

The Waterloo Institute for Nanotechnology

Presents

Intercalation of Chiral Ligand to Make Impact on Transition-Metal Asymmetric Catalysis

Professor Jing He

State Key Laboratory of Chemical Resource Engineering
Beijing University of Chemical Technology, Beijing, China

Transition-metal catalyzed asymmetric reaction is an important strategy to produce optically pure compounds. Recently, utilization of rigid or flexible confined spaces of inorganic hosts to improve enantioselectivity has attracted much attention in heterogeneous asymmetric catalysis. This work focuses on how to utilize the confinement of bi-dimensional flexible nanospace and the steric effect of rigid planar nanosheet of layered hosts to enhance the enantioselectivity in metal-catalyzed asymmetric synthesis. The layered host employed in our work is layered double hydroxides (LDHs), a kind of naturally-occurring or synthetic anionic clay.

The presentation includes:

1. Constraining a Titanium-Tartrate Complex to Induce Enantioselectivity

Titanium-tartrate complex was intercalated into the interlayer galleries of LDHs by ion-exchange. Constrained in the LDH interlayer region, titanium-tartrate complex showed obviously enhanced asymmetric induction in the heterogeneous sulfoxidation of pro-chiral methyl phenyl sulfide. Further studies proved that, in proper solvents, the interlayer region of titanium-tartrate intercalated LDHs could be swollen to accommodate the catalytic reactions. Obvious confinement from the bi-dimensional nanospace was clearly observed.

2. Orientation of Pre-Intercalated Tartrate to Impact Enantioselectivity

L-tartrate, the ligand for Ti (IV) centers, was intercalated into the interlayer galleries of LDHs and controlled as perpendicular-lying or flat-lying orientation. The interlayer tartrate in perpendicular orientation chelated Ti (IV) with both C-O-Ti and C=O-Ti coordination, not only displaying higher enantioselectivity for sulfoxide but also giving higher catalytic activity in the asymmetric sulfoxidation. The interlayer tartrate in a flat-lying orientation holds only the C-O-Ti coordination, contributing less to the improvement of enantioselectivity.

3. Attachment of Chiral α -Amino Acid Ligand to Nanosheet to Enhance Enantioselectivity

α -Amino acids, a kind of naturally occurring chiral unit, have been intercalated into the interlayer galleries of LDHs by ion-exchange or co-precipitation. The enantioselectivity in vanadium-catalyzed epoxidation of allylic alcohols was significantly enhanced by nanosheet attachment. Delamination allowed the catalytic reactions to be carried out under a pseudo-homogeneous condition, greatly increasing the catalytic efficiency while preserving enhanced enantioselectivity. Using water as medium, the catalyst can be directly recycled by simple liquid/liquid separation without loss of catalytic activity and enantioselectivity.



Monday, November 14th, 2011
11:00 am - 12:00 pm
Davis Centre 1304