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In Situ Generated Iron Oxide Nanocrystals as Efficient and Selective Catalysts for the Reduction of Nitroarenes Using a Continuous Flow Method


Reduction of Nitroarenes Using In Situ Generated Iron Oxide Nanocrystals

Reduction of nitroarenes using the batch system:

\[
\begin{align*}
\text{Fe(acac)}_3 (0.25 \text{ mol%}) + \text{N}_2\text{H}_4\cdot\text{H}_2\text{O (1.2 equiv)} \rightarrow \\
\text{NO}_2 \rightarrow \text{NH}_2
\end{align*}
\]

\text{MeOH, MW, 150 °C, 2–8 min}

20 examples 95–99% yield (eq. 1)

Selected examples:

- 2 min, 99% yield
- 2 min, 99% yield
- 8 min, 99% yield
- 4 min, 99% yield

Continuous-flow reduction of nitroarenes:

\[
\begin{align*}
\text{Fe(acac)}_3 (0.25 \text{ mol%}) + \text{N}_2\text{H}_4\cdot\text{H}_2\text{O (1.2 equiv)} \rightarrow \\
\text{NO}_2 \rightarrow \text{NH}_2
\end{align*}
\]

\text{MeOH, 150–170 °C, 6–12 mL/min}

\text{residence time: 1.3–1.6 min}

Selected examples:

- 6 mL/min, 150 °C
- 12 mL/min, 170 °C
- 10 mL/min, 170 °C

Comment: The reduction of nitroarenes was also performed using a continuous-flow system to afford the anilines in 95–97% yield (eq. 2). The in situ generated iron oxide nanoparticles were characterized by XRD and HRTEM analyses. ICP–MS showed 7.9% iron leaching from the catalyst during the reduction using the batch system.

Significance: Iron oxide nanocrystals, generated in situ from Fe(acac)_3 and hydrazine hydrate, catalyzed the reduction of nitroarenes with hydrazine hydrate under microwave conditions to give the corresponding anilines in 95–99% yield (20 examples, eq. 1). In the reduction of nitrobenzene to aniline using the batch system, the catalyst was magnetically separated from the reaction mixture and reused seven times.