

Manganese (III) Salen Supported Onto Hydrous Zirconia: Synthesis, Characterization, and Solvent Free Aerobic Oxidation of Styrene

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Solid catalysts comprising manganese salen and hydrous zirconia were synthesized and characterized, and catalytic activity was evaluated by carrying out solvent-free liquid phase aerobic oxidation of styrene. As solid catalysts show high conversion of styrene with good selectivity toward benzaldehyde and styrene epoxide. The recovery of the catalyst was readily accomplished by simple filtration. The recycled catalyst can be used up to four cycles without any loss in conversion as well as selectivity.

Keywords: manganese-salen, hydrous zirconia, styrene/styrene oxide, benzaldehyde

Introduction

Catalytic oxidation of alkenes into more valuable epoxides as well as oxygen containing carbonyl compound is one of the important synthetic reaction. Oxidation of styrene is an important organic transformation as the obtained benzalde-hyde is a very valuable chemical having widespread applications in perfumery, dye stuffs and agrochemicals,^[1] whereas epoxides can be easily transferred to a large variety of compounds via regio- and stereoselective ring opening reactions.^[2–4]

Typical oxidants compatible with a majority of oxidation system are various alkyl hydroperoxide, hypochlorite, or iodosylbenzene. A problem associated with these oxidants is their low active oxygen content. The major drawback associated with these oxidants is the waste generation. Hence, from an environment and economical point of view, molecular oxygen should be the preferred oxidant and considering its high active oxygen content and no by-products.

Among number of complexes, Mn-salen catalysts are preferred since manganese itself is a relatively nontoxic metal, and manganese complexes are superior for the selective oxidation of olefins, chiefly because of fewer side reactions over manganese complexes. Manganese Schiff base has been widely described as good epoxidation catalysts with different oxidants.^[5–7] Especially Mn(III)salen complexes have been proven excellent for their selectivity toward epoxidation.^[5–12] However these complexes are also suffer from the same traditional problem such as they can not be recovered in homogeneous medium. Further, deactivation results in the formation of μ -peoroxo dimer and other polymeric species^[13,14] mainly because of ligand oxidation.

To overcome the above mention problems Mn(III)salen complex are supported onto different types of supports, such as functionalized polymeric ionic liquid,^[15] organic polymers, ^[16,17] polymeric membranes,^[18] mesoporous materials,^[19–26] ion exchange resins,^[27] layered double hydroxides,^[28,29] zeolite,^[30] and pillared clay.^[31]

The Literature survey shows that the oxidation of styrene using supported Mn(III)salen was carried in different organic solvent using various types of oxidants such as NaClO, CPBA, and peroxides. Although few reports are available in the literature describing the aerobic oxidation of styrene in different solvent system such as dichloromethane, toluene, benzene under homogeneous and heterogeneous medium.^[4,32]

It was observed in the literature that no reports are available in the use of metal hydroxide for supporting Mn(III) salen. Among all-metal hydrous oxides, hydrous zirconia has drawn great attention. This may be due to the fact that its surface hydroxyl groups are able to undergo chemical interaction with active compounds. A literature survey also show that no reports are available on solvent free aerobic oxidation of styrene using Mn(III)salen supported onto hydrous zirconia. Hence, in the present work an attempt was made to use hydrous zirconia as a support for Mn(III)salen as well as to carry out solvent free aerobic oxidation of styrene.

A series of catalysts containing 20-40% loading of Mn(III) salen (Mn(salen)) onto hydrous zirconia (ZrO₂) were synthesized. The synthesized new catalysts was characterized by various physicochemical techniques such as chemical stability, elemental analysis, Fourier transform infrared spectroscopy (FT-IR), diffuse reflectance (DR-UV), thermal gravimetric

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analysis (TGA), surface area measurement (BET Method), scanning electron microscopy (SEM), and electron spin resonance (ESR). The catalytic activity was evaluated for aerobic oxidation of styrene. Among the series of the catalysts, 30% loaded complex (Mn(salen)₃₀/ZrO₂) was found to be excellent. Further study was carried out using this catalyst by varying different parameters such as amount of the catalyst and reaction time. The present catalyst can be regenerated and reused up to four cycles without loss any appreciable loss in% conversion and selectivity.

Experimental

Materials

All the chemicals used were of A. R. grade. Zirconium oxychloride (ZrOCl₂.8H₂O) (Loba Chemie, Mumbai), MnCl₂.4H₂O, salicylaldehyde, ethylene diamine, ethanol, methanol, dichloromethane, styrene, styrene oxide, and benzaldehyde were obtained from Merck and used as received.

Synthesis of the Catalyst

The synthesis of the catalyst was carried out in three steps.

Synthesis of the support, hydrous Zirconia

Hydrous zirconia was synthesized following the same procedure reported by Bhatt and Patel,^[33] by adding an aqueous ammonium solution to an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ and pH of the solution was adjusted to 8.5. The resulted precipitates were aged at 100°C over a water bath for 1 h, filtered, washed with distilled water until chloride free water was obtained, and dried at 100°C for 10 h. The obtained material is designated as ZrO_2 .

Synthesis of the complex, [Mn(salen)Cl]

The Mn(III) salen was synthesized by the method reported by Freie et al.^[2] The salen ligand (Schiff Base) was synthesized by refluxing the ethanolic solution of the ethylenediamine and salicyladehyde in a mole ratio of 1:2 for 1 h.

The Mn(III) salen complex was synthesized following the procedure given in the literature,^[2] by refluxing the ethanolic solution of salen ligand and methanolic solution of MnCl₂.4H₂O in a mole ratio of 1:1 for 2 h. During the reaction the bright yellow color of the solution changes to dark brown. The dark brown solution was concentrated to obtain a dark brown solid. The obtained dark brown solid (yield = 73%) was designated as Mn(salen).

Supporting of the Mn(salen) onto ZrO_2

A series of catalysts containing Mn(salen) (20–40%) was synthesized by impregnating ZrO_2 (1gm) with an ethanolic solution of Mn(salen) (0.2–0.4 g/20–40 mL of ethanol) and dried at 60°C for 3 h in oven and impregnated at 100°C for 10 h. The obtained materials were designated as Mn(salen)₂₀/ ZrO_2 , Mn(salen)₃₀/ ZrO_2 , and Mn(salen)₄₀/ ZrO_2 .

The catalytic reaction was optimized with 30% loaded [Mn (salen)Cl] complex. The observed values for the elemental

Table 1. EDX values of supported catalyst.

Element	EDX	Theoretical
0	34.90	34.38
Cl	7.91	7.54
Mn	5.29	5.05
Zr	51.90	52.29

analysis for $Mn(salen)_{30}/ZrO_2$ are in good agreement with the theoretical values. Theoretical: O, 34.90; Cl, 7.91; Mn, 5.29; Zr, 51.90; observed: O, 34.38; Cl, 7.54; Mn, 5.05; Zr, 51.29 (Table 1).

Characterization

Elemental analysis was carried out using the JSM 5610 LV EDAX-SEM analyzer. Thermogravimetric analysis was carried out on the Mettler Toledo Star SW 7.01 up to 600°C in air with the heating rate of 5°C/min. FT-IR spectra of the sample were obtained using the KBr wafer on the Perkin Elmer instrument. The UV-DR of samples was recorded at ambient temperature on Perkin Elmer 35 LAMDA instrument using the 1cm quartz cell using barium sulfate as a reference. The surface morphology of the support and supported catalyst were studied by SEM analysis using JEOL SEM instrument (Model-JSM-5610LV) with scanning electron electrode at 15 kV. Scanning was done at 1 mm range and image was taken at a magnification of $100 \times$ for ZrO₂ and Mn(salen)₃₀/ZrO₂. The specific surface area was calculated from adsorption-desorption isotherm using BET method on Micromeritics spectrophotometer (Model: Series ASAP 2020). The ESR spectra were recorded on a Varian E-line Century series X-band ESR spectrometer (room temperature and scanned from 2000 to 4000 Gauss).

Catalytic Reaction

Oxidation of styrene

The catalytic activity was evaluated for the solvent free oxidation of styrene using molecular oxygen as an 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 styrene (100 mmole) at 80° C. The reaction was started by bubbling O₂ into the reaction medium and was continuously stirred on magnetic hot plate.

In the oxidation of styrene, after completion of reaction the reaction mixture was allowed to cool to room temperature and then 10% aqueous solution Na₂CO₃ was added with constant stirring. The resultant mixture (organic and aqueous) was allowed to stand for 15–20 min in order to separate the two distinct layers. The aqueous layer was collected and concentrated HCl was added slowly with constant stirring. No white precipitate of benzoic acid was observed. The remained organic layer was extracted with dichloromethane and analyzed on a gas chromatograph (Nucon 5700 model) having a flame ionization detector and BP-1 capillary column (30 m, 0.25 mm i.d.).

Further the product identification was done by comparison with authentic samples and finally by a combined gas chromatography mass spectrometer (Hewlett-Packard) using HP-1 capillary column (30 m, 0.5 mm i.d.) with EI (70 eV).

The percentage conversion of the substrate and the percentage-selectivity of the products in the epoxidation reaction are calculated as

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

Selectivity(\%) =
$$\frac{\text{product formed(mol)}}{\text{Substrate converted(mol)}} \times 100$$

Results and Discussion

DR-UV of Mn(salen) show two characteristic absorption bands at 432 and 500 nm (Figure 1a) corresponding to metal-ligand charge transfer and d-d transition respectively.^[34] DR-UV of Mn(salen)₃₀/ZrO₂ show two absorption bands at 432 and 500 nm, which are identical with free Mn (salen) complex (Figure 1b), indicates no change in the local environment of the Mn(III) coordination centre after supporting.

Figure 2 shows FT-IR spectra of Mn(salen), ZrO₂, and Mn(salen)₃₀/ZrO₂. The characteristic absorption frequencies for Mn(salen), ZrO₂, Mn(salen)₃₀/ZrO₂, and reused catalyst are presented in Table 2. The main characteristic bands of Mn(salen) are observed at 1331cm^{-1} (ν (C-N)) and 1630 cm⁻¹ (ν (C-C, C=N)) and are in good agreement with reported value.^[35]

The FT-IR spectra of ZrO_2 shows a broad band in the region of 3400 cm⁻¹. This is attributed to asymmetric hydroxo (-OH) stretches. Two types of bending vibrations are observed at 1600 and 1370cm⁻¹, indicating the presence of (H-O-H) and (O-H-O) bending, and vibrations, respectively. It also shows a weak bending band at 600 cm⁻¹ attributed to the presence of Zr-O-H bond. The FT-IR spectra of Mn(salen)₃₀/ZrO₂ shows bands at 1333 cm⁻¹ and 1628 cm⁻¹ corresponding to C-N stretching vibration and C-C, C=N. The presence of these bands in Mn(salen)₃₀/ZrO₂ confirms that Mn(salen) keeps its structure undegraded after

supporting onto the hydrous zirconia. Apart from this the catalyst shows the considerable shift in C-O (1542 cm⁻¹) vibration band. This indicates the interaction of oxygen of C-O of Mn(salen) to the H of hydroxyl group of ZrO_2 . Hence, there must be strong hydrogen bond between Mn(salen) and ZrO_2 through surface hydroxyl groups of zirconia (Scheme 1).

It is known that Mn(salen) is not thermally stable (Figure 3b). In free complex, at 130°C there is a cleavage of Mn-Cl bond and release of chlorine as hydrogen chloride and at 300°C the free complex completely oxidises to give a dark manganese oxide. The TGA of support ZrO_2 (Figure 3a) shows initial weight loss up to 210°C which is due to loss of adsorbed water of crystallization. TGA of Mn(salen)₃₀/ZrO₂ (Figure 3b) shows first weight loss of 7% at 50°C is due to the adsorbed water molecule of hydrous zirconia. The second weight loss of 7% at 170°C is due to the cleavage of Mn-Cl bond. The final weight loss of 14% at 430°C is due to the decomposition of Mn(salen) on ZrO₂. The weight of the nonremovable residue for Mn(salen)₃₀/ZrO₂ is 4.1648mg (78.15%). This shows that supporting of Mn(salen) on the surface of hydrous zirconia increases the thermal stability of Mn(salen). An increase in thermal stability indicates the presence of strong interaction between Mn(salen) and support.

BET surface area of ZrO_2 and the $Mn(salen)_{30}/ZrO_2$ was found to be 170 m²g⁻¹ and 234.4 m²g⁻¹ respectively. The larger surface area of the 30% Mn(salen)/ZrO₂ compared to that of the support was because of supporting of Mn(salen) and it is as expected.^[36] The increases in the surface area of the supported catalyst may be due to the high dispersion of Mn(salen) onto the surface of ZrO₂.

Catalytic Reaction

Oxidation of styrene involves the formation of two products: (a) epoxide and (b) benzaldehyde. To ensure the catalytic activity, the same reaction was carried out without catalyst. It was found that no oxidation takes place. The support, ZrO_2 was also used as catalyst for oxidation of styrene and no conversion was observed.

Effect of % loading

The aerobic oxidation of styrene was carried using unsupported i.e. parent Mn(salen) and Mn(salen) supported



Fig. 1. DR-UV of (a) Mn(salen), (b) Mn(salen)₃₀/ZrO₂, and (c) recycled catalyst.



Fig. 2. FT-IR spectra of (a) Mn(salen), (b) ZrO_2 , and (c) Mn (salen)₃₀/ ZrO_2 .

onto ZrO_2 with different loading. The obtained results are presented in Table 3. As the% loading of the Mn(salen) complex (10–30%) increases, conversion also increases, as expected. The catalyst with 30% loading shows maximum conversion as well as selectivity toward epoxide. Further, increases in% loading from 30% to 50% results in decrease in conversion. This can be explained as follows. Up to 30% loading, the entire support surface is covered by monolayer of Mn(salen) complex. Hence, substrate is accessible to maximum active sites, which are responsible for maximum conversion. After 30% loading, due to

Table 2. Band assignment of (a) ZrO_2 , (b) Mn(salen), (c) Mn (salen)₃₀/ ZrO_2 , and (d) recycled catalyst.

Assignment	Wavenumber (cm ⁻¹)			
	ZrO ₂	Mn (salen)	Mn(salen) ₃₀ / ZrO ₂	Reused Catalyst
ν(-OH)	3400	_	3407	3406
δ(H-O-H)	1600		1602	1600
δ(Zr-O-H)	600		603	602
ν (C-C), ν (C=N)		1630	1628	1628
ν(C-O)		1535	1542	1543
ν(C-N)		1331	1333	1332



Sch. 1. Interaction of Mn(salen) with surface of ZrO_2 .

multilayer formation of Mn(salen) onto support surface, all the catalytically active sites may not be accessible to the substrate molecule, which results in decreases in conversion.



Fig. 3. TGA curve of (a) support (ZrO_2) and (b) Mn(salen) and Mn(salen)₃₀/ZrO₂.

Table 3. Effect% loading of Mn(salen) on to ZrO₂.

		Selectivity (%)		
Catalyst ^a	Conversion (%)	Benzaldehyde	Epoxide	
ZrO ₂ ^b				
Mn(salen) ^c	62	45	55	
$Mn(salen)_{20}/ZrO_2$	60	76	24	
$Mn(salen)_{30}/ZrO_2$	67	53	47	
$Mn(salen)_{40}/ZrO_2$	54	70	30	
$Mn(salen)_{50}/ZrO_2$	47	74	26	

^aConversion based on styrene; Styrene, 100 mmol; amount of catalyst, 25 mg; Oxidant, O_2 1 atm; reaction time 4 h; temperature, 80°C. ^bamount of ZrO₂ 19.3 mg. ^camount of catalyst (i.e., parent Mn(salen)) 5.7 mg.

The control experiments with ZrO_2 and Mn(salen) were also carried out under optimized conditions with O_2 and results are presented in Table 3. It can be seen from Table 3 that ZrO_2 is inactive toward the epoxidation of styrene indicating the catalytic activity is due to only Mn (salen). The same reaction was carried out by taking the active amount (5.7 mg) of Mn(salen). It was found that the active catalyst gives 62% conversion with 55% selectivity toward epoxide and 45% selectivity toward benzaldehyde. Almost the same activity and selectivity was obtained for supported catalyst. This indicates that Mn(salen) is the real active species. Thus, we were successful in supporting Mn (salen) onto ZrO_2 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Effect of the amount of the catalyst $(Mn(salen)_{30}/ZrO_2)$

The effect of amount of the catalyst was studied keeping all other parameters (temperature, reaction time) constant and the obtained results are shown in Table 4. With increase in the amount of catalyst the amount of active species (Mn) increases as a result % conversion increases. Further, the increase in amount the number active sites increases, the epoxide is readily converted to the benzaldehyde. To the known industrial importance of epoxide the amount of catalyst is optimize to 25 mg.

Effect of reaction time

It is seen, from Table 5 that with increase in reaction time the conversion also increases. Initially, the increase in the conversion after 8 h is slow. This may be due to the fact that the alkene is consumed during the reaction, as a result the amount of the reactant decreases, which then requires time to reversibly bind with the oxidant. Further, the rate of desorption of the products formed from the catalyst surface is faster as a result the overall rate of the reaction slows down resulting into slow increase in the conversion with time.

Test for leaching and heterogeneity

Any leaching of the active species from the support makes the catalyst unattractive and hence it is necessary to study the stability as well as leaching. The catalyst was filtered after completion of reaction and the filtrate was characterized for UV-VIS spectroscopy. For comparison, UV-VIS spectra of Mn(salen) complex in ethanol were also recorded (Figure 4). The absence of any characteristic peaks in filtrate (Figure 4) indicates that there is no leaching of Mn(salen) and the catalyst remains completely insoluble under reaction condition and could be reused.

Further leaching of the Mn(salen) from Mn(salen)₃₀/ ZrO₂ was confirmed by carrying out an analysis of the used catalyst (EDAX) as well as the product mixture (AAS). Analysis of the used catalyst did not show any appreciable loss in manganese content as compared to the fresh catalyst. Analysis of the product mixture also showed that if any Mn was present it was below the detection limit, which corresponded to less than 1 ppm. These observations strongly suggest no leaching of the Mn species from the support. Further, for the rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture at 80°C after 2 h and allowed the filtrate to react up to 4 h. The reaction mixture of 2 h and filtrate was analyzed on a gas chromatogram. Results are presented in Table 6. No change in % conversion as well as % selectivity was found. On the basis of the results, it can be concluded that there is no leaching of the Mn(salen) from the support and the present catalysts is truly heterogeneous in nature and fall into the category C.[37]

 Table 4. Effect of amount of the catalyst.

			Selectivity (%)	
Catalyst ^a	Amount (mg)	Conversion (%)	Benzaldehyde	Epoxide
Mn(salen) ₃₀ /	10	28	58	42
ZrO ₂	25	67	53	47
	35	66	61	39
	50	70	68	32
	75	74%	75%	25%

^aConversion based on styrene; Styrene, 100 mmol; Oxidant, O_2 1 atm; reaction time 4 h; temperature, 80°C.

 Table 5. Effect of reaction time.

		~ .	Selectivity (%)	
Catalyst ^a	Time (h)	Conversion (%)	Benzaldehyde	Epoxide
Mn(salen) ₃₀ /	2	23	60	40
ZrO_2	4	67	53	47
	8	76	65	35
	12	79	80	20
	16	81	81	19

^aConversion based on styrene; Styrene, 100 mmol; amount of catalyst, 25 mg; Oxidant, O_2 1 atm; temperature, 80°C.



Fig. 4. DR-UV spectra of (a) Mn(salen) and (b) filtrate.

Table 6. Heterogeneity test.

		Selectivity (%)	
Catalyst ^a	Conversion (%)	Benzaldehyde	Epoxide
$\frac{\text{Mn(salen)}_{30}}{\text{ZrO}_2(2, h)}$	23	60	40
Filterate (4 h)	23	60	40

^aConversion based on styrene; Styrene, 100 mmol; amount of catalyst, 25 mg; Oxidant, O_2 1 atm; reaction time 4 h; temperature, 80°C.

Table 7. Recycling of the catalyst.

		Selectivity (%)	
Catalyst ^a	Conversion (%)	Benzaldehyde	Epoxide
$\frac{Mn(salen)_{30}}{ZrO_2 (4 h)}$	67	53	47
R1	66	55	45
R2	66	55	45
R3	66	55	45
R4	66	55	45

^aConversion based on styrene; Styrene, 100 mmol; amount of catalyst, 25 mg; Oxidant, O_2 1 atm; reaction time 4 h; temperature, 80°C.

Table 8. Mn(salen) complex supported on to different supports.

		Selectivity (%)	
Catalyst	Conversion %	Epoxide	Benzaldehyde
$Mn(salen)_{30}/ZrO_2$	67	47	53
Mn(salen) ₃₀ /Alumina	53	40	60
Mn(salen) ₃₀ /MCM-41	57	38	62
Mn(salen) ₃₀ /SBA-15	55	43	57

Reaction conditions: Styrene, 100 mmol; amount of catalyst, 25 mg; Oxidant, O_2 1 atm; temperature, 80°C; time, 4 h.



The catalysts, $Mn(salen)_{30}/ZrO_2$ was recycled to test their activity as well as stability. To see any change in the structure of catalyst after completion of reaction, the DR-UV of used catalyst was recorded. Figure 1b and 1c illustrates the DR-UV of fresh catalyst as well as used catalyst. No difference in DR-UV indicates the stability of the used catalyst after the reaction.

The FT-IR spectra of reused catalyst show all the bands of C-N, C-C, C=N, and C-O stretching vibration. The presence of these bands confirms that Mn(salen) keeps its structure undegraded. This indicates that the catalyst is stable during the reaction conditions.

The regeneration of the catalyst was carried out and reused up to four cycles without any appreciable loss in catalytic activity. The distribution for the selectivity of the products is remains the same. The results are shown in Table 7.

To determine the effectiveness of the catalyst, the synthesized Mn-salen was supported on to neutral alumina, MCM-41, and SBA-15. The reactions were carried out under optimized conditions (Table 8).

Conclusion

In the present article, we report the use of hydrous zirconia as a support for Mn(salen). TGA indicates the stability of catalyst up to 430°C indicates the strong interaction between complex and support. FT-IR and DR-UV indicates the structure of Mn(salen) did not get destructed after supporting on the surface of ZrO₂. SEM image indicates the existence of highly charged species on the surface of support. The present contribution reports the solvent free liquid phase aerobic oxidation of styrene using Mn(salen) on ZrO₂, which is the first report made ever. The Mn(salen)₃₀/ZrO₂ gives 67% conversion with 47% selectivity of styrene oxide and 53% selectivity of benzaldehyde under mild reaction condition. The superiority of the work also lies in regenerating and reusing the catalyst with same % conversion, which indicates the stability of the catalyst in reaction condition.

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