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R. K. Sharma[a]; Chetna Sharma[a]
[a] Green Chemistry Network Centre, Department of Chemistry, University of Delhi, Delhi, India

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Efficient Oxidative Methyl Esterification of Aldehydes By Silica-supported Manganese Complex: Clean and Recyclable Catalyst

R.K. SHARMA* and CHETNA SHARMA

Green Chemistry Network Centre, Department of Chemistry, University of Delhi, Delhi, India

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An oxidative methyl esterification of aldehydes was carried out using hydrogen peroxide as oxidant and silica supported manganese complex as catalyst. The catalyst was prepared by grafting method and characterized by surface area analysis by the BET method, elemental and thermogravimetric analyses, FT-IR, ^{13}C-CPMAS spectral studies and atomic absorption spectrometry technique (AAS). The work-up procedure is very simple and products were obtained in moderate to high yields. The catalyst was reutilized during successive catalytic cycles.

Keywords: Heterogeneous catalyst, functionalized silica gel, oxidation, 30% aq hydrogen peroxide

1 Introduction

The direct oxidative transformation of aldehydes to esters is an extremely useful and selective functional group interconversion in organic synthesis (1), hence, much effort has been devoted to find newer methods and reagents that would make the process environmentally benign. So far, this process of oxidative esterification has been accomplished in a variety of ways. A two-step reaction sequence involving the oxidation of hemiacetal (2a), acetal (2b) or cyanohydrins (2c) can bring about this conversion or several one-pot conversions using different transition metal oxidants such as pyridinium dichromate (3a), MnO_2 (3b), electrochemical oxidation (3c), as well as very recently using catalyst V_2O_5/H_2O_2 (4a), oxone (4b), titanosilicate (5), $NaIO_4/LiBr$ (6), $Fe(ClO_4)_3.xH_2O$ (7), Pd-Al_2O_3(8), KI/t-BHP (9). Though, most of these methods are useful for direct oxidative esterification of aldehydes to corresponding esters, many methods suffer from disadvantages such as use of an amount of expensive and polluting reagents, drastic reaction conditions, an inert atmosphere, and electrochemical conditions. Moreover, these reactions proceed with homogeneous catalysts which usually cause a serious problem of toxicity (10) as the separation of toxic metal ions from the reaction mixture becomes difficult and hence, is one of the major contributors to waste in chemical processes. Therefore, the development of a catalytic route with respect to environmentally benign catalyst and reagent, cost-effectiveness, mild reaction condition, and facile isolation of required product is favourable and one of the major goals of green chemistry (11). Considering all these facts, we used silica as a solid support since it displays many advantageous properties such as high surface area, excellent stability (chemical and thermal), good accessibility, and organic groups can be robustly anchored to the surface; to provide catalytic centres (12).

In the present study we report the synthesis of silica supported manganese catalyst and investigated it in the oxidative esterification of a variety of aldehydes with methanol as solvent in combination with H_2O_2 as oxidant at reflux in air.

2 Experimental

2.1 Materials

3-Aminopropyltriethoxysilane (Fluka) and silica gel (Qualigens) were commercially obtained and used as such in this study. Starting materials and reagents used in the reactions were obtained commercially from Thomas Baker and Spectrochem Pvt. Ltd. and used without purification. All of the solvents used in the present study were purified before use.

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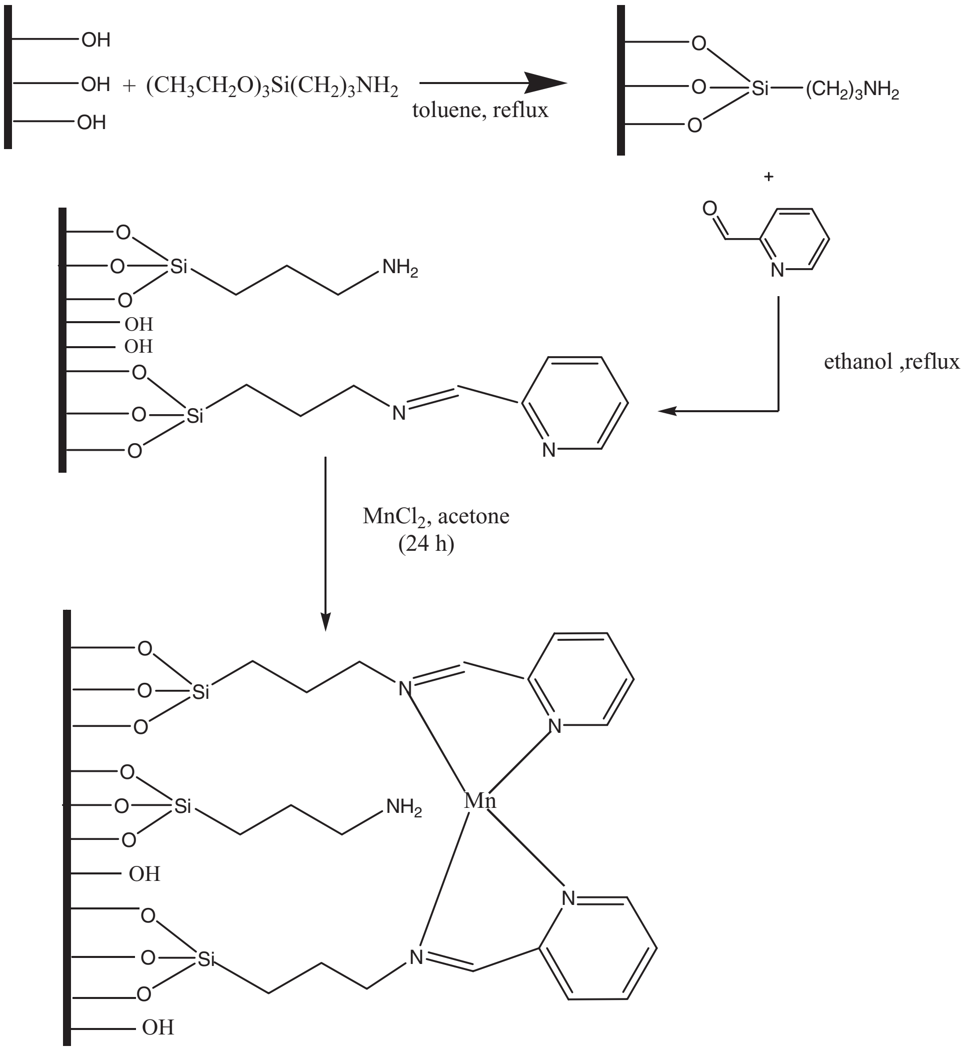
*Address correspondence to: R. K Sharma, Green Chemistry Network Center, Department of Chemistry, University of Delhi, New Delhi 110007, India. Tel/Fax: +91-011-27666250; E-mail: rksharmagreenchem@hotmail.com



Sch 1. Synthesis of covalently anchored manganese complex onto silica.

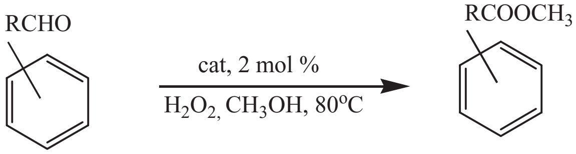
2.2 Preparation of Catalyst

The immobilized catalyst has been prepared by the post-modification method according to Scheme 1. Silica gel was functionalized using 3-aminopropyltriethoxy silane to yield aminopropyl silica gel (APSG) according to a reported procedure (12b). The grafting of APSG with pyridine-2-carboxaldehyde, followed by its complexation with manganese(II) chloride was undertaken to yield a catalyst.

A mixture of APSG (4 g) and pyridine -2-carboxaldehyde (4.0 mmol) in ethanol was stirred for 18 h at room temperature. The modified silica was dried at 90°C overnight. It was then reacted with a solution of manganese chloride (1.5 mmol) in acetone. The mixture was stirred for 24 h and the catalyst was filtered off and washed thoroughly with acetone until the washings were colourless. The catalyst was dried overnight in air at 90°C. The resulting brown supported catalyst was conditioned for a total of 27 h by refluxing in ethanol, toluene and then acetonitrile so as to remove any surface physisorbed managanese. The conditioned catalyst was dried overnight in vacuum oven at 90°C.

2.3 General Procedure for Oxidative Methylation of Aldehydes

To a stirred mixture of benzaldehyde (1 mmol) and catalyst (2 mol%) in methanol (3 mL) was added dropwise aqueous 30% hydrogen peroxide (2 mmol) at reflux (Sch. 2). The progress of the reaction was monitored by TLC. At



Sch 2. Synthesis of aromatic esters from their corresponding aldehydes.

Table 1. Physico-chemical parameters of silica gel (SG), aminopropyl silica gel (APSG) and catalyst (Mn-Py-SG)

Material	*Elemental Analysis* %C	%H	%N	C/ per N	*BET surface area* $/m^2g^{-1}$	*Thermal Analysis* Δm^a/%	ΔT^b / °C
SG	—	—	—	—	235.67	—	—
APSG	5.281	1.269	2.046	2.58	151.91	3.3	0–180
						8.57	180–600
Mn-Py-SG	8.082	2.248	1.779	9.08	132.35	4.7	0–180
						12.9	180–600

[a] change in mass of material
[b] change in temperature

the end of the reaction, the excess hydrogen peroxide was deactivated by the addition of aq. sodium bisulfite followed by filtration through a small Buckner funnel. The catalyst was regenerated after washing with ethanol, acetone and drying in air. The methyl esters obtained were purified by column chromatography (silica gel, hexane: ethylacetate = 20:1). The products were characterized by comparison of their spectroscopic (IR, ^{1}H-NMR) data, and melting points with those of authentic samples.

2.4 Characterization Techniques

The IR spectra were recorded on Perkin-Elmer Spectrum 2000 Fourier transform infrared (FT-IR) spectrometer. Thermal analysis was performed with the help of Shimadzu DTG-60 instrument. N_2 adsorption analysis was carried out at 77 K by Model 2010, Micromeritics, USA. The analytical data were processed by the BET equation for surface areas. Elemental analysis was performed on an Elementar Analysensysteme GmbH VarioEL V3.00. ^{13}C-CPMAS spectra were recorded on a Bruker DSX-300 NMR spectrometer at 75.47 MHz. The content of manganese in the heterogeneous catalyst was determined by Perkin-Elmer AANALYST 200 AAS after digesting the sample in aqua regia. ^{1}H-NMR spectra for the products were recorded on Bruker 300 MHz instrument using TMS as internal standard. Melting points were recorded on a Buchi R-535 apparatus and are uncorrected.

3 Results and Discussion

3.1 ^{13}C CP-MAS NMR Analysis

The catalyst synthesis was confirmed by various instrumental techniques. The three signals at 9.3, 22.3 and 42.9 ppm observed in the ^{13}C-CPMAS NMR spectrum of APSG due to –Si–CH_2–, –CH_2– and –N–CH_2– groups, respectively, authenticate the synthesis of APSG. The immobilization of pyridine-2-carboxaldehyde on silica gel was further confirmed by ^{13}C CP-MAS NMR spectroscopy (Fig. 1a). In the Py-SG spectrum, nine well-formed peaks were observed. These peaks are numbered sequentially in Figure 1b. First three peaks are attributed to the precursor carbon atoms numbered 1, 2, and 3, as indicated in Figure 1b. On complexation, a –N–CH_2– peak shifts to 63.29 ppm whereas, the peak at 41.5 ppm refers to the uncomplexed –N–CH_2– group. The aromatic carbon atoms at meta position to nitrogen were assigned to that numbered 5 at 122.9 ppm whereas the one at para position was assigned 6th peak at 135.6 ppm. The aromatic carbons bonded to nitrogen were numbered 7 and 8 with the peaks at 148.4 and 154.3, respectively. The Schiff base condensation was also confirmed by the presence of C=N peak (assigned number 9 in Fig. 1b) at 161.4 ppm.

3.2 FTIR Spectroscopy

Figure 2 shows the spectra of Py-SG (a) and Mn-Py-SG (b). The spectra of the silica gel and the modified support (see supplementary material) are dominated by strong bands characteristic of the support matrix. These bands are due to surface hydroxyl groups, in the range of 3770–3300 cm^{-1}, and to lattice vibrations, in the range of 1300–750 cm^{-1}. Two strong bands are present at about 1094 cm^{-1} and 797 cm^{-1}, which can be assigned to ν_{as}(Si–O–Si) and ν_s(Si–O–Si), respectively. No significant changes are observed in the silica gel structure sensitive vibrations, after its modification, which is an indication that its framework remained unchanged. The spectrum of APSG (b) exhibits an additional band at about 2924 cm^{-1} due to the aliphatic (–CH_2) stretching of the propyl chain of the silylating agent, thus suggesting that the silica gel surface was functionalized with the linking agent. The infrared spectrum of the chemically modified silica prior to complexation with the metal shows a band at 1666 cm^{-1} attributed to the C=N stretching vibration of the imine. Upon complexation with manganese, the band shifts to 1657 cm^{-1}indicative of the metal-ligand bond formation (13).

3.3 Surface Area Analysis

As expected, the BET surface area strongly decreased after grafting (14), according to the sequence SG > APSG > Mn-Py-SG. The reduction in surface area in this sequence confirms the functionalization of silica gel with

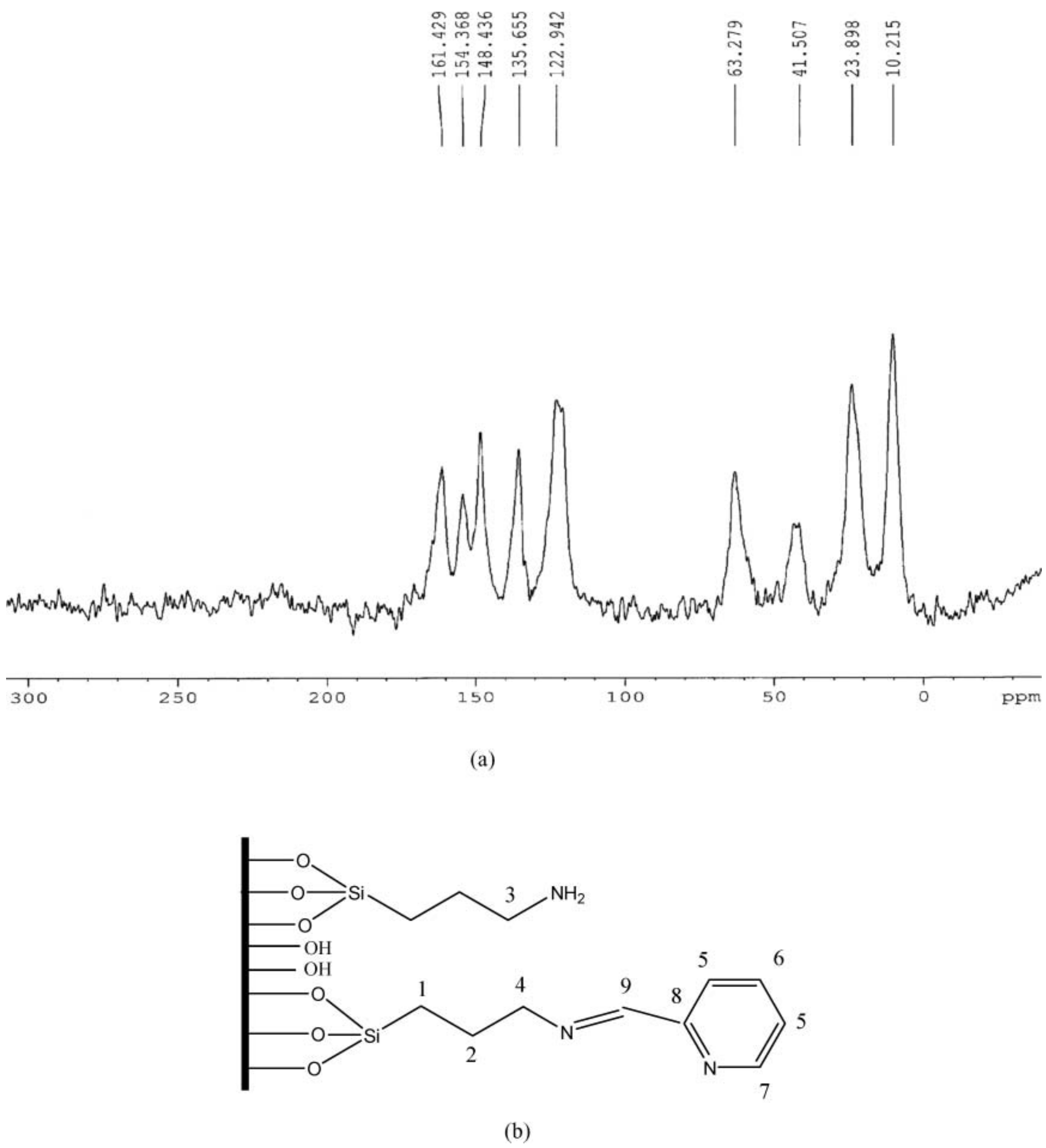


Fig 1. (a) ^{13}C-NMR spectrum of Py-SG; (b) labelling of carbon atoms in Py-SG in order of the peaks obtained in the spectrum in Figure 1a.

3-aminopropyltriethoxysilane to give APSG, and its modification with pyridine-2-carboxaldehyde followed by metallation, to yield a catalyst. The BET surface area of silica gel (SG), aminopropylsilica gel (APSG) and catalyst Mn-Py-APSG were measured and are represented in Table 1.

3.4 Elemental and Thermogravimetric Analyses

The quantitative estimation of organic functional group covalently anchored onto the surface of silica gel was performed with elemental, and thermogravimetric analyses. The results obtained from these two techniques have also been compared to authenticate the synthesis of APSG and catalyst.

Elemental analysis was carried out for SG, APSG and Mn-Py-SG. The nitrogen content of APSG was 2.046%. According to this value, the amount of the ligand, which was attached to silica gel, was 1.46 mmol/g of support. The observed carbon and nitrogen contents of APSG shows C/N ratio to be ~3 thereby confirming the incorporation of 3-aminopropyltriethoxy ligand into the silica matrix.

Thermogravimetric curves showed two distinct stages of decomposition. The one between 30 and 180°C was related to adsorbed water and other one between 180 and 600°C was assigned to decomposition of organic matter and water from silanol groups condensation. The detailed thermogravimetric data are presented in Table 1. The weight loss due to the decomposition of organic matter gives rise to the grafting capacity of 1.47 mmol g^{-1} which is in good agreement with the results of elemental analysis.

The TG curve of Mn-Py-SG shows that water loss is 4.7%, whereas the organic degradation ends at 600°C (12.9%). Consequently, the weight loss due to pyridine-2-carboxaldehyde moiety is calculated from elemental analysis to be only 12.11% enabling a theoretical capacity of 0.38 mmol g^{-1} of Mn-Py-SG. The metal loading of Mn-Py-SG, which was determined by AAS, was obtained to be 0.37 mmol/g. This value is in good agreement with ligand content of the material and shows that complexation of the supported material has nearly been completed.

Table 2. Effect of solvent on oxidation of benzaldehyde using Mn-Py-SG as catalyst and H_2O_2 as oxidant at room temperature

Entry	*Solvent*	*Reaction time/h*	*Yield*[a]*/%*
1	Methanol	5.0	26[b]
2	Ethanol	5.0	19[c]
3	i-PrOH	12.0	11[d]
4	t-BuOH	12.0	No reaction

[a] Isolated yield after preparative liquid chromatography
[b] 5% benzoic acid
[c] 2% benzoic acid
[d] traces of benzoic acid

3.5 Catalytic Activity of Mn-Py-SG in the Oxidative Methylation of Aldehydes

To evaluate the effect of catalyst, oxidation of benzaldehyde was carried out in the presence of different alcohols (Table 2). It has been observed that respective esters have been formed and declining yields with increase in the alkyl group of alcohol is attributed to the steric hinderance due to the bulkier alkyl groups. From Table 2, it could be seen that conversion of aldehydes to their respective esters is not 100% complete, minor amounts of acids have also been obtained that is due to the over-oxidation as it has been proposed that the formation of methyl ester is not a

Fig 2. (a) FT-IR spectrum of Py-SG (before complexation); (b) FT-IR spectrum of Mn-Py-SG (after metal-ligand bond formation).

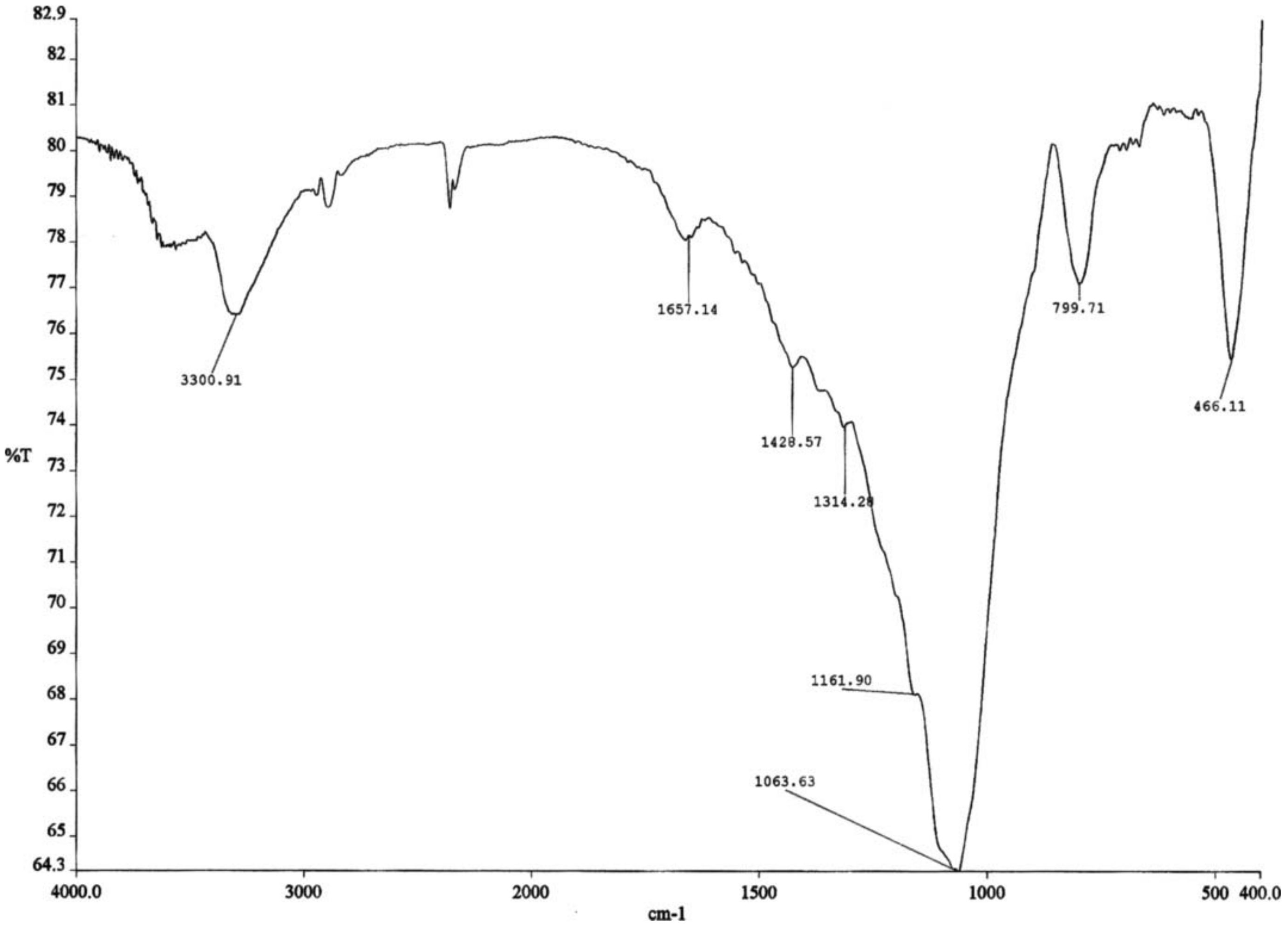


Fig 2. (*Continued*)

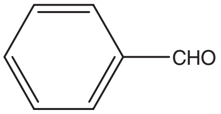
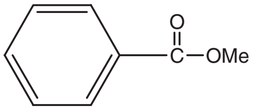
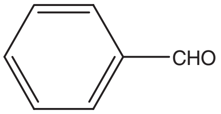
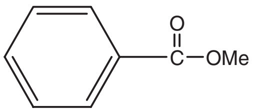
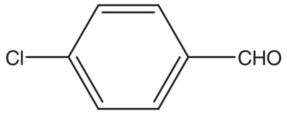
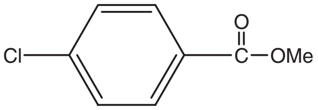
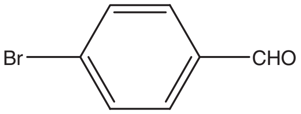
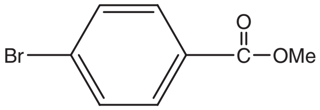
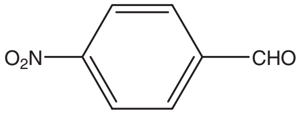
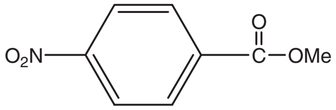
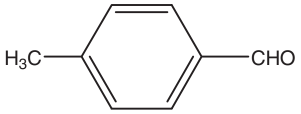
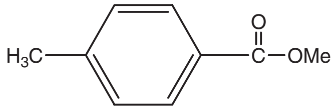
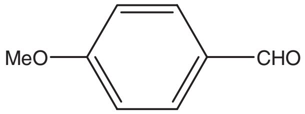
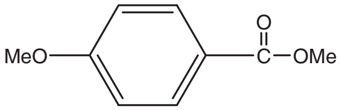
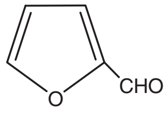
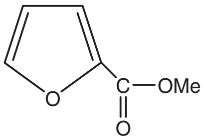
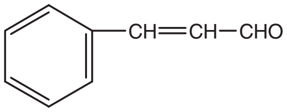
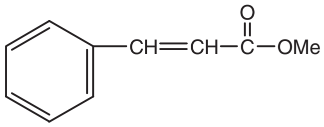
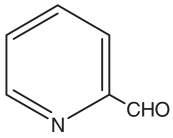
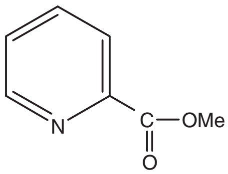
two-step procedure that involves first the oxidation of aldehyde to acid followed by its subsequent oxidation to give the ester rather conversion of aldehyde to ester involves hemiacetal formation.

Furthermore, we carried out the blank oxidative methylation of benzaldehyde with hydrogen peroxide alone under similar reaction conditions without using catalyst. The oxidation was found to be very slow and gave a very poor yield of the oxidized product. We also found that the addition of hydrogen peroxide in one portion gave a poor yield of the desired product, while its dropwise addition gave maximum yield of the product in shorter reaction time.

The effect of temperature and time on product yield was also studied for oxidative methyl esterifaction of benzaldehyde and it has been found that yields of products are a function of temperature. The results show that product yield increased as the reaction temperature was raised (Fig. 3). Since methanol has been used as solvent, the maximum temperature could not exceed the boiling point of methanol when there is still a scope of reaction in terms of product yield, as predicted from the sharp rise in the curve in Figure 3. Therefore, reaction was continued and some controlled experiments showed that the yields of esters are also a function of time: the longer the time, the higher the yield and finally, no increase in the product yield was found after 8 h.

Once the reaction conditions were optimized, oxidative methylation of benzaldehyde to its methyl ester was carried out in the presence of homogeneous, as well as heterogenized managanese catalyst. As expected, turn over numbers for the latter were significantly much higher than the former, so reactions were performed in the presence of Mn-Py-SG as catalyst and results are presented in Table 3. The efficacy of present methodology is further demonstrated by esterification of unsaturated aldehyde such as cinnamaldehyde (entry 9) but on the contrary, existing protocol does not hold well for heterocyclic aldehydes (entries 8 and 10) that may be due to an unfavorable equilibrium in hemiacetal formation. After the completion of reaction, the catalyst was recovered by simple filtration and washed with acetone and air-dried. The recovered catalyst was reused and almost consistent activity was noticed even after fifth cycle. When a fresh reaction was conducted with the filtrate

Table 3. Oxidative esterification of benzaldehyde using Mn-Py-SG as catalyst and H_2O_2 as oxidant at reflux[a]

Entry	Substrate	Product	Time/h	Isolated Yield[b]/% (TON $\times 10^3$)[d]
1.[c]			6.5	90 (4.5)
2.			8.0	88(44) 82, 79, 77, 75[e]
3.			6.5	84(42)
4.			6.5	82(41)
5.			11.0	85(42.5)
6.			10.5	80(40)
7.			10.0	83(41.5)
8.			12.0	Trace
9.			9.0	74(37)
10.			12.0	Trace

[a] Reaction condition: Reaction condition: substrate (1 mmol), Mn-Py-SG catalyst (2 mol%), aq. 30 wt% H_2O_2 (2 mmol) in methanol (3 mL) at reflux.

[b] Yields after column chromatography.

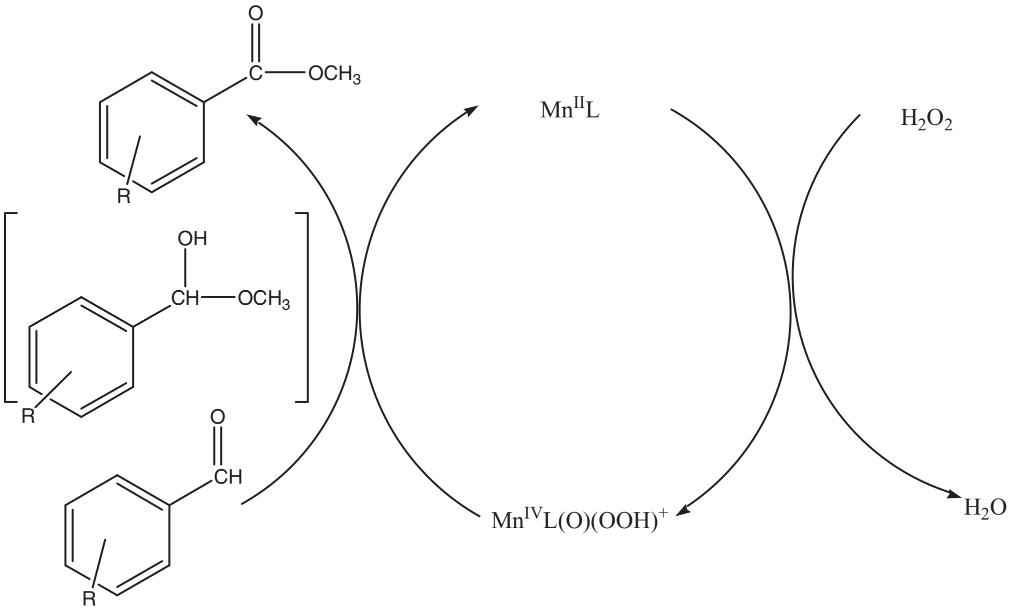
[c] Reaction condition: substrate (1 mmol), $MnCl_2$catalyst (20 mol%), aq. 30 wt% H_2O_2 (2 mmol) in methanol (3 mL) at reflux.

[d] Turnover number (TON) = mole of product formed/mole of metal present in the catalyst.

[e] Same catalyst is used for several runs after its regeneration.

obtained at the end of the reaction, almost no catalytic activity of the filtrate was observed.

It seems plausible that the aldehyde is oxidized with Mn-Py-SG to the corresponding acid, which is esterified immediately with alcohol. However, when benzoic acid is used instead of benzaldehyde under identical conditions, no methyl benzoate could be obtained. It is most probable that this oxidation of aldehydes in an alcoholic medium proceeds through hemiacetal formation as indicated in Scheme 3. Most likely, supported Mn(II) catalyst was oxidized to the Mn(IV) complex in the presence of aq H_2O_2 (15).



Sch 3. Proposed Mechanism of oxidative esterification.

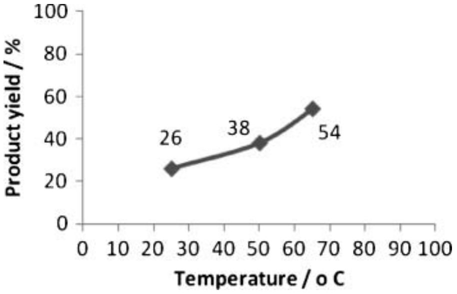


Fig 3. Effect of temperature on the product yield (reaction was carried out for 5 h).

4 Conclusions

In summary, we have developed a manganese-based catalyst system for efficient oxidative esterification of aldehydes with methanol as solvent and H_2O_2 under mild conditions, which represents an excellent complement to the previously established protocols. Although the literature enumerates a number of procedures for conversion of aldehydes into esters, the simplicity, environmental acceptability, recyclability of the catalyst and inexpensiveness of our procedure makes it a practical alternative. Furthermore, the use of hydrogen peroxide as oxidant is quite attractive, as it possesses several advantages such as low price, ease of handling, absence of toxic waste and formation of only water as a by-product (16).

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