

# A new magnetic nanoparticle-supported Schiff base complex of manganese: an efficient and recyclable catalyst for selective oxidation of alcohols

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A new magnetic nanoparticle-supported Schiff base complex of manganese was prepared via the copper-catalyzed 'click' reaction of an aminosilylidene manganese complex bearing terminal alkynyl with azide-functionalized shell-core magnetic nanoparticles. The as-prepared catalyst was applied in the oxidation of alcohols to corresponding aldehydes or ketones with high yield and selectivity when the reaction was carried out in dimethylsulfoxide at 110°C for 4 h using *tert*-butyl hydroperoxide as oxidant. Moreover, the catalyst can be easily separated from the reaction mixture using an external magnet and reused five times with no significant loss of catalytic activity. Copyright © 2016 John Wiley & Sons, Ltd.

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**Keywords:** manganese Schiff base; heterogeneous catalyst; oxidation; recycling; magnetic nanoparticle

## Introduction

The oxidation of alcohols to their corresponding carbonyl compounds is a very important reaction for the synthesis of drugs and spices.<sup>[1]</sup> There are many oxidizing reagents and catalysts for the oxidation of alcohols.<sup>[2]</sup> Traditionally this reaction is carried out with a stoichiometric amount of oxidants such as pyridinium chlorochromate and Dess–Martin periodinane, but these reagents are toxic and produce large amounts of hazardous waste causing serious environmental problems.<sup>[3]</sup> Thus, from the viewpoints of environment and economy, it is necessary to develop highly active, selective and recyclable catalysts.<sup>[4]</sup>

With the advantages of low cost, ease of preparation and chemical and thermal stability, transition metal Schiff base complexes have attracted extensive attention. Tong *et al.* reported chitosan–Schiff base Co(II) and Pd(II) complexes for aerobic oxidation of cyclohexane.<sup>[5]</sup> Gava *et al.* developed an efficient copper complex catalyst for C–H bond functionalization of methane.<sup>[6]</sup> Hanhan *et al.* prepared binuclear Pd(II) complex catalysts for Suzuki coupling in water.<sup>[7]</sup> Meanwhile, there are many transition metal Schiff base complexes, such as Fe,<sup>[8]</sup> V,<sup>[9]</sup> Cu,<sup>[10]</sup> Co,<sup>[11]</sup> Ag,<sup>[12]</sup> Pd<sup>[12]</sup> and Mn,<sup>[13]</sup> that are widely used in catalytic oxidation of alcohols. Although these homogeneous transition metal complexes provide satisfying outcomes in the oxidation of alcohols to corresponding carbonyl compounds, they are still more or less associated with problems including contamination of reaction products and difficulty of separation.<sup>[14]</sup> Consequently, the heterogenization of homogeneous catalysts through covalently immobilizing on inert supports has attracted enormous interest, since the immobilized complexes can be easily separated from the product and effectively reused.<sup>[15]</sup> There are many appropriate organic and inorganic supports, such as microporous polymers,<sup>[16]</sup> mesoporous silica,<sup>[17]</sup> metal oxides<sup>[18]</sup> and carbon materials.<sup>[19]</sup>

Because of the advantages of high surface area and low porosity, nanoparticles have recently been considered as excellent supports for homogeneous catalysts.<sup>[20]</sup> However, they still have the drawbacks of inconvenient separation, recovery and obvious leaching owing to their colloidal nature. Application of magnetic nanoparticles (MNPs) as supports is a promising way to solve these problems, because MNPs can be simply and quantitatively recovered from the reaction system using a magnet.

Recently, we have synthesized a MNP-supported dual acidic ionic liquid and MNP-supported palladium catalyst and used them in multicomponent condensation and Suzuki–Miyaura coupling reactions, respectively.<sup>[21,22]</sup> In continuation of the research on MNP-supported catalysts, herein we report the synthesis of a new MNP-supported manganese catalyst (Mn@MNP) and its application in alcohol oxidation reactions. Mn@MNP was prepared via the copper-catalyzed 'click' reaction of an aminosilylidene manganese complex bearing terminal alkynyl with azide-functionalized silica-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles (1).

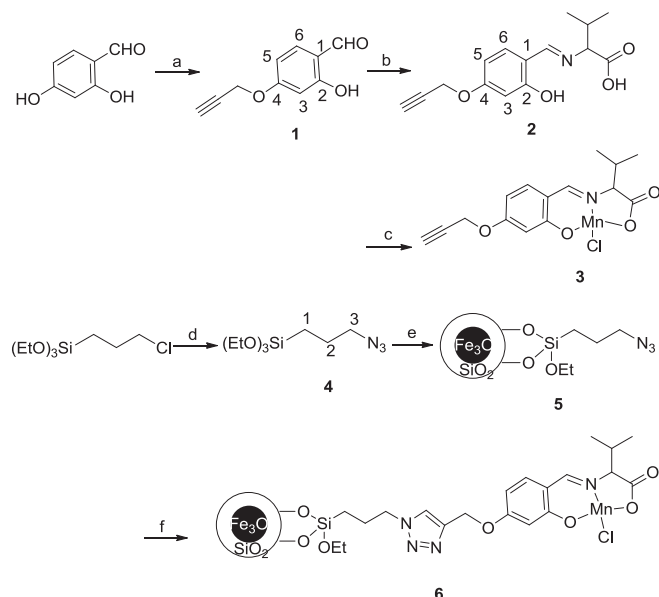
## Experimental

### General remarks

All of the reagents and solvents are commercially available and were used without further purification. Transmission electron microscopy (TEM) images were obtained using a JEM-2100 instrument. Fourier transform infrared (FT-IR) spectra were obtained with a Nicolet

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**Scheme 1.** Synthetic route to MNP-supported manganese catalyst Mn@MNP (**6**).

spectrometer (KBr).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker DRX500 spectrometer. X-ray diffraction (XRD) was conducted using a Bruker D8 Advance instrument. Elemental analysis was performed with an Elementar Vario EL  $\beta$  recorder. Manganese content of the catalyst was measured using inductively coupled plasma (ICP) with an L-PAD analyzer (Prodigy). Thermogravimetric analysis was performed with a Shimadzu TGA-50 spectrometer. Magnetization curves were obtained using vibrating sample magnetometry (VSM; Lakeshore 7304). Quantitative analysis of the products was conducted using GC (Varian CP-3800).

### Synthesis of Mn@MNP

#### Synthesis of 2-hydroxy-4-(prop-2-ynoxy)benzaldehyde (**1**)<sup>[23]</sup>

A mixture of 2,4-dihydroxybenzaldehyde (2.8 g, 20 mmol), potassium carbonate (2.8 g, 20 mmol) and acetone (20 ml) was heated to 50°C. Then a solution of propargyl bromide (2.4 g, 20 mmol) in acetone (10 ml) was slowly added through a dropping funnel and the mixture was stirred for 3 h under reflux. After completion of the reaction, the mixture was cooled to ambient temperature and then filtered. The filtrate was concentrated under vacuum and then treated with dichloromethane (100 ml). The organic layer was washed four times with water, dried over sodium sulfate, filtered and concentrated under vacuum. The desired product **1** was obtained by purification with silica gel chromatography (petroleum ether–ethyl acetate, 15:1) as a white solid (1.2 g, 6.8 mmol, 34%).

#### Synthesis of Schiff base ligand (**2**)

L-Valine (1.17 g, 10 mmol) and **1** (1.76 g, 10 mmol) were added into 25 ml of ethanol and the resulting mixture was stirred under reflux for 5 h. Then the mixture was concentrated to nearly dry, 30 ml of ether was added and immediately much yellow solid precipitated. The mixture was then filtered and the solid was washed with ether three times. Ligand **2** was obtained by drying under vacuum overnight (0.88 g, 3.2 mmol, 32%).  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 13.98 (s, 1H, COOH), 8.39 (s, 1H, Ph-CH-N), 7.33 (d,  $J = 9$  Hz, 1H, Ph- $H^6$ ), 6.44 (m, 2H, Ph- $H^3$ , Ph- $H^5$ ), 4.81 (s, 2H, Ph-O-CH<sub>2</sub>-C-CH), 3.82

(d,  $J = 5.2$  Hz, 1H, N-CH-COOH), 3.59 (t,  $J = 2$  Hz, 1H, Ph-O-CH<sub>2</sub>-C-CH), 2.22 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.88 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 167.46 (COOH), 161.30 (Ph-C<sup>4</sup>), 159.77 (Ph-C<sup>2</sup>), 156.32 (Ph-CH-N), 128.48 (Ph-C<sup>6</sup>), 107.60 (Ph-C<sup>1</sup>), 101.64 (Ph-C<sup>5</sup>), 97.11 (Ph-C<sup>3</sup>), 73.96 (Ph-O-CH<sub>2</sub>-C-CH), 73.65 (Ph-O-CH<sub>2</sub>-C-CH), 69.79 (N-CH-COOH), 50.66 (Ph-O-CH<sub>2</sub>-C-CH), 26.10 (CH(CH<sub>3</sub>)<sub>2</sub>), 14.34 (CH(CH<sub>3</sub>)<sub>2</sub>), 12.70 (CH(CH<sub>3</sub>)<sub>2</sub>).

#### Synthesis of manganese complex (**3**)

A flask was charged with **2** (0.275 g, 1 mmol) and ethanol (25 mL). The mixture was heated to 50°C, and then a solution of manganese (II) acetate tetrahydrate (0.245 g, 1 mmol) in ethanol (10 ml) was added through a dropping funnel. After reacting for 10 h, the mixture was filtered, the solid was washed with ethanol three times, dried under vacuum overnight and used for the next reaction directly.

#### Synthesis of 3-azidopropyltriethoxysilane (**4**)<sup>[24]</sup>

A mixture of 3-chloropropyltriethoxysilane (9.64 g, 40.0 mmol), sodium azide (3.90 g, 60.0 mmol), tetrabutylammonium bromide (TBAB; 2.58 g, 8.0 mmol) and dry acetonitrile (150 ml) was stirred under reflux for 48 h under a nitrogen atmosphere. After completion of the reaction, the mixture was cooled to ambient temperature and then filtered. The filtrate was concentrated under vacuum and then ether (30 ml) was added. The mixture was filtered and washed with ether (2  $\times$  10 ml). The combined filtrate was concentrated under vacuum to afford the product **4** as a pure and colorless liquid (7.92 g, 80%).

#### Synthesis of silica-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles<sup>[22]</sup>

A mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (10.8 g, 40.0 mmol), FeCl<sub>2</sub>·4H<sub>2</sub>O (4.0 g, 20.0 mmol) and deionized water (250 ml) was stirred at 85°C under nitrogen. Then concentrated ammonia was added to the solution to adjust the pH to 9. Four hours later, the precipitate was washed with deionized water several times. The black precipitate (Fe<sub>3</sub>O<sub>4</sub>) was collected using a permanent magnet. To coat a layer of silica on the surface of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Fe<sub>3</sub>O<sub>4</sub> (2.0 g) was fully dispersed in ethanol (400 ml) under ultrasonic irradiation for half an hour, and then tetraethylorthosilicate (4.0 ml) and concentrated ammonia (12 ml) were added. After stirring for 24 h, with the help of a permanent magnet, the black precipitate (SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>) was collected, then washed with ethanol three times and dried in a vacuum.

#### Synthesis of azide-functionalized MNPs (**5**)

A mixture of SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> (1.5 g) and dry toluene (75 ml) was subjected to ultrasonic treatment for 1 h, and then **4** (0.5 g, 2.02 mmol) was added. After stirring under reflux for 24 h under a nitrogen atmosphere, the reaction mixture was cooled. The product **5** was collected using a permanent magnet, washed with toluene and acetone several times and dried in a vacuum overnight.

#### Synthesis of manganese catalyst Mn@MNP (**6**)

Complex **3** (0.2 g, 0.55 mmol), CuI (22 mg, 0.11 mmol) and **5** (1 g) were mixed in *N,N*-dimethylformamide (DMF)–tetrahydrofuran (THF) (1:1, 10 ml) under nitrogen, and *N,N*-diisopropylethylamine (DIPEA; 2 ml) was added by injection. After stirring at room temperature for three days, the solid was collected using a permanent magnet, then washed with ether (3  $\times$  20 ml), water (3  $\times$  20 ml) and acetone (3  $\times$  20 ml). Mn@MNP (1.068 g) was obtained after fully drying under vacuum. The content of Mn was calculated to be 0.55% using ICP–atomic emission spectrometry.

### General procedure for oxidation catalyzed by Mn@MNP

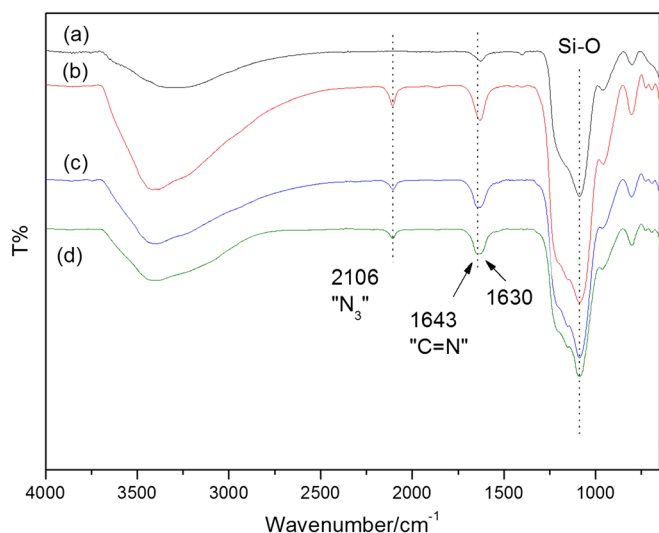
Mn@MNP (0.002 mmol), dimethylsulfoxide (DMSO; 3 ml), alcohol (1 mmol) and *tert*-butyl hydroperoxide (TBHP; 1.5 mmol) were charged in a 10 ml round-bottomed flask equipped with a magnetic stirrer. The mixture was stirred at 110°C and the progress of the reaction was monitored using GC. After completion of the reaction, the catalyst was separated using a permanent magnet, washed with water and ethanol, and dried under vacuum. The recovered Mn@MNP could be used for the next run without any other treatment. The oxidation products are all known and identified by comparing their retention times with those of authentic samples.

### Results and discussion

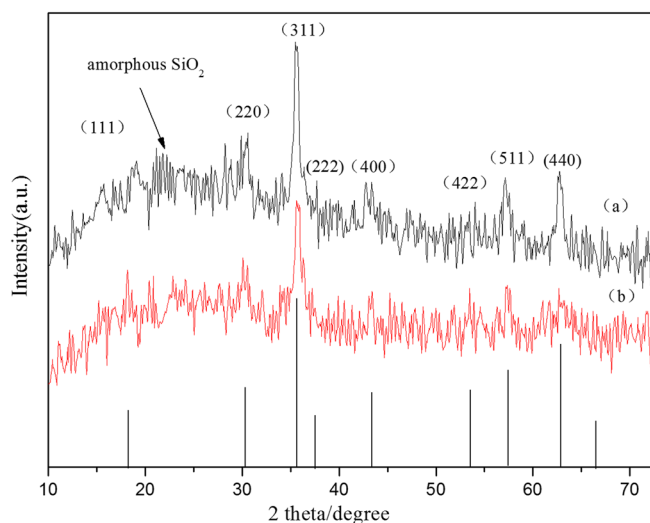
The Mn@MNP catalyst was prepared following the procedure shown in 1. Firstly, salicylaldehyde went through a direct propargylation with propargyl bromide to afford intermediate **1**, which underwent a simple condensation with *L*-valine to afford Schiff base **2**, which was then treated with a solution of Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O and LiCl under reflux conditions to provide complex **3**. The azide-functionalized MNPs **5** were prepared according to our previously reported method,<sup>[19]</sup> with the loading of the azide groups being determined as 0.28 mmol g<sup>-1</sup> from elemental analysis of the nitrogen content. Finally, **5** was reacted with an excess of complex **3** using CuI as catalyst in the presence of DIPEA.

Figure 1 shows the FT-IR spectra of SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>, **5** and **6**. After introducing azido groups, a strong absorption band at 2106 cm<sup>-1</sup> appears in Fig. 1(b) compared with Fig. 1(a). After 'click' reaction, the absorption band at 2106 cm<sup>-1</sup> reduces obviously owing to the formation of the 1,2,3-triazole (Fig. 1(c)). The typical band for C-N vibration is observed at around 1643 cm<sup>-1</sup> (Fig. 1(c)). These results indicate that complex **3** is successfully immobilized onto SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>. And after being reused five times, the FT-IR spectrum (Fig. 1(d)) of the recovered catalyst is almost the same as that of fresh catalyst.

Figure 2 shows the high-angle XRD pattern of the catalyst. The diffraction peaks (220), (311), (400), (422), (511) and (440) are attributed to the standard Fe<sub>3</sub>O<sub>4</sub> sample (JCPDS file no. 19-0629; Fig. 2). The peak at 2θ from 20° to 30° belongs to amorphous silica layer.



**Figure 1.** FT-IR spectra of (a) SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>, (b) azide-functionalized MNPs (**5**), (c) MNP-supported Mn catalyst (**6**) and (d) catalyst after being reused five times.

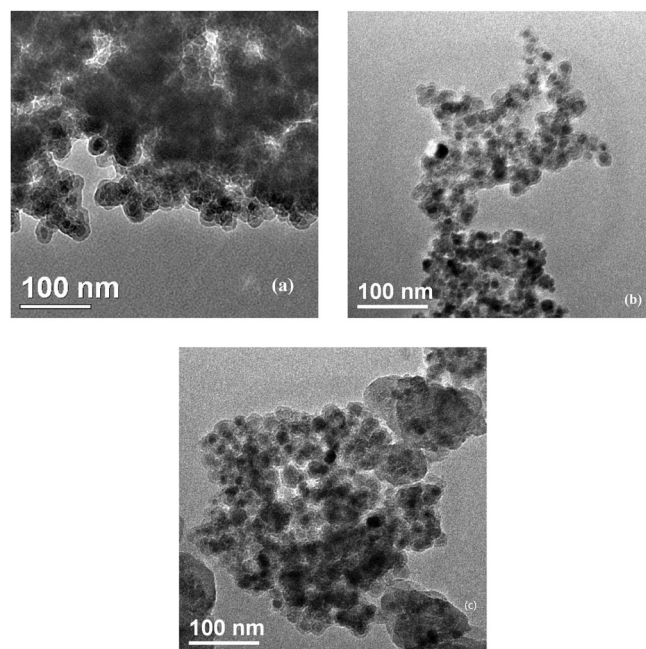


**Figure 2.** XRD pattern of (a) SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> and (b) Mn@MNP catalyst.

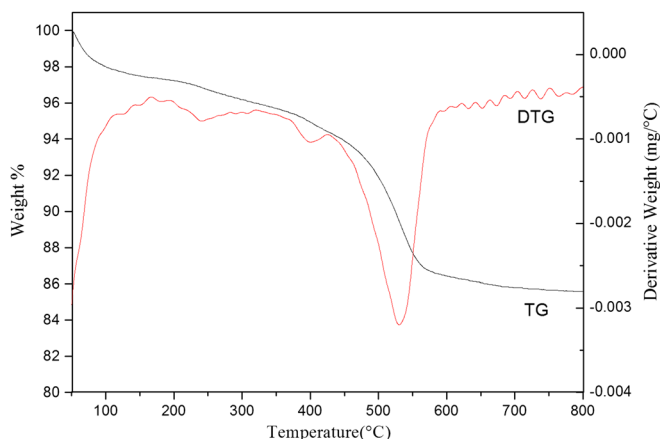
No characteristic peaks for Mn are observed, which proves the excellent dispersion of the Mn sites on the MNPs.<sup>[25]</sup> According to the Bragg diffraction angle and full width at half maximum of (311) peaks, the average crystal size of the Fe<sub>3</sub>O<sub>4</sub> cores, calculated using the Scherrer formula, is about 11 nm.

Figure 3 shows TEM images of the SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> support, the Mn@MNP catalyst and catalyst reused five times. As shown in Fig. 3 (a), the average size of the Fe<sub>3</sub>O<sub>4</sub> cores is about 8–12 nm, and the cores are surrounded by grey silica shells. After anchoring of the complex **3**, the support particles are about 20–30 nm (Fig. 3(b)). And after being reused five times, the morphology of the catalyst does not show an obvious change (Fig. 3(c)).

The thermostability of Mn@MNP was investigated using thermogravimetric analysis. As shown in Fig. 4, there is an initial weight loss



**Figure 3.** TEM images of (a) SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>, (b) Mn@MNP catalyst and (c) catalyst after being reused five times.

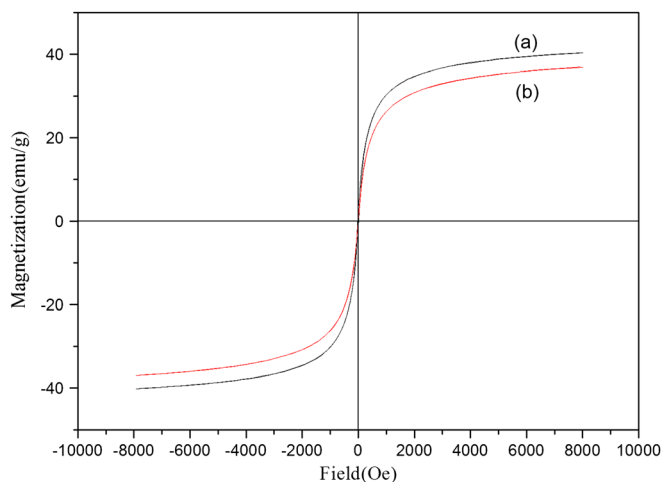


**Figure 4.** Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for MNP-supported Mn catalyst (**6**).

of 2.5% up to 140°C, which is ascribed to the adsorbed water on the catalyst surface. Thermal degradation occurs after 220°C, which indicates the catalyst has excellent thermostability. A main weight loss of 9.5% is observed from 330 to 590°C, which is attributed to the destruction of organic structure. And the derivative thermogravimetric curve shows the organic structure decomposes in one step. From 600 to 800°C, the weight of the sample no longer changes, which also means that the organic structure had decomposed already. Hence, the thermostability of Mn@MNP is excellent.

The magnetic properties were evaluated using VSM at room temperature. The VSM magnetization curve of the sample (Fig. 5) goes through the zero point, so the catalyst has no magnetic hysteresis phenomenon, which indicates that the as-prepared catalyst is superparamagnetic. As a result, the catalyst can be easily separated from the reaction system using an external magnet.

The activity of Mn@MNP was investigated in the oxidation of benzyl alcohol to benzaldehyde. Our initial study centered on determining the optimal conditions (solvent, oxidant, reaction temperature and time) and the results are summarized in Table 1. When the model reaction is carried out in MeCN using H<sub>2</sub>O<sub>2</sub> as oxidant, no reaction occurs (Table 1, entry 1). But when TBHP is used as oxidant, a moderate yield is obtained (Table 1, entry 2).



**Figure 5.** Magnetization curves of (a) SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> and (a) MNP-supported Mn catalyst (**6**).

**Table 1.** Optimization of reaction conditions<sup>a</sup>

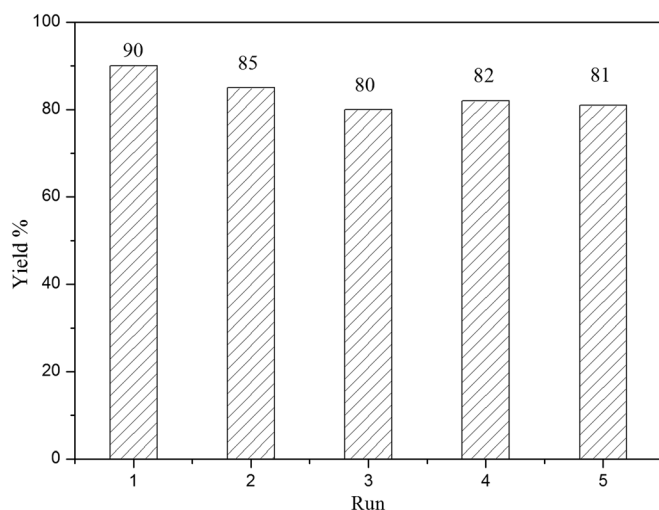
Entry	Solvent	Oxidant	Time (h)	Catalyst (mol%)	Temp. (°C)	Yield (%) <sup>b</sup>
1	MeCN	H <sub>2</sub> O <sub>2</sub>	24	0.2	80	0
2	MeCN	TBHP	4	0.2	80	42
3	CH <sub>2</sub> Cl <sub>2</sub>	TBHP	4	0.2	Reflux	36
4	THF	TBHP	4	0.2	Reflux	19
5	PhMe	TBHP	4	0.2	90	34
6	DMF	TBHP	4	0.2	90	32
7	DMSO	TBHP	4	0.2	90	55
8	DMSO	None	4	0.2	90	0
9	DMSO	TBHP	4	0.2	100	79
10	DMSO	TBHP	4	0.2	110	90
11	DMSO	TBHP	4	0.2	120	77
12	DMSO	TBHP	2	0.2	110	79
13	DMSO	TBHP	4.5	0.2	110	86
14	DMSO	TBHP	4	0.8	110	87
15	DMSO	TBHP	4	0	110	35
16	DMSO	TBHP	4	0.1	110	76

<sup>a</sup>Reaction conditions: benzyl alcohol (1 mmol), H<sub>2</sub>O<sub>2</sub>/TBHP (1.5 mmol), solvent (3 ml).  
<sup>b</sup>GC yields.

So TBHP was selected as the oxidant for further research. Some other solvents including CH<sub>2</sub>Cl<sub>2</sub>, THF, toluene, DMF and DMSO were used as reaction media, among them DMSO affording the best results (Table 1, entries 2–7). So DMSO was selected as the optimal solvent for further studies. As DMSO has some oxidation ability, in order to identify whether TBHP is necessary for the reaction or not, a control experiment without TBHP was carried out and gave no detectable reaction (Table 1, entry 8). So oxidant is necessary for the reaction. When the reaction temperature is increased from 90 to 110°C, the yield increased accordingly (Table 1, entries 7, 9, 10). However, further increase of temperature to 120°C results in decreased yield (Table 1, entry 11). Consequently, 110°C is the optimal reaction temperature. Finally, reaction time and loading amount of catalyst were investigated. The results indicate that 0.2 mol% loading of Mn@MNP and reacting for 4 h afford the best result (Table 1, entries 10, 12–16).

The recyclability of the MNP-supported Mn catalyst was then investigated using the above model reaction under the optimized conditions. After completion of the reaction, the catalyst was simply recovered using an external magnet, washed with water and ethanol, and dried under vacuum. As can be seen from Fig. 6, the catalyst can be recycled five times with no significant loss in activity. After the catalyst was separated, the filtrate was used for ICP analysis. The result shows the Mn content in the filtrate is less than 0.18 ppm, which indicates that the as-prepared catalyst is very stable and rules out the possibility that the reaction is catalyzed by leached Mn.

Under the optimized reaction conditions, a variety of alcohols were used to test the scope of this method. The results are summarized in Table 2. For benzyl alcohols, electron-donating groups such as methyl and methoxyl favor the oxidation in comparison to electron-withdrawing ones including nitro, chlorine and bromine. When nitro group is attached to the aromatic ring, a markedly decreased yield is obtained (Table 2, entry 4). The reason might



**Figure 6.** Recycling experiment of the MNP-supported Mn catalyst (6).

$\text{R}-\text{CH}(\text{OH})-\text{R}' \longrightarrow \text{R}-\text{C}(=\text{O})-\text{R}'$				
Entry	R	R'	Time (h)	Yield (%) <sup>b</sup>
1	4-Methoxyphenyl	H	4	92
2	4-Methylphenyl	H	4	94
3	4-Chlorophenyl	H	4	92
4	4-Nitrophenyl	H	8	51
5	2-Methoxyphenyl	H	4	90
6	2-Methylphenyl	H	4	91
7	2-Chlorophenyl	H	4	79
8	2-Bromophenyl	H	4	76
9	2-Pyridyl	H	4	91
10	Phenyl	methyl	4	86
11	Cyclohexyl	H	24	58
12	<i>n</i> -Nonyl	H	24	8

<sup>a</sup>Reaction conditions: alcohol (1 mmol), TBHP (1.5 mmol), DMSO (3 ml), 0.2 mol% catalyst.  
<sup>b</sup>GC yields.

be attributed to the much stronger electron-withdrawing ability of nitro group than chlorine and bromine. In addition, steric effects clearly influence the reaction, which can be seen from a comparison of the results for 4-chlorobenzyl alcohol and 2-chlorobenzyl alcohol (Table 2, entries 3 and 7). Because the vicinal steric effect is greater than the contrapuntal one, 4-chlorobenzyl alcohol shows higher reactivity than 2-chlorobenzyl alcohol. Furfural and  $\alpha$ -methylbenzyl alcohol also present high reactivity and afford excellent yields. Aliphatic alcohols show low reactivity in this reaction. Moderate yield is obtained when cyclohexanol is used as substrate and extremely low yield is obtained when laurinol is used.

In comparison with other catalysts employed for the oxidation of alcohols, the as-prepared Mn@MNP catalyst is more efficient (Table 3). Reaction time and yield are the essential factors in view of efficiency. As is evident from Table 3, the reported catalysts require a longer reaction time, or benzaldehyde is obtained in low yield.

**Table 3.** Comparison of Mn@MNP with some other catalysts for the oxidation of benzyl alcohol

Entry	Catalyst	Solvent	Oxidant	Time (h)	Yield (%)	Ref.
1	CoO-CeO <sub>2</sub>	<i>n</i> -Hexane	TBHP	8	55	[26]
2	Cr(salen)-NH <sub>2</sub> -MCM-41	Solvent free	H <sub>2</sub> O <sub>2</sub>	4	53	[27]
3	[Mn(bp)(N <sub>3</sub> )(CH <sub>3</sub> OH)]	CH <sub>3</sub> CN	H <sub>2</sub> O <sub>2</sub>	4	42	[28]
4	SBA-15Co-Si	<i>n</i> -Hexane	TBHP	6	57	[29]
5	Mn@MNP	DMSO	TBHP	4	90	This work

## Conclusions

We have developed a new MNP-supported Mn catalyst via a 'click' route. The catalyst shows high activity in the selective oxidation of alcohols to afford aldehydes or ketones. Furthermore, the catalyst can be simply recovered from the reaction system using magnetic separation and can be reused several times without a significant loss in activity.

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