Hydrogenation on NHC-Modified Ru/K-Al₂O₃ Catalysts

Preparation:

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\begin{align*}
R^1 \text{N} & \text{N} - R^2 \\
\text{BF}_4^- \\
\text{IMes HBF}_4 (R = \text{mesityl}) \quad \text{or} \\
\text{ICy HBF}_4 (R = \text{Cy})
\end{align*}
\]

\[
\text{I-BuOK} \quad \text{PhMe} \quad \text{Ru/K-Al}_2\text{O}_3 \quad \text{IMes \ or ICy} \quad \text{PhMe} \quad \text{IMes/Ru/K-Al}_2\text{O}_3 \quad (R = \text{mesityl}) \quad \text{or} \\
\text{ICy/Ru/K-Al}_2\text{O}_3 \quad (R = \text{Cy})
\]

Selected examples:

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\begin{align*}
1 & \quad \text{H}_2 \quad (10 \text{ bar}) \quad \text{hexane, 25 °C, 16 h} \\
& \quad \text{NHC} = \text{IMes, ICy}
\end{align*}
\]

\[
\begin{align*}
2 & \quad + \quad 3 \\
2 \% & \quad 3 \% = \quad 0:95 \\
& \quad (\text{Ru/K-Al}_2\text{O}_3) \\
89:0 & \quad (\text{IMes/Ru/K-Al}_2\text{O}_3) \\
92:0 & \quad (\text{ICy/Ru/K-Al}_2\text{O}_3)
\end{align*}
\]

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 ^13^C 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, ^13^C NMR spectroscopy confirmed that the carbene carbon was directly attached to the ruthenium nanoparticles.