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Manganese (III) salophen supported on nanosilica triazine dendrimer as a selective heterogeneous catalyst for oxidation of alcohols with sodium periodate

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Abstract In this paper, we present an efficient and practical method for oxidation of alcohols to their corresponding carbonyl compounds catalyzed by [Mn(salophen)@nSTD]. This catalyst was synthesized, and characterized by FT-IR, UV–Vis, TGA, SEM and TEM. The results of experiments proved that this catalyst has excellent selectivity and high activity in the oxidation of different primary and secondary alcohols to their corresponding aldehyde and ketone at room temperature. The effects of important factors in the oxidation of alcohols such as kind of oxidant, solvent and amount of catalyst were investigated in the oxidation of 4-chlorobenzyl alcohol. This catalyst shows high stability and reusability after six catalytic runs.

Keywords Manganese (III) salophen \cdot Heterogeneous catalyst \cdot Nanosilica triazine dendrimer \cdot Oxidation of alcohols

Introduction

High selective oxidation of primary and secondary alcohols to their corresponding carbonyl compounds has gathered much attention in both organic synthesis and industrial applications. These products are used as important precursors and intermediates for many drugs, vitamins and fragrances. Numerous methods for oxidation of alcohols have been reported, but most of them suffer from toxic, unsafe, unstable and expensive classical reagents such as

Majid Moghadam moghadamm@sci.ui.ac.ir persulfate, potassium permanganate, and chromate [1-5]. Therefore, remarkable investigations have been conducted to apply environmentally friendly catalytic systems with a moderate oxidant, high activity and selectivity in the oxidation of alcohols.

P-450 enzymes are able to oxidize a wide variety of organic compounds and are the most efficient catalysts found in all domains of life. In recent years, numerous biomimetic systems such as transition metal Schiff base complexes have been developed to mimic the action of P-450 enzymes. Schiff base transition metal complexes have been used as suitable oxidation catalysts due to their easy preparation, low cost, chemical and thermal stability, and high activity in various oxidation reactions such as oxidation of alkenes, sulfides, amines, alcohols and imidazolines [6-16].

Among different metal Schiff base complexes, manganese Schiff bases complexes due to their attractive redox active systems, and high catalytic activity and selectivity are the most appropriate oxidation catalysts. However, the formation of inactive di- μ -oxo-bridged manganese dimers leads to inactivation of catalyst which is the main drawback of these catalysts. Anchoring these homogeneous catalysts onto organic and inorganic supports is a worthy way to overcome this problem [17–20].

Dendrimers have been attracted much attention in different fields such as target drug delivery, gene therapy, additives and medical chemistry [21–25]. Moreover, in last decades, dendrimers have been used in catalyst fields because of their abundant functional groups, spatial backbones and tridimensional structures [26, 27]. Immobilization of dendrimer catalysis on nanoparticles has gained maximum benefits from economic and environmental points of view because of their easy reusability and recoverability [26, 28, 29].

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Recently, we have reported the use of manganese salophen supported on nanosilica triazine dendrimer in epoxidation of different alkenes [17]. High catalytic activity and selectivity of this catalyst are the most important reasons which motivated us to investigate the potential of this catalyst in oxidation of alcohols with a mild oxidant at room temperature (Scheme 1). Reusability and stability of this catalyst were also investigated in this study.

Experimental

Materials

All materials were obtained from Merck and Aldrich chemical companies. Salophen ligand was prepared and metallated according to the literature [30].

Physicochemical measurements

FT-IR spectra were obtained by a Jasco 6300 spectrophotometer. Elemental analysis was carried out on a LECO, CHNS-932 analyzer. Thermogravimetric analvsis (TGA) was carried out by a Mettler TG50 instrument under oxygen flow at a uniform heating rate of 20 °C min⁻¹ in the range of 25–600 °C. Gas chromatography (GC) experiments were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20M. The scanning electron microscope measurement was taken on a Hitachi S-4700 field emission scanning electron microscope (FE-SEM). The transmission electron microscopy (TEM) was performed on a Philips CM10 Transmission Electron Microscope operating at 100 kV. Manganese content of the catalyst was determined by a Jarrell-Ash 1100 ICP analyser.

Preparation of nanosilica triazine dendrimer

Nanosilica triazine dendrimer was synthesized according to our previously work [31–33]. Concisely, activated nanosilica was functionalized with 3-aminopropyltrimethoxysilane (APTS). In the next step, aminopropylfunctionalized nanosilica, AP-nSiO₂, was reacted with



Scheme 1 Oxidation of alcohols to their corresponding carbonyl compounds by [Mn (salophen)@nSTD]

cyanuric chloride at 0 °C. Then, the obtained white powder was modified with bis(3-aminopropylamine) in the presence of *N*,*N*-diisopropylethylamine (DIPEA) to give the first generation of nanosilica triazine dendrimer (G₁). Finally, G₁ was converted to the CC2 and second generation (G₂), respectively, upon reaction with cyanuric chloride and bis(3-aminopropyl)amine.

Preparation of manganese(III) salophen supported on nanosilica triazine dendrimer, [Mn(salophen)Cl@ nSTD]

To a solution of manganese salophen (0.2 g) in acetonitrile (50 ml), nanosilica triazine dendrimer (1 g) was added. Next, the mixture was refluxed for 48 h. At the end of the reaction, the mixture was cooled and filtered. The obtained brown precipitated was washed with acetonitrile, methanol and acetone successively. In the final step, the catalyst was dried under vacuum at room temperature for several hours. The steps of nanocatalyst synthesis are shown in Scheme 2.

Typical procedures of oxidation of alcohols to their corresponding carbonyl compounds with NaIO₄ catalyzed by [Mn(salophen)@nSTD]

A solution of NaIO₄ (1 mmol) in H₂O (2.5 ml) was added to a mixture of alcohol (0.5 mmol) and [Mn(salophen)@ nSTD] (150 mg, 0.02 mmol) in CH₃CN (5 ml). The mixture was stirred at room temperature, and the progress of the reaction was monitored by GC. The products were identified by comparison with known standard samples. At the end of the reaction, organic compounds were extracted with Et₂O and purified with a silica gel plate or a silica gel column.

Results and discussion

Characterization of catalyst [Mn(salophen)@nSTD]

Surface morphology and the size of the heterogeneous catalyst and nanosilica triazine dendrimer particles were studied by field emission scanning electron microscopy (FE-SEM). After the immobilization of manganese salophen complex, a clear change in the morphology of the particles was observed (Fig. 1). The size of particles declined and the agglomerates were broken. The field transmission electron microscopy image of [Mn(salophen)@nSTD] shows dark regions corresponded to manganese and colorless



Scheme 2 Synthesis of manganese salophen supported on nanosilica triazine dendrimer, [Mn (salophen)@nSTD]

regions attributed to nanosilica triazine dendrimer and salophen ligand (Fig. 2) [17].

Catalytic experiments

The prepared catalyst was used for oxidation of alcohols with sodium periodate at room temperature. To this end, optimization of reaction parameters such as amount of catalyst, kind of solvent and oxidant was vital for obtaining higher catalytic activity.

Effect of catalyst contents on the oxidation of 4-chlorobenzyl alcohol

First, the effect of different content of catalyst on the oxidation of 4-chlorobenzyl alcohol was investigated (Table 1). It is noteworthy that in the absence of catalyst no progress was observed. The data in Table 1 show the yield of 4-chlorobenzaldehyde increased with increasing the amount of catalyst from 25 mg to 150 mg (TOF = 11.5 h^{-1}), and no obvious increase in the yield

Fig. 1 FE-SEM image of a nSTD, b [Mn(salophen)@ nSTD]



SEM RV: 15.00 kV VID: 5.502 mm [________ View field: 1.445 µm Det: InBeam 200 nm SEM MAG: 150.00 kc Date(m/d/y): 01/25/15

IROST View field: 2.167 µm Det: InBeam 500 nm Sea MAG: 100.00 kx Date(mMdy): 01/25/15 IROST



Fig. 2 TEM image of [Mn(salophen)@nSTD]

Table 1 Effect of the catalyst amount on the oxidation of 4-chlorobenzyl alcohol with $NaIO_4$

Catalyst amount (mg)	Catalyst amount (mmol)	Yield (%) ^a	
0	0	5	
25	0.003	32	
50	0.006	53	
100	0.0013	81	
150	0.02	94	
200	0.026	96	

Reaction conditions: 4-chlorobenzyl alcohol (0.5 mmol), $NaIO_4$ (1 mmol), CH_3CN/H_2O (5 ml/2.5 ml)

^a GC yield

 Table 2
 Influence of different oxidants on the oxidation of 4-chlorobenzyl alcohol catalyzed by [Mn(salophen)Cl@nSTD]

Oxidant	Solvent	Yield (%) ^a
NaIO ₄	CH ₃ CN/H ₂ O	94
H_2O_2	CH ₃ CN/H ₂ O	72
NaOCl	CH ₃ CN	25
ТВНР	CH ₃ CN	10

Reaction conditions: 4-chlorobenzyl alcohol (0.5 mmol), oxidant (1 mmol), catalyst (150 mg, 0.02 mmol Mn) CH_3CN/H_2O (5 ml/2.5 ml)

^a GC yield

Table 3Effect of different solvents on the oxidation of 4-chloroben-zyl alcohol with sodium periodate catalyzed by [Mn(salophen)Cl@nSTD]

Entry Solvent		Yield (%) ^a		
1	CH ₃ CN/H ₂ O	94		
2	CHCl ₃ /H ₂ O	18		
3	CH ₂ Cl ₂ /H ₂ O	45		
4	CH ₃ COCH ₃ /H ₂ O	75		
5	CH ₃ CH ₂ OH/H ₂ O	53		
6	CH ₃ OH/H ₂ O	60		

Reaction conditions: 4-chlorobenzyl alcohol (0.5 mmol), $NaIO_4$ (1 mmol), catalyst (150 mg, 0.02 mmol Mn), solvent (5 ml/2.5 ml) ^a GC yield

of the product was observed by using 200 mg of catalyst (TOF = 9.23 h⁻¹). Therefore, 150 mg of catalyst was chosen as the optimized amount of catalyst.

 Table 4
 Oxidation of alcohols

 using sodium periodate by
 [Mn(salophen)Cl@nSTD]^a

 catalyst
 [Mn(salophen)Cl@nSTD]^a

Entry	Alcohol	Product	Time (h)	Yield (%) ^b	Selectivity (%)	TOF (h^{-1})
1	СН2ОН	Сно	2	92	100	11.5
2	СН2ОН	СНО	2.5	85	100	8.5
	O ₂ Ń	O ₂ N				
3	O2N-CH2OH	О2N-СНО	2	88	100	11
4	СН2ОН	СНО	2	86	100	10.75
	н₃со	н₃со				
5	Br-CH ₂ OH	Br-CHO	2	87	100	10.87
6	СІСН2ОН	СІ—СНО	2.5	81	100	8.1
7		СІ-СНО	2	94	100	11.75
8	ОН		3.25	69	100	5.31
9	ОН	°	3	73	100	6.08
10	сн ₂ он	СНО	3.5	65	100	4.64

 $^{\rm a}$ Reaction conditions: alcohols (0.5 mmol), NaIO_4 (1 mmol), catalyst (150 mg, 0.02 mmol Mn), CH_3CN/ H_2O (5 ml/2.5 ml)

^b GC yield

Table 5 Comparison of the catalytic activity of [Mn(salophen)Cl@nSTD] with some of previously reported systems in oxidation of benzyl alcohol

Row	Catalyst	Reaction	Reaction conditions			Yield (%)	$TOF(h^{-1})$	[Ref.]
		Time (h)	Catalyst (mol%)	T (°C)	Oxidant			
1	Manganese (III) salophen supported on nanosilica triazine dendrimer	2	2	RT	NaIO ₄	92	11.5	This work
2	Ru supported on alumina	1	2.5	80	O ₂	99	39.6	[34]
3	(Bpy)CuI/TEMPO	3	5	RT	air	95	6.3	[35]
4	Encapsulation of Pd-NP into the PMO-based yolk-shell hybrid materials	8	5	50	O ₂	94	2.35	[36]
5	Cp*Ir complex	20	1.5	Reflux, H ₂ O	air	92	0.76	[37]
6	Mesoporous channels of SBA-15 in stabiliz- ing palladium nanoparticles	5.5	0.4	80	O ₂	83	37.7	[38]
7	PEG-stabilized palladium nanoparticles	13	10	80	O ₂	83.1	1.27	[39]
8	Nanoparticles of palladium-supported amphiphilic resin particles	24	0.2	60	O ₂	99	4.12	[40]
9	Palladium-Schiff base-triphenylphosphine	2.5	2	Reflux, CH ₂ Cl ₂	NMO	87	17.4	[41]



Fig. 3 Results of catalysts recovery in the oxidation of 4-chlorobenzyl alcohol with sodium periodate after six consecutive times

 Table 6
 Amounts of manganese leached in the oxidation of 4-chlorobenzyl alcohol with sodium periodate

Mn (mmol/g) ^a	Number
0.134	Fresh catalyst
0.126	After 6 time use

Reaction conditions: 4-chlorobenzyl alcohol (0.5 mmol), $NaIO_4$ (1 mmol), catalyst (150 mg), CH_3CN/H_2O (5 ml/2.5 ml)

^a Determined ICP analysis



Fig. 4 FT-IR spectrum of: a [Mn(salophen)Cl@nSTD] and b recycled catalyst

Effect of various oxidants on the oxidation of 4-chlorobenzyl alcohol catalyzed by [Mn(salophen)@ nSTD]

Another prominent factor in the oxidation of alcohols is the nature of oxidant. The ability of different single oxygen donors, such as $NaIO_4$, H_2O_2 , NaOCl, and *tert*-BuOOH, was tested in the oxidation of alcohols. The results show that $NaIO_4$ compared with other oxygen donors has the best yield (Table 2).

Effect of various solvent on the oxidation of 4-chlorobenzyl alcohol by [Mn(salophen)@nSTD]

Catalytic activity can be enhanced by an accurate choice of solvent. Hence, the effect of different solvents on the oxidation of 4-chlorobenzyl alcohol was studied. Among the mixture of methanol, ethanol, acetone and acetonitrile (single phase systems), dichloromethane and carbon tetrachloride (two-phase systems with *n*-Bu₄NBr as phase transfer catalyst), the 2:1 mixture of acetonitrile/water is the most appropriate solvent for oxidation of alcohols due to its higher carbonyl yield (Table 3). The higher catalytic activity in aqueous acetonitrile is corresponded to the polarity of the solvent and higher solubility of periodate in CH₃CN/H₂O mixture.

Oxidation of alcohols with sodium periodate catalyzed by [Mn(salophen)@nSTD]

Under optimized conditions and room temperature, the ability of this heterogeneous catalyst in the oxidation of primary and secondary alcohols was investigated. The results are summarized in Table 4. This catalyst gave high yields in the oxidation of benzyl alcohols. After 2h reaction, 94% of the benzyl alcohol was oxidized solely to benzaldehyde, giving a considerably high TOF of 11.5 h⁻¹ (entry 1). 4-Chlorobenzyl alcohol was oxidized to 4-chlorobenzaldehyde with 100% selectivity (entry 7). The effect of electron-donating (e.g., -CH₃ and -CH₃O) and electron-withdrawing substitutes (such as -NO₂ and -Br) on benzene ring of alcohols was examined. 4-Chlorobenzyl alcohol and 4-bromobenzyl alcohol were converted to the corresponding aldehyde in 94 and 87% yield, respectively (entries 7 and 5). 3-Nitrobenzaldehyde and 3-methoxybenzaldehyde were obtained in 85 and 86% (entries 2 and 4). It was clear that the nature of substitutes does not have a significant role on the yield of carbonyl compounds. In this catalytic system, benzyl alcohols reacted in shorter times and higher yields compared with secondary alcohols, whereas 1-heptanol as a primary aliphatic alcohol (entry 10) reacted more slowly compared to the other alcohols. Most importantly, all liner and benzyl alcohols had been selectivity converted to their corresponding aldehydes and ketones without producing any carboxyl compound as a by-product.

The performance of [Mn(salophen)Cl@nSTD] catalyst in the oxidation of benzyl alcohol was compared with some of the previously reported catalysts (Table 5). It is noteworthy that this catalytic system is superior in terms of turnover frequency (TOF), catalyst amount, reaction temperature or reaction time in comparison with others.

Catalyst reusability

The reusability of catalysts is highly desired for "greening" chemical manufacturing processes. In order to examine reusability and stability of the catalyst, [Mn(salophen) Cl@nSTD] was reused for several times in the oxidation of 4-chlorobenzyl alcohol. At the end of each run, this catalyst was separated from the reaction mixture and washed completely with acetonitrile and H₂O, and dried. Results obtained by GC showed that the catalyst was reused for six consecutive times. The amount of Mn leached after sixth run, measured by ICP, shows a value of about 6% of its initial amount (Fig. 3; Table 6).

The nature of the recovered catalyst was monitor by FT-IR spectroscopy. No difference was observed in FT-IR spectrum of the recovered catalyst compared to the spectrum of the fresh catalyst (Fig. 4).

Conclusion

In conclusion, we have successfully developed an efficient catalytic system for oxidation of alcohols. This catalyst is able to oxidize different benzyl alcohols and aliphatic alcohols to their corresponding carbonyl compounds in mild condition with high yield and excellent selectivity. Furthermore, due to strong covalent bond between manganese salophen and amine groups at the surface of triazine dendrimer, the catalysts could be recovered and reused several times by simple filtration without significant loss of activity.

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