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Chiral self-dimerization of vanadium complexes on a SiO_2 surface: the first heterogeneous catalyst for asymmetric 2-naphthol coupling†

Mizuki Tada, Toshiaki Taniike, Lakshmi M. Kantam and Yasuhiro Iwasawa*
Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: iwasawa@chem.s.u-tokyo.ac.jp; Fax: (+81)3-5800-6892

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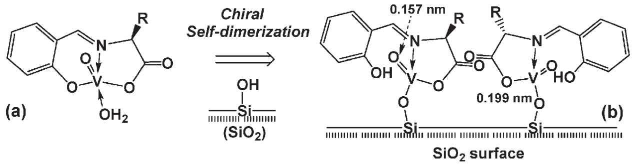
The self-dimerized chiral assembly of vanadium–Schiff-base complexes was found to occur on a SiO_2 surface and to be the first heterogeneous catalyst for the asymmetric oxidative coupling of 2-naphthol with 100% selectivity and 90% enantioselectivity.

The fine design of chirality on heterogeneous catalyst surfaces is still a serious challenge to be tackled. A simple application of strategy for the design of homogeneous chiral catalysts to heterogeneous systems is not the way to success generally,[1] and a new strategy to construct novel chirality on surfaces is indispensable for heterogeneous asymmetric catalysis. The oxidative coupling of 2-naphthol is a representative reaction mode for a direct synthesis of 1,1′-binaphthol (BINOL) whose optically pure derivatives are regarded as versatile chiral auxiliaries and ligands in asymmetric syntheses.[2] Nevertheless only few studies have been reported for the asymmetric coupling of 2-naphthols in homogeneous systems.[3–5] To our knowledge, this is the first heterogeneous catalyst for the asymmetric coupling reaction.

Several V-monomer precursors with Schiff-bases obtained from α-amino acids (L-valine, L-isoleucine, L-leucine and L-phenylalanine) (Scheme 1(a)) were synthesized according to the literature.[6] The attachment of the precursors on SiO_2 (Aerosil 200; calcined at 773 K for 2 h) was performed by impregnation of each V complex in dehydrated ethanol, followed by evacuation of the solvent. The V monomers selectively reacted with surface silanols leading to the structural reconstruction of the tridentate Schiff-ligand coordination species, as characterized by ESR, XPS, UV/VIS, FT-IR, XAFS and DFT calculation (ESI†). The Ph–O moiety of the Schiff-base ligand transformed to the Ph–OH configuration *via* selective reaction with surface Si–OH, and the coordination number of V–O(N) single bonds analyzed by EXAFS was reduced from 3.8 to 2.8 on the surface. Thus, the V monomers convert to a coordinatively unsaturated metal conformation on the SiO_2 surface (Scheme 1(b)), which can behave as an active site for the coordination of 2-naphthol.

Fig. 1 shows ESR spectra for the supported V complex (b) in the presence and absence of O_2 measured at 6 K. The hyperfine signals of the supported complex ($g_\parallel = 1.948$, $A_\parallel = 17.01\ \mathrm{cm}^{-1}$; $g_\perp = 1.991$, $A_\perp = 6.49\ \mathrm{cm}^{-1}$) and the relationship between the hyperfine coupling constants ($g_\parallel < g_\perp$ and $A_\parallel \gg A_\perp$) demonstrate an axially compressed $d_{xy}{}^1$ configuration of a V=O complex. Furthermore, a broad peak was observed on the hyperfine signals, and it greatly increased after the adsorption of O_2 as shown in Fig. 1 (A2). The peak was accompanied with the appearance of a new peak attributed to the half band of $|\Delta M_s| = 2$ (A1). The results demonstrate that another V complex is located near a V complex to form a dimer assembly. The V–V distance in the V dimer produced by self-assembly on the surface is estimated to be 0.40 ± 0.05 nm by the relative intensity of the forbidden half-field transition ($|\Delta M_s| = 2$) to the allowed transition ($|\Delta M_s| = 1$).[7] After evacuation of the O_2-adsorbed sample, the intensity returns completely to the original level and the change in the ESR signal occurs reversibly. This reversible adsorption of O_2 molecules means that the supported V catalyst possesses capacity for O_2 activation that is indispensable for the oxidative coupling reaction. After the coordination of 2-naphthol, the V assembly also adsorbs O_2 (Fig. 1 (B1) and (B2)). The broad signal and the behavior for oxygen molecules were observed in the range of V loading 0.3–3.4 wt%, indicating that the chiral self-dimerization of the V precursors occurs independently of V loading on the SiO_2 surface.



Scheme 1 Preparation of the self-dimerized chiral assembly of vanadium monomers on a SiO_2 surface.

The Ph–OH moiety formed by the surface reaction undergoes hydrogen bonding with the C=O group of the ligand to assemble the supported V complexes on the surface. Indeed, a difference (232 cm^{-1}) in the frequencies of $\nu_{\mathrm{asym}}(\mathrm{COO})$ and $\nu_{\mathrm{sym}}(\mathrm{COO})$ in the FT-IR spectrum indicates the occurrence of hydrogen bonding at the C=O oxygen. The hydrogen bonding between Ph–OH and C=O is responsible for the V-complex dimerization.

We have performed modeling by the DFT calculation for the self-assembled V complex based on the characterization of the V assembly on the surface (Fig. 2). Two V=O bonds are directed to the opposite sides mutually from the principal molecular plane of the V complex, similarly to a structural unit in the V complex crystal,[10] and a favorable reaction space for the oxidative coupling of two 2-naphthols is created between the two unsaturated V centers. Other configurations have not given any stable dimer structure that agrees with the experimental results. In solution, two chiral isomers with different V=O directions toward a plane

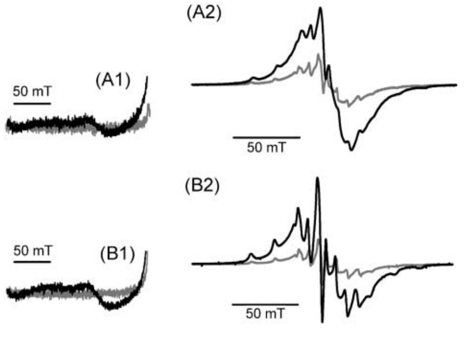


Fig. 1 ESR spectra for the supported V dimer (V 3.4 wt%) in the absence (gray) and presence (black) of O_2 at 6 K. (A) Supported catalyst; (B) supported catalyst after coordination with 2-naphthol. Left (1): half-band; right (2): main signal.

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† Electronic supplementary information (ESI) available: Fig. S1: V K-edge XANES spectra for the V precursor, the supported V catalyst and the supported V catalyst treated with 2-naphthol. Fig. S2: V K-edge EXAFS Fourier-transformed spectra for the V precursor, the supported V 3.4 wt% catalyst and the supported V catalyst treated with 2-naphthol. Table S1: Frequencies of vibration modes for the V precursors labeled with isotopes (^{13}C and ^{15}N) and the supported V catalyst (3.4 wt%) measured by FT-IR and calculated by DFT. See http://www.rsc.org/suppdata/cc/b4/b410307f/

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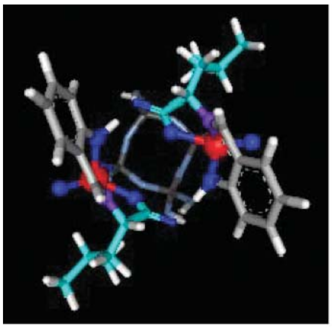
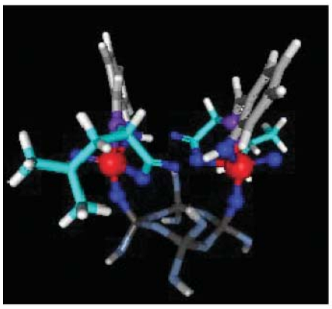


(Top view)



(Side view)

Fig. 2 The structure of the V dimer on a SiO_2 cluster modeled by DFT. Two V complexes have the interaction between Ph–OH on a V complex and C=O on another V complex (*vice versa*) to form the dimer structure. All *ab initio* calculations for a number of possible surface structures were performed using a density functional code, DMol3[8] where the exchange–correlation interaction was treated by the Perdew–Wang 91 functional (PW91).[9] For valance electrons the double-numeric basis set with polarization functions (DNP) was employed, while for core electrons the effective core potentials (ECP) were used. Red: vanadium atom; blue: oxygen atom; sky: chiral isobutyl group; gray: phenyl ring.

constructed of the tridentate ligand coordination coexist in a similar concentration because of a low energy difference between the two isomers.[11] Thus the SiO_2 surface selectively creates novel and unique chirality by the chiral self-dimerization, which cannot be realized in solution.

We have found that the supported V catalyst is highly active for the coupling of 2-naphthol under aerobic conditions (Table 1). On the SiO_2-supported V catalysts, the conversion reaches a maximum of 96%, and the reaction rate in toluene is higher than that in $CHCl_3$. The supported V catalyst is perfectly selective (100% selectivity) and reusable for the BINOL synthesis as shown in Table 1. The homogeneous V precursor is inactive for the reaction.[12] The V complexes supported on Al_2O_3 and TiO_2 are not selective for the coupling (Table 1).

Table 1 Catalytic performances of homogeneous and heterogeneous V catalysts for the asymmetric oxidative coupling of 2-naphthol

Catalyst-V wt%[a]	Temp./K	Time/day	Solvent	Conv. (%)	Selectivity (%)	ee (*R*) (%)
Precursor[b]	293	5	$CHCl_3$	0	0	—
SiO_2-0.3[c]	263	6	Toluene	12	100	14
SiO_2-0.3[d]	263	5	$CHCl_3$	6	100	51
SiO_2-0.3[e]	263	5	$CHCl_3$	9	100	56
SiO_2-0.3	293	5	$CHCl_3$	76	100	19
SiO_2-0.3	263	5	$CHCl_3$	9	100	54
SiO_2-0.3	293	5	Toluene	96	100	13
SiO_2-0.3	263	5	Toluene	11	100	32
SiO_2-0.3[f]	263	5	Toluene	10	100	33
SiO_2-0.3[g]	263	6	Toluene	9	100	31
SiO_2-0.8	263	5	Toluene	33	100	39
SiO_2-1.6	263	5	Toluene	42	100	48
SiO_2-3.4	263	11	Toluene	93	100	90
SiO_2-3.4[f]	263	11	Toluene	91	100	89
Al_2O_3-1.7	293	5	$CHCl_3$	69	53	−2
TiO_2-0.8	293	5	$CHCl_3$	52	0	—

[a] All the reactions were performed in 5 ml of solvent. Catalyst amount (supported catalyst) is 100 mg, and 1 wt% corresponds to 9.8×10^{-6} mol of V dimer, while the molar ratio V/reactant is always 1/36. [b] Ligand: L-leucine. [c] Homogeneous reaction.[12] [d] L-Valine. [e] L-Isoleucine. [f] L-Phenylalanine. [g] Reuse. [h] Hydroxynaphthaldehyde was used instead of salicylaldehyde.

The nature of the ligands shows less effect on the enantioselectivity for the oxidative coupling (56 ee%). Thus, the leucine-based catalysts were used for detailed investigation of the catalytic performances. With an increase in V loading (0.3 to 3.4 wt%) the enantioselectivity remarkably increases as shown in Table 1. The highest enantio excess 90% was achieved on the supported 3.4 wt% V catalyst. This ee% is equivalent to the highest ee% (91%) among the values reported thus far for the oxidative coupling of 2-naphthol without functional groups on its naphthyl ring in homogeneous systems.[5c] From the estimation of the cross section of the V precursor, the V loading of 3.4 wt% corresponds to full coverage of the complex on the SiO_2 surface, where the configuration and reaction environment of the V dimer on the surface are regulated rigidly for the achievement of the high enantioselectivity compared to the lower V loadings.

In conclusion, we have found the chiral self-assembly of vanadium Schiff-base monomers on a SiO_2 surface to provide a novel SiO_2-supported chiral V dimer, which exhibits enantioselective catalysis for 2-naphthol oxidative coupling. The V-monomer precursor reacts on the surface selectively to assemble with each other, and the formed V dimer with unsaturated chiral V centers is active for the catalytic 2-naphthol coupling reaction. The SiO_2-supported V catalyst exhibits 100% selectivity for the BINOL synthesis, and the highest enantioselectivity of 90% is accomplished on the full-coverage V catalyst. This is the first heterogeneous catalyst with an active self-assembly structure for the asymmetric oxidative coupling of 2-naphthol. The self-assembly on surfaces provides a new promising way to produce active species for heterogeneous enantioselective catalysis.

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