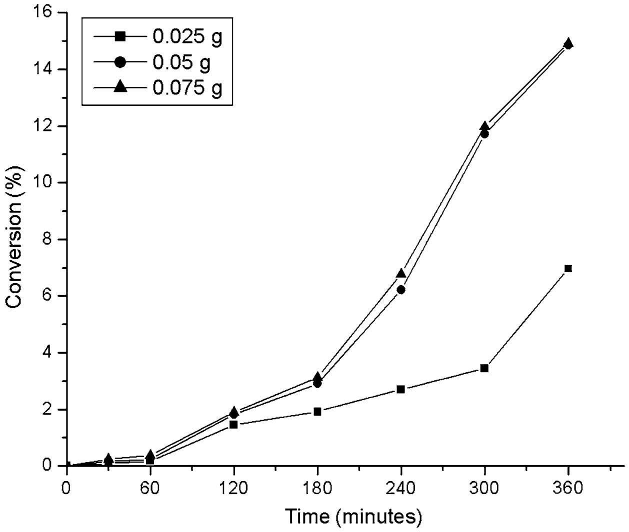


Fig. 7 Effect of amount of catalyst on the oxidation of cyclohexane catalyzed by α-TiP.Co(salicylaldimine)

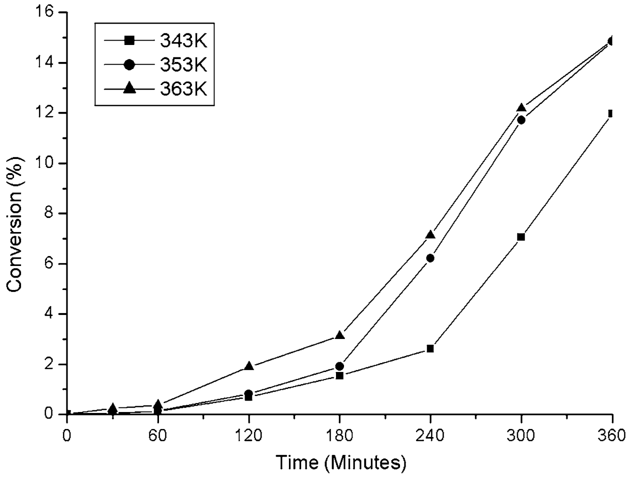


Fig. 8 Effect of temperature on the oxidation of cyclohexane catalyzed by α-TiP.Co(salicylaldimine)

cyclohexane is plotted against time at different temperature. It is evident from Fig. 8, the conversion of cyclohexane increases from 11.98 to 14.85 % with increase in reaction temperature from 343 to 353 K. Further increase in temperature to 363 K the conversion of cyclohexane, 14.90 %, remains almost same. This is due to decomposition of TBHP at higher temperature which results in lower conversion of cyclohexane. Similar type of observation is reported by many researchers [37, 56]. The results of the conversion of cyclohexane, TBHP consumption, TBHP efficiency, selectivity of the products and TON are summarized in Table 7. It is found that when the temperature increased from 343 to 363 K, the efficiency of TBHP increased while its consumption decreased which also confirmed the thermal decomposition of TBHP at higher temperatures. The selectivity of KA-oil decreased from 99.10 to 91.93 % with increasing temperature from 343 to 363 K. Cyclohexanone was the major product in the oxidation of cyclohexane. Thus the maximum conversion (14.85 %) 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 8, we have compared our catalytic system with the other catalytic system reported in literature. It was found that in most of cases conversion of cyclohexane and selectivity of KA-oil are lesser in comparison with the present work. Here, we are reporting the oxidation of cyclohexane catalyzed by α-TiP.Co(salicylaldimine) using TBHP under solvent free condition, under the optimum condition, a maximum 14.85 % conversion of cyclohexane with 92.13 % was obtained after 6 h of reaction time.

3.3 Recyclability and Heterogeneity of the Catalyst

The stability of the heterogeneous catalyst plays an important role in a catalytic activity study. It is verified by the use of catalyst, α-TiP.Co(salicyaldimine) in successive cycles. To examine the recyclability of the catalyst, the used α-TiP.Co(salicyaldimine) was recovered from the reaction media by simple filtration and washing with methanol followed by dichloromethane before being dried at 110 °C for overnight, then subjected to further catalytic reaction under similar reaction conditions. The catalyst, {α-TiP.Co(salicylaldimine)} was recycled for the five 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 9). The conversion of cyclohexane was reduced by 0.87 % from first to fifth cycle. The cobalt content was reduced by 2.93–1.45 % from first to fifth cycle. The reduction in metal contents after fifth cycle suggests that metal-leaching has occurred, which is observed in several catalytic systems [50, 58]. The regenerated catalyst was further characterized by ICP-AES, XRD, BET surface area and FTIR analysis after five cycles (data are given in corresponding tables). No significant changes in metal content, composition and morphology were observed in regenerated catalyst after fifth cycle. This suggests that the catalyst was stable during catalytic reaction and suitable for recycling. After fifth cycle only small loss in metal content was observed.

Further experiments on the stability of the catalyst during oxidation of cyclohexane were performed by hot filtration technique. The catalyst was filtered out at 353 K after 1 h in order to avoid re-adsorption of leached cobalt onto the catalyst surface. The filtrate collected after 1 h of first cycle of cyclohexane oxidation 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 in the oxidation of cyclohexane. The solution did not exhibit any colour due to the absence of cobalt, which was estimated using ICP-AES. The result suggested that no cobalt-leaching occurred during the catalytic reaction. This observation indicates that the catalyst is heterogeneous in nature.

4 Conclusions

A new catalyst, α-TiP.Co(salicylaldimine) was synthesized and characterized by ICP-AES, SEM, EDX, XRD, BET surface area, FTIR, UV–Vis spectroscopy and TGA analysis. The catalytic activity of α-TiP.Co(salicylaldimine) with TBHP as an oxidant for oxidation of cyclohexane was studied. The catalyst, α-TiP.Co(salicylaldimine) was found to have potential catalytic activity for oxidation of cyclohexane. Reaction conditions have been optimized considering various parameters viz. effects of various oxidants, solvents, cyclohexane to TBHP molar ratio, catalyst amount and reaction temperature to get maximum conversion of cyclohexane. The maximum, 14.85 % conversion of cyclohexane with 92.13 % selectivity of KA-oil was obtained. The major oxidation products follow the order: cyclohexanone (59.30 %) > cyclohexanol (32.83 %) > other products (7.87 %). The catalyst, α-TiP.Co(salicylaldimine) was found to be stable enough for oxidation of cyclohexane, it can be recycled five times.

Table 8 Comparison of literature catalysts and our catalyst system for oxidation of cyclohexane

Entry	Catalytic system	Reaction condition	Conversion (%)	Selectivity (%) (*KA-oil)
1	Ebadi and Nikbakht [18]	CoPc/c-alumina (1.0 g), TBHP, DMF/CH_2Cl_2 (3:7), reflux temperature, 8 h	12.96	100
2.	Anand et al. [19]	Co-TUD-1 (0.1 mmol), TBHP, solvent free, 70 °C, 18 h	10.3	90.52
3.	Xia et al. [15]	Cosalen-NaY(0.1 g), O_2, solvent free, 150 °C, 3 h	13.40	23.5
4.	Pingping et al. [16]	CoAlPO-5 (200 mg), O_2, 130 °C, 8 h	1.60	56.7
5.	Carneiro et al. [17]	Co/ZSM-5 (100 mg), O_2, 100 °C, 4 h	7.5	92.4
6.	Yuan et al. [21]	Co-ZSM-5(200 mg), O_2, solvent free, 100 °C, 4 h	7.22	90.7
7.	Jin et al. [22]	Cu–salpn/Y (0.1 g), H_2O_2, Acetonitrile, 60 °C, 2 h	2.3	100
8.	Chen et al. [23]	CoPh-HMS (0.12 g), O_2, solvent free, 115 °C, 6 h	6.7	80.5
9.	Present work	α-TiP.Co(salicylaldimine), TBHP, 80 °C, solvent free, 6 h	14.85	92.13

*KA-oil: cyclohexanone (K): cyclohexanol (A)

Table 9 Recycling experiment

No. of cycle	Cyclohexane conversion (%)	Product selectivity (%)			Selectivity (%) (ol + none = *KA-oil)	TON	Metal content (%)
		Cyclohexanol	Cyclohexanone	Other products			
Fresh	14.85	32.83	59.30	7.87	92.13	184.01	2.93
1	14.85	32.83	59.30	7.87	92.13	184.01	2.93
2	14.60	32.46	59.11	7.43	92.05	182.76	2.90
3	14.40	32.13	57.69	0.80	91.93	180.64	2.88
4	14.19	31.87	57.31	0.67	91.85	178.43	2.25
5	13.98	31.25	56.90	0.37	90.10	172.98	1.45

*KA-oil: cyclohexanone (K): cyclohexanol (A)

Acknowledgments The authors are thankful to UGC-DAE Consortium of scientific Research, Central Salt and Marines Chemical Research Institute Bhavnagar, Gujarat and Sophisticated Analytical Instrumental Facilities (SAIF), IIT, Powai, Mumbai (Maharashtra), and Punjab University Chandigarh for providing analytical facilities.

References

1. Ingold KU (1989) Aldrichim Acta 22:69
2. Salavati-Niasari M, Salimi Z, Bazarganipour M, Davar F (2009) Inorg Chim Acta 362:3715
3. Salavati-Niasari M (2008) Polyhedron 27:3132
4. Salavati-Niasari M (2009) J Coord Chem 62:980
5. Zhou L, Xu J, Miao H, Wang F, Li X (2005) Appl Catal A 292:223
6. Singh AP, Torita N, Shylesh S, Iwasa N, Arai M (2009) Catal Lett 132:492
7. Anisia KS, Kumar A (2007) J Mol Catal A 271:164
8. Gupta KC, Sutar AK (2008) J Mol Catal A 280:173
9. Gupta KC, Sutar AK (2008) Coord Chem Rev 252:1420
10. Gupta KC, Sutar AK, Li CC (2009) Coord Chem Rev 253:1926
11. Karabach YY, Kirillov AM, Haukka M, Kopylovich MN, Pombeiro AJL (2008) J Inorg Biochem 102:1190
12. Salvati-Niasari M, Bazarganipour M (2009) Bull Korean Chem Soc 30:355
13. Salvati-Niasari M, Bazarganipour M (2008) Trans Met Chem Soc 33:751
14. Khare S, Shrivastava S (2004) J Mol Catal A 217:51
15. Xia Y, Fang L, He'an L (2007) J Cent South Univ Technol 01:0078
16. Pingping W, Peng B, Kian PL, Zhao XS (2010) Catal Today 158:220
17. Carneiro JT, Yang CC, Moma JA, Moulijn JA, Mul G (2009) Catal Lett 129:12
18. Ebadi A, Nikbakht F (2011) React Kinet Mech Catal 104:37
19. Anand R, Hamdy MS, Hanefeld U, Maschmeyer T (2004) Catal Lett 95:3
20. Anand R, Hamdy MS, Gkourgkoulas P, Maschmeyer T, Jansen JC, Hanefeld U (2006) Catal Today 117:279
21. Yuan HX, Xia QH, Zhan HJ, Lu XH, Su KX (2006) Appl Catal A 304:178
22. Jin C, Fan W, Jia Y, Fan B, Ma J, Li R (2006) J Mol Catal A 249:23
23. Chen C, Zhou L, Zhang Q, Ma H, Miao H, Xu J (2007) Nanotechnology 18:1
24. Salavati-Niasari M, Shakouri-Arani M, Davar F (2008) Microporous Mesoporous Mater 116:85
25. Salavati-Niasari M, Sobhani A (2008) J Mol Catal A 285:58
26. Guo CC, Chu MF, Liu Q, Liu Y, Guo DC, Liu XQ (2003) Appl Catal A 246:303
27. Parton RF, Peere GJ, Neys PE, Jacobs PA, Claessens R, Baron GV (1996) J Mol Catal A 113:445
28. Fan B, Li H, Fan W, Jin C, Li R (2008) Appl Catal A 340:67
29. Tembe GL, Ganeshpure PA, Satish S (1997) J Mol Catal A 121:17
30. Cruz RSda, S-Silva JM, Arnold U, Schuchardt U (2001) J Mol Catal A Chem 171:251
31. Carvalho WA, Wallau M, Schuchardt U (1999) J Mol Catal A 144:91
32. Clearfield A, Frianeza TN (1978) J Inorg Nucl Chem 11:1925
33. Thakkar R, Chudasama U (2009) J Sci Ind Res 68:312
34. Alfonsoa BF, Trobajob C, Salvadò MA, Pertierrac P, Garcìa-Grandac S, Rodrìguez Fernándezd J, Blancoa JA, Garcìab JR (2005) Z Anorg Allg Chem 631:2174
35. Clearfield A, Thakur DS (1986) Appl Catal 26:1
36. Khare S, Chokhare R (2012) J Mol Catal A 353:138
37. Khare S, Chokhare R (2011) J Mol Catal A 344:83
38. Hamdy MS, Ramanathan A, Maschmeyer T, Hanefeld U, Jansen JC (2006) Chem Eur J 12:1782
39. Swern D (1971) Organic peroxide. Wiley, New York **357**
40. Sun L, Boo WJ, Sue HJ, Clearfield A (2007) New J Chem 31:39
41. Chisem IC, Rafelt J, Shieh MT, Chisen J, Clark JH, Jachuck R, Macquarrie D, Ramshaw C, Scott K (1998) Chem Commun 1949:1950
42. Mlumbazo N, Malpolie SF (2009) J Mol Catal A 312:70
43. Singh UG, Williams RT, Hallam KR, Allen GC (2005) J Solid State Chem 178:3405
44. Ray S, Mapolie SF, Darkwa J (2007) J Mol Catal A 267:143
45. Slade RCT, Knowles JA, Jones DJ, Rozière J (1997) Solid State Ionics 96:9
46. Mostafaa SI, Ikedab S, Ohtanic B (2005) J Mol Catal A 225:181
47. Tordin E, List M, Monkowius U, Schindler S, Knör G (2013) Inorg Chim Acta 402:90
48. Uguina MA, Delgade JA, Carretero J, Gomez-Diaz D, Rodrigez G (2009) Ind Eng Chem Res 48:4671
49. Ammoumraoui IR, Braham AC, Roy LP, Kappenstein C (2011) Bull Mater Sci 34:1127
50. Zhao R, Wang Y, Guo Y, Liu X, Zhang Z, Zhan W, Lu G (2006) Green Chem 8:459
51. Schuchardt U, Cardoso D, Serchelic R, Pereira R, Cruz RS, Guerreiro MC, Mandelli D, Spinacé EV, Pires EL (2001) App Catal A 211:1

52. Davood H, Faraji AR (2013) C R Chim 16:888
53. Farzaneh F, Majidian M, Ghandi M (1999) J Mol Catal A 148:227
54. Maksimchuk NV, Kovalenko KA, Fedin VP, Kholdeeva OA (2012) Chem Commun 48:6812
55. Pala N, Pramanik M, Bhaumik A, Ali M (2014) J Mol Catal A 392:299
56. Lu XH, Yuan HX, Zhang JL, Zhou AA, Xia QH (2012) Ind J Chem 51:420
57. Jianying W, Hua Z, Xiangjing Z, Runjing L, Yongqi H (2008) J Chem Eng 16:273
58. Masters AF, Beattie JK, Roa AL (2001) Catal Lett 75:3