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Zeolite Supported Permanganate : An Efficient Catalyst for Selective Oxidation of Enamines, Alkylarenes and Unsaturated Alcohols.

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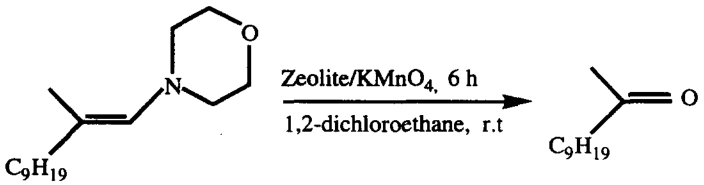
Abstract : Potassium permanganate supported on zeolite can be used for the selective oxidation of various enamines, alkylarenes and unsaturated alcohols to the corresponding ketones, in good yield. Arenes were selectively oxidized at the benzylic position. If the benzylic carbon is secondary, ketones are obtained, and alcohols are produced if the benzylic position is tertiary. In contrast unsaturated secondary alcohols selectively undergo oxidation to the corresponding olefinic ketones without affecting the carbon-carbon double bonds. © 1997 Elsevier Science Ltd.

Over the last two decades the use of zeolite, an environmentally attractive solid catalyst, in synthetic chemistry has become more and more popular due to their characteristic properties such as shape selectivity, thermal stability, acidic and basic nature coupled with the ease of set-up and work-up procedure.[1] Eventhough potassium permanganate is a powerful oxidizing agent, its utility in organic synthesis has been severely limited by solubility problems.[2] Studies by Lee and others have shown that the adsorption of potassium permanganate on to solid support changes the reactivity and selectivity in various reactions.[3]

In this paper, we wish to report a mild and convenient heterogeneous catalytic methodology for the selective oxidation of enamines, arenes and unsaturated alcohols using zeolite supported potassium permanganate. The zeolites were synthesized according to the reported procedure.[4] Potassium permanganate was impregnated on to the zeolite and analyzed as reported elsewhere.[5] The amount of potassium permanganate loaded on to the zeolite used for the present investigation was 0.25 mmol/g. These zeolite supported potassium permanganate reagents showed remarkable selectivity towards the oxidation of enamines, arenes and unsaturated alcohols.

A number of different reagents have been developed for the oxidative cleavage of the enamines double bond in the past such as sodium periodate,[6] sodium dichromate in acid,[7] nitrous acid,[8] and molecular oxygen with copper ion systems.[9] The general procedure for the oxidative cleavage of various enamines to the corresponding ketones over zeolite supported potassium permanganate was as follows. The enamine (1 mmol)



dissolved in 1,2-dichloroethane (50 mL) was added to $KMnO_4$/Zeolite reagent (5 g) and stirred for 6 h in a round bottom flask at room temperature. After 6 h, the reaction mixture was filtered and the zeolite was washed with methanol (3 x 25 mL). Removel of solvent from the combined filtrate furnished the crude material, which was further purified by column chromatography using hexane/ethyl acetate resulted the corresponding ketone in good yield. The results with other enamines and zeolites are summarized in Table 1.

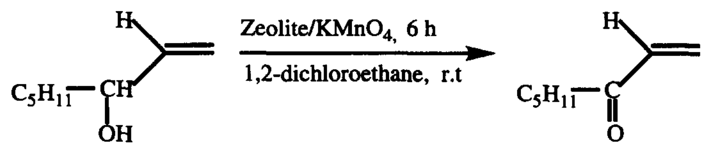
Table 1 Zeolite supported permanganate conversion of enamines and unsaturated alcohols. t = 6 h ; T = r.t .

Entry	Substrates	Products [a]	Yield [b]	
			Y-Zeolite	Zeolite beta
1	1-(4-morpholino)-2-phenyl propene	acetophenone	95 (88)	92
2	1-(4-morpholino)-2,2-diphenyl ethene	benzophenone	81 (85)	77
3	2-ethyl-1-(4-morpholino)-1-butene	3-pentanone	84 (76)	80
4	1-morpholino cyclohexene	cyclohexanone	91	88
5	2-methyl-1-(4-morpholino)-1-pentene	2-pentanone	93	90
6	1-(4-morpholino)-2-methyl-1-undecene	2-undecanone	94	91
7	1-octen-3-ol	1-octene-3-one	83 (89)	87
8	1-hepten-3-ol	1-hepten-3-one	85 (80)	81
9	1-nonen-3-ol	1-nonen-3-one	89 (90)	85
10	1-phenyl-1-buten-3-ol	1-phenyl-1-buten-3-one	78 (81)	76

[a] Products were characterized by comparing melting points, NMR, IR spectra with authentic compounds. [b] Isolated pure yields and the yields with commercial Y-Zeolite are shown in parentheses.

In a control experiment, 1-morpholino cyclohexene (1 mmol) dissolved in 50 mL of 1,2-dichloroethane was added to stirred mixture of $KMnO_4$ (1 mmol) and unsupported Y-Zeolite (5 g) in a round bottom flask and continued the stirring for another 6 h at room temperature. The yield of cyclohexanone obtained from the above reaction was only 38%.

Another example for the remarkable selectivity of $KMnO_4$/Zeolite reagent is in the case of oxidation of unsaturated secondary alcohols to the corresponding ketones without affecting the carbon-carbon double bond. In solution $KMnO_4$ oxidizes unsaturated alcohols preferentially at the double bond, whereas $KMnO_4$/Zeolite reagent converts the unsaturated secondary alcohols to the corresponding olefinic ketones under mild condition



in good yield.[10] Regen *et al* had reported the oxidation of various alcohols over molecular sieves supported potassium permanganate and clay in benzene at 70 °C.[5] The procedure for the oxidation of unsaturated alcohol to olefinic ketone was same as in the case of enamines and the results are listed in Table 1.

Potassium permanganate adsorbed on zeolite can be used to selectively oxidize aromatics at the benzylic position. This heterogeneous permanganate oxidation is a mild and simple procedure. Diphenyl methane (1 mmol) was dissolved in 1,2-dichloroethane (DCE, 50mL) in a round bottom flask and $KMnO_4$/Zeolite reagent (4 g) was added to the reaction mixture under stirring. The progress of the reaction was monitored by TLC. After 4 days, it was filtered, and the zeolite was washed with methanol (3 x 25 mL). The removal of solvent furnished benzophenone in 98% yield as the only product. This technique has been successfully applied to the selective oxidation of several other benzylic compounds to the corresponding ketones/alcohols and the results are illustrated in Table 2. If the benzylic position is secondary, ketones are formed in high yields, whereas alcohols are produced if the benzylic carbon is tertiary.

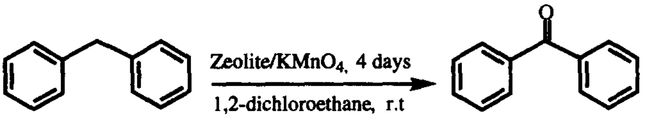
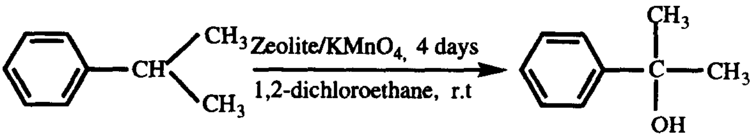


Table 2 Comparison of the yield of ketones/alcohols over various zeolite Supported Permanganate.t = 4 days ; T = r.t .

Entry	Substrates	Products [a]	Yield[b]	
			Y-Zeolite	Zeolite beta
1	diphenyl methane	benzophenone	98 (94)	94
2	fluorene	9-fluorenone	90 (92)	85
3	xanthene	xanthone	78 (74)	80
4	9,10-dihydro anthracene	anthraquinone	72 (77)	69
5	ethylbenzene	acetophenone	93 (86)	91
6	propylbenzene	propiophenone	90	92
7	cumene	2-phenyl-2-propanol	88	85
8	Sec.butylbenzene	2-phenyl-2-butanol	84	82

[a] All ketones and alcohols were characterized by comparing melting points, NMR, IR spectra with authentic compounds. [b] Isolated pure yields and the yields with commercial Y-Zeolite are shown in parentheses.



We have thus developed a mild heterogeneous catalytic method for the oxidation of various organic compounds using zeolite supported potassium permanganate reagent. The major advantages of this method over the corresponding homogeneous reactions are that the products can be easily isolated by filtration followed by removal of solvent, exhibit high selectivity for oxidation, lack of corrosiveness and other environmental hazards, ease of set-up and handling, regeneration and reuse of zeolite after activation.

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