Facile Fabrication of Magnetically Recyclable Metal-Organic Framework Nanocomposites for Highly Efficient and Selective Catalytic Oxidation of Benzylic C–H Bonds

Oxidation of Benzylic C–H Bonds with HKUST-1@Fe₃O₄

Preparation of HKUST-1@Fe₃O₄:

\[
\begin{align*}
\text{HKUST-1@Fe₃O₄} & \quad \text{Cu(OAc)}_2\text{H}_2\text{O} \\
\text{Fe₃O₄-CO₂H} & \quad \text{Cu}^{2+} \\
\text{PVP} & \quad \text{BTC} \\
\end{align*}
\]

Oxidation of benzylic hydrocarbons:

\[
\begin{align*}
\text{94.7% conversion} \quad \text{95.2% selectivity} \\
\text{99% conversion} \quad \text{99% selectivity} \\
\text{98.3% selectivity} \\
\text{97.1% selectivity}
\end{align*}
\]

Significance: The magnetic core–shell nanocomposites HKUST-1@Fe₃O₄ were prepared from Fe₃O₄-CO₂H (Φ 20 nm), polyvinylpyrrolidone (PVP), Cu(OAc)$_2$ and trimesic acid (BTC), in which the iron-based nanoparticles were encapsulated by the resulting HKUST-1 shell [for the copper-organic framework of Cu(OAc)$_2$ and trimesic acid, see: Chui et al. Science 1999, 283, 1148]. The oxidation of benzylic C–H bonds was carried out with HKUST-1@Fe₃O₄ and TBHP to give the corresponding desired carbonyl products in up to >99% conversion and >99% selectivity.

Comment: The catalyst was characterized by SEM, HR-TEM, PXRD, BET, and FT-IR analyses. Elemental analysis revealed a ratio of copper and iron of 19.34% and 28.63%. The catalyst was recovered by an external magnet and reused twice without significant loss of the catalytic activity.