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Mn(II) salen complex immobilized on nano silicagel as a recyclable heterogeneous catalyst for oxidation of alcohols to their corresponding carbonyl compounds

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Abstract

Mn(II) salen complex immobilized on nano silicagel was prepared by incorporating Mn(II) salen complex into a nanosilica matrix and characterized by TGA, XRD, atomic absorption spectroscopy and was successfully applied as catalyst for the oxidation of alcohols to their corresponding carbonyl compounds. Oxidation of a series of alcohols in acetonitrile over immobilized Mn(II) salen complex using tetrabutylammonium peroxymonosulfate (TBAO) as oxidant were resulted in the corresponding carbonyl compounds selectively in moderate to high yields. It is noteworthy that the aldehydes do not undergo further oxdation to carboxylic acids. The yields of aromatic alcohols are higher than those of alcohols with aliphatic groups. The catalyst has been reused several times without observable loss of its activity and selectivity.

Keywords: Immobilized Mn salen; oxidation of alcohols; nano silicagel.

Introduction

Schiff base ligands with more flexible structures are easily synthesized and form a complex with almost all metal ions. Many Schiff base complexs show excellent catalytic activity in various reactions [1-4]. One of the most important challenges in catalysis is to transform a successful homogeneous catalyst into a heterogeneous one, due to the intrinsic advantages of heterogeneous systems, namely easy catalyst separation/recycling and products separation

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[5,6]. The simplest methodology to accomplish heterogenization is to support the active salen-metal complex onto or into an insoluble solid. The interaction between the complex and the support can range from physisorption to Coulombic forces and covalent anchoring. Heterogenization of metal complexs has been carried out using supports such as zeolite, clays, silicious materials and activated carbon [7–12]. With the advancement of nanoscience and nanotechnology, nano silicagel is becoming increasingly interesting due to its unique properties which differ significantly from bulk material. Due to the high surface area and volume ratios, nanoparticles can effectively improve the loading and the catalytic efficiency of immobilized catalysts. This improvement permits to turn to the advantages of both homogeneous (selectivity, activity) and heterogeneous (separation, recovery, recycling) catalysts [13,14].

The oxidation of alcohols is an attractive and important transformation in organic chemistry, since carbonyl compounds are useful building blocks in organic synthesis and also they play the key role in activation of enzymes. These products are important intermediates in the synthesis of many drugs, vitamins and fragrances. [15,16]. For this purpose, manganese complexes of the Schiff base (Salen complexes) have long been used as efficient catalysts in catalytic oxidation reactions due to their high oxidation ability. Therefore, there is more interest to introduce more efficient manners for synthesis of reuseable catalyst, especially from the standpoint of green chemistry. In continuation of our work on the synthesis of recyclable catalysts and their application in the oxidation reaction [17, 18], we have covalently bonded Mn(II) salen complex to the nano silicagel support and the catalyst has been used for conversion of alcohols to aldehydes/ ketones using TBAO as oxidant at room temperature.

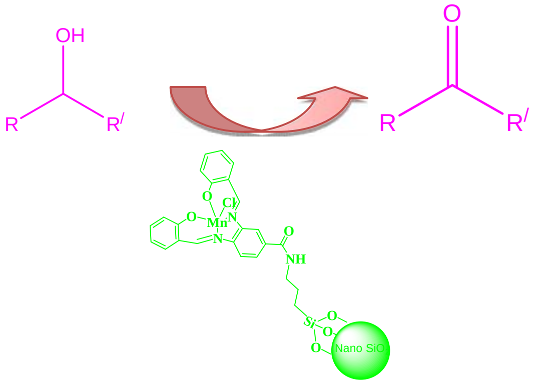


Figure 1.

Experimental

Chemicals

Reagents and solvents were purchased from Merck or Fluka Chemical Companies. Purity determinations of the products were accomplished by TLC on silica-gel polygram SILG/UV 254 plates and GC spectrometer.

Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a 780 Perkin Elmer spectrometer in KBr pellets and reported in cm^{-1}. NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in DMSO-d$_6$ with chemical shift (ò) given in ppm relative to TMS as internal standard.

Catalyst preparation

Procedure for the synthesis of compound (cyclohexylamino) (cyclohexylimino) methyl 3,4-diaminobenzoate (3)

A few drops of NEt$_3$ was added to the suspension of 3,4-diamino benzoic acid (1.52 g, 10 mmol) and DCC (3.09 g, 15 mmol) in dry tetrahydrofuran. The reaction mixture was stirred for 2 h under reflux condition and the progress of the reaction was monitored by TLC. Upon completion, the solvent was evaporated in vacuum. After purification by short column chromatography (n-hexan, ethylacetat, 1:3), the solution was cooled to 0 °C and the crude white solid product was filtered off. Compound 3 was characterized on the basis of its spectroscopic data.White solid crystal, m.p. = 94-96 ^{o}C, IR (KBr, v_{max}, cm^{-1}): 3450-3100 (N-H), 2925, 2835, 1680, 1615, 1575, 1505, 1435, 1340, 1290, 1210, 1150, 1080, 880, 820, 715. ^{1}H NMR (400MHz, CDCl$_3$): δ 0.9-2.1 (m, 20 H, cyclohexyl), 3.4 (s, 2H, NH$_2$), 3.5 (m, 1H), 3.7 (s, 2H, NH$_2$), 4.16 (m, 1H), 5.9 (s, 1H, NH), 6.65 (d, 1H, J= 8 Hz), 6.97-7.01 (m, 2H). ^{13}C NMR (62.9 MHz, CDCl$_3$): 24.4, 25.3, 26.3, 30.9, 32.3, 49.6, 53.5, 56.9, 115.2, 116.4, 120.5, 127.6, 133.3, 138.5, 155.0, 171.3. MS: m/z(%) 358(25, M$^+$), 258(43), 233(22), 222(9), 177(49), 151(38), 135(100), 107(21), 83(20),55(41).

Procedure for the synthesis of compound (cyclohexylamino) (cyclohexylimino) methyl4-{[(E)-1-(2 hydroxyphenyl)methylidene]amino}-3-{[(z)-1-(2-hydroxyphenyl (methylidene]amino}benzoate (4)

Compound 3 (3.58 g, 10 mmol) was dissolved in methanol (30 mL) and salicylaldehyde (20 mmol, 2 mL) was added to the test tube and were refluxed for 2 h. The crude solid yellow product was filtered and washed thoroughly with ethanol(3*10 mL) and recrystallized successively from solutions of hot ethanol. Yellow solid, m.p. = 179-181^{o}C, IR (KBr, v_{max}, cm^{-1}): 3300, 2910, 2845,1665,1640, 1615, 1490, 1470, 1320, 1250, 1220, 1180, 1130, 770. ^{1}H NMR (400MHz, CDCl$_3$): δ 0.82-2.15 (m, 20 H, cyclohexyl), 3.56(m, 1H), 4.15(m, 1H), 6.19(s, 1H, NH), 6.91-7.58(c, 11H), 8.63(s, 1H, CH=N), 8.67(s, 1H, CH=N), 12.81(s, 2H, OH). ^{13}CNMR, (62.9 MHz, CDCl$_3$): 24.5, 25.3, 26.2, 30.9, 32.4, 39.8, 56.5, 57.3, 117.6, 118.5, 119.0, 119.2, 119.7, 122.0, 126.1, 132.6, 133.7, 135.7, 136.0, 139.4, 142.6, 164.55, 164.8, 169.9. MS: m/z(%) 566(0.2, M^+), 505(25), 386(13), 242(11), 142(19), 125(20), 99(24), 77(21), 56(37), 43(68), 41(100).

Procedure for the synthesis of Mn(II) salen complex 5

$Mn(OAc)_2.4H_2O$ (2.94 g, 12 mmol) was added to a suspension of compound 4 (5.66 g, 10 mmol) in hot ethanol (20 mL) and the suspension was stirred under reflux condition for 1 h. A brown-yellow solid started to precipitate from the reaction mixture, which was kept at room temperature for a further 5 min. The yellow solid was filtered and washed with ethanol leading to the pure product 5.

Procedure for the synthesis of Nano-SiO_2

The synthesis of Nano-SiO_2 was achieved by the ammonia-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS) in a mixed solvent of deionized water and ethanol using PEG as the surfactant agent in the process at room temperature. In a typical procedure, 100 mL ethanol and 20 mL deionized water were mixed together in a beaker, and then 1.0 g of PEG (MW 6000) was dispersed into the mixture by ultrasonication. After adding ammonia water (2.5 mL), tetraethyl orthosilicate (TEOS, 2 mL) was added to the reaction solution. The resulting dispersion was mechanically stirred continuously for 20 h at room temperature. The resultant products were collected and washed with ethanol and deionized water in sequence., and then dried under vacuum at 60 ˚C for 2 h for further use.

Covalent bonding of (3-Aminopropyl)trimethoxysilane to nano silicagel

(3-Aminopropyl)trimethoxysilane (10.0 mL), nano silicagel (2.00 g) and dry toluene (100.0 mL) were refluxed for 28 h and the crystalline product was isolated by filtration. The collected powder 6 was washed for 12 h in a soxhlet extractor using 2-propanol as a solvent and dried in vacuo at 90 ˚C for 12 h to remove adsorbed water.

Immobilization of the salen complex

Compound 5 (6.54 g, 10 mmol) was dissolved in hot toluene (100 mL) and then compound 6 (2 g) was added gradually. The mixture stirred for 15 h and the resulting suspension was filtered with a fine-porous filter paper. The collected powder 7 was washed for 15 h in a soxhlet extractor using aceton and for 12 h in a soxhlet extractor using ethanol as a solvent and dried in vacuo at 90 ˚C for 6 h.

General procedure for oxidation of alcholes

A mixture of alcohole compounds (1 mmol), TBAO (0.17 mmol), Mn(II) salen complex-immoblized on nano silicagel (0.007 mmol) and CH_3CN (2 mL) was stirred at room temperature for 5 min. After completion of the reaction (TLC or GC), the reaction mixture was centrifuged to separate the catalyst. Evaporation of the solvent under reduced pressure gave almost pure products. Further purification was preceded by vacuum distillation or recrystalization to afford pure carbonyl compound.

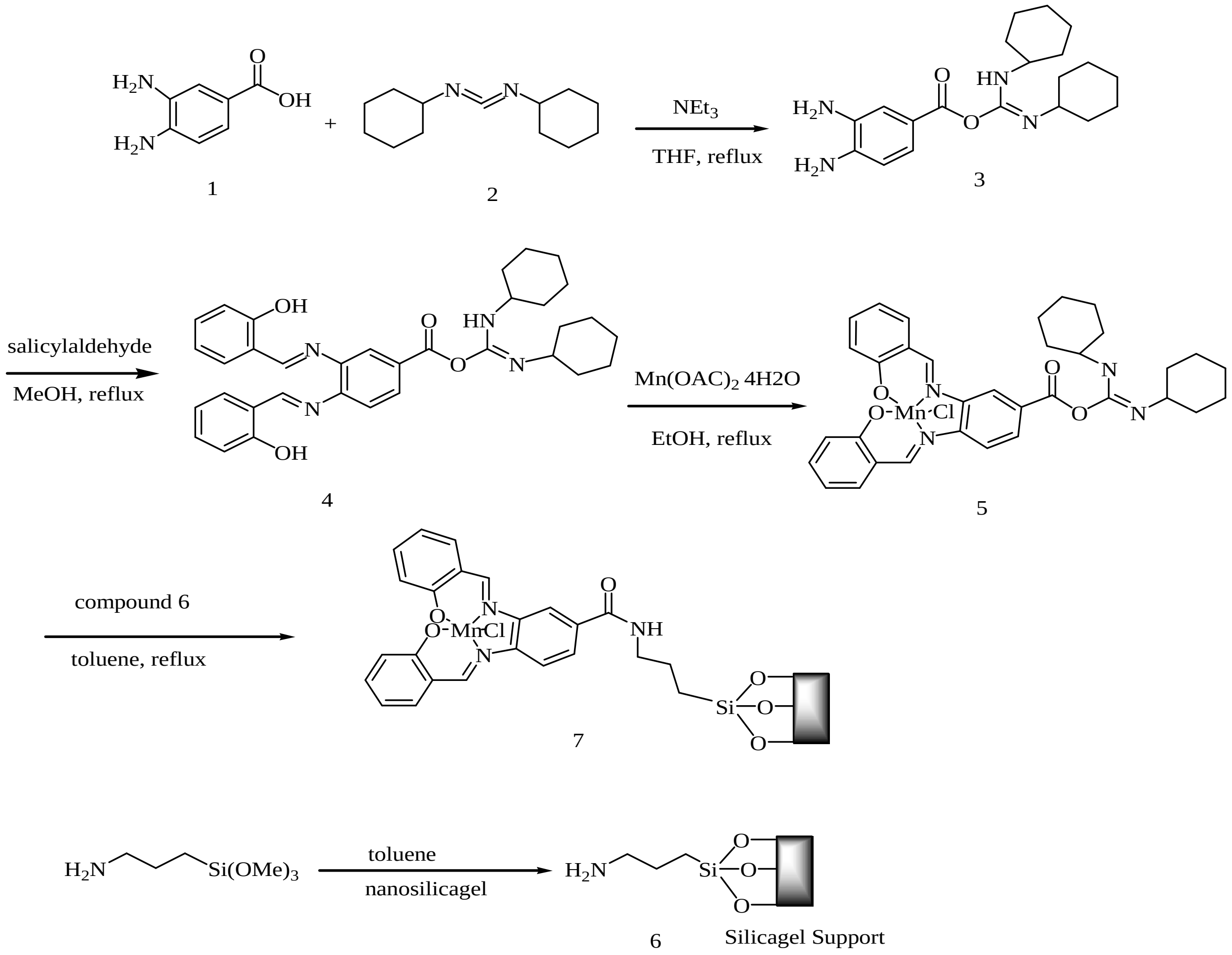
Results and discussion

Catalyst characterization

Preparing heterogeneous catalysts by immobilizing the homogenous precursors on solid support is one of the important routes for developing novel heterogeneous catalysts. In most of these cases, the immobilized catalysts so prepared could provide advantages over their unsupported counterparts in terms of separation, reusability, and particularly, the ability to provide practical conveniences in a continuous system that is valued in industry.

Due to the reasonable needs to clean and green recovery of the heterogenous catalyst, especially salen complexs, we synthesized Mn(II) complex of (cyclohexylamino) (cyclohexylimino) methyl4-{[(E)-1-(2-hydroxyphenyl)methylidene]amino}-3 [(z)-1-(2-hydroxyphenyl(methylidene]amino} benzoate immobilized on nano silicagel as a new heterogeneous system (Scheme 1). Firstly, (cyclohexylamino) (cyclohexylimino) methyl 3,4-diaminobenzoate **3** was prepared by the reaction of 3,4-diamino benzoic acid with dicyclohexyl carbodiimide (DCC). The structure of compound **3** was established on the basis of its spectroscopic data. The IR spectrum of the compounds exhibited the absorption band at around 3100-3450 cm^{-1} indicating the secondary amine stretching vibration (NH). Mass spectrum of compound 3 showed its respective $[M^+]$ peaks (M/Z=358). In the ^{1}HNMR spectrum, the aliphatic proton pertaining to the cyclohexyl group were observed at around 0.9-2.1 ppm. The amine proton (NH) was appeared at around 5.9 ppm. The resulting compound was treated with salicylaldehyde in a 1:2 molar ratio in methanol for 2 h to give the corresponding schiff base **4**. IR absorption bands in the 3300 cm^{-1} region can be attributed to the OH stretching vibrations. In the ^{1}H NMR spectrum, the secondary amine proton (NH) was appeared at around 6.19 ppm while the imine proton was observed in 8.63 ppm. The phenol proton was observed at around 12.81 and the aliphatic protons (CH_2)

of cyclohexyl group were appeared at around 0.82- 2.15 ppm.



Scheme 1.

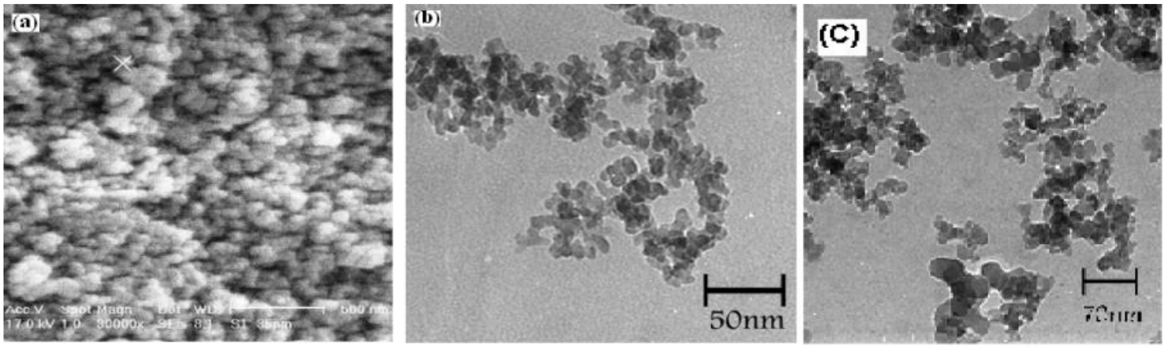


Figure 2. (a) SEM image of Nano-SiO_2 (b)TEM image of Nano-SiO_2 (c) TEM image of nanoSiO_2- salen complex

The reaction of the schiff base lignd **4** with $Mn(OAc)_2.4H_2O$ gave manganese salen complex **5**. The structures and purities of the schiff-base ligand and of the metal complex were confirmed by IR and UV-Vis spectroscopy. The infrared spectrum of free ligand (i.e. prior to complexation with the metal) shows a band about 1615 cm^{-1} attributed to the C=N stretching vibration of the imine. This is reduced under 1600 cm^{-1} upon complexation of Mn^{+2} ion. Then, pretreated 3-aminopropylated nano silicagel **6** (produced from threatment of 3-aminopropyltrimethoxysilane and nano silicagel in dry toluene) was stirred with a toluene solution of complex **5** under reflux condition for 15 h to prepare complex-anchored nanosilica material (compound 7). The synthesized Mn(II) salen complex - nano silicagel was characterized by different methods such as XRD, TGA and TEM techniques. The amount of complex loaded on the surface of nano silicagel was determined by atomic absorption spectroscopy.

Transmission electron microscopy (TEM)

The morphology and grain size of the complex was investigated by TEM (Figure 2). They have a narrow distribution of sizes, from 15 nm to 20 nm.

X-ray diffraction (XRD) analysis

Figure 2 shows XRD pattern of $NanoSiO_2$-salen complex. One broadened XRD peak for amorphous silica was recorded at $2\theta = 23^{o}$ (Figure 3).

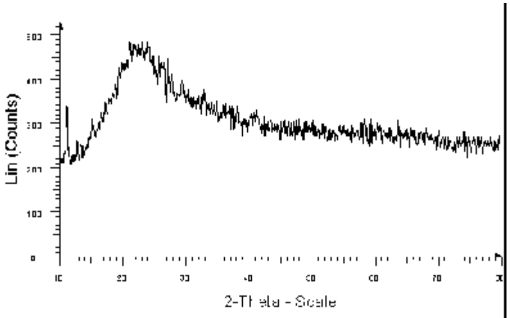


Figure 3. XRD pattern of nanoSiO2- salen complex

Thermal gravimetric analysis (TGA) and atomic absorption spectroscopy

The thermal behavior of Mn(II) salen complex-nanocilicagel is shown in Figure 4. A significant decrease in the weight percentage of the Mn(II) salen complex-nanocilicagel at about 183 °C is related to desorption of water molecules from the catalyst surface. This was evaluated to be ~1.2 % according to the TGA analysis. In addition, the analysis showed other decreasing peak appeared at temperature around 450 °C due to the decomposition of the organic spacer group (decomposition of the catalyst from the silica surface). Therefore, the covalent bonds in the catalyst endow it with high thermal stability. According to the atomic absorption spectroscopy, the amount of Mn(II) salen complex functionalized on nanocilicagel is evaluated to be 1.4 mmol /g.

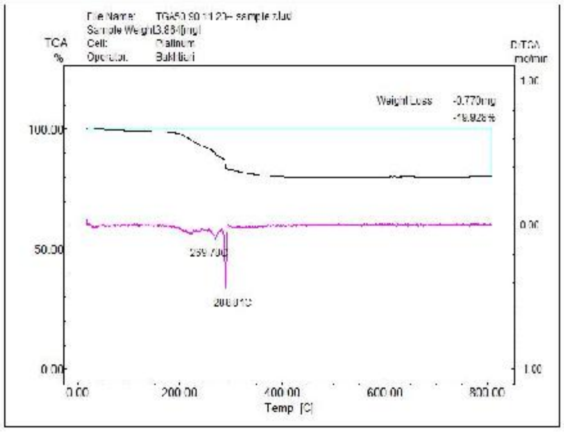


Figure 4. TGA pattern of the synthesized Mn(II) salen complex-nano silicagel

Catalytic activity of nanosilica-Mn(II) salen complex for the oxidation of alcohols

In order to show the merit of synthesized heterogeneous catalyst in organic reactions, the new nanosilica-supported Mn(II) salen complex was used~~,~~ as an efficient and recyclable heterogeneous catalyst for oxidation of various alcohols into the corresponding carbonyl compounds. For this purpose, benzyl alcohol was taken as the model substrate. We examined this reaction in various solvents and oxidants (Table 1).

The results indicate that different solvents affected the efficiency of the reaction. In the presence of TBAO as oxidant, acetone and dichloromethane afforded low yield (50%), while water and chloroform could improve the yield of benzaldehyde (Table 1, Entries 2-5).

Table1. Effect of solvents and oxidants on the oxidation of benzyl alcohol by Mn(II) salen Complex immobilized on nano-SiO_2 [a]

Entry	Solvent	Oxidant	Yield(%)[b]
1	CH_3CN	TBAO	95
2	$CHCl_3$	TBAO	75
3	CH_2Cl_2	TBAO	50
4	$(CH_3)_2CO$	TBAO	50
5	H_2O	TBAO	80
6	CH_3CN	PhIO	19
7	$CHCl_3$	PhIO	25
8	CH_2Cl_2	PhIO	10
9	$(CH_3)_2CO$	PhIO	10
10	H_2O	PhIO	80
11	CH_3CH_2OH	PhIO	-
12	CH_3CN	UHP	40
13	CH_3CN	Oxone	-
14	CH_3CN	H_2O_2	-
15	CH_2Cl_2	UHP	-

[a]Reaction condition: benzyl alcohol (1mmol), solvent (2cc) under ambient condition.

[b]GC Yields

Finally, when acetonitrile was used, the yield increased to 95% better than any other solvents that were examined here. The model reaction was examined in the presence of different oxidant and TBAO was the most effective oxidant and the reaction was completed in 5 min. To obtain the optimized reaction conditions, we also changed the amount of catalyst and oxidant. The results are summarized in Table 2 and 3.

Table 2. Effect of the amount of Mn(II) salen complex on the oxidation of benzyl alcohol[a]

Entry	Catalyst (g)	Yield (%)[a]
1	0.1	50
2	0.016	80
3	0.005	95
4	0.001	80

[a]Reaction condition: benzyl alcohol (1mmol), CH_3CN (2cc), TBAO(0.07 g) under ambient condition

.[b]GC Yields

Table 3. Effect of the amount of oxidant on the oxidation of benzyl alcohol by Mn(II) salen complex [a]

Entry	TBAO (g)	Yield (%)[a]
1	0.01	40
2	0.03	50
3	0.05	90
4	0.07	95
5	0.1	95

[a]Reaction condition: benzyl alcohol (1mmol), CH_3CN (2mL), Mn(II) salen Complex (0.005 g) under ambient condition

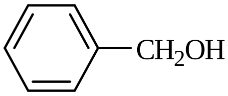
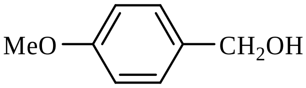
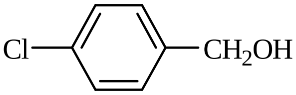
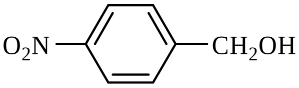
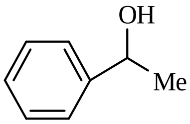
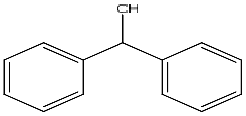
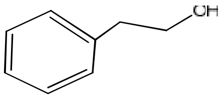
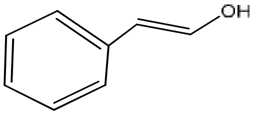
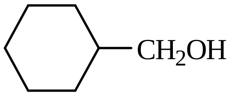
[b]GC Yields

Consequently, we found that the yield of the product was improved to 95% when the mixture of TBAO (0.07 g) and catalyst (0.005 g) was used. In addition, the catalytic behaviour of the immobilized Mn(II) salen complex was also compared with pure Mn(II) salen complex in homogeneous system.

Control experiments indicate that in the absence of the catalyst, the oxidation of benzyl alcohol at the same condition gives benzaldehyd in a rather low yield of 21%.

To ascertain the scope and limitation of the present reaction, with above optimized conditions at hand, a variety of alcohols were examined and these results were summarized in Table 4. We were pleased to find that all substrates were converted to the corresponding carbonyls in good to excellent yields (40-100%). It is noteworthy that the aldehydes do not undergo further oxdation to carboxylic acids. The oxidation yields of aromatic alcohols are higher than those of alcohols with aliphatic groups. In Table 5, the efficiency of our method for the oxidation of alcoholes is compared with some other published works in literature. Each of these methods have their own advantages, but they often suffer from some troubles including necessity of temperature control (Entries 2-6), long reaction time (Entries 2-7) and employ of non-recyclable catalyst (Entry 2).

Table 4. The oxidation of alcohols catalyzed by Mn(II) salen complex-nanosilicagel in ambient condition[a]

Entry	Reagent	Yield (%)[b]
1		95
2		98
3		98
4		40
5		100
6		76
7		72
8		75
9		50

[a] Reaction conditions: alcohol (1mmol), TBAO (0.17mmol, 0.07g), catalyst (0.007mmol, 5 mg), CH_3CN (2 mL), stirred at room temperature for 5 min

[b] GC yields

Table 5. Comparison of results using Mn(II) salen complex-nanosilicagel with results obtained by other works for the oxidation of alcohols

Entry	Catalyst	Condition	Yield (%)	Ref
1	Current	CH_3CN, r.t., 5min	98 [a]	-
2	V_2O_5	Toluene, 100 °C, 22h	92 [a]	19
3	$Ru/AlO(OH)_3$	Toluene, 80°C, 8h	99 [a]	20
4	Pd complex	Toluene, 60 °C, 3.5h	99 [a]	21
5	TEMPO	Ionic liquid, 65°C, 8h	88 [b]	22
6	V_2O_5	Toluene, 100 °C, 25h	79 [b]	19
7	Pd/C	$MeOH/H_2O$,r.t, 12h	44 [b]	23

[a] 4- methoxy benzyl alchole

[b] 4- nitro benzyl alchole

At the end of the reaction, the catalyst was recovered by centrifuge and reused for several times. The recycled catalyst was washed with dichloromethane and subjected to a second reaction process. The results show that the yield of product after five runs was only slightly reduced (Table 6).

Table 6. Recyclability of Mn(II) salen complex - nano silicagel as a catalyst in the oxidation of benzylalcohol[a]

Entry	Cycle	Yield (%)[b]
1	0	95
2	1	95
3	2	93
4	3	93
5	4	91
6	5	88

[a] Reaction conditions: benzylalcohol (1mmol), TBAO (0.17mmol, 0.07g), catalyst (0.007mmol, 5 mg), CH_3CN (2 mL), stirred at room temperature for 5 min.

[b] GC yields

Acknowledgements

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