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SiO_2-Supported Chiral V Catalysts for Asymmetric Oxidative Coupling of 2-Naphthol

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Introduction

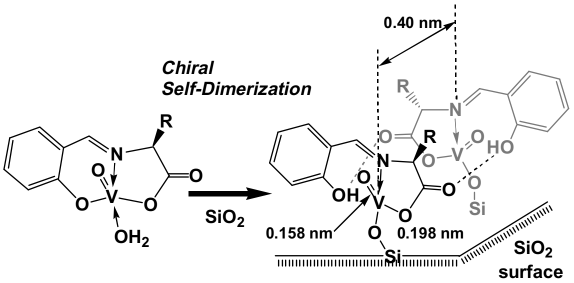
1,1'-binaphthol (BINOL) and its derivatives have been utilized as versatile chiral sources for asymmetric catalysis, and efficient catalysts for their syntheses are ultimately requested in many chemical fields. The oxidative coupling of 2-naphthols is a direct synthesis of BINOL derivatives, but only few homogeneous metal complexes have been reported for the asymmetric coupling of 2-naphthols. We found that a chiral structure is created by the surface-mediated self-dimerization of V complexes on SiO_2 and the designed V complexes supported on the surface are active and enantioselective for the asymmetric oxidative coupling of 2-naphthol: 96% conversion, 100% selectivity to BINOL, and 90% enantioselectivity to (R)-BINOL. The structure of the active V dimer and the reaction mechanism of the oxidative coupling reaction were studied by means of FT-IR, XPS, DR-UV/VIS, ESR, DFT, and V K-edge XAFS. This is the first heterogeneous catalyst for the asymmetric oxidative coupling of 2-naphthol.

Experimental

V-monomer complexes with chiral Schiff-base ligands were impregnated with SiO_2, Al_2O_3, and TiO_2 in ethanol under N_2. The solvent was evaporated, and the sample was dried under vacuum for 7 h. V loadings were changed in the range of 0.3-3.4 wt%, which were determined by XRF (Scheme 1).

XAFS spectra at V K-edge were measured in a transmission mode at 15 K at the BL-9A, 9C, and 12C station. Background subtraction was conducted by the AUTOBK program, and Fourier-transformed spectra were fitted in R space by FEFFIT program.

The oxidative coupling reaction was performed in absolute toluene, and the reaction was monitored by HPLC. The coordination of 2-naphthol was investigated by XAFS after the evacuation of the solvent.



Scheme 1 The preparation of the supported V-dimer catalyst on a SiO_2 surface.

Results and Discussion

A sharp pre-edge peak at 5469.2 eV attributed to the V=O bond for the V precursor did not disappear in the spectrum of the supported V complex, indicating that the V=O double bond remained unchanged upon supporting of the V precursor on SiO_2. The pre-edge peak position (5469.2 eV) of the supported V catalyst was same as that of the precursor. Hence the valence of the V center is four (V^{4+}) on the surface. No spectral changes were observed upon the coordination of 2-naphthol.

The XANES spectra for both the precursor and the supported V complex demonstrated the existence of a V=O double bond. A V=O bond at 0.157 ± 0.001 nm is similar to that of the precursor at 0.158 nm, while the CN of V-O bonds at 0.199 ± 0.002 nm decreased from 3.8 ± 0.4 to 2.8 ± 0.5. Thus an unsaturated V center was formed on the surface. Longer-distance bonding was not observed with all the catalysts, indicating that there was no direct V-V bonding in the supported V catalysts. Combined by FT-IR and ESR spectra, we proposed the active structure of the supported V complex as shown in Scheme 1. The Ph-O moiety of the Schiff-base ligand was selectively reacted with surface Si-OH, forming Ph-OH and unsaturated V center. The Ph-OH group coordinated with COO of another V complex by hydrogen bonding. Thus the unsaturated active V site and chiral V center were created on the SiO_2 surface. There were no significant differences in the structures of the supported V complexes with different V loading (0.3-3.4 wt%).

The treatment of the supported V catalyst with 2-naphthol caused recovery of the CN of V-O bonds to 4.0 ± 0.6 at 0.199 ± 0.002 nm. The V=O double bond was at 0.157 ± 0.002 nm, similar to that of the fresh sample before the 2-naphthol coordination. The CN of V-O did not increase after the addition of excess 2-naphthol and the V center could activate one 2-naphthol molecule.

References

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