

The Structures of Surface-Functionalized Chiral Cu-BOX Complexes for Asymmetric Diels-Alder Reaction

Satoka TANAKA, Mizuki TADA, and Yasuhiro IWASAWA*
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Introduction

The design of asymmetric heterogeneous catalysts is still a challenging topic in catalytic chemistry. We have designed and prepared surface-functionalized SiO₂-supported Cu-bis(oxazoline) (BOX) complexes for asymmetric Diels-Alder reaction and found that the surface functionalization with an achiral silane-coupling reagent 3-methacryloxypropyltrimethoxysilane remarkably amplified enantioselectivity for the reaction. 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(ClO₄)₂·6H₂O to the SiO₂-supported BOX ligand (a). The surface supporting the BOX ligand was functionalized with methacryloxypropyltrimethoxysilane, followed by the coordination of the Cu precursor (c).

EXAFS measurements and analysis: Cu K-edge EXAFS spectra were measured at 298 K in a transmission and a fluorescence mode at BL-9C and 12C stations. Background was subtracted by AUTOBK and then *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

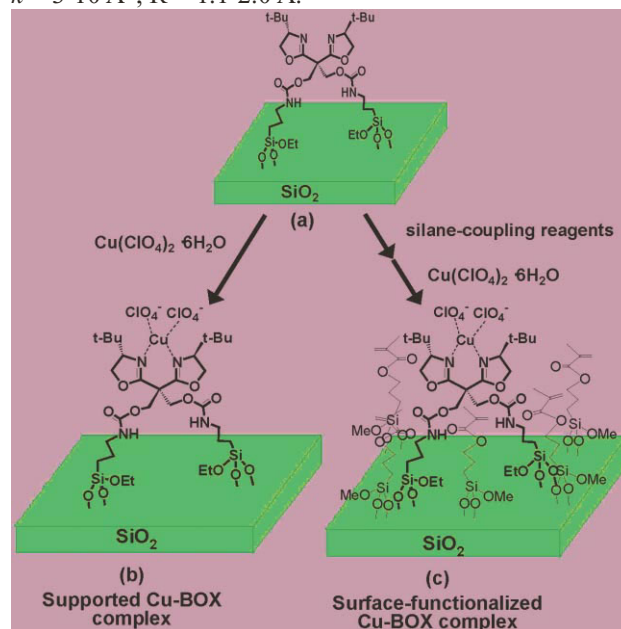
Similar Cu K-edge XANES spectra were observed for homogeneous Cu(BOX)(ClO₄)₂, (b), and (c), indicating bivalent Cu species. Table 1 shows the curve-fitting results of EXAFS functions at Cu K-edge for Cu(BOX)(ClO₄)₂, (b), and (c). UV/VIS and ESR spectra suggested that both supported Cu complexes (b) and (c) possessed two Cu-N bonds. The curve-fitting analysis for three Cu-BOX complexes was carried out with Cu-N shell, whose bond distance and CN were 1.98 Å and 4, respectively, for all Cu-BOX complexes (Table 1). Fitting with Cu-O shell was suggested similar 4-coordinated Cu complexes. Therefore, the supported complexes (b) and (c) had two Cu-O bonds and two Cu-N coordination bonds, which were similar to Cu(BOX)(ClO₄)₂. According to *g*-values calculated from ESR spectra, both (b) and (c) complexes have square-planar conformation on the surface. The determined structures of the supported Cu-BOX catalysts are presented in Scheme 1.

Asymmetric Diels-Alder reactions were carried out on (b) and (c). While the supported complex (b) showed low enantioselectivity (15 ee%), the achiral methacryloxy-functionalized complex (c) amplified the enantioselectivity up to 65 ee%. The EXAFS analysis showed that there was no change in the local coordination of the Cu-BOX complexes (b) and (c). Thus, it is suggested that the oxygen of methacryl moiety may interact with the NH group of the chiral BOX ligand by hydrogen bonding and an asymmetrically-assembled structure may be created, resulting in the large increase in enantioselectivity on the surface.

Table 1: Curve-fitting results of Cu K-edge EXAFS spectra for homogeneous Cu(BOX)(ClO₄)₂, supported Cu-BOX complex (b), and surface-functionalized Cu-BOX complex (c) measured at 293 K

Sample	Shell	CN	R / Å	$\sigma^2 / \text{Å}^2$
Cu(BOX)(ClO ₄) ₂	Cu-N	4.5±0.6	1.98±0.01	(4±1)×10 ⁻³
(b)	Cu-N	4.4±0.5	1.99±0.01	(2±1)×10 ⁻³
(c)	Cu-N	4.1±0.5	1.98±0.01	(4±1)×10 ⁻³

k = 3-10 Å⁻¹, R = 1.1-2.0 Å.



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

* iwawasa@chem.s.u-tokyo.ac.jp