

Selective Aerobic Oxidation of Alcohols by Using Manganese Oxide Nanoparticles as an Efficient Heterogeneous Catalyst

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Abstract: Manganese oxide (Mn₃O₄) nanoparticles have been successfully innovated to be efficient catalysts not only for the aerobic oxidation of various alcohols to aldehydes or ketones, but also for the selective aerobic oxidation of mixed alcohols.

Keywords: alcohols; heterogeneous catalysts; manganese oxide; nanoparticles; oxidation

The oxidation of alcohols to the corresponding carbonyl products is one of the most fundamental reactions in organic chemistry.^[1] A variety of methods has been reported for the selective oxidation of alcohols. However, most of them have to be performed with a stoichiometric amount of toxic or expensive oxidants.^[2] From the environmental and economic points of view, the aerobic oxidation of alcohols has attracted considerable attention during the past decade,^[3] among which the development of efficient and recyclable heterogeneous catalysts is of particular interest. Several excellent heterogeneous catalysts have been reported,^[4] most of these catalysts involved expensive noble metals as the components. Innovating cheap transition metal-based heterogeneous catalytic systems with simple manipulation for this important transformation is thus highly desirable but challenging. Among these systems, there are few reports on the use of Mn species as catalysts for the oxidation of alcohols.^[5] Herein, we report that Mn₃O₄ nanoparticles catalyzed the aerobic oxidation of various alcohols to corresponding aldehydes or ketones with high

efficiency and very good recyclability. Moreover, Mn₃O₄ nanoparticles exhibited very high selectivity in the aerobic oxidation of mixed alcohols.

Mn₃O₄ nanoparticles were prepared according to a modified literature procedure.^[6] Selective-area electron diffraction (ED) and X-ray diffraction (XRD) patterns (see Figure S1d and Figure S3a in the Supporting Information) confirm the phase of as-synthesized nanoparticles to be tetragonal Mn₃O₄ (JCPDS 24-0734). Afterwards, the as-synthesized Mn₃O₄ nanoparticles and other Mn-based compounds were examined as potential catalysts for the aerobic oxidation of benzyl alcohol in CH₃CN at 80 °C. As shown in Table 1, Mn₃O₄ nanoparticles gave a better result after reaction for 8 h (Table 1, entry 1) whereas commercial Mn₃O₄ and other manganese oxides showed poorer catalytic activities (Table 1, entries 2–4). Manganese salts, such as MnCl₂·4H₂O and Mn(OAc)₂·4H₂O, could only give the corresponding product with the yields of 20% and 25%, respectively (Table 1, entries 5 and 6). Without catalyst the reaction hardly occurred (Table 1, entry 7). We also prepared octahedral Mn₃O₄ nanocrystals^[7] and examined them in the reaction. Our experimental results indicated that octahedral Mn₃O₄ nanoparticles showed lower catalytic activity than polyhedral Mn₃O₄ nanoparticles (Table 1, entry 8). The higher activity of polyhedral Mn₃O₄ nanoparticles could be attributed to their high specific surface area since the catalyst can expose a large number of active sites.

Inspired by these intriguing results, we optimized the reaction conditions further. After a series of experiments, DMF proved to be the best solvent, affording benzaldehyde with an isolated yield of 84%

Table 1. Aerobic oxidation of benzyl alcohol catalyzed by different Mn-based catalysts.^[a]

PhCH ₂ OH 1a		Mn catalyst CH ₃ CN, 80 °C	PhCHO 2a	
Entry	Catalyst	Conv. [%] ^[b]	Yield [%] ^[b]	
1	Mn ₃ O ₄ nanoparticles	65	65	
2 ^[c]	Mn ₃ O ₄	48	48	
3	Mn ₂ O ₃	46	46	
4	MnO ₂	40	40	
5	MnCl ₂ ·4 H ₂ O	20	20	
6	Mn(OAc) ₂ ·4 H ₂ O	29	29	
7	-	<5	<5	
8	Mn ₃ O ₄ octahedrons	15	15	

^[a] Reaction conditions: benzyl alcohol (1 mmol) and 5 mol% Mn catalyst in CH₃CN at 80 °C for 8 h.

^[b] Determined by GC-MS analysis.

^[c] Commercial Mn₃O₄.

(Table 2, entry 3) in the presence of 5 mol% catalyst. When the catalyst loading was increased to 10 mol%, benzaldehyde can be obtained with an isolated yield of 96% after reaction for 4 h (Table 2, entries 8–10). Even with a very low catalyst loading (1 mol%), a 93% yield of benzaldehyde could still be obtained after prolonging the reaction time to 18 h (Table 2, entry 11). More importantly, an almost equal yield of benzaldehyde was obtained when the oxidant air was replaced with an oxygen balloon under the same condition (Table 2, entry 12). Thus, the optimum reaction conditions were obtained as follows: 10 mol% Mn₃O₄ nanoparticles as catalyst, DMF as solvent, air as the oxidation and the reaction temperature at 80 °C for 4 h.

With the optimal conditions in hand, the generality of alcohol substrates was examined. As shown in Table 3, both electron-rich and electron-poor benzylic alcohols could be efficiently oxidized to aldehydes. Moreover, the over-oxidized carboxylic acid were not observed even when the reaction time was prolonged (Table 3, entries 1–10). As for the oxidation of alcohols containing heteroatoms which are hardly amenable to catalyzed reaction, the Mn₃O₄ nanoparticles also exhibit quite high catalytic activity (Table 3, entry 10). When a primary aliphatic alcohol was employed as the reaction substrate, the oxidation can be carried out smoothly to afford the corresponding product with good yield after prolonging the reaction

Table 2. Optimization of the reaction conditions for oxidizing benzyl alcohol to benzaldehyde.^[a]

PhCH ₂ OH 1a		Mn ₃ O ₄ nanoparticles solvent, 80 °C	PhCHO 2a	
Entry	Solvent	Yield [%] ^[b]		
1	ClCH ₂ CH ₂ Cl	21		
2	CH ₃ CN	65		
3	DMF	84		
4	CHCl ₃	40		
5	EtOH	48		
6	toluene	20		
7	1,4-dioxane	17		
8 ^[c]	DMF	96		
9 ^[d]	DMF	85		
10 ^[e]	DMF	82		
11 ^[f]	DMF	93		
12 ^[g]	DMF	96		

^[a] Reaction conditions: benzyl alcohol (1 mmol), 5 mol% Mn₃O₄ nanoparticles, 80 °C, 8 h.

^[b] Isolated yield.

^[c] 10 mol% Mn₃O₄ nanoparticles, 4 h.

^[d] 15 mol% Mn₃O₄ nanoparticles, 4 h.

^[e] 20 mol% Mn₃O₄ nanoparticles, 4 h.

^[f] 1 mol% Mn₃O₄ nanoparticles, 18 h.

^[g] An O₂ balloon was employed.

time a little (Tables 3, entry 11). An allylic alcohol, such as cinnamyl alcohol, could be selectively oxidized to cinnamaldehyde and no epoxidized product was detected (Tables 3, entry 12). Secondary alcohols could also be efficiently oxidized to the corresponding ketones although a prolonged reaction time was required (Tables 3, entries 13–15). It is noteworthy that this reaction can be scaled up to a gram scale, giving the product with 93% isolated yield (Table 3, entry 16). A high turnover frequency (TOF) of 1678 h⁻¹ at 80 °C was achieved in the initial 30 min (see the Supporting Information). The TOF of the reaction catalyzed by Mn₃O₄ nanoparticles is higher than that of the Mn oxide catalysts reported previously,^[8] which could be attributed to its high specific surface area.

Besides the high catalytic activity, these Mn₃O₄ nanoparticles exhibited good catalytic selectivity for different alcohols in the aerobic oxidation (Table 4).

Table 3. Oxidation of various alcohols catalyzed by Mn₃O₄ nanoparticles.^[a]

$\text{R}-\text{CH}(\text{OH})-\text{R}' \xrightarrow[\text{DMF, 80 }^\circ\text{C}]{\text{Mn}_3\text{O}_4 \text{ nanoparticles}} \text{R}-\text{C}(=\text{O})-\text{R}'$				
Entry	R	R'	2	Conv. ^[b] /Yield [%] ^[c]
1	2-CH ₃ OC ₆ H ₄	H	2b	100/95
2	4-CH ₃ OC ₆ H ₄	H	2c	100/91
3	2-CH ₃ C ₆ H ₄	H	2d	100/92
4	4-CH ₃ C ₆ H ₄	H	2e	100/93
5	2-ClC ₆ H ₄	H	2f	100/95
6	4-ClC ₆ H ₄	H	2g	100/93
7	2-NO ₂ C ₆ H ₄	H	2h	96/90
8	4-NO ₂ C ₆ H ₄	H	2i	100/94
9	2,4,6-(CH ₃) ₃ C ₆ H ₂	H	2j	88/80
10	4-CF ₃ C ₆ H ₄	H	2k	100/92
11	2-Py	H	2l	95/90
12 ^[d]	CH ₃ (CH ₂) ₅	H	2m	80/75
13 ^[e]	C ₆ H ₅ CH=CH	H	2n	100/92
14 ^[f]	cyclohexanol	-	2o	87/80
15 ^[f]	C ₆ H ₅	CH ₃	2p	90/84
16 ^[f]	C ₆ H ₅	C ₆ H ₅	2q	87/80
17 ^[g]	C ₆ H ₅	H	2a	100/93

^[a] Reaction conditions: alcohol (1 mmol), 10 mol% Mn₃O₄ nanoparticles, DMF (0.5 mL), 80 °C, 4 h.

^[b] Determined by GC-MS analysis.

^[c] Isolated yield.

^[d] 24 h.

^[e] 2 h.

^[f] 12 h.

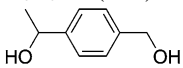
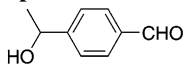
^[g] Benzyl alcohol (10 mmol), 10 mol% of Mn₃O₄ nanoparticles, 80 °C, 18 h.

When a mixture of 4-methylbenzyl alcohol and 1-phenylethanol was employed as the reaction substrate, 4-methylbenzyl alcohol was fully converted to 4-methylbenzaldehyde with 92% isolated yield whereas only a 5% isolated yield of acetophenone was obtained from the oxidation of 1-phenylethanol (Table 4, entry 1). When a mixture of 4-methylbenzyl alcohol and cinnamyl alcohol was oxidized, cinnamyl alcohol was selectively converted into cinnamaldehyde with an isolated yield of 83% (Table 4, entry 2)

while 4-methylbenzaldehyde was obtained with a lower yield of 12%. When cinnamyl alcohol coexisting with secondary alcohols was used as the reactant, cinnamyl alcohol was selectively oxidized to the corresponding aldehyde and very low conversion of the secondary alcohol was observed (Table 4, entry 3). For the competition between 4-methylbenzyl alcohol and 1-heptanol, an isolated yield of 86% for 4-methylbenzaldehyde was achieved but no oxidation product of 1-heptanol was observed (Table 4, entry 4). As for the mixture of 1-phenylethanol and 1-heptanol, 1-phenylethanol was selectively oxidized and 1-heptanol remained unconverted (Table 4, entry 5). When the primary and the secondary benzylic alcohol sites coexisted in the same molecule, only the primary alcohol was selectively oxidized (Table 4, entry 6). Thus the catalytic selectivity of these polyhedral Mn₃O₄ nanoparticles towards alcohols in the aerobic oxidation could be deduced to the order as below: allylic primary alcohols > benzylic primary alcohols > benzylic secondary alcohols > aliphatic alcohols. In contrast, when commercial Mn₃O₄ was employed as the catalyst for this oxidation, no catalytic selectivity was observed (see Table S1 in the Supporting Information). Similarly, no catalytic selectivity was detected either when pyridinium chlorochromate (PCC) was used as a catalyst in this oxidation (see Table S2 in the Supporting Information). These results clearly demonstrate the advantage of our polyhedral Mn₃O₄ nanoparticles in the selective aerobic oxidation of alcohols.

The catalytic selectivity perhaps originated from the selective chemisorption of alcohols on the surface of the Mn₃O₄ nanoparticles. The infrared spectrum of Mn₃O₄ nanoparticles exposed to the of 1-heptanol and 1-phenylethanol (purple line in Figure S7 in the Supporting Information) was more similar to that exposed to 1-phenylethanol than to that exposed to 1-heptanol, which implied that the chemisorption of 1-phenylethanol was stronger than that of 1-heptanol. This was consistent with the selective aerobic oxidation of 1-phenylethanol in the mixture of 1-phenylethanol and 1-heptanol (Table 4, entry 5). Similarly, the IR spectra of Mn₃O₄ nanoparticles exposed to individual 4-methylbenzyl alcohol (blue line in Figure S8 in the Supporting Information), individual cinnamyl alcohol (red line in Figure S8 in the Supporting Information) and the mixture of 4-methylbenzyl alcohol and cinnamyl alcohol (purple line in Figure S2 in the Supporting Information) demonstrated the selective chemisorption of cinnamyl alcohol, agreeing with the selective aerobic oxidation of cinnamyl alcohol in the mixture of 4-methylbenzyl alcohol and cinnamyl alcohol (Table 4, entry 2). Therefore, the Mn₃O₄ nanoparticles exhibited a high selectivity for the chemisorption of mixed alcohols, leading to a high selectivity for the subsequent aerobic oxidation of mixed alcohols.

Table 4. Selective aerobic oxidation of mixed alcohols catalyzed by Mn₃O₄ nanoparticles.^[a]

Entry	Alcohols	Products	Yield [%] ^[b]
1	4-CH ₃ C ₆ H ₄ CH ₂ OH + C ₆ H ₅ CH(OH)CH ₃	2e + 2p	92 + 5
2 ^[c]	4-CH ₃ C ₆ H ₄ CH ₂ OH + C ₆ H ₅ CH=CHCH ₂ OH	2e + 2n	12 + 83
3	C ₆ H ₅ CH=CHCH ₂ OH + C ₆ H ₅ CH(OH)CH ₃	2n + 2p	87 + 3
4	4-CH ₃ C ₆ H ₄ CH ₂ OH + CH ₃ (CH ₂) ₅ CH ₂ OH	2e + 2m	86 + n.r.
5 ^[d]	C ₆ H ₅ CH(OH)CH ₃ + CH ₃ (CH ₂) ₅ CH ₂ OH	2p + 2o	50 + n.r.
6			87

^[a] 1 mmol each of both alcohols were treated with 10 mol% Mn₃O₄ nanoparticles in DMF (0.5 mL) at 80 °C for 4 h.

^[b] Isolated yield.

^[c] 2 h.

^[d] 8 h.

Table 5. Reuse of Mn₃O₄ nanoparticles.^[a]

Run	Mn ₃ O ₄ nanoparticles							
	1st	2nd	3rd	4th	5th	6th	7th	11th
Yield [%] ^[b]	96	96	96	96	95	95	95	94

^[a] Reaction conditions: benzyl alcohol (1 mmol), 10 mol% Mn₃O₄ nanoparticles, 80 °C, 4 h.

^[b] Isolated yield.

hols. These results provide a new vision on the catalytic oxidation of alcohols.

This Mn₃O₄ nanoparticles catalyst was not only highly active and selective but also robust in the aerobic oxidation of alcohols. The recyclability of Mn₃O₄ nanoparticles catalyst was excellent. Its catalytic activity in the aerobic oxidation of benzyl alcohol was not reduced even after 11 cycles of catalytic activity evaluation (Table 5). The TEM image (Figure 1, b), XRD pattern (Figure S3b in the Supporting Information), and Mn 2p XPS spectrum (Figure S4 in the Supporting Information) of polyhedral Mn₃O₄ nanoparticles after the 10th catalytic activity evaluation experiment

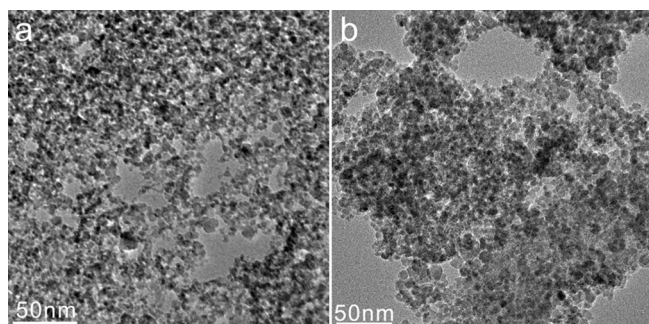


Figure 1. TEM images of (a) fresh polyhedral Mn₃O₄ nanoparticles and (b) Mn₃O₄ nanoparticles after the tenth cycle of use.

were similar to those of as-synthesized Mn₃O₄ nanoparticles, demonstrating that the structure of the Mn₃O₄ nanoparticles changed little after the recycling reactions.

In summary, we have successfully developed a new catalytic system for the selective aerobic oxidation of alcohols by using polyhedral Mn₃O₄ nanoparticles as a cheap, efficient and re-useable heterogeneous catalyst. Benzylic alcohols, allylic alcohols and even aliphatic alcohols could be oxidized to the corresponding aldehydes or ketones efficiently without the formation of over-oxidized carboxylic acids. Moreover, the Mn₃O₄ nanoparticles catalyst exhibited high selectivity and excellent recyclability in the chemisorption of mixed alcohols. These results open up a door for the innovation of economic, green and efficient heterogeneous catalysts for important organic reactions.

Experimental Section

General Procedure

10 mol% Mn₃O₄ nanoparticles was added into a DMF (0.5 mL) solution containing the alcohol (1 mmol). The mixture was stirred at 80 °C for 4 h under an air atmosphere. After completion of the reaction, the catalyst was separated by filtration. Then the solution was extracted with ethyl acetate (20 mL × 3). The combined layer was washed sequentially with water and brine, and then dried over anhydrous Na₂SO₄. The organic phase was concentrated under vacuum and purified with column chromatography on silica gel to afford the pure product.

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