Room temperature Aldol reactions using magnetic Fe_3O_4@ $Fe(OH)_3$ composite microspheres in Hydrogen-bond catalysis

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Supporting Information

Experimental Details:

Preparation of Fe_3O_4@$Fe(OH)_3$ composite microspheres: Fe_3O_4 microspheres were prepared according to the reported method with minor modifications.[1] $FeCl_3 \cdot 6H_2O$ (2.0 mmol) and sodium acetate (17.4 mmol) were dissolved in 20 ml of ethylene glycol with magnetic stirring at room temperature for 2h. The resulted yellow solution was then transferred to a Teflon stainless-steel autoclave and sealed. After a reaction at 200 °C for 10 h, the resulted Fe_3O_4 microspheres were magnetically gathered and washed with water and ethanol three times. Then, 0.2 g of the as-prepared Fe_3O_4 microspheres and 12.4 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ were ultrasonically dispersed into 5 ml of ethanol. After totally dissolution and dispersion, the Fe_3O_4 microspheres were magnetically separated from the ethanol solution and dried at 80 °C for 5h. Fe_3O_4@$Fe(OH)_3$ composite microspheres were then prepared via adding 2 ml of $NH_3 \cdot H_2O$ aqueous solution (17%) to the dried brown Fe_3O_4 microspheres under vigorous stirring. The as-prepared Fe_3O_4@$Fe(OH)_3$ composite microspheres were magnetically gathered and washed with water 5 times, and was dried at 110 °C overnight for further usage.

Preparation of Fe_3O_4@$Fe(OD)_3$ composite micropheres:

At first, 100 ml/min of ammonia gas was bubbled into 10 ml D_2O for 10 minutes to prepare $NH_3.D_2O$ solution at room temperature. Then 0.2 g of the dried Fe_3O_4 microspheres and 12.4 mmol of anhydrous $Fe(NO_3)_3$ was ultrasonically dispersed into 5 ml of ethanol. After totally dispersion and dissolution, the Fe_3O_4 microspheres were magnetically separated from the ethanol solution and dried at 80 °C for 5h. Fe_3O_4@$Fe(OD)_3$ composite microspheres were then prepared via adding 2 ml of self-prepared $NH_3 \cdot D_2O$ solution to the dried brown Fe_3O_4 microspheres under vigorous stirring. The as-prepared Fe_3O_4@$Fe(OD)_3$ composite microspheres were magnetically separated and washed with D_2O several times, followed dry at 110 °C overnight for reaction.

Characterization of Fe_3O_4@$Fe(OH)_3$ composite microspheres: The as-obtained Fe_3O_4@$Fe(OH)_3$ composite microspheres were characterized by transmission electron microscopy (TEM, JEOL JEM-1011), X-ray diffraction (XRD, D/max-2500), and Thermo Gravimetric Analyzer (TGA).

General procedure for Aldol reactions in Table 1:

Under air atmosphere, 2 ml of acetone and 0.2 mmol of aromatic aldehydes were mixed together with 128 mg of Fe_3O_4@$Fe(OH)_3$ composite microspheres under vigorous stirring at room temperature. After 24 h of reaction, Fe_3O_4@$Fe(OH)_3$ composite microspheres were magnetically separated from the reaction mixture and the resulted solution was purified by flash column chromatography on silica gel (mixture of petroleum ether/ethyl acetate) to give the desired product.

^{1}H NMR and MS data for products in Table 1:

(E)-4-phenylbut-3-en-2-one (Table 1, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 6.67 (d, *J* = 16.2 Hz, 1H), 7.3-7.5 (m, 5H), 7.6 (d, *J* = 16.3 Hz, 1H); GC-MS m/z: 146 ($C_{10}H_{10}O$, 146.07).

4-hydroxy-4-(4-nitrophenyl)butan-2-one (Table 1, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.84 (d, 2H), 3.5 (br s, 1H), 5.25 (q, 1H), 7.53 (d, 2H), 8.21 (d, 2H); GC-MS m/z: 209 ($C_{10}H_{11}NO_4$).

(E)-4-(4-chlorophenyl)but-3-en-2-one (Table 1, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 6.71 (d, *J* = 16.1 Hz, 1H), 7.40 (d, 2H), 7.58 (d, 2H), 7.65 (d, *J* = 16.3 Hz, 1H); GC-MS m/z: 180 ($C_{10}H_9ClO$).

(E)-4-(4-bromophenyl)but-3-en-2-one (Table 1, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 6.67 (d, *J* = 16.4 Hz, 1H), 7.5 (d, 2H), 7.63 (d, 2H), 7.65 (d, *J* = 16.1 Hz, 1H); GC-MS m/z: 224 ($C_{10}H_9BrO$, 225.08).

(E)-4-(3-oxobut-1-enyl)benzonitrile (Table 1, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 6.8 (d, *J* = 16.3 Hz, 1H), 7.5 (d, *J* = 16.2 Hz, 1H), 7.63 (d, 2H), 7.70 (d, 2H); GC-MS m/z: 171 ($C_{11}H_9NO$, 171.20).

(E)-4-p-tolylbut-3-en-2-one (Table 1, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 6H), 6.69 (d, *J* = 16.2 Hz, 1H), 7.23 (d, 2H), 7.45 (d, 2H), 7.51 (d, *J* = 16.3 Hz, 1H); GC-MS m/z 160 ($C_{11}H_{12}O$, 160.21).

(E)-4-(4-methoxyphenyl)but-3-en-2-one (Table 1, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.84 (s, 3H), 6.63 (d, *J* = 16.2 Hz, 1H), 6.92 (d, 2H), 7.49 (d, *J* = 16.2 Hz, 1H), 7.51 (d, 2H); GC-MS m/z: 176 ($C_{11}H_{12}O_2$, 176.21).

(E)-4-(3-(trifluoromethyl)phenyl)but-3-en-2-one (Table 1, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 6.74 (d, *J* = 16.3 Hz, 1H), 7.2-7.6 (m, 4H), 7.62 (d, *J* = 16.1 Hz, 1H); GC-MS m/z: 214 ($C_{11}H_9F_3O$, 214.18).

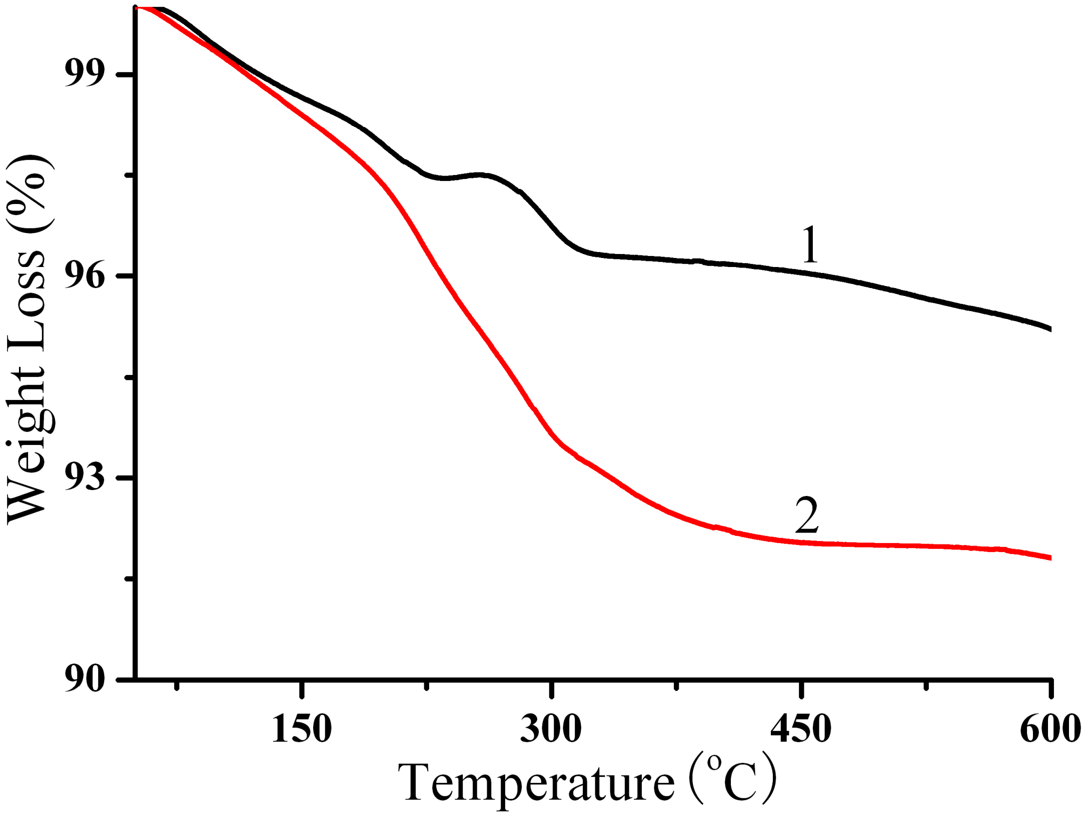

Figure S1 TGA results of (1) Fe_3O_4 microspheres and (2) $Fe_3O_4@Fe(OH)_3$ composite microspheres under nitrogen atmosphere

Table S1 Aldol reaction between acetone and 4-chlorobenzaldehyde catalyzed by $Fe_3O_4@Fe(OH)_3$ composite microspheres and Fe_3O_4 microspheres

Entry[a]	Catalyst	Cycle[b]	Reaction time (h)	Yields (%)
1	42 mg $Fe_3O_4@Fe(OH)_3$	-	24	46
2	84 mg $Fe_3O_4@Fe(OH)_3$	-	24	76
3	128 mg $Fe_3O_4@Fe(OH)_3$	1	24	88
4	128 mg $Fe_3O_4@Fe(OH)_3$	2	24	93
5	128 mg $Fe_3O_4@Fe(OH)_3$	3	24	91
6	128 mg $Fe_3O_4@Fe(OH)_3$	4	24	89
7	128 mg $Fe_3O_4@Fe(OH)_3$	5	24	87
8	No catalyst	-	120	ND[c]
9[d]	Fe_3O_4	-	30	trace

[a] Reaction conditions: 0.2 mmol of 4-chlorobenzaldehyde, 2 ml of acetone, certain amount of $Fe_3O_4@Fe(OH)_3$ composite microspheres, room temperature, 24-120h. [b] The $Fe_3O_4@Fe(OH)_3$ composite microspheres were magnetically recovered and reused for several times. [c] Not detected. [d] 128 mg of Fe_3O_4 microsphere was used.

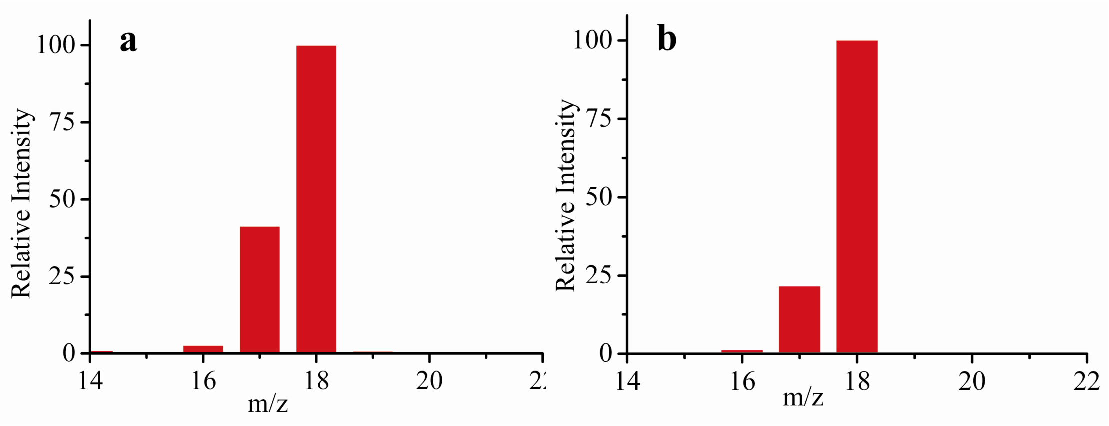

Figure S2 Molecular ion mass patterns for water in reaction 1 using (a) $Fe_3O_4@Fe(OH)_3$ composite microspheres and (b)$Fe_3O_4@Fe(OD)_3$ composite microspheres as catalysts, respectively.

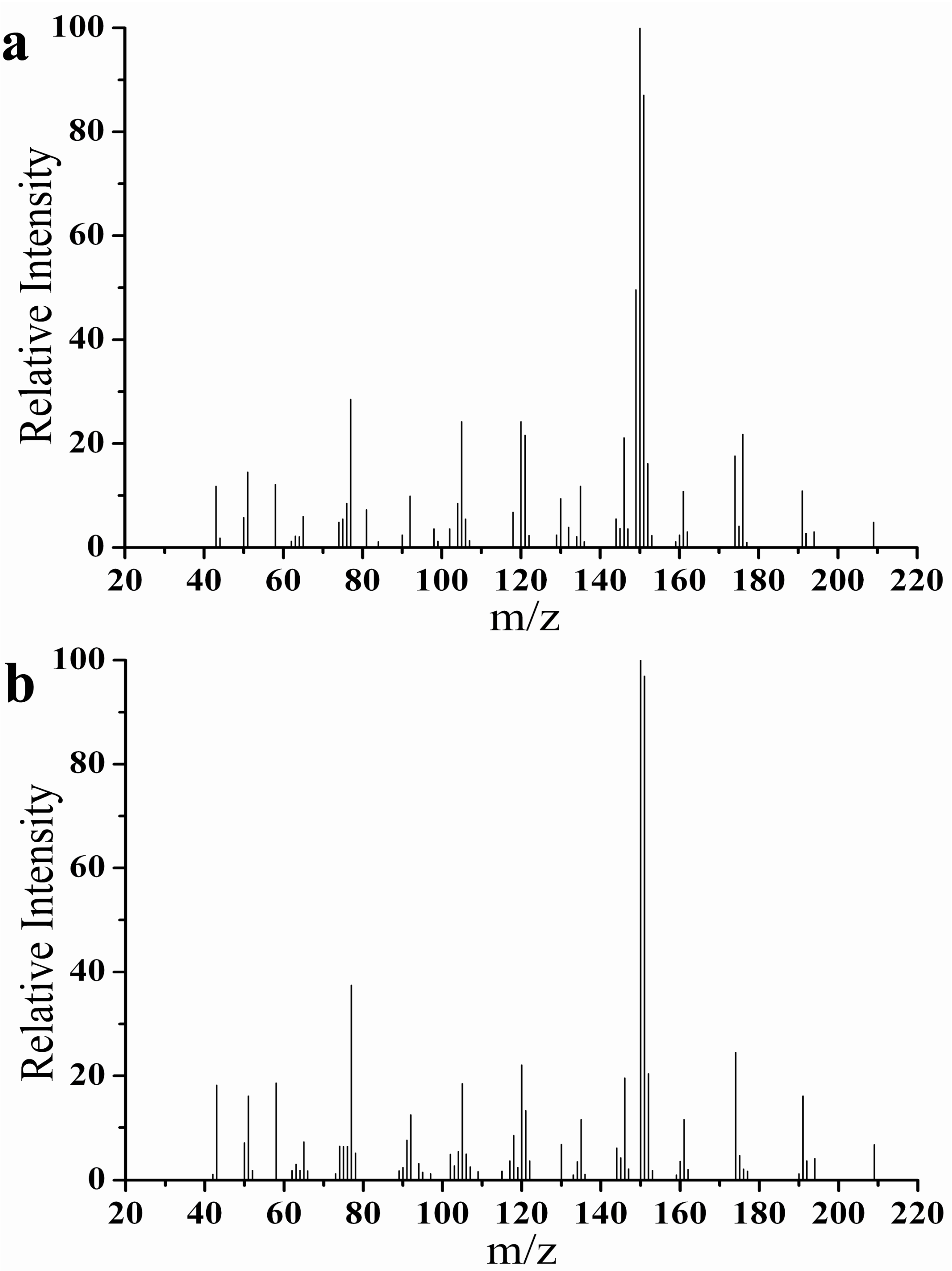

Figure S3 Molecular ion mass patterns for product 3 in reaction 2 using (a) $Fe_3O_4@Fe(OH)_3$ composite microspheres and (b) $Fe_3O_4@Fe(OD)_3$ composite microspheres as catalysts, respectively.

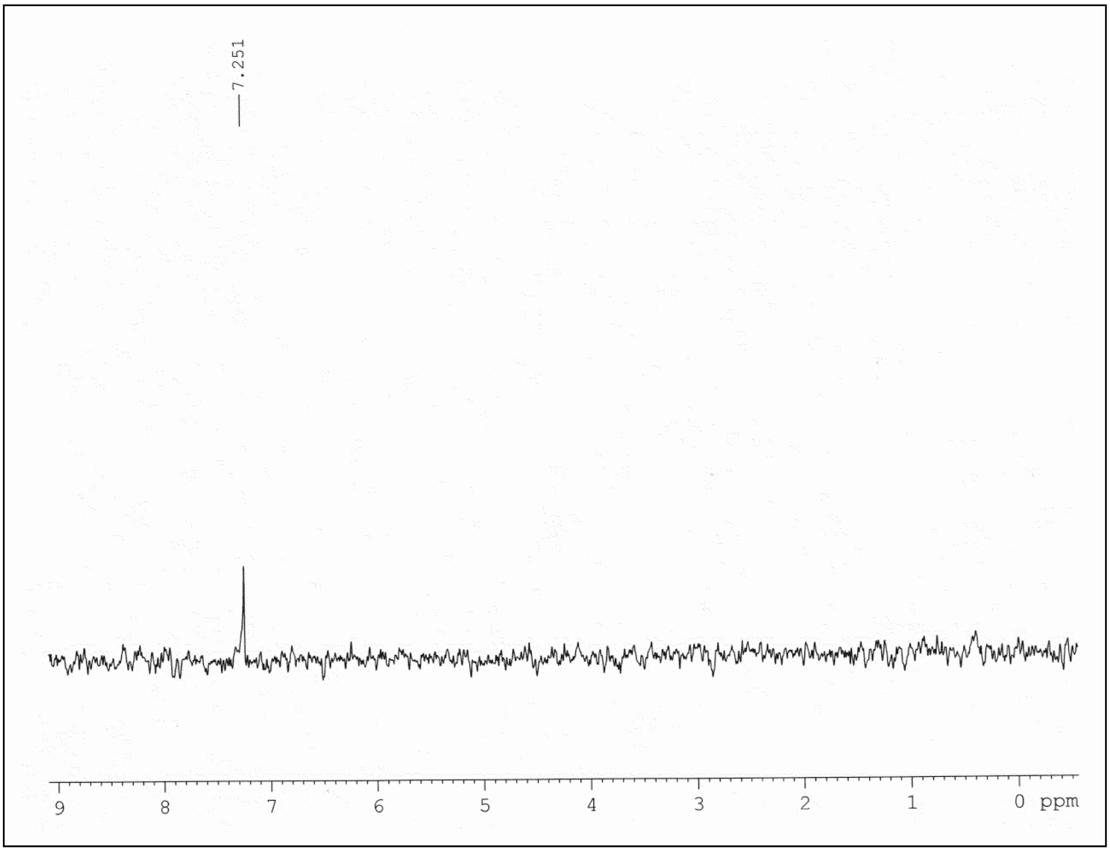

Figure S4 $^{3/2}$D NMR spectrum of product 3 in reaction 2 using Fe_3O_4@$Fe(OD)_3$ composite microspheres as catalysts. $\delta = 7.251$ is signal from $CDCl_3$ (impurity in the $CHCl_3$ solvent).

Reference

1. S.-H. Xuan, Y.-X. J. Wang, J. C. Yu and K. C.-F. Leung, *Langmuir*, 2009, **25**, 11835-11843.