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Heterogeneous catalyst Mn(salicylaldimine) complex covalently bonded to α-titanium phosphate: Synthesis, characterization and catalytic activity for oxidation of cyclohexane

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A new heterogeneous catalyst, Mn(salicylaldimine) complex covalently bonded to α-titanium phosphate has been synthesized by *in situ* method and characterized by BET surface area, X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, Fourier transform infrared spectra, X-ray photoelectron spectroscopy and inductively coupled plasma atomic emission spectroscopy. The catalytic activity of α-TiP.Mn(salicylaldimine) is studied for the liquid phase oxidation of cyclohexane using *tert*-butylhydroperoxide as an oxidant under solvent-free condition. In the oxidation reaction, cyclohexane is oxidized to cyclohexanol, cyclohexanone and some unidentified products. A maximum conversion (14.75%) of cyclohexane with 91.70% selectivity of KA-oil is obtained at 353 K after 6 h of reaction time. The catalyst can be reused for four cycles without significant loss of catalytic activity.

Keywords: Catalysts, Heterogeneous catalysts, Oxidation, Titanium phosphate, Cyclohexane, Salicylaldimine, *tert*-Butylhydroperoxide

Oxidation of cyclohexane is an important industrial process because it gives cyclohexanol and cyclohexanone. The mixture of cyclohexanol (A) and cyclohexanone (K) is known as KA-oil which is an important intermediate in the bulk production of polyamide fibers and plastics such as nylon-6 and nylon-66[1,2]. The current industrial process of cyclohexane oxidation is carried out at 423–433 K and 15 bar in the presence of catalysts. In this process the conversion of cyclohexane is 4% with 85% selectivity in the presence of soluble cobalt salt of KA-oil[3]. This process is environmentally hazardous and generates plenty of by-products and wastes. However, large scale oxidation of cyclohexane to KA-oil is of importance and continues to be a challenge[4-6]. The reaction in homogeneous medium is not very efficient because the organic ligand of transition metal complexes used as catalysts can be degraded[7,8]. Furthermore, it is difficult to separate the catalyst and the products from the reaction mixture in the homogeneous system. Heterogeneous catalysts offer merits of high catalytic activity and stability and several other benefits of catalysis like easy separation and reusability. In this context, several heterogeneous catalysts have been studied using various oxidants such as *tert*-butyl hydroperoxide (TBHP), molecular oxygen and hydrogen peroxide (H_2O_2)[9-17]. Many attempts have been made to synthesize more efficient heterogeneous catalysts for the oxidation of cyclohexane using various supports such as alumina, silica, polymers, zeolites, MCM-41, carbon tubes[18-24], etc. Immobilization of transition-metal ions on layered compounds by ion-exchange method to synthesize catalysts is better because it provides temperature and solvent stable supports of known structure[25, 26].

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[27-30]. 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[26,31]. Herein we report the synthesis of heterogeneous catalyst, Mn(salicylaldimine) complex covalently bonded to α-titanium phosphate, abbreviated as α-TiP.Mn(salicylaldimine) by an *in situ* method and its catalytic activity, for oxidation of cyclohexane using TBHP as an oxidant under solvent free condition.

Materials and Methods

Titanium(IV) isopropylate (97%, Aldrich), phosphoric acid, hydrofluoric acid, manganese(II) acetate ($Mn(CH_3COO)_2.4H_2O$), salicylaldehyde, (3-aminopropyl)triethoxysilane and cyclohexane were of reagent grade (E Merck). Cyclohexane was checked by gas chromatography (GC) to ensure 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 saturating the aqueous layer with NaCl[32]. 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 samples of catalytic products were prepared by the standard procedure[33]. ICP-AES (Inductively coupled plasma atomic emission spectroscopy) was used for estimation of manganese(II). Energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) were performed using a Jeol JSM 6100 electron microscope, operating at 20 KV. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer in the 2θ range of 5°- 40° using Cu-Kα radiation (λ = 1.5418 Å) at a scanning speed of 2º/min with step size 0.02°. 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 Fourier transform infrared (FTIR) spectra were recorded on Perkin Elmer (model 1750) instrument in KBr. Electronic spectra were recorded on Shimadzu UV-1800 spectrophotometer. X-ray photoelectron spectrometer (VSW Ltd, UK) at a base pressure better than 3×10^{-9} Torr was used for XPS studies. Al Kα radiation (1486.6 eV) was employed for the 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 the external reference. To correct the shift in binding energies of core levels due to the charging effect, the graphitic C 1*s* peak at 284.6 eV was used as the internal reference. Analytical gas chromatography was carried out on a Shimadzu gas chromatograph GC-14B with dual flame ionization detector (FID) and attached with a Shimadzu printer having SE-30 ss column at 393 K. The oxidation products were identified by GC–MS (Hewlett Packard, GCD-1800 A) with an electron ionization detector using Perkin-Elmer Clasus 500 column (30 m×60 mm).

Preparation of catalyst

The catalyst, α-TiP.Mn(salicylaldimine), was prepared in two steps. In the first step, α-titanium phosphate (abbreviated *α*-TiP) was prepared by reported method[34]. A sample of 10 mL Ti(IV)isopropylate (97%) was mixed with 100 mL of 3 M H_3PO_4 in a flask then, 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 ºC. After the reaction, the product was washed with distilled water until the *p*H of the supernatant liquid was 5, and then dried at 110 ºC for 24 h. The final product was identified as α-TiP. Finally, the structure of α-TiP was confirmed by powder XRD.

In the second step, the ligand, salicylaldimine, was synthesized by the condensation of (3-aminopropyl) triethoxysilane (1 mol) and salicyaldehyde (1 mol) in ethanol (40 mL), the solution instantly becomes yellow due to imines formation[35]. Then ethanolic solution of metal acetate (0.5 mol) was added and the mixture was stirred for 30 min at room temperature. After 30 min, α-TiP (1 g) was added and the mixture was stirred overnight at room temperature. The final product was washed with distilled water and ethanol. Finally, the product was soxhlet extracted to remove uncomplexed ligand using solvents such as methanol, dichloromethane and diethyl ether 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, SEM, EDX and ICP-AES analyses.

Catalytic oxidation of cyclohexane

The catalytic oxidation of cyclohexane was carried out using {α-TiP.Mn(salicylaldimine)} catalyst in a three-necked round bottom flask (100 mL) equipped with a refluxed condenser. In a typical experiment, the flask was loaded with catalyst (50 mg) and 5 mL of a mixture of cyclohexane (17.86 mmol%) and TBHP (38.89 mmol%). An additional amount of cyclohexane (1.59 mmol%) was added to maintain molar ratio1:2 for cyclohexane-to-TBHP. The mixture was stirred at the desired temperature for 6 h. After completion of the reaction, the contents of the flask were 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 ºC.

The products were identified by GC-MS. The GC-MS analysis revealed cyclohexanol, cyclohexanone and some unidentified products in the reaction.

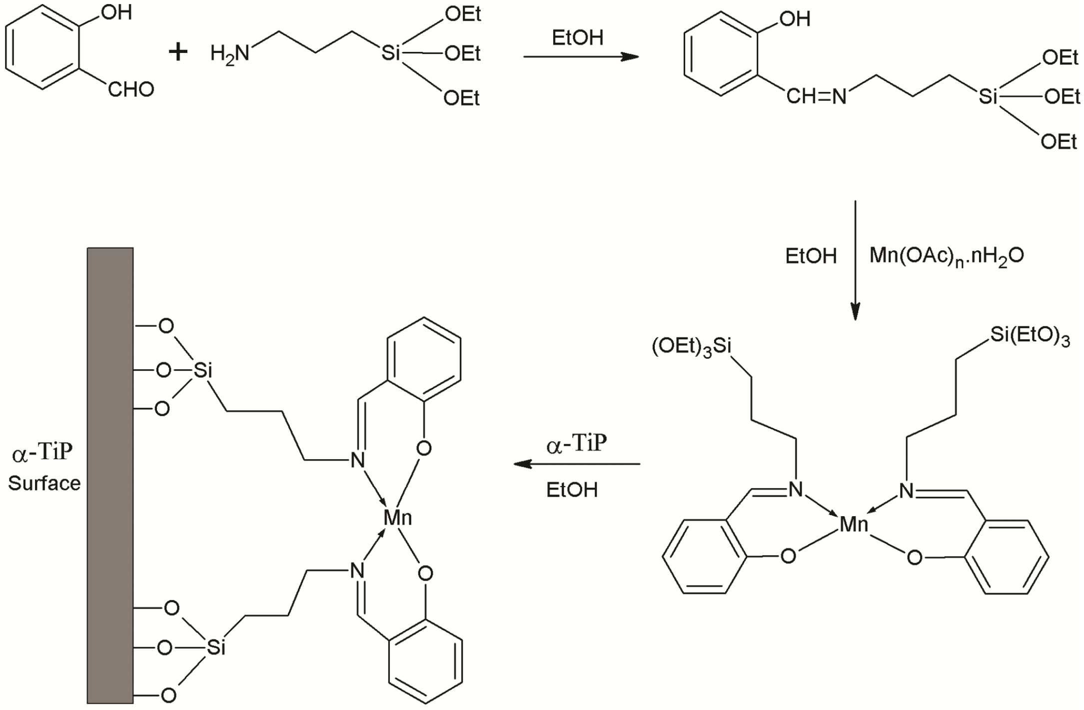
The effect of various parameters such as various oxidants, solvents, TBHP concentration, amount of catalyst and reaction temperature were studied by varying one parameter and keeping other parameteters constant.

Results and Discussion

Characterization of catalyst

The α-TiP.Mn(salicylaldimine) was synthesized by the covalent bonding of Mn(salicylaldimine) on supported α-TiP. The synthetic route of α-TiP.Mn(salicylaldimine) is described in Scheme 1. Physical and surface properties of all compounds are given in Table 1. The colours of α-TiP and α-TiP.Mn(salicylaldimine) were different before and after four reaction cycles due to change in metal content, as determined by ICP-AES analysis. The colour of α-TiP was white while the colour of α-TiP.Mn(salicylaldimine) was green due to presence of manganese. The elemental composition of α-TiP.Mn(salicylaldimine) was determined by EDX analysis. The presence of titanium (11.14%), phosphorous (14.48%) and oxygen (74.38%) in α-TiP and titanium (9.39%), phosphorous (12.11%), oxygen (67.66%), nitrogen (3.12%), silicon (6.12%) and manganese (1.60%) in α-TiP.Mn(salicylaldimine) confirms the formation of α-TiP.Mn(salicylaldimine). The EDX spectra of α-TiP and α-TiP.Mn (salicylaldimine) are shown Fig. 1 (Inset). The SEM images, which allow us to monitor how the morphology of the sample evolves during the studied process, are shown in Fig. 1. The SEM image of α-TiP (Fig. 1 (a)) reveals the presence of well-defined hexagonal plates with smooth surfaces. The SEM images of α-TiP.Mn(salicylaldimine) (Fig. 1 (b)) are less ordered than that of α-TiP and contains both sheets and spheres of different shapes and sizes, which indicates the presence of homogeneous complex on the surface.

The powder XRD patterns of support, α-TiP and heterogeneous catalyst, α-TiP.Mn(salicylaldimine) before and after catalytic reaction are shown in Fig. 2. The *d*-spacing of the most intense reflection corresponding to the (002) plane of α-TiP was 7.56 Å which was virtually constant in the α-TiP.Mn (salicylaldimine) catalysts, indicating that the metal complex was present on the surface of TiP. Thus,



Synthetic route of formation of α-TiP.Mn(salicylaldimine)

Scheme 1

Table 1—Physical data of α-TiP.Mn(salicylaldimine)

Catalyst	Colour	Metal content (%)	BET surface area (m^2/g)	Pore vol. (cm^3g^{-1})	Pore size (Å)	*d*-spacing (Å)
α-TiP	White	-	5.46	0.04	23.51	7.56
α-TiP. Mn(salicylaldimine)[b]	Green	2.3	5.23	0.03	21.90	7.56
α-TiP. Mn(salicylaldimine)[a]	Brown	1.9	4.34	0.03	19.56	7.55

[a]after catalysis (fourth cycle), [b]before catalysis.

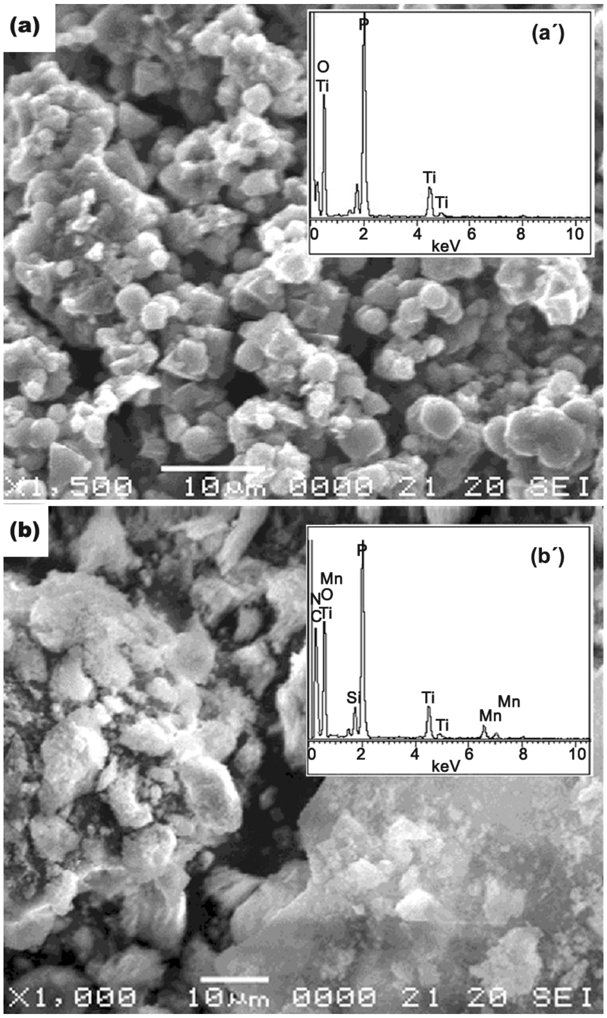


Fig. 1—SEM images of (a) α-TiP and (b) α-TiP.Mn (salicylaldimine). [Inset: EDX spectra of (a′) α-TiP, and, (b′) α-TiP.Mn (salicylaldimine)].

XRD reveals that the support retains its crystallinity and structure after covalently bonding of the Mn(salicylaldimine) complex on α-TiP. The results of BET surface area, pore volume and pore size of support, α-TiP and heterogeneous catalyst, α-TiP.Mn(salicylaldimine) before and after catalytic reaction are incorporated in Table 1. The surface area of α-TiP is 5.46 m^2/g, whereas the surface area of α-TiP.Mn(salicylaldimine) before and after four reaction cycles are 5.23 m^2/g and 4.34 m^2/g respectively, which is lower than that of the support indicating that covalent bonding of Mn (salicylaldimine) complex leads to marginal decrease in surface area. Similar observations are also reported in literature[36]. 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 decreased in the α-TiP.Mn(salicylaldimine). The surface area, pore volume and pore size of the α-TiP is lowered slightly after covalent bonding of the metal complexes on its surface, indicating the formation of the α-TiP.Mn (salicylaldimine) catalyst.

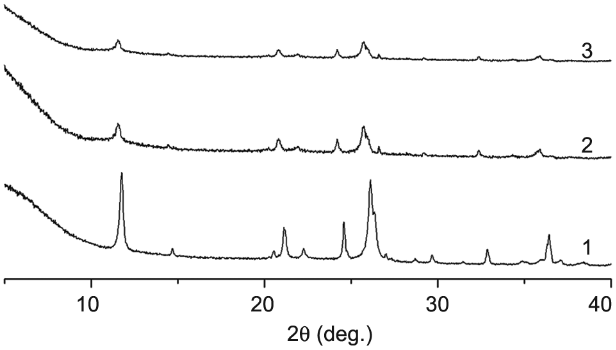


Fig. 2—XRD patterns of α-TiP (1), α-TiP.Mn(salicylaldimine) before reaction (2) and α-TiP.Mnsalicylaldimine) after reaction (3).

FTIR spectra of free ligand, neat Mn (salicylaldimine) complexes, α-TiP.Mn (salicylaldimine) and α-TiP are shown Fig. 3. Free ligand shows bands at 1627 and 1280 cm^{-1} due to C=N and C-O stretching frequency respectively. The bands due to C=N and C-O are shifted to lower frequency, 1614 cm^{-1} and 1196 cm^{-1}, upon coordination in metal complexes. The Si-O vibration of ligand observed at ν 1192 cm^{-1} is also shifted to lower frequency at 1118 cm^{-1} in metal complexes due to coordination. These data are in good agreement with reported data[37]. The bands at 3400 and 1635 cm^{-1} in the spectrum of α-TiP are due to the presence of external water in addition to the strongly hydrogen-bonded OH or extremely strong coordinated H_2O[38]. A band in the region ~1038 cm^{-1} is attributed to the presence of

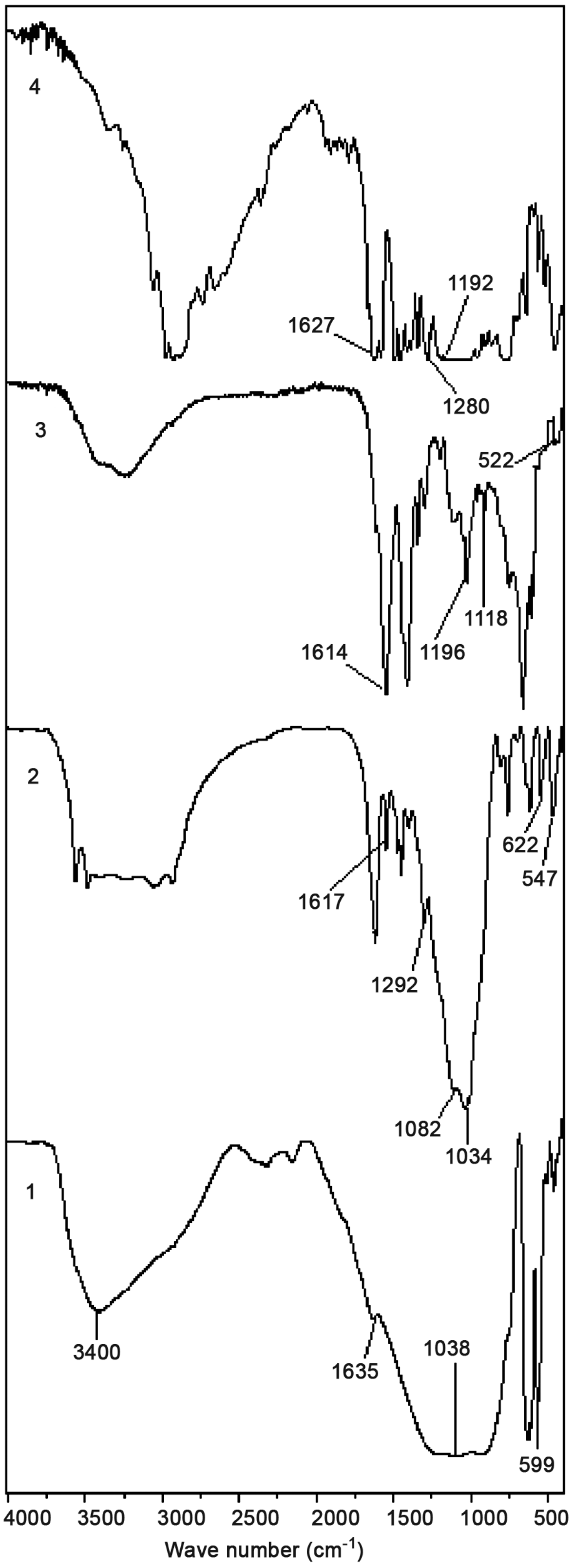


Fig. 3—FTIR spectra of α-TiP (1), α-TiP.Mn(salicylaldimine) (2), Mn(salicylaldimine) (3), and, free ligand (4).

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. The band at 599 cm^{-1} is due to stretching vibration of Ti-O. The band positions of PO$_4^{3-}$ in the spectrum of covalently bonded heterogeneous catalyst, α-TiP.Mn(salicylaldimine), is shifted to lower frequencies while that of Ti–O is shifted to higher frequencies due to presence of Mn-O interaction. The C=N stretching frequency of the imines group metal complexes is much weaker and shifts to higher frequency at 1617 cm^{-1} in α-TiP.Mn(salicylaldimine). The Si-O vibration of metal complexes is slightly merged with of PO$_4^{3-}$ stretching vibration of α-TiP in α-TiP.Mn (salicylaldimine). A comparison of FTIR spectra of α-TiP, α-TiP.Mn(salicylaldimine), Mn (salicylaldimine) and ligand provides evidence of coordination of the metal complexes on α-TiP.

A typical electronic spectra of free ligand and neat Mn(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, which are assigned to φ→φ, π→π* and n→π* transitions respectively. The band at 251 nm is assigned 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 wavelength of 372 nm in metal-complex due to ligand-to-metal charge transfer transition, which indicates the coordination of phenolate oxygen of ligand to an empty *d* orbital of metal ions.

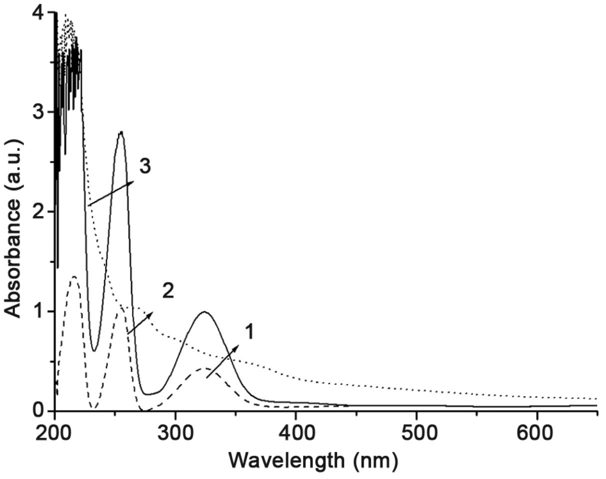


Fig. 4—UV-visible spectra of ligand-salicylaldimine (10^{-5} *M*) (1), and ligand-salicylaldimine (10^{-4} *M*) (2) solution in methanol, and, Mn(salicylaldimine) complex in methanol (3).

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. A change in the chemical and oxidation state of an element can cause small changes in its binding energy and this has been used for assignment of the oxidation states of elements in oxide cathodes. Figure 5(a) shows the peaks corresponding to Ti2p, P2p and O1s. The carbon peak was also scanned for the compensation of charging effect. The binding energies of core levels Ti2p$_{3/2}$ (458.28 eV), P2p$_{3/2}$ (131.62 eV) and O1s (530.27 eV) showed slight variations from earlier reported values for α-TiP due to change in the chemical environment[39,40]. Figure 5(b), shows the peaks corresponding to Ti2p, P2p, O1s, Si2p, N1s and Mn2p. The binding energy of core levels energies are Ti2p (457.43 eV), P2p (130.57 eV), O1s (529.51 eV), Si2p (98.04 eV), N1s (396.54 eV) and Mn2p (640.21 eV). The binding energy of core level energy of Mn2p$_{3/2}$ peak appears at 638.55 eV, which is always associated with satellite peak at 645.5 eV[41]. It is in good agreement with that reported for Mn(Salen) complex immobilized on zirconium polystyerene-phosphate[42]. This confirms that the oxidation state of Mn is +3 in α-TiP.Mn (salicylaldimine). These results indicates that the Mn(salicylaldimine) was successfully covalently anchored onto α-TiP.

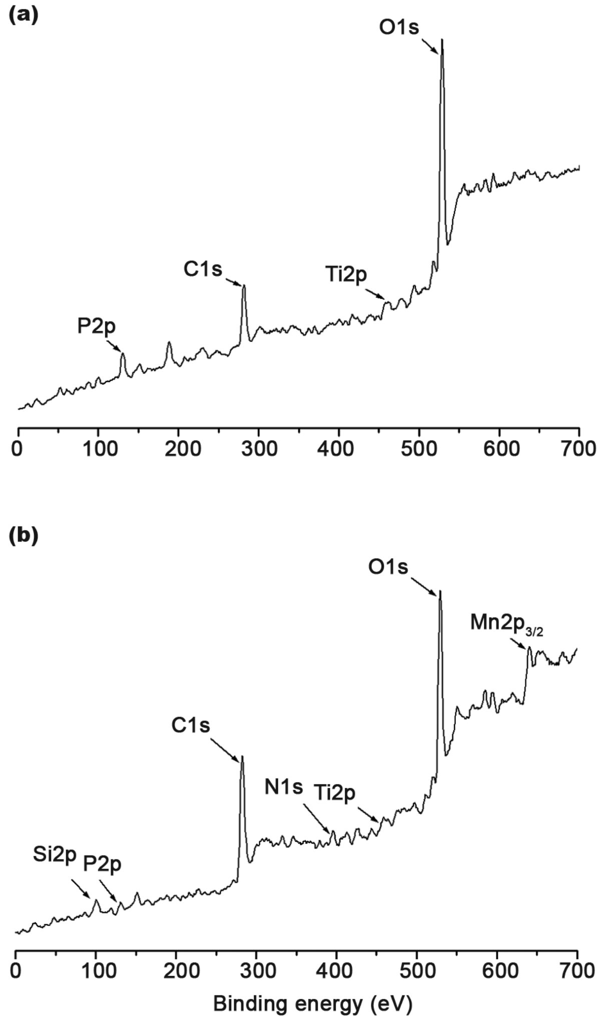


Fig. 5—XPS spectra of (a) α-TiP and (b) α-TiP.Mn (salicylaldimine).

Catalytic oxidation of cyclohexane

The solvent-free oxidation of cyclohexane, catalyzed by α-TiP.Mn(salicylaldimine) with *tert*-butylhydroperoxide as an oxidant was investigated. Under similar experimental conditions, the support, α-TiP, homogeneous complex, Mn(salicylaldimine) complexes and heterogeneous catalyst, α-TiP.Mn (salicylaldimine) were tested. It was observed that the support, α-TiP, was catalytically inactive in the oxidation of cyclohexane (Table 2). The catalysts, Mn(salicylaldimine) and α-TiP.Mn(salicylaldimine), oxidized cyclohexane to cyclohexanol, cyclohexanone and some other products. Furthermore, it was observed that while the homogeneous Mn(salicylaldimine) complex does not show high catalytic activity for the oxidation of cyclohexane, (probably due to the partial solubility of homogeneous Mn(salicylaldimine) complex in cyclohexane), the heterogeneous catalyst, α-TiP.Mn(salicylaldimine) show high catalytic activity. The oxidation of cyclohexane catalyzed by α-TiP.Mn(salicylaldimine)/TBHP system can be explained by Scheme 2. In all catalytic reactions, the yields of the products were calculated using internal standard method and the consumption of TBHP was determined iodometrically after each set of reaction. TBHP consumed and the efficiency of TBHP were calculated according to reported formula[43] given below.

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

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

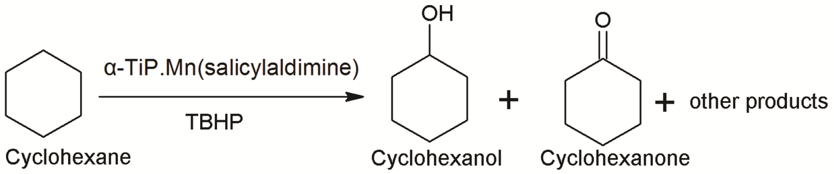
The percentage conversion of the substrate, percentage selectivity and TON (turnover number) of the products were calculated as follows.[44]

Substrate conv. (%) = [substrate converted (moles)/ substrate used (moles)] × 100

Table 2—Effect of oxidant, solvent, support, homogeneous and heterogeneous catalysts on the oxidation of cyclohexane at 6 h reaction time

Catalyst	Oxidant/Solvent	Cyclohexane conv. (%)	Product sel. (%)		TON
			KA oil[a]	Other products	
α- TiP	TBHP/Solvent-free[b]	-	-	-	-
Mn(salicylaldimine)	TBHP/Solvent-free[b]	5.26	98.98	1.02	67.76
α- TiP.Mn(salicylaldimine)[c]	H_2O_2/Solvent-free	-	-	-	-
α- TiP.Mn(salicylaldimine)	70% TBHP/Solvent-free	2.47	99.40	0.60	41.87
α- TiP.Mn(salicylaldimine)	TBHP/Solvent-free[b]	14.85	98.70	1.30	177.89
α- TiP.Mn(salicylaldimine)	TBHP/Acetonitrile[b]	9.21	81.21	18.79	93.34
α- TiP.Mn(salicylaldimine)	TBHP/Acetone[b]	8.34	79.23	20.77	90.23
α- TiP.Mn(salicylaldimine)	TBHP/Dichloromethane[b]	8.21	77.03	22.97	90.14

[a]KA oil = cyclohexanol+cyclohexanone mixture; [b]TBHP = TBHP(70% in cyclohexane); [c]Time = 1 h.



Oxidation of cyclohexane catalyzed by α-TiP.Mn(salicylaldimine)/TBHP system

Scheme 2

Product sel. (%) = [Product formed (moles)/ substrate conv. (moles)] × 100

TON = mmol of products / mmol of catalyst

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

The effect of various solvents, viz., acetonitrile, acetone and dichloromethane on the oxidation of cyclohexane catalyzed by α-TiP.Mn(salicylaldimine) was studied to develop an efficient catalytic system. The results are incorporated in Table 2. It was observed that in presence of solvents, the conversion of cyclohexane decreases in the following order: solvent-free (14.75%) > acetonitrile (9.21%) > acetone (8.34%) > dichloromethane (8.21%). It can be seen that the selectivity of KA-oil is high with a dipolar aprotic solvent, the selectivity of KA-oil follows the order; acetonitrile (81.21%) > acetone (79.23%) > dichloromethane (77.30%). 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[45,46]. A maximum of 14.75% conversion of cyclohexane with 91.70% selectivity of KA-oil (cyclohexanol, 33.83% + cyclohexanone, 57.87%) was obtained under solvent-free condition.

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.Mn(salicylaldimine) was studied to select the best oxidant. The results are incorporated in Table 2. It was observed that in the case of 30% H_2O_2 leaching of the catalyst occurred after 15 minutes and no products were formed. In the case of 70% TBHP, leaching of catalyst was also observed after 1 h with negligible 2.47% conversion of cyclohexane. The TBHP (70% in cyclohexane) effectively oxidized cyclohexane to cyclohexanol, cyclohexanone and some other unidentified products. The conversion of cyclohexane was 14.75% and the selectivity of products cyclohexanone and cyclohexanol (KA-oil) was 91.70 %. Thus, the best oxidant for our catalytic system is TBHP (70% in cyclohexane) to obtain maximum conversion of cyclohexane.

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. It was observed that when cyclohexane-to-TBHP molar ratio increases from 1:1 to 1:2, the conversion of cyclohexane increases from 12.52% to 14.75%. On further increase in cyclohexane-to-TBHP molar ratio to 1:2.18, the conversion of cyclohexane increased slightly to 14.79%. The results of the conversion of cyclohexane, TBHP efficiency, consumption, product selectivity and TON are presented in Table 3. The selectivity of KA-oil decreased from 97.36 to 90.77% 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[11,47,48]. This is probably due to the non-productive decomposition of TBHP at higher concentration. Similar observation is reported in the case of TS-1/ionic liquid/TBHP system[14]. At all molar ratio of cyclohexane-to-TBHP, cyclohexanone was the major product. Moreover, since higher concentration of oxidant showed little increases in conversion, we have chosen 1:2 molar ratio of cyclohexane-to-TBHP as the best from the economic point of view.

The effect of the catalyst amount on the conversion of cyclohexane was investigated by considering three different amounts, i.e., 25, 50, and 75 mg of catalyst. When catalyst amount increased from 25 mg to 50 mg, the conversion increased from 12.57% to 14.75%. On further increase in catalyst amount (75 mg), conversion of cyclohexane increased to 14.76%. Very little increase in conversion was observed at higher catalyst amount. Similar result is observed with Co_3O_4-I/O_2 system also[49]. The results of the conversion of cyclohexane, TBHP efficiency, TBHP consumption, selectivity of products and TON are incorporated in Table 3. The selectivity of KA-oil decreased from 97.33% to 91.25% with increasing amount of catalyst. 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 25 mg to 75 mg. Therefore, 50 mg was considered optimum amount for the studied reaction.

To study the effect of temperature on the catalytic oxidation of cyclohexane, the reaction was carried out at three different temperatures, i.e., 343 K, 353 K and 363 K for 6 h. The results of the conversion of cyclohexane, TBHP efficiency, TBHP consumption, selectivity of the products and TON are given in Table 3. On increasing temperature from 343 K to 353 K, conversion of cyclohexane increased from 12.40% to 14.75%. On further increase in temperature to 363 K, conversion of cyclohexane increased only to 14.78%, i. e., it remains almost the same. This is due to decomposition of TBHP at higher temperature which does not increase the conversion of cyclohexane appreciably. Similar observation has been reported by many researchers[14,26]. It is found that when the temperature increased from 343 to 363 K, the efficiency of TBHP increased while its consumption decreased which also confirms the thermal decomposition of TBHP at higher temperatures (Table 3). The selectivity of KA-oil decreased from 97.75 to 90.59% with increasing temperature from 343 to 363 K. Thus, the best temperature to carry out oxidation of cyclohexane was 353 K.

Thus, the optimum reaction conditions for obtaining maximum conversion of cyclohexane is 1:2 molar ratio of cyclohexane-to-TBHP, 50 mg catalyst and 353 K temperature.

Recyclability of the catalyst

To check the reusability of α-TiP.Mn (salicylaldimine), we have carried out repeated reaction cycles under similar reaction conditions.

Table 3—Effect of cyclohexane:TBHP molar ratio, catalyst amount and temperature for oxidation of cyclohexane catalyzed by α-TiP.Mn(salicylaldimine) /TBHP[a]

Cyclohexane/TBHP (molar ratio)	Catalyst amt (mg)	Temp. (K)	Conv. (%)	TBHP consumption (%)	TBHP efficiency (%)	Product sel. (%)		TON
						KA-oil[b]	Others	
1:1	50	353	12.52	87.48	14.31	97.36	2.64	142.09
1:2	50	353	14.75	85.25	43.43	91.70	8.30	177.89
1:2.18	50	353	14.79	85.21	17.36	90.77	1.55	178.14
1:2	25	353	12.57	87.43	14.38	97.33	2.67	141.76
1:2	75	353	14.76	85.24	17.32	91.25	8.75	178.17
1:2	50	343	12.40	87.59	14.16	97.75	2.25	141.23
1:2	50	363	14.78	85.22	17.34	90.59	9.41	178.25

[a]TBHP (70% in cyclohexane); [b]KA-oil = cyclohexanol (A) + cyclohexanone (K).

After completion of reaction, the catalyst was recovered by simple filtration, washed with methanol and dried at 110 °C and then reused. The catalyst, α-TiP.Mn(salicylaldimine), was recycled for four runs for oxidation of cyclohexane without significant loss of catalytic activity. The cyclohexane conversion remained the same in second cycle (14.6%) then gradually decreased to 13.89% in fourth cycle. The conversion of cyclohexane was reduced to 0.96% from the first to the fourth cycle. This decrease in conversion is also due to the loss of catalyst during filtration and washing. The results of recycling suggest that the catalyst is stable during the catalytic reaction. The recycled catalyst was further characterized by BET surface area, XRD, FTIR, SEM, and ICP-AES. The results of these analyses indicate that catalyst remained almost the same after catalytic reaction. Only a little leaching of catalyst was observed which was confirmed by ICP-AES analysis after the fourth run. Metal leaching has been observed in several catalytic systems[46,50].

Conclusions

The catalyst, α-TiP.M(salicylaldimine) was prepared by covalent anchoring on α-TiP and characterized by BET surface area, XRD, SEM, EDX, FTIR and ICP-AES. Its catalytic activity for oxidation of cyclohexane using TBHP (70% in cyclohexane) as an oxidant was studied under solvent-free condition. In the oxidation reaction, cyclohexane was oxidized to cyclohexanol, cyclohexanone and other products. A maximum, (14.75%) conversion of cyclohexane with 91.70% selectivity of KA-oil was obtained with 1:2 molar ratio of cyclohexane-to-TBHP, 50 mg catalyst and 353 K temperature. The catalyst was recyclable up to four cycles.

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