Oxidation of benzylic alcohols to carbonyl compounds with hydrogen peroxide catalysed by manganeses chloride supported on montmorillonite K10

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Manganeses(II) chloride supported on montmorillonite K10 was found to be an efficient catalysts for the oxidation of alcohols to carbonyl compounds with hydrogen peroxide as oxidant.

Keywords: oxidation, hydrogen peroxide, montmorillonite K10, manganese (II) chloride, benzylic alcohols

Oxidation of benzylic alcohols to carbonyl compound is a fundamental transformation in organic synthesis and numerous methods utilising various reagents have been reported.[1-8] Aldehydes and ketones are important precursors and intermediates for many drugs, vitamins and fragrances.[9,10] Metal ions play a significant role in many of theses reactions.[11-13] Oxidation of organic compounds in combination with hydrogen peroxide as the oxidant is of importance in synthetic organic chemistry for both environmental and economical reasons.[14, 15]

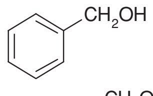
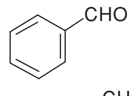
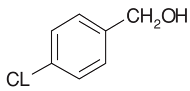
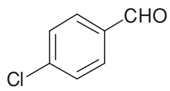
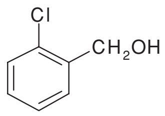
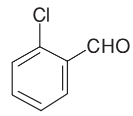
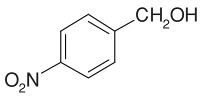
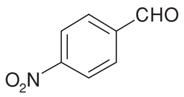
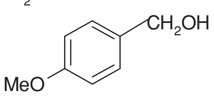
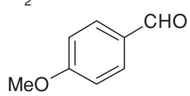
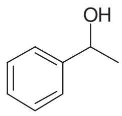
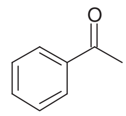
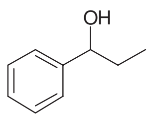
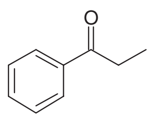
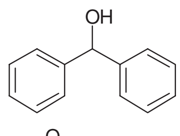
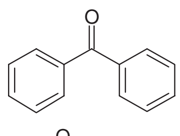
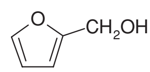
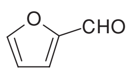
Manganeses salts as the catalyst or oxidant are used for oxidation of organic compounds consistently[16,17] typically as manganese oxide[18-21] and potassium permanganate.[22-25]

Many organic reactions have been devised in which the reagents are deposited on various inorganic solid supports. These novel reagents have advantages over the conventional homogeneous solution techniques: easy set-up and of work-up, mild experimental conditions, high yields and/or selectivity.[26, 27] Montmorillonite K10 has been inset extensively for this purpose.[28, 29]

In this work, benzylic alcohols (primary and secondary) were subjected to the oxidation by hydrogen peroxide on clay-supported manganeses (II) chloride. The overall reaction is best formulated as shown in Scheme 1.

Various solvents were examined for oxidation of benzylic alcohols and the best results are shown in Table 1.

Table 1 Oxidation of benzylic alcohols with hydrogen peroxide catalysed by manganese (II) chloride supported on Montmorillonite K10

Entry	Alcohol	Product	Solvent	Time/h	Yield[a]/%
1			Acetonitrile	2	91
2			Acetonitrile	2.5	88
3			Acetonitrile	2.5	80
4			Toluene	3.5	83
5			Toluene	3.5	85
6			Acetonitrile	3	90
7			acetonitrile	2	87
8			Acetonitrile	2	85
9			Toluene	4.5	95

[a]All yields refer to isolated products.

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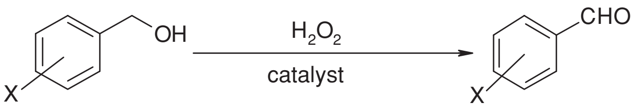

Scheme 1

Toluene was found to be a very good solvent for most of the benzylic alcohols such as *para* methoxy benzyl alcohols in this oxidation method. Manganese (II) chloride supported on wet montmorillonite K10 (80% w/w) was used for the oxidation of benzylic alcohols to carbonyl compounds and exhibited high selectivity and stability. It was prepared by mixing manganeses (II) chloride and montmorillonite K10 as the support and could be used several times. In this method work-up is simply separation of the hetrogeneous-supported catalyst by filtration, then removal of the solvent, followed by purification of the residue using column chromatography to give pure products in high yields. The results are summarised in Table 1.

The effect of catalyst on the reaction (time/yield) was investigated using benzyl alcohol, as shown in Table 2. Association of catalyst with oxidant resulted in increased yield and decrease of reaction time (Table 2).

Clay-supported manganeses (II) chloride can be recovered after use as a catalyst for oxidation of alcohols. In a typical procedure, the catalyst after the first use for the oxidation of benzylic alcohols was recovered by washing with diethyl ether and *n*-hexene (2×30ml) followed by drying at 100°C for 6h and then it was reused for the oxidation of benzyl alcohol to benzaldehyde. The second and third run according to this procedure showed little decrease in the reaction yield (Table 3).

In conclusion, clay supported manganeses (II) chloride can be used as an efficient and recoverable catalyst for controlled oxidation of benzylic alcohols to their carbonyl compounds, high yields, easy work-up and reusability of the catalyst are the most significant aspects of this method.

Experimental

Chemicals were purchased from Merck, Fluka and Aldrich chemical companies and were used without further purification.

All products are known compounds and were identified by their IR and ^{1}H NMR spectra.

Catalyst preparation: Manganese (II) chloride (4 g) was added to deionised water (500 ml) and the mixture was stirred vigorously in the presence of air for 10 min until complete dissolution of the manganeses (II) chloride. Clay (montmorillonite K10) (40 g) was then added. The resulting suspension was refluxed for 24 h then the solvent was evaporated and the resulting dry solid was placed in an oven at 100 for 12 h.

Typical procedure for the oxidation of benzyl alcohol: Benzyl alcohol (1 mmol) was dissolved in acetonitrile (15 ml), then the catalysts (0.25 g) and hydrogen peroxide (50 mmol) were added and the mixture was refluxed with stirring. The progress of the reaction was monitored by TLC (ethyl acetate in petroleum ether), then mixture was filtered and the residue was washed with dichloromethane (2×10 ml). The combined filtrates were evaporated, and the residue was passed through a short column of silica gel [eluent: petroleumether, ethyl acetate (4:1)] to obtain pure benzaldehyde.

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Table 2 Effect of catalyst in reaction (time/yield)

Substrate	Reaction condition	Time/h	Yield/%
$C_6H_5CH_2OH$	A	2	91
$C_6H_5CH_2OH$	B	4	30
$C_6H_5CH_2OH$	C	4	35

A: typical procedure.
B: typical procedure without catalyst.
C: typical procedure with clay instead of catalyst.

Table 3 Reusability of catalysts

Experimental trail	Substrate	Product	Yield/%^{a}
1st	$C_6H_5CH_2OH$	C_6H_5CHO	91
2nd	$C_6H_5CH_2OH$	C_6H_5CHO	89
3rd	$C_6H_5CH_2OH$	C_6H_5CHO	86

^{a}All reactions were carried out according to the typical procedure.

References

1 B.M. Trost, I. Fleming and M.F. Semmelhack, In *Comprehensive Organic Synthesis*, Pergamon, New York, 1991, p.7.
2 R.C. Larock, *Comprehensive Organic Transformations*, Wiley, New York, 1999, p.1234.
3 E.J. Corey and G. Schmidt, *Tetrahedron Lett.*,1979, 399.
4 A.J. Mancuso and D. Swern, *Synthesis*, 1981, 165.
5 A.J. De, *Scient. Ind. Res.*, 1982, **41**, 484.
6 D.B. Dess and J.C. Martin, *J. Org. Chem.*, 1983, **48,** 4155.
7 J.J. Abbot, *Mol. Catal.*, 1984, **26,** 117.
8 R.A. Sheldon, I.W.C.E. Arends and A. Dijkman, *Catal. Today*, 2000, **57**, 157.
9 R.A. Sheldon and J.K. Kochi, *Metal Catalyzed Oxidation of Organic* Compounds, Academic Press, New York, 1981.
10 M. Hudlicky, *Oxidation in Organic Chemistry*, ACS, Washington DC, 1990.
11 Z. Tyeklar and K.D. Karlin, *Acct Chem. Res*, 1989, **22,** 241.
12 C.G.M. Gavino and P. Bruno, *Reactive Polymers*, 1990, **12,** 219.
13 E.R.M. Alami and G. Cahiez, *Tetrahedron Lett.*, 1997, **38**, 14397.
14 A. Corma, V. Fomes, S. Iborra, M. Mifusd and M. Renz, *J. Catalysis*, 2004, **221,** 67.
15 A.O. Terentev, A.V. Kutkin, M.M. Platonov, Y.N. Ogibin and G.I. Nikishin, *Tetrahedron Lett.*, 2003, **44,** 7359.
16 E.I. Ochiai, *Nucl Chem Lett.*, 1973, **9**, 987.
17 P. Capdevielle and M. Maumy, *Tetrahedron Lett.*, 1990, **31**, 3891.
18 L.M. Gandia, M.A. Viecente and A.M. Gil, *Applied Catalysis*, 2002, **38**, 295.
19 H. Einaga and S. Futamura, *J. Catalysis*, 2004, **227**, 304.
20 L.M. Gandiam, M.A. Viecente and A. Gil, *Appl. Catalysis B: Environ.*, 2002, **38**, 295.
21 P. Fabrizioli, T, Burgi and A. Baiker, *J. Catalysis*, 2002, **207**, 88.
22 G.V. Ambulgekar, S.D. Samant and A.B. Pandit, *Ultrasonics Sonochemistry*, 2005, **12**, 85.
23 A. Shabani, P. Mirzaei, S. Naderi and G.L. Donald, *Tetrahedron*, 2004, in press.
24 L. Ji-Dong, W. Miao, Z. Li-Yun and F. Zhi-Gang, *Catalysis Commun.*, 2003, **4**, 647.
25 M.H. Schroth, M. Oostron, T.W. Wietsma and J.D. Istok, *J. Contam. Hydrol.*, 2001, **50**, 79.
26 G.H. Ponser, *Angew Chem*, 1978, **90**, 527 and *Angew Chem. Int. Ed. Engl.*, 1978, **17**, 478.
27 A. Mckillop and D.W. Young, *Synthesis*, 1979, **401**, 481.
28 M. Balogh and P. Laszlo, *Chemistry Using Clays*, Springer-Verlag, Berlin, 1993.
29 O. Sieskind and P. Alberch, *Tetrahedron Lett.*, 1993, **34**, 1197.