Shape-Selective Hydrogenation of Nitroarenes by Using Zeolite-Encaged Single-Atom Rhodium Catalysts

\[ \text{[Rh(NH}_2\text{CH}_2\text{CH(NH}_2\text{))Cl}_3] \quad \overset{\text{n-Pr}_4\text{NOH}, 10 \text{min}}{\longrightarrow} \quad \overset{\text{Si(OEt)}_4, \text{hydrothermal process}}{\longrightarrow} \quad \overset{\text{H}_2 \text{O}, 10 \text{h}, 170 \, ^\circ\text{C, 3 d}}{\longrightarrow} \quad \overset{\text{H}_2 \text{flow (60 mL/min), 500 \, ^\circ\text{C, 4 h}}}{\longrightarrow} \quad \text{Rh@S-1-H} \quad (1) \]

\[ \text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \quad \overset{\text{Rh@S-1-H (0.11 mol% Rh), H}_2\text{O, 298 K, 6.33 min}}{\longrightarrow} \quad 3\text{H}_2 + \text{NH}_4^+ + \text{BO}_2^- \quad (2) \]

\[ \overset{\text{TOF: 432 molH}_2 \text{molRh}^{-1} \text{min}^{-1}}{\longrightarrow} \]

\[ \overset{\text{Rh@S-1-H (1.1 mol% Rh), MeOH–H}_2\text{O, 298 K, 1.5–60 min}}{\longrightarrow} \]

Results:

- \[ \text{100\% conversion} \]
- \[ \text{>99\% selectivity} \]
- \[ \text{1.5 min} \]
- \[ \text{10.0 equiv} \]
- \[ \text{3\text{H}_2} \]
- \[ \text{NH}_4^+ \]
- \[ \text{BO}_2^- \]

Significance: A single-atom rhodium catalyst immobilized on silicate-1 zeolite (Rh@S-1-H), prepared as shown in equation 1, catalyzed the hydrolysis of ammonia–borane with a turnover frequency of 432 molH\textsubscript{2} molRh\textsuperscript{-1} min\textsuperscript{-1} (eq. 2). A sequential hydrolysis of ammonia–borane and hydrogenation of nitroarenes also proceeded in the presence of Rh@S-1-H (eq. 3).

Comment: As shown in equation 3, \textit{p}-substituted nitrobenzenes were reduced to the corresponding anilines with 100% conversion and >99% selectivity, whereas \textit{m}-substituted nitrobenzenes were almost intact after the hydrogenation reaction. Rh@S-1-H was characterized by means of \textsuperscript{13}C MAS-NMR, TGDTA, PXRD, ICP-AES, HAADF-STEM, HRTEM, SEM, EDS, XPS, XANES, EXAFS, and CO-DRIFTS measurements.