Room temperature Aldol reactions using magnetic Fe$_3$O$_4$@Fe(OH)$_3$ composite microspheres in Hydrogen-bond catalysis

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Supporting Information

Experimental Details:

Preparation of Fe$_3$O$_4$@Fe(OH)$_3$ composite microspheres: Fe$_3$O$_4$ microspheres were prepared according to the reported method with minor modifications.\textsuperscript{1} FeCl$_3$·6H$_2$O (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$_3$O$_4$ microspheres were magnetically gathered and washed with water and ethanol three times. Then, 0.2 g of the as-prepared Fe$_3$O$_4$ microspheres and 12.4 mmol of Fe(NO$_3$)$_3$·9H$_2$O were ultrasonically dispersed into 5 ml of ethanol. After totally dissolution and dispersion, the Fe$_3$O$_4$ microspheres were magnetically separated from the ethanol solution and dried at 80 °C for 5h. Fe$_3$O$_4$@Fe(OH)$_3$ composite microspheres were then prepared via adding 2 ml of NH$_3$·H$_2$O aqueous solution (17%) to the dried brown Fe$_3$O$_4$ microspheres under vigorous stirring. The as-prepared Fe$_3$O$_4$@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$_3$O$_4$@Fe(OD)$_3$ composite microspheres: At first, 100 ml/min of ammonia gas was bubbled into 10 ml D$_2$O for 10 minutes to prepare NH$_3$.D$_2$O solution at room temperature. Then 0.2 g of the dried Fe$_3$O$_4$ 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$_3$O$_4$ microspheres were magnetically separated from the ethanol solution and dried at 80 °C for 5h. Fe$_3$O$_4$@Fe(OD)$_3$ composite microspheres were
then prepared via adding 2 ml of self-prepared NH$_3$·D$_2$O solution to the dried brown Fe$_3$O$_4$ microspheres under vigorous stirring. The as-prepared Fe$_3$O$_4$@Fe(OD)$_3$ composite microspheres were magnetically separated and washed with D$_2$O several times, followed dry at 110 °C overnight for reaction.

**Characterization of Fe$_3$O$_4$@Fe(OH)$_3$ composite microspheres:** The as-obtained Fe$_3$O$_4$@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$_3$O$_4$@Fe(OH)$_3$ composite microspheres under vigorous stirring at room temperature. After 24 h of reaction, Fe$_3$O$_4$@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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_9$ClO).

- **(E)-4-(4-bromophenyl)but-3-en-2-one (Table 1, entry 4):** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_9$BrO, 225.08).

- **(E)-4-(3-oxobut-1-enyl)benzonitrile (Table 1, entry 5):** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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_{10}NO, 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$_{9}$F$_3$O, 214.18).

Figure S1 TGA results of (1) Fe$_3$O$_4$ microspheres and (2) Fe$_3$O$_4$@Fe(OH)$_3$ composite microspheres under nitrogen atmosphere
Table S1  Aldol reaction between acetone and 4-chlorobenzaldehyde catalyzed by Fe₃O₄@Fe(OH)₃ composite microspheres and Fe₃O₄ microspheres

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Cycle</th>
<th>Reaction time (h)</th>
<th>Yields (%)</th>
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<tr>
<td>1</td>
<td>42 mg Fe₃O₄@Fe(OH)₃</td>
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</tr>
<tr>
<td>2</td>
<td>84 mg Fe₃O₄@Fe(OH)₃</td>
<td>-</td>
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<td>76</td>
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<tr>
<td>3</td>
<td>128 mg Fe₃O₄@Fe(OH)₃</td>
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<td>24</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>128 mg Fe₃O₄@Fe(OH)₃</td>
<td>2</td>
<td>24</td>
<td>93</td>
</tr>
<tr>
<td>5</td>
<td>128 mg Fe₃O₄@Fe(OH)₃</td>
<td>3</td>
<td>24</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>128 mg Fe₃O₄@Fe(OH)₃</td>
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<td>24</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>128 mg Fe₃O₄@Fe(OH)₃</td>
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<td>87</td>
</tr>
<tr>
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<td>120</td>
<td>ND</td>
</tr>
<tr>
<td>9d</td>
<td>Fe₃O₄</td>
<td>-</td>
<td>30</td>
<td>trace</td>
</tr>
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</table>

a Reaction conditions: 0.2 mmol of 4-chlorobenzaldehyde, 2 ml of acetone, certain amount of Fe₃O₄@Fe(OH)₃ composite microspheres, room temperature, 24-120h. b The Fe₃O₄@Fe(OH)₃ composite microspheres were magnetically recovered and reused for several times. c Not detected. d 128 mg of Fe₃O₄ microsphere was used.

Figure S2  Molecular ion mass patterns for water in reaction 1 using (a) Fe₃O₄@Fe(OH)₃ composite microspheres and (b)Fe₃O₄@Fe(OD)₃ composite microspheres as catalysts, respectively.
**Figure S3** Molecular ion mass patterns for product 3 in reaction 2 using (a) Fe$_3$O$_4$@Fe(OH)$_3$ composite microspheres and (b) Fe$_3$O$_4$@Fe(OD)$_3$ composite microspheres as catalysts, respectively.
Figure S4 3/2D NMR spectrum of product 3 in reaction 2 using Fe$_3$O$_4$@Fe(OD)$_3$ composite microspheres as catalysts. $\delta = 7.251$ is signal from CDCl$_3$ (impurity in the CHCl$_3$ solvent).

Reference