Supporting information

Application of nickel ferrite and cobalt ferrite magnetic nanoparticles in C-O bond formation: A comparative study between their catalytic activities

Firouz Matloubi Moghaddam*, Ghazal Tavakoli, Ali Aliabadi

Synthesis of Nickel Ferrite (NiFe$_2$O$_4$) nanoparticles

The solutions of iron chloride (FeCl$_3$.6H$_2$O) (100 mL, 0.2 M) and nickel chloride (NiCl$_2$.6H$_2$O) (100 mL, 0.1 M) were prepared separately and mixed together. The solution was stirred for an hour. Then, in order for pH to reach 13, a solution of NaOH (~15 mL, 3 M) was added slowly to the flask. Finally, oleic acid (3 drops) was added to the solution as surfactant to prevent the aggregation and agglomeration of the nanoparticles. Then, the suspension was vigorously stirred using a magnetic stirring bar at 60 °C for 2 h. After complete precipitation, the residue was washed with double distilled water (3×25 mL) and dried in an oven at 90 °C over night; then it was calcinated at 600 °C for 4 h. The final product is a black-brown powder showing magnetic properties.

Synthesis of Cobalt Ferrite (CoFe$_2$O$_4$) nanoparticles

The solutions of iron nitrate (Fe(NO$_3$)$_3$.9H$_2$O) (100 mL, 0.2 M) and cobalt nitrate (Co(NO$_3$)$_2$.6H$_2$O) (100 mL, 0.1 M) were prepared separately and mixed together. After stirring for an hour, a solution of NaOH (~15 mL, 3 M) was added slowly (during 30 minutes) to the flask in order for pH to reach 12. Finally, oleic acid (3 drops) was added to the solution as surfactant to prevent the aggregation and agglomeration of the nanoparticles. Then, the suspension was vigorously stirred using a magnetic stirring bar at 90 °C for 2 h. After complete precipitation, the residue was washed with double distilled water (3×25 mL) and dried in an oven at 90 °C over night; then it was calcinated at 600 °C for 5 h. The final product is a black powder showing magnetic properties.

Characteristic data of the some selected products

Diphenyl ether (entries 1-3)$^1$

\[
\begin{array}{c}
\text{H NMR (400 MHz, CDCl$_3$, ppm): } \\
\delta 7.36 (m, 4H), 7.09 (m, 2H), 7.04 (m, 4H).
\end{array}
\]

\[
\begin{array}{c}
\text{C NMR (400 MHz, CDCl$_3$, ppm): } \\
\delta 160.6 (2C), 131.7 (4C), 126.4 (2C), 119.0 (4C).
\end{array}
\]

1-Methyl-4-phenoxybenzene (entry 4)$^1$

\[
\begin{array}{c}
\text{H NMR (400 MHz, CDCl$_3$, ppm): } \\
\delta 7.36 (m, 4H), 7.09 (m, 2H), 7.04 (m, 4H).
\end{array}
\]

\[
\begin{array}{c}
\text{C NMR (400 MHz, CDCl$_3$, ppm): } \\
\delta 160.6 (2C), 131.7 (4C), 126.4 (2C), 119.0 (4C).
\end{array}
\]
1H NMR (400 MHz, CDCl₃, ppm):  δ 7.31 (t, 2H, J = 7.6 Hz), 7.15 (d, 2H, J = 8.2 Hz), 7.10 (m, 1H), 7.02 (d, 2H, J = 8.1 Hz), 6.93 (d, 2H, J = 8.0 Hz), 2.36 (s, 3H).

13C NMR (400 MHz, CDCl₃, ppm): δ 160.9, 157.7, 134.7, 132.5, 129.3, 124.0, 119.9, 119.1, 24.2.

2-Phenoxy-4-phenyl acetophenone (entry 5)

1H NMR (400 MHz, CDCl₃, ppm):  δ 7.85 (d, 1H, J = 7.8), 7.31-7.44 (m, 5H), 7.20-7.25 (m, 4H), 6.94-6.99 (m, 3H), 2.61 (s, 3H).

13C NMR (400 MHz, CDCl₃, ppm): δ 196.6, 158.3, 155.1, 142.3, 136.2, 129.9, 129.4, 129.0 (2C), 128.8 (2C), 127.8 (2C), 123.5, 122.0, 120.4, 118.7 (2C), 115.5, 31.1.

1-Methoxy-4-phenoxybenzene (entry 6-8)

1H NMR (400 MHz, CDCl₃, ppm): δ 7.31 (m, 2H), 7.05 (m, 1H), 7.01 – 6.97 (m, 2H), 6.92 (d, J = 7.8 Hz, 2H), 6.90 (m, 2H), 3.84 (s, 3H).

13C NMR (400 MHz, CDCl₃, ppm): δ 161.5, 157.8, 152.2, 142.3, 136.2, 129.9, 129.4, 129.0 (2C), 128.8 (2C), 122.6, 118.9, 116.7, 58.5.

4-(4-methoxyphenoxy)benzonitrile (entry 9)

1H NMR (400 MHz, CDCl₃, ppm): δ 7.53 (d, 2H, J = 7.4), 7.08 (d, 2H, J = 7.4), 6.90 (d, 2H, J = 7.6), 6.79 (d, 2H, J = 7.6), 3.89 (s, 3H).

1-(4-(4-Methoxyphenoxy)phenyl)ethanone (entry 10)
4,4'-oxybis(methoxybenzene) (entry 11)

\[ \text{MeO} - \text{O} - \text{Me} \]

$^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 6.96 (m, 4H), 6.90 (m, 4H), 3.81 (s, 6H).

$^{13}$C NMR (400 MHz, CDCl$_3$, ppm): δ 157.4, 152.6, 122.7, 117.1, 57.0.

1-phenoxynaphthalene (entry 13)

\[ \text{PhO} - \text{O} - \text{Ph} \]

$^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 8.24 (m, 1H), 7.91 (m, 1H), 7.70 (m, 1H), 7.59 – 7.50 (m, 2H), 7.44 (m, 3H), 7.06 (t, $J = 7.7$ Hz, 1H), 7.00 (d, $J = 8.2$ Hz, 2H), 6.96 (d, $J = 7.7$ Hz, 1H).

$^{13}$C NMR (400 MHz, CDCl$_3$, ppm): δ 155.9, 152.4, 134.0, 130.1, 128.3, 126.5, 126.1, 124.9, 124.7, 123.5, 122.7, 121.9, 119.4, 112.0.

4-(1-naphthoxy) toluene (entry 15)

\[ \text{PhO} - \text{O} - \text{Ph} \]

$^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.87 (d, 1H, $J = 7.6$), 7.49 (d, 1H, $J = 7.7$), 7.12-7.31 (m, 4H), 7.06 (d, 2H, $J = 7.8$), 6.74-6.79 (m, 3H), 2.31 (s, 3H).

1-(4-(1-naphthoxyphenyl))ethanone (entry 16)
$^{1}H$ NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.90 (d, 1H, $J = 8.0$), 7.82 (d, 2H, $J = 7.8$), 7.59 (d, 1H, $J = 7.8$), 7.30-7.36 (m, 3H), 7.15 (m, 1H), 7.00 (d, 2H, $J = 7.5$), 6.79 (d, 1H, $J = 7.9$), 2.63 (s, 3H).

$^{13}C$ NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 199.0, 160.5, 150.2, 135.7, 130.3, 129.0 (2C), 128.2, 127.4, 127.1, 126.2 (2C), 122.5, 121.6, 118.7 (2C), 110.3, 30.9.

2-Formyl diphenyl ether (entry 19)

$^{1}H$ NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 10.36 (s, 1H), 7.83 (d, 1H, $J = 7.7$), 7.54 (t, 1H, $J = 7.6$), 7.20-7.25 (m, 3H), 7.09 (d, 1H, $J = 7.6$), 6.93-6.97 (m, 3H).

$^{13}C$ NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 193.3, 158.9, 155.4, 135.2, 132.4, 130.1, 129.3 (2C), 123.0, 121.8, 119.1, 118.4 (2C).

2,2’-diformyl diphenyl ether (entry 20)

$^{1}H$ NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 10.28 (s, 2H), 7.76 (m, 2H), 7.48-7.51 (m, 2H), 7.13-7.20 (m, 4H).

$^{13}C$ NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 190.6(2C), 156.8(2C), 135.7(2C), 131.2(2C), 130.6(2C), 123.1(2C), 118.8(2C).

4-phenoxy-2H-chromen-2-one (entry 22)
1H NMR (400 MHz, CDCl₃, ppm): δ 7.16-7.28 (m, 4H), 6.85 (m, 2H), 6.76-6.83 (m, 3H), 5.79 (s, 1H).
13C NMR (400 MHz, CDCl₃, ppm): δ 169.1, 161.2, 157.0, 153.1, 130.6 (2C), 128.5, 127.4, 126.6, 123.0, 122.1, 118.8 (2C), 117.6, 99.7.

3-Methoxy diphenyl ether (entry 23)

1H NMR (400 MHz, CDCl₃, ppm): δ 7.28 (m, 2H), 7.15 (m, 1H), 6.95-6.99 (m, 3H), 6.49-6.52 (m, 2H), 6.48 (s, 1H), 3.92 (s, 3H).
13C NMR (400 MHz, CDCl₃, ppm): δ 162.4, 160.1, 159.3, 130.2, 121.6 (2C), 120.3, 109.3, 108.9, 104.0, 56.1.

2-Methyl-4'-methoxy diphenyl ether (entry 24)

1H NMR (400 MHz, CDCl₃, ppm): δ 7.02-7.05 (m, 2H), 6.81-6.88 (m, 4H), 6.77 (d, 2H, J = 7.8), 3.78 (s, 3H), 2.31 (s, 3H).
13C NMR (400 MHz, CDCl₃, ppm): δ 156.3, 152.7, 150.2, 129.9, 128.1, 126.8, 122.3, 119.7 (2C), 118.4, 115.1 (2C), 56.3, 15.1.

4-Allyl-2,4'-dimethoxy diphenyl ether (entry 25)

1H NMR (400 MHz, CDCl₃, ppm): δ 6.80-6.74 (m, 4H), 6.69-6.57 (m, 3H), 6.23 (m, 1H), 5.01 (dd, 1H, J = 15.9, J = 2.8), 4.98 (dd, 1H, J = 8.6, J = 2.8), 3.26 (m, 2H), 3.84 (s, 3H), 3.69 (s, 3H).
13C NMR (400 MHz, CDCl₃, ppm): δ 155.2, 153.4, 150.0, 144.9, 136.6, 131.4, 121.1, 119.3 (2C), 119.0, 118.1, 114.5 (2C), 112.9, 58.8, 56.7, 49.1.

4. References
