



Cobalt (II) exchanged supported 12-tungstophosphoric acid: Synthesis, characterization and non-solvent liquid phase aerobic oxidation of alkenes

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ABSTRACT

Co²⁺ exchanged supported 12-tungstophosphoric acid was synthesized and characterized. Its catalytic activity was evaluated for the oxidation of alkenes such as styrene, cyclohexene and *cis*-cyclooctene under mild conditions. The superiority of the catalyst lies efficiently in catalyzing the non-solvent liquid phase oxidation of alkenes, especially oxidation of cyclohexene with 98% conversion and 57% selectivity for cyclohexene oxide, with molecular oxygen at 1 atm pressure. The active intermediate, responsible for the oxidation of alkenes, was also isolated and characterized by ESR. Its catalytic activity was evaluated for the oxidation of styrene under optimized conditions. Based on the above study a probable reaction mechanism was also proposed.

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1. Introduction

In recent years, supported heteropolyacids (HPAs) have received much attention as solid acid catalysts [1–9]. The presence of replaceable H⁺ is known to be responsible for acid catalyzed reactions [10]. The protons in the secondary structure of the heteropolyacids can be easily exchanged, completely or partially, with different cations without affecting the primary Keggin structure [11].

Due to the known advantages, use of Co containing catalytic systems for the oxidation of organic substrates has attracted much attention [12]; however, reports using molecular oxygen are very scanty. Use of Co complexes for the oxidation of terminal olefins using molecular oxygen [13–15] with sacrificial co-reductant, isobutyraldehyde, has been reported. Oxidation of styrene using Co exchanged faujasite type zeolites [16] and oxidation of cyclic olefins as well as terminal olefins over Co exchanged zeolites have been reported by Jasra et al. [17,18]. In both cases, DMF was used as solvent and reactions were carried out at 60 psi (4 atm) pressure.

Thus, almost all reported oxidation reactions with molecular oxygen are carried out using solvent under high-pressure conditions. It would be interesting if oxidation reactions could be

carried out without organic solvents with molecular oxygen under mild conditions. This could be possible by designing a catalyst possessing advantages of supported HPAs as well as Co. In the present paper, we report the results for solvent-free oxidation of alkenes with molecular oxygen under mild conditions over a new catalyst. We have made use of supported HPAs as exchanging agent. Cobalt was exchanged with available protons of supported 12-tungstophosphoric acid (TPA/ZrO₂). The resulting amorphous catalyst, Co exchanged supported 12-tungstophosphoric acid (CoTPA/ZrO₂), was characterized by various physico-chemical techniques such as elemental analysis, thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and surface area measurement (BET method). The oxidation state of Co was confirmed by magnetic moment studies and ESR. The catalytic activity was evaluated for the non-solvent liquid phase oxidation of alkenes with molecular oxygen as the oxidant and *tert*-butyl hydroperoxide (TBHP) as an initiator under mild conditions.

2. Experimental

2.1. Materials

All chemicals used were of A.R. grade. 12-Tungstophosphoric acid and zirconium oxychloride were obtained from Loba Chemie, Mumbai. Cobalt acetate tetrahydrate and styrene were obtained

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from Merck and used as received. Cyclohexene and *cis*-cyclooctene were obtained from Spectrochem, Mumbai.

2.2. Synthesis of catalyst

The Co exchanged supported 12-tungstophosphoric acid was synthesized in two-step process. The first step involves the synthesis of the supported 12-tungstophosphoric acid while the second step involves the synthesis of cobalt exchanged supported 12-tungstophosphoric acid.

2.2.1. Synthesis of supported 12-tungstophosphoric acid (TPA/ZrO₂)

30% of 12-tungstophosphoric acid (TPA) supported onto ZrO₂ was synthesized by impregnation as reported by us earlier [19].

2.2.2. Synthesis of cobalt exchanged supported 12-tungstophosphoric acid (Co TPA/ZrO₂)

This was followed by the wet impregnation of 1 g of TPA/ZrO₂ with 25 mL 1% aqueous solution of Co(CH₃COO)₂·4H₂O for 24 h with stirring. The solution was then filtered, washed with distilled water in order to remove the excess of cobalt and dried at 100 °C for 1 h. The resulting material was designed as CoTPA/ZrO₂.

2.3. Characterization

The filtrate and solid CoTPA/ZrO₂ were analyzed for Co as well as acetate anion. The analysis of filtrate showed the presence of acetate anions and excess of Co ions, which were determined by UV–vis spectroscopy. The analysis of the product mixtures for any leaching of Co was carried by using atomic absorption spectrometer AAS GBC-902 instrument. Elemental analysis for cobalt estimation was carried out by using a JSM 5610 LV EDX-SEM analyzer. FT-IR spectrum of the sample was obtained by using the KBr wafer on a PerkinElmer instrument. TGA of the samples was carried out on a Mettler Toledo Star SW 7.01 in the temperature range of 50–600 °C under nitrogen atmosphere with a flow rate of 2 mL/min and a heating rate of 10 °C/min. Magnetic susceptibility measurements were carried out with the Gouy Balance method at 25 °C by applying Pascal corrections. The ESR spectra were recorded on a Varian E-line Century series X-band ESR spectrometer (at room temperature and scanned from 2000 to 4000 G). The XRD pattern was obtained by using a Philips PW-1830 diffractometer. The conditions were: Cu K α radiation (1.54 Å), scanning angle from 0° to 60°. Adsorption–desorption isotherms of samples were recorded on a Micromeritics ASAP 2010 surface area analyzer at –196 °C.

2.4. Oxidation of alkenes

The catalytic activity was evaluated for the oxidation of alkenes using molecular oxygen as oxidant and TBHP as co-oxidant. Oxidation reaction was carried out in a batch type reactor operated under atmospheric pressure. In a typical reaction, a measured amount of catalyst was added to a three-necked flask containing alkene and initiator TBHP (0.15 mmol) at 80 °C (for styrene) and 50 °C (for cyclic alkenes). The reaction was started by bubbling O₂ into the liquid. The reaction was carried out by varying different parameters such as the amount of the catalyst and reaction time. After completion of the reaction, the liquid product was extracted with dichloromethane, dried with magnesium sulphate and analyzed on a gas chromatograph (Nucon 5700 model) having a flame ionization detector and an SE-30 packed column (2 m length and 10% silica based stationary phase. Product identification was done by comparison with authentic samples and finally by a combined gas chromatography mass spectrometer (Hewlett-Packard) using an

Table 1
FT-IR frequencies of the materials.

Materials	FT-IR band frequencies (cm ⁻¹)					
	H–OH	Zr–O–H	P–O	W=O	W–O–W	Co–O
ZrO ₂	3400 1600 1370	600	–	–	–	–
TPA/ZrO ₂	3400	600	1070	964	812	–
CoTPA/ZrO ₂	3306 1622	–	1058	943	851	475

HP-1 capillary column (30 m, 0.5 mm id) with EI (70 eV). The conversion was calculated on the basis of mole percent of alkenes:

$$\text{conversion (\%)} = \frac{(\text{initial mol \%}) - (\text{final mol \%})}{\text{initial mol \%}} \times 100$$

3. Results and discussion

The amount of exchanged Co was 72 mg/g of TPA/ZrO₂. The FT-IR bands for zirconia (ZrO₂), TPA/ZrO₂ and CoTPA/ZrO₂ are shown in Table 1. The FT-IR spectrum for ZrO₂ shows the bands at 3400 cm⁻¹ corresponding to symmetric aquo stretching, and two bending vibrations at 1600 and 1370 cm⁻¹ for the O–H–O and H–O–H vibrations. It also shows a weak bending vibration at 600 cm⁻¹ attributed to the Zr–O–H vibration. The FT-IR spectrum of TPA/ZrO₂ shows additional stretching vibrational bands for W–O–W, W=O and P–O at 812, 964 and 1070 cm⁻¹ respectively. The FT-IR spectrum of CoTPA/ZrO₂ shows bands at 851, 943 and 1058 cm⁻¹ corresponding to the symmetric stretching for W–O–W, W=O and P–O. The shift in the band positions as compared to those of TPA/ZrO₂ may be due to the change in the environment. An additional bending vibration at 475 cm⁻¹ corresponds to the Co–O vibration and indicates the presence of Co in the synthesized material.

The TGA curve of TPA/ZrO₂ shows 12.6% weight loss in the temperature range of 70–100 °C indicating the loss of adsorbed water. Further, there is no weight loss observed up to 450 °C indicating the stabilization of the supported material. TGA of CoTPA/ZrO₂ shows 10.2% weight loss in the temperature range of 100–150 °C due to the loss of adsorbed water. No appreciable weight loss is observed up to 400 °C indicating that the synthesized catalyst is stable up to 400 °C.

The magnetic susceptibility value for TPA/ZrO₂ is 0.2 μ B indicating the diamagnetic nature of TPA/ZrO₂. The magnetic susceptibility value for CoTPA/ZrO₂ is 1.5 μ B (after applying Pascal corrections), which corresponds to one unpaired electron. The magnetic study indicates the presence of paramagnetic Co species (low spin $t_{2g}^6 e_g^1$; $S = 1/2$), which was further confirmed by ESR spectra. TPA/ZrO₂ is ESR silent indicating the presence of diamagnetic TPA/ZrO₂ system. The room temperature X-band ESR of CoTPA/ZrO₂ shows a typical anisotropic spectrum for Co(II), $S = 1/2$ spin system revealing the presence of paramagnetic Co with g_{\perp} 2.706 and g_{\parallel} 2.723.

The XRD patterns of TPA/ZrO₂ and CoTPA/ZrO₂ are presented in Fig. S1. XRD pattern of CoTPA/ZrO₂ shows the amorphous nature of the catalyst. It does not show any characteristic diffraction line indicating a very high dispersion of solute in a non-crystalline form on the surface of TPA/ZrO₂. This observation was further supported by BET surface area values. The increase in surface area for the CoTPA/ZrO₂ (307 m²/g) as compared to that of TPA/ZrO₂ (146 m²/g) indicates high uniform dispersion of the Co on the surface of TPA/ZrO₂.

Table 2
Oxidation of styrene using different concentrations of catalyst with molecular oxygen.

Catalyst ^a	Amount of catalyst (mg)	Concentration of the active catalyst (mmol) on TPA/ZrO ₂	Conversion (%)	Selectivity (%)	
				Benzaldehyde	Styrene oxide
CoTPA/ZrO ₂	25	0.03	23	52	48
	50	0.06	49	65	35
	75	0.09	62	>99	–
	100	0.122	76/95 ^b	>99	–
	200	0.244	77/95 ^b	>99	–

^a Conversion is based on styrene; styrene, 100 mmol; oxidant, O₂ 1 atm; TBHP 0.15 mmol; temperature, 80 °C; time, 4 h.

^b Conversion is based on styrene; styrene, 100 mmol; oxidant, O₂ 1 atm; TBHP 0.15 mmol; temperature, 80 °C; time 24 h.

3.1. Oxidation of alkenes

A detailed study was carried out on the oxidation of styrene to optimize the conditions. TPA/ZrO₂ was almost inactive for the oxidation of alkenes under the present reaction conditions. The effect of concentration of the catalyst on the conversion is shown in Table 2.

With an increase in the amount of Co, % conversion also increases. This suggests that Co functions as active sites for oxidation. The obtained results are in good agreement with a reported one [16]. It is very interesting to observe the difference in the selectivity of the products with an increase in the concentration of the catalyst. As shown in Table 2, with 0.03 mmol concentration of active catalyst, epoxide is selectively obtained. On increasing the concentration of the catalyst, the product selectivity shifts from the less stable intermediate (epoxide) towards the more stable product (benzaldehyde). This may be due to the fact that with increase in the amount of the active species the reaction becomes very fast which favours the conversion of the formed styrene oxide to benzaldehyde.

The catalytic performances of the catalyst for the oxidation of cyclic alkenes are shown in Table 3. It has been reported by Kanmani and Vancheesan [20] that the use of TBHP with transition metal based catalysts activates the metal centre. The inter-conversion of the two oxidation states for the metal complexes, corresponding to an oxidative addition and reductive elimination, are responsible for effective catalysis. Hence, the activated catalysts, attack the C=C site of styrene and preferentially lead to an oxidative cleavage rather than epoxide formation [21]. While in the case of cyclic olefins, an allylic attack is preferred, giving rise to epoxide which in turn rearranges by reductive elimination of the catalyst resulting in further oxygenated products. Thus the obtained results are in good agreement with the reported explanation.

The observed order for the reactivity of cyclic olefins is cyclohexene > *cis*-cyclooctene. The lower conversion for *cis*-cyclooctene is mainly due to two factors: (i) the bulkiness of the cyclic ring as well as ring strain makes it difficult to coordinate and thus partially prevents the oxidation process (ii) initially the rate of desorption of the product (i.e. cyclooctene oxide) from the catalyst surface is high but as the concentration of the bulky product increases in the reaction mixture, the rate becomes slow.

Table 3
Oxidation of alkenes using molecular oxygen.

Catalyst ^a	Alkene	Conversion (%)	Products	Selectivity (%)	TON
CoTPA/ZrO ₂	Styrene	76	Benzaldehyde	>99	623
	Cyclohexene	98	Cyclohexene oxide	57	803
			Cyclohexanol	43	
<i>cis</i> -Cyclooctene	21	Cyclooctene oxide	>99	172	

^a Conversion is based on substrate; substrate, 100 mmol; oxidant, O₂ 1 atm; TBHP 0.15 mmol; catalyst 0.12 mmol; temperature, 80 °C; reaction time 4 h (for styrene), 24 h (for cyclic olefins).

In the case of oxidation of cyclohexene, besides cyclohexene oxide, cyclohexanol was also obtained which is unusual as compared to the reported results. Cyclic alkenes generally follow allylic oxidation resulting in 2-cyclohexene-1-one or 2-cyclohexene-1-nol as products rather than the epoxidation or bond cleavage mechanism. Oxidation of cyclohexene has been reported by a number of groups [18,22], when a peroxide type of oxidants is used, resulting in allylic oxidation products. In the present study bond cleavage was observed giving rise to cyclohexanol. This could be explained on the basis that the oxidant used contains the highest content of active oxygen. Also the catalyst used is highly acidic with acidity equivalent to superacids. Under these extreme acidic oxidation conditions the bond cleavage mechanism is preferred to the typical allylic oxidation.

3.2. Test for heterogeneity

The leaching of Co from CoTPA/ZrO₂ was confirmed by carrying out an analysis of the used catalyst (EDX) as well as the product mixtures (AAS). Analysis of the used catalyst did not show appreciable loss in the cobalt content as compared to the fresh catalyst. Analysis of the product mixtures showed that if any cobalt was present it was below the detection limit, which corresponded to less than 1 ppm. These observations strongly suggest that the present catalyst is truly heterogeneous in nature.

Heterogeneity test was carried out for the oxidation of styrene as an example. For the rigorous proof of heterogeneity, a test [23] was carried out by filtering catalyst from the reaction mixture at 80 °C after 4 h and the filtrate was allowed to react up to the completion of the reaction (6 h). The reaction mixture of 4 h and the filtrate were analyzed by gas chromatography. No change in the % conversion as well as % selectivity was found indicating the present catalyst fall into category C [23]. The results are presented in Table 4.

3.3. Recycling of catalyst

The catalyst remains insoluble in the present reaction conditions and hence can be easily separated by simple filtration followed by washing. The catalyst was washed with dichloromethane and dried at 100 °C. Oxidation of styrene was carried out with the recycled catalyst under the optimized conditions. The catalyst was recy-

cluded in order to test its activity as well as stability. The obtained results are presented in Table 5. As seen from Table 5, the recycled catalyst did not show any appreciable change in the activity, indicating that the catalyst is stable and can be regenerated for repeated use.

Similarly, recycling of the catalyst was carried out for the oxidation of cyclic alkenes. No appreciable change in conversion as well as selectivity indicates that the catalyst can be reused.

3.4. Reaction mechanism

In order to study the reaction mechanism the same sets of reactions were carried under two different conditions: (i) alkene + oxidant + TBHP and (ii) alkene + oxidant + CoTPA/ZrO₂. In both the cases the reaction did not progress significantly. These observations indicate that the liberation of O₂ from TBHP was not sufficient to induce the reaction as well as the activation of Co²⁺ to Co³⁺ being necessary for provoking the reaction under the optimized conditions. Hence it may be concluded that in the present study TBHP acts as an initiator only.

Based on the above observations a tentative reaction mechanism for styrene, as an example, is proposed in Scheme 1. It has been reported that the catalyst containing metal cations in low valency states and involving O₂ as an oxidant always follow the radical chain mechanism induced by M–O₂ intermediate [24,25]. In the present catalytic system, the mechanism involving the Co species is expected to follow the same path. As described in the proposed reaction mechanism, for the catalytic reaction to proceed activation of Co²⁺ is required. The activation of Co²⁺ species takes place through attack of TBHP followed by the formation of an active intermediate, [•]OCo³⁺TPA/ZrO₂. It is expected that TBHP gets reduced to form *tert*-butyl alcohol and in turn oxidizes Co²⁺ → Co³⁺ *in situ*. The liberated oxygen from TBHP attacks Co³⁺ to form [•]OCo³⁺TPA/ZrO₂. This formed intermediate is responsible for the activation of alkenes.

This activated species ([•]OCo³⁺TPA/ZrO₂) gets attached with O₂ species and forms [•]OOCo³⁺TPA/ZrO₂ radical (i.e. Co–O₂ metal–superoxo intermediate) which then attacks the substrate. The metal–superoxo intermediate reversibly binds to the alkene attacking the reaction site, resulting in oxidation of substrate to form products. Further, oxidation of alkenes via radical chain mechanism is a known process [24,25].

In order to confirm the role of formed active intermediate, it was isolated and characterized by ESR. Further, its catalytic activity

Table 4

% Conversion and % selectivity for the oxidation of styrene (with and without catalyst).

Catalyst	% Conversion	% Selectivity Benzaldehyde
CoTPA/ZrO ₂ (4 h)	76	>99
Filtrate (6 h)	75.6	>99

% Conversion is based on alkene; catalyst, 0.122 mmol; oxidant, O₂; TBHP 0.15 mmol; reaction temperature 80 °C.

Table 5

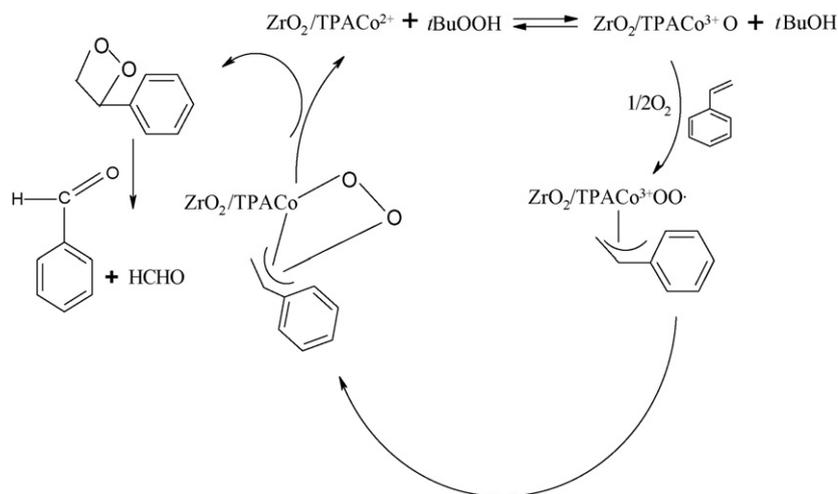
Oxidation of styrene with fresh and regenerated catalyst.

^a Catalyst	% Conversion	% Selectivity Benzaldehyde
CoTPA/ZrO ₂	76	>99
R1-CoTPA/ZrO ₂	72	>99
R2-CoTPA/ZrO ₂	72	>99

^a Styrene, 100 mmol; oxidant, 1 atm O₂; TBHP 0.15 mmol; reaction time, 4 h; catalyst, 0.122 mmol; temperature 80 °C.

was also evaluated for the oxidation of alkenes, especially styrene. The room temperature X-band ESR ([•]OCo³⁺TPA/ZrO₂) shows a typical anisotropic ESR with splitting of the ESR signal which may be due to the presence of a radical electron (Fig. S2). The broadening of the signal may be due to the presence of a transition metal ion (i.e. Co³⁺). The anisotropic ESR signal is indicative of the presence of a free radical. The free radical resides on O-atom and it is strongly coupled with Co³⁺. The reported, *g*-value of organic free radicals is 2.0023 [26]. The average *g*-value calculated for the present system is 2.01. The observed higher *g*-value may be due to the nature of the formed radical intermediate. In the present system the nature of the radical is inorganic and hence the result is as expected. The ESR studies strongly support the proposed mechanism.

Oxidation of styrene was carried out by using [•]OCo³⁺TPA/ZrO₂ under optimized conditions (100mmol styrene; 0.15 mmol TBHP; 1 atm O₂; conc. of catalyst 100 mg; temperature 80 °C; reaction time 4 h). 76% conversion with >99% selectivity for benzaldehyde was obtained with CoTPA/ZrO₂ for the oxidation of styrene. If oxidation reaction follows the proposed reaction mechanism, [•]OCo³⁺TPA/ZrO₂ must give almost the same conversion as well as selectivity. The results are as expected. 73% conversion with >99%



Scheme 1. Proposed reaction mechanism for the oxidation of styrene.

Table 6
Comparison of conversion and selectivity values for the oxidation of alkenes.

Catalyst	Alkene	^a Reaction conditions	Conversion (%)	Products/selectivity	TON
CoTPA/ZrO ₂ NaCoX96 [17]	Styrene	100;4;1;0;100	76	BA/ >99	623
		10;4;4;20;200	100	BA/67 StyO/33	16.0
Co ²⁺ X [16]			44	StyO/60	13.0
CoTPA/ZrO ₂ NaCoX96 [18]	Cyclohexene	8;24;1;0;100	98	Cy6O/57	803
		2;8;4;40;200	26	Cy6O/48	–
CoTPA/ZrO ₂ NaCoX96 [18]	<i>cis</i> -Cyclooctene	8;24;1;0;100	21	<i>cis</i> -Cy8O/>99	172
		2;8;4;40;200	47	<i>cis</i> -Cy8O/100	

^a Substrate (mmol): reaction time (h): pressure (atm): solvent (mL): amount of catalyst (mg). 1 atm = 14.5 psi.

selectivity for benzaldehyde was obtained. Thus the ESR studies and catalytic study strongly support the proposed mechanism confirming that the formed intermediate is only responsible for higher conversion.

3.5. Comparison with reported catalysts

The superiority of the present catalyst lies in obtaining higher conversion as well as selectivity, especially in the case of cyclohexene, than NaCoX96. It is seen from the Table 6 that in the case of styrene, 100% conversion was obtained with NaCoX96 but the selectivity for benzaldehyde is 67%. In the case of Co²⁺-X, styrene oxide and benzaldehyde were the two main products along with minor quantities of styrene glycol, benzoic acid and mandelic acid, only 44% conversion being obtained. The present catalyst gives 76% conversion with >99% selectivity for benzaldehyde. Other products obtained were less than 1%. In the case of oxidation of cyclic alkenes, especially for cyclohexene, results are very unique and outstanding. The present catalyst gives 98% conversion and 57% selectivity for cyclohexene oxide.

Further, all reported reactions were carried out in DMF as solvent under 60 psi pressure (4.1 atm) conditions, while the present reactions are non-solvent reactions under ambient pressure. It is also interesting to note that the present catalyst gives very high TON as compared to the reported catalysts.

4. Conclusion

In conclusion, we have come up with a new oxidation catalyst; Co exchanged supported 12-tungstophosphoric acid. The present contribution reports solvent-free liquid phase aerobic oxidation of alkenes at lower temperature and ambient pressure. The superiority of the present catalyst lies, in obtaining 98% conversion for cyclohexene with 57% selectivity for cyclohexene oxide as well as in obtaining very high turnover number (TON) for all oxidation reactions. The active intermediate, responsible for oxidation, was isolated and studied for ESR as well as catalytic activity. Based on the results, a probable mechanism for the oxidation of alkenes was also proposed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.01.014.

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