Hydrogenation on NHC-Modified Ru/K-Al₂O₃ Catalysts

**Preparation:**

- IMes·HBF₄ (R = mesityl)
- ICy·HBF₄ (R = Cy)

**Selected examples:**

1. Preparation of NHC/Ru/K-Al₂O₃ catalysts:
   - NHC = IMes, ICy
   - H₂ (10 bar), hexane, 25 °C, 16 h
   - NHC = IMes, ICy

2. Reaction of ethynylbenzene (1) with H₂ (10 bar), hexane, 25 °C, 16 h
   - Product: Ethylbenzene (2) and Ethylcyclohexane (3)
   - Yield: 1313 (Ru/K-Al₂O₃), 89:0 (IMes/Ru/K-Al₂O₃), 92:0 (ICy/Ru/K-Al₂O₃)

**Significance:** A surface-modification method was developed for tuning the catalytic performance of ruthenium nanoparticles supported on K-doped alumina (Ru/K-Al₂O₃) by using N-heterocyclic carbenes (NHC) ligands. For example, the hydrogenation of ethynylbenzene (1) under hydrogen in the presence of unmodified Ru/K-Al₂O₃ gave ethylcyclohexane (3) as the sole product in 95% yield, whereas the use of IMes/Ru/K-Al₂O₃ or ICy/Ru/K-Al₂O₃ (2 mol% ruthenium, NHC-modified Ru/K-Al₂O₃, 3.0 equiv of the NHC based on surface ruthenium) as a catalyst under similar conditions gave ethylbenzene (2) as the sole product in 89% and 92% yield, respectively.

**Comment:** The catalysts were characterized by means of ¹³C solid-state NMR, Ru 3p XPS, Ru K-edge EXAFS, and TEM. The particle size of ruthenium (TEM), the oxidation state of ruthenium (XPS), and the Ru–Ru coordination number (EXAFS) remained unchanged after the surface modification. In addition, ¹³C NMR spectroscopy confirmed that the carbene carbon was directly attached to the ruthenium nanoparticles.