

Structures of Surface-Functionalized Chiral Cu-BOX Complexes for Asymmetric Cyclopropanation

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Introduction

The design of asymmetric heterogeneous catalysts is still a challenging topic in chemistry. We have designed and prepared surface-functionalized SiO₂-supported Cu-bis(oxazoline) (BOX) complexes [1] and found that the surface functionalization with achiral silane-coupling reagents such as 3-methacryloxypropyltrimethoxysilane and octadecyltriethoxysilane had the positive effect for the amplification of enantioselectivity for asymmetric cyclopropanation. The structures of active Cu complexes were characterized by Cu K-edge XAFS.

Experimental

Preparation

(*S*)-*t*-Bu-BOX modified with two triethoxysilyl groups was immobilized on a SiO₂ surface. The SiO₂-supported Cu-BOX complex (Scheme 1 (b)) was prepared by the coordination of Cu(OTf)₂ to the SiO₂-supported BOX ligand (a). The surface supporting BOX ligands was functionalized with 3-methacryloxypropyltrimethoxysilane (c) and octadecyltriethoxysilane (d), followed by the coordination of the Cu precursor.

EXAFS measurements and analysis

Cu K-edge EXAFS spectra were measured at 298 K in a fluorescence mode at BL-9C and 12C stations. Background was subtracted by AUTOBK and *k*³-weighted EXAFS functions were Fourier-transformed into *R* space. FT spectra were fitted in *R* space by FEFFIT program. Backscattering amplitudes and phase shifts were calculated by FEFF8 code.

Results and discussion

Similar Cu K-edge XANES spectra were observed for Cu(BOX)(OTf)₂ complex, supported catalyst (b), surface-functionalized catalysts (c) and (d), indicating the surface Cu complexes were bivalent. Table 1 shows the curve-fitting results of EXAFS spectra at Cu K-edge for (b), (c), and (d). The curve-fitting analysis for three Cu-BOX complexes was carried out with a Cu-O shell, whose coordination number was 4 for all the Cu-BOX complexes (Table 1). From UV/Vis analysis in homogeneous phase, the BOX ligand is known to make a 1:1 complex with Cu(OTf)₂. Therefore, the supported complexes (b), (c), and (d) had two Cu-O and two Cu-N coordination bonds, attributed to Cu(BOX)(OTf)₂ (Scheme 1).

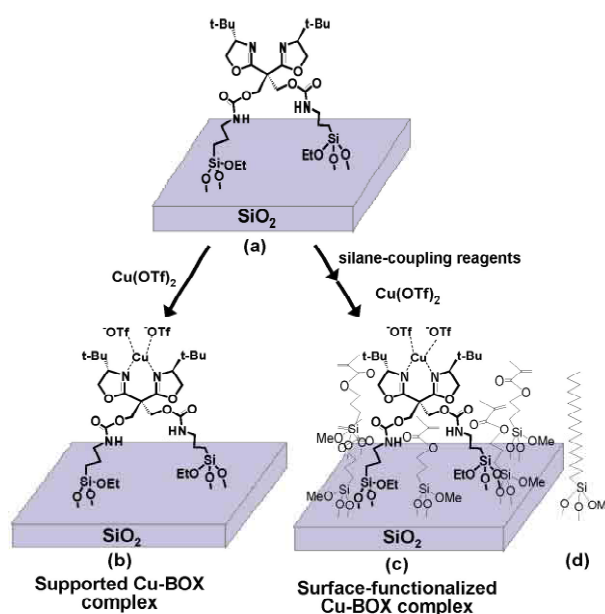
The asymmetric cyclopropanation of styrene and ethyl diazoacetate was carried out on (b), (c), and (d) at 293 K. While the simple supported complex (b) showed 55% ee for trans products, the methacryl-functionalized complex

(c) amplified the enantioselectivity up to 72% ee. The octadecyl-functionalized complex (d) also showed the larger ee (68% ee) than (b). The EXAFS analysis showed that there was no significant change in the local coordination of the Cu-BOX complexes (b), (c), and (d). Thus, it is suggested that the conformations of achiral organic groups such as methacryl and octadecyl groups could enhance the chiral environment around the Cu-BOX complex on SiO₂, resulting in the increases in the enantioselectivity.

Table 1: Curve-fitting results of Cu K-edge EXAFS spectra for supported Cu-BOX complex (b), and surface-functionalized Cu-BOX complexes (c) (methacryl-functionalized), and (d) (octadecyl-functionalized) measured at 293 K

Sample	Shell	CN	R / Å	$\sigma^2 / \text{Å}^2$
(b)	Cu-O	4.1±0.4	1.99±0.01	(6±1)×10 ⁻³
(c)	Cu-O	4.4±0.3	1.96±0.01	(6±1)×10 ⁻³
(d)	Cu-O	4.4±0.3	1.95±0.01	(4±1)×10 ⁻³

$k = 3-11 \text{ Å}^{-1}$, $R = 1.1-2.0 \text{ Å}$.



Scheme 1: Preparation of supported Cu-BOX complex (b) and surface-functionalized Cu-BOX complexes (c) and (d) on SiO₂.

Reference

[1] M. Tada, S. Tanaka, and Y. Iwasawa, Chem. Lett. 34, 1362 (2005).

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