Heterogenized Cobalt Oxide Catalysts for Nitroarene Reduction by Pyrolysis of Molecularly Defined Complexes


Co$_3$O$_4$–Nitrogen Complex for Hydrogenation of Nitroarenes

Significance: A carbon-supported cobalt oxide-nitrogen catalyst 1 was prepared by pyrolysis (800 °C) of Co(phen)$_2$(OAc)$_2$ on Vulcan XC72R (an activated carbon). The hydrogenation of nitroarenes was carried out with 1 (1 mol% copper) in THF–H$_2$O under 50 bar of H$_2$ to give the corresponding anilines 2a–j in up to 99% yield.

Comment: The catalyst was reused nine times in the reaction of nitrobenzene where catalytic activity gradually decreased. The catalyst was characterized with TEM, energy-dispersive X-ray (EDX), XPS, and electron paramagnetic resonance (EPR).

**Preparation of a carbon-supported cobalt oxide nitrogen catalyst 1:**

$$\text{Co}_3\text{O}_4 + \text{nitrogen} \rightarrow \text{catalyst 1}$$

$$\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O} + \text{EtOH} \rightarrow \text{Vulcan XC72R}$$

$$\text{EtOH, r.t., 30 min} \rightarrow 60 ^\circ \text{C, 4 h} \rightarrow 800 ^\circ \text{C, 2 h} \rightarrow \text{Ar}$$

$$\text{Co}_3\text{O}_4$$

Results:

- 2a: 4 h, 91% yield
- 2b: 4 h, 99% yield
- 2c: 4 h, 99% yield
- 2d: 6 h, 97% yield
- 2e: 6 h, 94% yield
- 2f: 6 h, 93% yield
- 2g: 12 h, 96% yield
- 2h: 4 h, 99% yield
- 2i: 6 h, 96% yield
- 2j: 4 h, 97% yield

**Key words:** nitroarenes, cobalt oxide, phenanthroline, hydrogenation