Chiral Polymer Stabilized Bimetallic Nanocatalysts for Asymmetric Oxidations

Position-selective oxidation of cyclic diols

Selected example:

\[
\text{Pd/Au (3:1)-1 (0.15 mol\%)} + \text{O}_2 (30 \text{ psi}), \text{H}_2\text{O}, 120 \degree \text{C}, 3 \text{ d}
\]

Dihydroxylation of alkenes

Selected example:

\[
\text{Pd/Au (3:1)-1 (0.5 mol\%)} + \text{O}_2 (30 \text{ psi}), \text{H}_2\text{O}, 25 \degree \text{C}, 3 \text{ d}
\]

C–H oxidation of cycloalkanes

Selected example:

\[
\text{Cu/Au (3:1)-1 (1 mol\%)} + 30\% \text{H}_2\text{O}_2, \text{MeCN}, 50 \degree \text{C}, 7 \text{ d}
\]

**Significance:** A 3:1 Pd/Au bimetallic nanocatalyst stabilized by the chiral substituted poly(N-vinylpyrrolidinone) 1, prepared according to eq. 1, catalyzed the selective oxidation of 1,2- and 1,3-cyclic diols (eq. 2; 15 examples), and the dihydroxylation of alkenes under oxygen in water (eq. 3; 7 examples, to afford the corresponding chiral products in high yields and high enantiomeric excesses. Cu/Au (3:1–1), prepared by a similar method, catalyzed the C–H oxidation of cycloalkanes with H₂O₂ to give the corresponding ketones with high enantioselectivity (eq. 4).

**Comment:** In the oxidation of (±)-cyclohexane-1,3-diol, the catalyst was recovered and reused twice with a sharp decrease in its catalytic activity (first run: 49% yield; 99% ee; second run: 39% yield, 99% ee; third run: 18% yield, 98% ee).