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Sonochemical Activation of Manganese Dioxide

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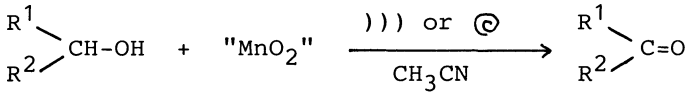
Ultrasonic irradiation accelerated the oxidation of alcohols to carbonyl compounds with 99% crystalline manganese dioxide. The preparation of sonochemically activated manganese dioxide was developed.

Activated manganese dioxide is a useful oxidant for many oxidative transformations such as a selective dehydrogenation.[1] However, current methods for preparing or activating this material are experimentally so tedious. We have been studying on the accerelation of solid-liquid heterogeneous reactions by the irradiation of ultrasound.[2] In this communication we report the sonochemical accerelation of manganese dioxide oxidation of alcohols and the new preparation of the sonochemically activated manganese dioxide.



It is well known that crystalline manganese dioxide is a poor oxidant. Figure 1 shows that commercially available 99% MnO_2 crystals (purchased from Nacalai Tesque, INC., Japan) are inactive toward the oxidation of cinnamyl alcohol to cinnamaldehyde under the stirring condition (a). However, the irradiation of ultrasound by using a ultrasonic cleaning bath allows this reaction to be performed; in 45 h the oxidation was completed (b). Sigmoidal reaction profile was observed. In contrast, when 99% MnO_2 was irradiated by ultrasound in CH_3CN for 12 h before the addition of cinnamyl alcohol, irradiated MnO_2 showed the oxidizing ability under the stirring conditions (c). In this case, the additional ultrasonic irradiation (d) accelerated the reaction.

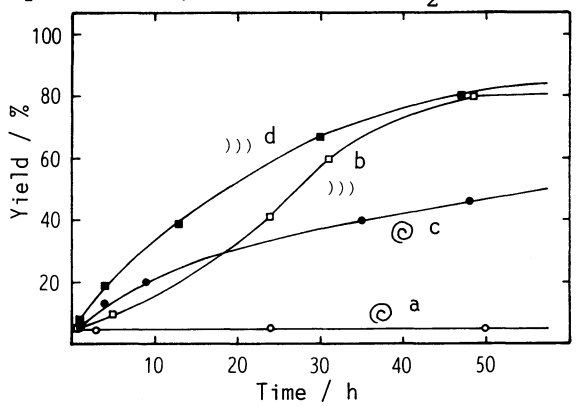


Fig. 1. Reaction profile of cinnamyl alcohol oxidation with 99% MnO_2 under the stirring and ultrasonic irradiation conditions.

Thus we examined the activation of 99% MnO_2 crystals by irradiation of ultrasound under several different conditions. Table 1 shows the comparative reactivities of ultrasonically treated MnO_2s including

mortar-ground 99% MnO_2 toward the oxidation of cinnamyl alcohol. Mechanical pulverization (MnO_2-1), sonomechanical pulverization in benzene (MnO_2-2), and the pulverization by the powerful but short time irradiation of ultrasound by using a cell distruptor (MnO_2-3) could not activate 99% MnO_2. MnO_2-4, -5, and -6 were most active. It seems that pH conditions do not obviously affect the reactivity, though the reactivity slightly increased in the order of MnO_2-4 (acidic), MnO_2-5 (neutral), and MnO_2-6 (alkaline).

Table 1 summarizes the results of the oxidations of several alcohols with MnO_2-5, the simplest sonochemically activated MnO_2 under the neutral conditions. Although the activity of MnO_2-5 was milder than that of the material described by Attenburrow and coworkers,[3] allylic alcohols and benzhydrol were oxidized with MnO_2-5 to corresponding carbonyl compounds in high yields.

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Table 1. Oxidation of Alcohols with MnO_2[a]

Alcohol	MnO_2[d]	))) [b] (17 °C, 8 h) Yield/%	@ [c] (17 °C, 8 h) Yield/%	@ [c] (50 °C, 0.5 h) Yield/%
Cinnamyl alcohol	1			0
	2			1
	3			9
	4			87
	5	99	100	97
	6			100
Geraniol	5	86	100	87
$PhCH_2OH$	5	61	40	49
Ph(Me)CHOH	5	22	17	46
Ph_2CHOH	5	90	100	100
2-Octanol	5	11	2	5
1-Octanol	5	1	2	5

a) See Ref. 4. b) The reaction was carried out under the irradiation of ultrasound. The temperature was maintained on 17 °C by circulating water through the cleaning bath. c) The reaction was carried out with stirring. d) See Ref. 5.

References

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3) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, J. Chem. Soc., 1952, 1094.
4) Typical reaction was as follows : A mixture of cinnamyl alcohol (0.1 g) and "MnO_2" (2.0 g) in CH_3CN (5 mL) containing diphenyl as an internal standard for GC analysis was stirred at 50 °C for 0.5 h. After dilution of the reation mixture with wet ether and centrifugation, the organic layer was analyzed quantitatatively by GC.
5) MnO_2-1 : ground by a mortar and a pestle. MnO_2-2-6 : irradiated ultrasound under following conditions; -2 : in benzene for 12 h by the cleaning bath, -3 : in water for 1 h by a cell distruptor, -4 : in 0.1 M HNO_3 for 12 h by the cleaning bath, -5 : in water for 12 h by the cleaning bath, -6 : in 0.1 M NaOH for 12 h by the cleaning bath. After the irradiation, MnO_2 was thoroughly washed with water and dried at 100 °C/0.1 mmHg for 12 h. The particle size employed was over 200 mesh, that is smaller than 0.075 mm.

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