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:

\[
\text{Fe(acac)₃ (0.25 mol\%)} + \text{N₂H₄ ⋅ H₂O (1.2 equiv)} \rightarrow \text{R- NH}_2
\]

MeOH, MW, 150 °C, 2–8 min

Selected examples:

\[
\begin{align*}
\text{NO₂} & \rightarrow \text{NH}_2 & \text{NO₂} & \rightarrow \text{NH}_2 & \text{NO₂} & \rightarrow \text{NH}_2 & \text{NO₂} & \rightarrow \text{NH}_2 \\
\text{Cl} & \rightarrow \text{NH}_2 & \text{Cl} & \rightarrow \text{NH}_2 & \text{Cl} & \rightarrow \text{NH}_2 & \text{Cl} & \rightarrow \text{NH}_2 \\
\text{MeO} & \rightarrow \text{NH}_2 & \text{MeO} & \rightarrow \text{NH}_2 & \text{MeO} & \rightarrow \text{NH}_2 & \text{MeO} & \rightarrow \text{NH}_2
\end{align*}
\]

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

6 min, 99% yield 6 min, 95% yield 4 min, 99% yield 2 min, 99% yield 4 min, 98% yield

Continuous-flow reduction of nitroarenes:

\[
\text{Fe(acac)₃ (0.25 mol\%)} + \text{N₂H₄ ⋅ H₂O (1.2 equiv)} \rightarrow \text{R- NH}_2
\]

MeOH, 150–170 °C, 6–12 mL/min

Residence time: 1.3–1.6 min

Selected examples:

\[
\begin{align*}
\text{NO₂} & \rightarrow \text{NH}_2 & \text{NO₂} & \rightarrow \text{NH}_2 & \text{NO₂} & \rightarrow \text{NH}_2 \\
\text{Cl} & \rightarrow \text{NH}_2 & \text{Cl} & \rightarrow \text{NH}_2 & \text{Cl} & \rightarrow \text{NH}_2 \\
\text{MeO} & \rightarrow \text{NH}_2 & \text{MeO} & \rightarrow \text{NH}_2 & \text{MeO} & \rightarrow \text{NH}_2
\end{align*}
\]

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

Residence time: 1.6 min 1.3 min 1.5 min

96% yield 95% yield 97% yield

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.

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.