Remarkable Effect of Alkalis on the Chemoselective Hydrogenation of Functionalized Nitroarenes over High-Loading Pt/FeOₓ Catalysts


Chemoselective Hydrogenation of Functionalized Nitroarenes to Anilines

**Significance:** A sodium-containing FeOₓ-supported platinum catalyst (Na-Pt/FeOₓ) was prepared by mixing H₂PtCl₆ and Fe(NO₃)₃ with (NH₄)₂CO₃ in water, followed by the treatment with NaNO₃, calcination, and reduction with hydrogen (eq. 1). Na-Pt/FeOₓ catalyzed the chemoselective hydrogenation of substituted nitroarenes under hydrogen pressure to afford the corresponding anilines in 95–97% yield (eq. 2). In the hydrogenation of 3-nitrostyrene, Na-Pt/FeOₓ promoted the hydrogenation of the nitro group to give 3-aminostyrene in 95% conversion with 98% selectivity (eq. 3). The catalyst was reused three times without significant loss of its catalytic activity or chemoselectivity.

**Comment:** Other alkali-metal-containing Pt/FeOₓ catalysts (Li-Pt/FeOₓ and K-Pt/FeOₓ) also promoted the selective hydrogenation of 3-nitrostyrene to 3-aminostyrene in 96 to >99% conversion and 94–95% selectivity. Compared with alkali-metal-containing catalysts, alkali-metal-free Pt/FeOₓ showed a lower selectivity (99% conversion and 66% selectivity). The authors have previously reported the chemoselective hydrogenation of functionalized nitroarenes to the corresponding anilines by using FeOₓ-supported platinum catalysts prepared from H₂PtCl₆, Fe(NO₃)₃, and Na₂CO₃ (Nat. Commun. 2014, 5, 5634).

**Equations:**

1. H₂PtCl₆ + Fe(NO₃)₃ + H₂(CO)₆ + (NH₄)₂CO₃ + NaNO₃ + H₂(10%)/He
   50 °C 400 °C 250 °C (Na: 5 wt%, Pt: 2 wt%)
   Na-Pt/FeOₓ

2. R-NO₂ → NH₂
   H₂ (3–6 bar), PhMe 40–50 °C, 20–85 min
   Na-Pt/FeOₓ (0.2–0.4 mol% Pt)
   97% yield
   96% yield
   95% yield
   97% yield
   96% yield

3. R-NO₂ + alkali-metal-Pt/FeOₓ
   (0.2 mol% Pt)
   H₂ (3 bar), PhMe 40 °C, 31–39 min
   Na-Pt/FeOₓ : 95% conversion, 98% selectivity
   Li-Pt/FeOₓ : 96% conversion, 95% selectivity
   K-Pt/FeOₓ : >99% conversion, 94% selectivity
   Pt/FeOₓ (alkali metal-free) : 99% conversion, 66% selectivity

**Keywords:** chemoselectivity, hydrogenation, platinum catalysis, nitroarenes, anilines