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Catalyst design for selective oxidation with molecular oxygen by metal-complex attachment

Mizuki Tada [*], Rajaram Bal, Yasuhiro Iwasawa

Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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Abstract

We have prepared novel metal-ensemble catalysts by chemical attachment of metal-complex precursors, *N*-interstitial Re_{10} cluster supported on HZSM-5 and chiral self-dimerized V-dimer on SiO_2, which are active and highly selective for selective oxidation with molecular oxygen. The $Re_{10}(N)_2$/HZSM-5 catalyst exhibited 87.7% (steady-state reaction) and 93.9% (pulse reaction) selectivity for direct phenol synthesis from benzene with molecular oxygen. The structures of active metal species were characterized by EXAFS, TPD and DFT calculations. The chiral self-dimerized V-dimer catalyst was found to be the first heterogeneous catalyst for the asymmetric oxidative coupling of 2-naphthol with molecular oxygen, which exhibited 100% selectivity and 90% enantioselectivity.

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1. Introduction

Selective oxidation with molecular oxygen has received much attention to date, but it is still difficult to activate molecular oxygen, while suppressing undesirable combustion under oxidation reaction conditions. While it has been recognized that the design of catalytically active structures and ensembles and the control of their reactivity based on in situ characterization are critical in achieving high catalytic performance with good selectivity, these issues, which are a serious challenge to particularly selective oxidation catalysis, have yet to be adequately addressed. We have succeeded in preparing highly selective oxidation catalysts for valuable selective oxidation with molecular oxygen by metal-complex attachment on oxide supports choosing appropriate metal-complex precursors. The present study emphasizes novel phenomena and concepts for the design of new catalytic structures for selective oxidation with molecular oxygen, presenting two examples we have recently discovered: *N*-interstitial Re_{10} cluster for direct phenol synthesis from benzene [1] and chiral self-dimerized V catalysts for asymmetric oxidative coupling of 2-naphthol [2,3].

2. Experimental

2.1. Preparation of N-interstitial Re$_{10}$ cluster supported on HZSM-5

HZSM-5 with a SiO_2/Al_2O_3 ratio of 19 was synthesized [4] and other zeolites were brought from TOSOH. The supported Re catalysts were prepared by a conventional impregnation method using NH_4ReO_4 and a chemical vapor deposition (CVD) method using CH_3ReO_3 (MTO). In the CVD procedure, ZSM-5, Beta, USY and Mordenite were pressed and sieved to 355–710 μm granules and calcined at 873 K for 2 h and then the zeolites were further treated at 673 K for 0.5 h under vacuum. Next, heating the whole apparatus at 333 K, the zeolites were exposed to MTO vapor for 14 h. The impregnation and CVD catalysts were pretreated in a He flow at 673 K for 1 h and cooled in a He flow before use as catalysts.

2.2. Preparation of chiral self-dimerized V-dimer on SiO$_2$

V-monomer precursors with Schiff-base ligands were synthesized by a reported method [5]. The V-monomer precursors were dissolved in dehydrated ethanol and impregnated with SiO_2 (Degussa; Aerosil 200), Al_2O_3 (Degussa; Allon C) and TiO_2 (Degussa; P-25) under nitrogen atmosphere. After

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[*] Corresponding author. Fax: +81 3 5841 4364.
E-mail address: mtada@chem.s.u-tokyo.ac.jp (M. Tada).

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stirring for 1 h at ambient temperature, the solvent was evaporated and the sample was dried under vacuum for 7 h. V loadings were in the range of 0.3–3.4 wt%, which were determined by XRF.

2.3. Catalyst characterization

XAFS spectra at V K-edge and Re L_{III}-edge were measured in a transmission mode at 15 K at the BL-9A and BL-9C stations of the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF). X-rays from the storage ring were monochromatized by a Si(1 1 1) double-crystals monochrometor and higher harmonics were removed by Rh-coated cylindrically bent mirrors. The EXAFS spectra were analyzed with the UWXAFS package [6]. Background was subtracted by the AUTOBK program and the obtained k^3-weighted EXAFS data were Fourier transformed into R-space. Phase shifts and backscattering amplitudes were calculated by the FEFF8 code [7].

ESR X-band spectra for the supported V catalysts (0.3–3.4 wt%) were recorded on JEOL JES-RE2X equipment at 6 K. The ESR spectrum was measured under vacuum and then measured in the presence of O_2. The adsorption of oxygen was performed twice after evacuation at 293 K. The changes in ESR spectra were examined for both forbidden half-field ($|\Delta Ms| = 2$) and allowed ($|\Delta Ms| = 1$) transitions. The interatomic distance of V–V was evaluated by the relative intensities of a half-field transition ($|\Delta Ms| = 2$) to a main ($|\Delta Ms| = 1$) transition, which are inversely proportional to the sixth power of r (r: V–V distance) [8]. Two V-dimers with O═V···V═O conformations (two V═O are directed opposite), $K_4[VO(cit)]_2$ $6H_2O$ (cit: citrate) with 0.3301 nm of V–V distance [9] and $Na_4[VO(d\text{-tart})]_2$ (tart: tartrate) with 0.435 nm of V–V distance [10,11] were used as references for the determination of the coefficient of the inverse proportion. The V–V distances of the supported V catalysts before and after the coordination of 2-naphthol were estimated after O_2 adsorption.

2.4. Selective oxidation with benzene and molecular oxygen to phenol

The selective catalytic reactions were conducted in a fixed-bed down-flow reactor by charging 0.2 g of a catalyst. A typical composition of the reaction gases was He:O_2:NH_3:benzene = 46.4:12.0:35.0:6.6 (mol%) and W/F was typically 6.7 g_{cat} h mol^{-1}. The products were analyzed by two on-line GCs with a FID detector using a NEUTRABOND-1 column for hydrocarbons and with a TCD detector using a Unibeeds C column for inorganic materials. Pulse experiments were carried out using 0.1 g of a catalyst and the volume of each pulse was 0.42 ml.

2.5. The asymmetric oxidative coupling of 2-naphthol with molecular oxygen

The oxidative coupling of 2-naphthol was carried out on both homogeneous and heterogeneous V catalysts in the temperature range of 263–293 K under O_2 atmosphere (101.3 kPa). The molar ratio of V-dimer to 2-naphthol was basically fixed to 1/36 and 5 ml of toluene or chloroform was used as solvents. The reaction in the absence of oxygen was also performed under nitrogen atmosphere.

3. Results and discussion

3.1. N-interstitial Re_{10}-cluster/HZSM-5 catalyst for direct phenol synthesis from benzene with molecular oxygen

Phenol is one of the most important chemicals and has been produced from benzene by the three-steps cumene process in industries, which is not only energy consuming but also less efficient, showing very low phenol yield and producing lots of by-products. Direct phenol synthesis from benzene is an alternative way to overcome these problems and O_2 [12–15], H_2O_2 [16,17], N_2O [18–25], $H_2 + O_2$ [26,27], air/CO [28] and O_2/H_2O [29] have been used as oxidants. Despite the good performances with N_2O and H_2O_2 as oxidants, any economically and environmentally favorable benzene-O_2 catalytic systems with high selectivity for phenol synthesis have not been discovered to date because molecular oxygen is hardly activated to selectively oxidize benzene to phenol.

We have succeeded in preparing HZSM-5-supported Re-cluster catalysts, which were active for the direct phenol synthesis with high phenol selectivity [15]. Nevertheless, selectivity of the benzene oxidation to phenol with O_2 reported to date has not exceeded 60% [14]. The prepared Re-cluster catalyst is tremendously selective (87.7% in the steady-state reaction and 93.9% in the pulse reaction) for the benzene oxidation with O_2 under coexisting NH_3 [1].

Table 1 shows the performances of the Re/zeolite catalysts for the selective oxidation of benzene with O_2. A Re-CVD/HZSM-5 catalyst (SiO_2/Al_2O_3 = 19) preferentially produced phenol with 87.7% selectivity in the presence of NH_3 (Table 1). No other liquid products were detected and only a by-product was gaseous CO_2. The activity and selectivity of the Re-CVD/HZSM-5 catalyst did not decrease for at least 6 h under the steady-state conditions. It is to be noted that the coexistence of NH_3 is indispensable for the selective oxidation. Neither benzene oxidation nor combustion proceeded in the absence of NH_3. The phenol formation rate and selectivity increased with increasing NH_3 pressure because the coexisting NH_3 produces active Re clusters as described hereinafter and reached maxima around 35–42 kPa of partial NH_3 pressure [1]. Excess ammonia decreased the rate and selectivity for the phenol synthesis by competitive adsorption against benzene and undesirable poisoning. The NH_3 pretreatment of the catalyst for longer than 1 h was required to generate the selective catalysis, indicating the formation of an active structure in situ under the catalytic reaction conditions in the presence of NH_3.

Impregnation and physically mixing catalysts were much less active and much less selective for the phenol synthesis (Table 1). The CVD catalyst was almost 18 times more active than the impregnation catalyst. In the physically mixing and

Table 1
Catalytic performances of Re/zeolite catalysts for the direct phenol synthesis from benzene with molecular oxygen at 553 K[a]

Catalyst	SiO_2/Al_2O_3	Method	Re/wt%	TOF/10^{-5} s^{-1}[b]	PhOH selec. (%)[c]
HZSM-5	19	–	–	Trace	0
Re/HZSM-5[d]	19	CVD	0.58	Trace	0
Re/HZSM-5	19	CVD	0.58	65.6	87.7
Re/HZSM-5[e]	19	CVD	0.58	51.8	85.6
Re/HZSM-5[f]	19	CVD	2.2	83.8	82.4
Re/HZSM-5[g]	19	CVD	0.58	74.6	93.9
Re/HZM-5[h]	19	CVD	0.58	86.1	90.6
Re/HZSM-5	19	Imp.[i]	0.6	11.8	27.7
Re/HZSM-5	19	Phys.[j]	0.6	Trace	0
Re/HZSM-5[d]	23.8	CVD	0.58	Trace	0
Re/HZSM-5	23.8	CVD	0.58	36.2	68.0
Re/HZSM-5	39.4	CVD	0.59	31.0	48.0
Re/H-Beta	37.1	CVD	0.53	18.5	12.0
Re/H-USY	29	CVD	0.60	Trace	0
Re/H-Mordenite	220	CVD	0.55	26.3	23.4
SiO_2-Al_2O_3	19	–	0	0	0
Re/SiO_2-Al_2O_3	19	Imp.[i]	1.2	trace	0

[a] Catalyst = 0.20 g; W/F = 6.7 g_{cat} h mol^{-1}; He/O_2/NH_3/benzene = 46.4/12.0/35.0/6.6 (mol%). The detailed carbon mass balance and material balance were examined in most of the experimental runs and the values were between 97 and 99%.

[b] Consumed benzene/Re/s.

[c] Phenol selectivity in carbon (%).

[d] In the absence of NH_3.

[e] W/F = 5.2 g_{cat} h mol^{-1}.

[f] W/F = 10.9 g_{cat} h mol^{-1}; He/O_2/NH_3/benzene = 46.4/12.0/35.0/6.6 (mol%).

[g] Pulse reaction on the NH_3-pretreted catalyst (0.1 g); 1 pulse of benzene + O_2 (He/O_2/benzene = 81.4/12.0/6.6 (mol%)).

[h] Pulse reaction on the NH_3-pretreated catalyst (1.0 g); 1 pulse of benzene + O_2 (He/O_2/benzene = 81.4/12.0/6.6 (mol%)).

[i] Impregnation catalyst.

[j] Physical mixing of MTO and HZSM-5.

impregnation catalysts Re^{7+} precursors were transformed to partly aggregated and ill-defined Re species unlike active Re clusters in the CVD catalyst. The phenol selectivity highly depended on the structure, acid strength and SiO_2/Al_2O_3 ratio of zeolites as shown in Table 1. The decrease in the SiO_2/Al_2O_3 ratio caused large increases in the catalytic activity (TOF: $31.0 \times 10^{-5}\ s^{-1}$–$65.6 \times 10^{-5}\ s^{-1}$) and the phenol selectivity (48.0–87.7%). The rate of phenol formation decreased in the order; HZSM-5 ($SiO_2/Al_2O_3 = 19$) > HZSM-5 ($SiO_2/Al_2O_3 = 23.8$) > HZSM-5 ($SiO_2/Al_2O_3 = 39.4$) ≫ H-Mordenite > H-beta > H-USY. Thus, HZSM-5 ($SiO_2/Al_2O_3 = 19$) among the employed zeolites is the most favorable support for the Re species. It is suggested that Al-OH in the HZSM-5 framework is a bonding site for active Re species. The phenol selectivity in the steady-state reaction decreased from 87.7 to 82.4% a little by increasing Re loading (0.58 → 2.2 wt%) and W/F (6.7 → 10.9 g_{cat} h mol^{-1}), while the conversion increased from 0.75% to 5.8% as shown in Table 1.

The Re L_{III}-edge EXAFS analysis revealed significant changes in the structure of supported Re species on HZSM-5 (Fig. 1). The NH_3 treatment of the Re/HZSM-5 prepared by CVD of MTO at the reaction temperature brought about the appearance of catalytic activity for the phenol synthesis. The phenol formation rate increased with an increase in the period of NH_3 (75 kPa) treatment at 553 K and reached a saturated value of 3.8 μmol g_{cat}^{-1} s^{-1} after the NH_3-treatment for 2 h, which indicates that the structural transformation to active Re species is completed by the 2 h-NH_3 treatment. The CN of Re–Re bonds was 5.2 ± 0.3 at 0.276 ± 0.002 nm, demonstrating the formation of Re clusters. Assuming Re_6 octahedron as a cluster unit [30], the CN of Re–Re bonds indicates Re_{10} clusters edge-shared with two Re_6 octahedra. Furthermore, it was found that the NH_3-treated Re-cluster catalyst released N_2 molecules at 685 K in TPD spectra. The number of encapsulated nitrogen atoms was 0.12 N_2/Re, which corresponds to be one nitrogen atom per a Re_6 octahedron. An NH_3-treated HZSM-5 without Re showed no N_2 desorption in TPD. The Re–N(O) bonds in the NH_3-treated Re-CVD/HZSM-5 catalyst were observed at 0.204 ± 0.001 nm (CN = 2.8 ± 0.3) and Re=O double bonds at 0.172 ± 0.001 nm (CN = 0.3 ± 0.2) were also observed by EXAFS [1]. DFT calculations for the Re clusters revealed that a nitrogen atom is located at the interstitial position of each Re_6 octahedral framework of a Re_{10} cluster which is attached on the wall of a zeolite pore via Re–O bonds [1]. It is to be noted that the interstitial nitrogen atoms are the key element to stabilize the Re_{10} clusters. The DFT-calculated structure of the Re cluster embedded in the pore of HZSM-5 is illustrated in Scheme 1.

The Re_{10} clusters with interstitial nitrogen atoms were highly selective for the catalytic phenol synthesis as shown in Table 1. Benzene was immediately converted to phenol by a pulse of a mixture of benzene and O_2 on 0.1 g of the NH_3-pretreated catalyst. It is to be noted that the selective benzene oxidation with O_2 on the active Re_{10} clusters proceeds without NH_3 with 93.9% selectivity. In the absence of O_2, the Re clusters did not produce phenol, suggesting that the oxygen of

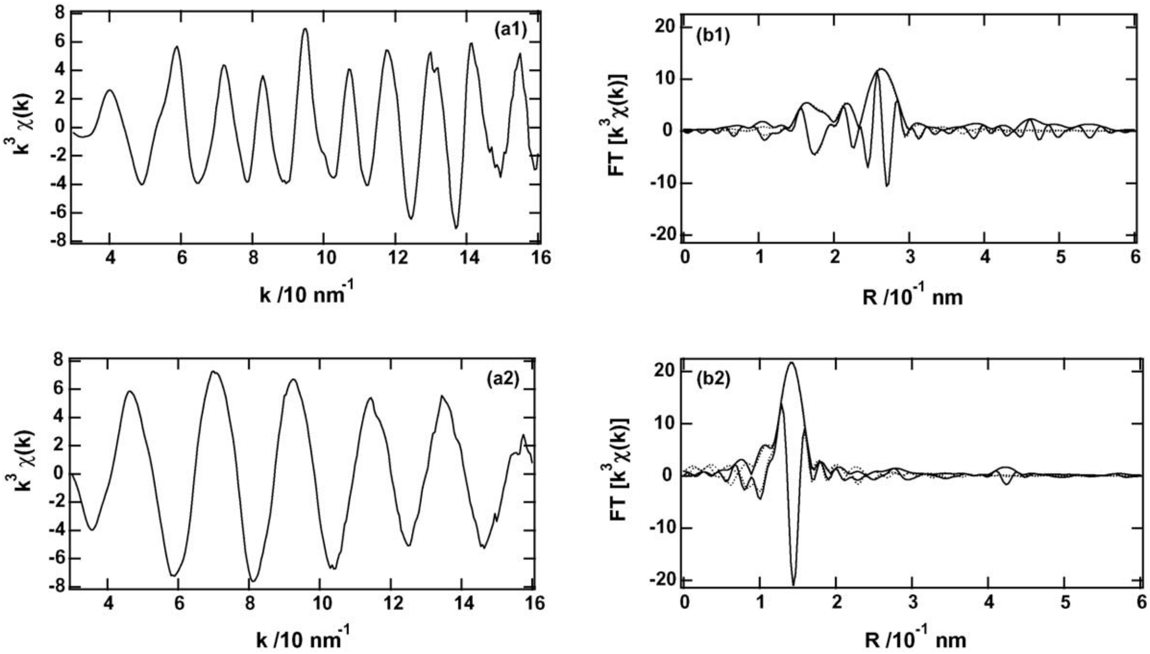


Fig. 1. Re L_{III}-edge EXAFS oscillations (a) and their associated Fourier transforms (b) measured at 15 K for the NH_3-treated Re-CVD/HZSM-5 catalyst (1) and the Re-CVD/HZSM-5 catalyst after the four pulse reactions with benzene and O_2 (2). The solid and dotted lines in the right FT represent absolute and imaginary parts of observed and fitted spectra, respectively.

the active Re-cluster framework is not active for the selective benzene oxidation. In the pulse reaction on 1.0 g of the NH_3-pretreated catalyst the conversion of benzene to phenol increased to 9.9% (TOF: $86.1 \times 10^{-5}\ s^{-1}$), while keeping a high phenol selectivity of 90.6% as shown in Table 1.

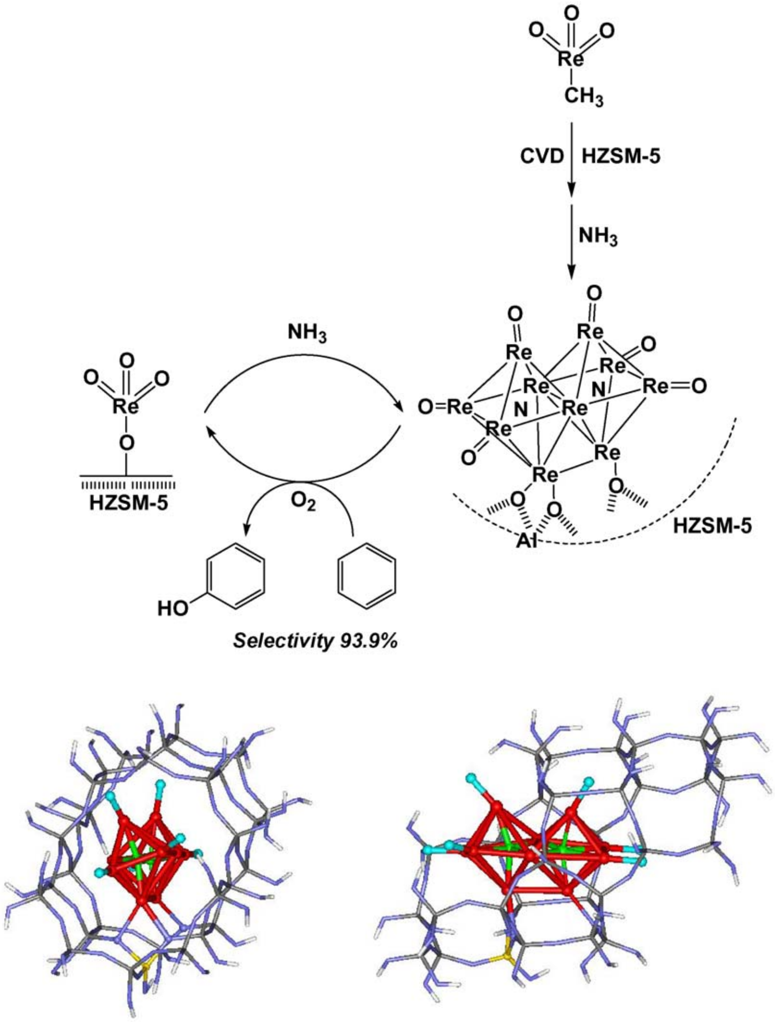
After the four pulse reactions with a mixture of benzene and O_2, the Re species showed no Re–Re bond, while Re=O and Re–O bonds were observed at 0.173 ± 0.001 nm (CN = 3.7 ± 0.2) and at 0.213 ± 0.003 nm (CN = 1.3 ± 0.7) as shown in Fig. 1. The XPS Re 4f peak was observed at 48.5 eV. These results demonstrate that the Re_{10} clusters were oxidized with O_2 and decomposed to inactive ReO_4-monomers with Re^{7+} as shown in Scheme 1. The ReO_4-monomers were transformed to the Re_{10} clusters by NH_3. The formation and decomposition of the cluster are balancing in the steady-state reaction.

3.2. *Chiral self-dimerized V-dimer on SiO_2 for asymmetric oxidative coupling of 2-naphthol*

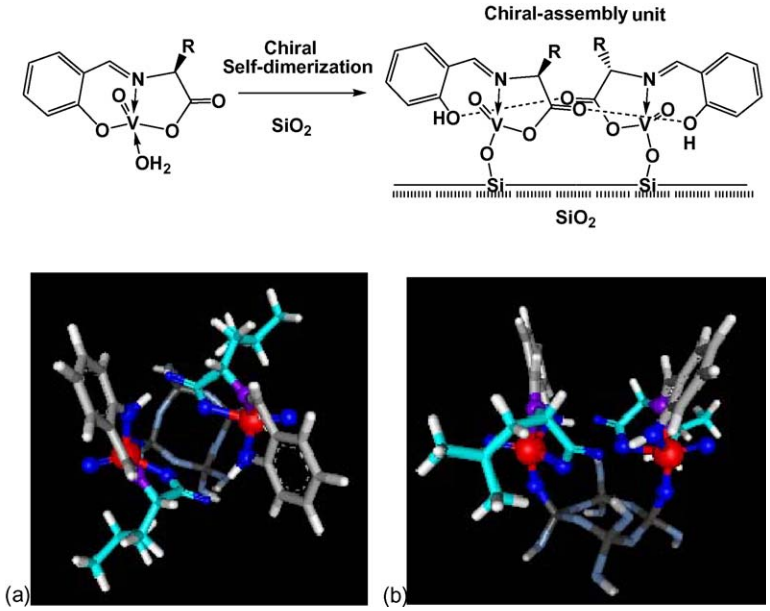
The oxidative coupling of 2-naphthol is a representative reaction mode for a direct synthesis of 1,1′-binaphthol (BINOL) whose optically pure derivatives are regarded as versatile chiral auxiliaries and ligands in asymmetric syntheses [31]. Nevertheless only a few studies have been reported for the asymmetric coupling of 2-naphthols in homogeneous systems [32–34]. We have found novel chiral self-dimerization of V-monomers on a SiO_2 surface [2,3]. The obtained V-dimer is highly enantioselective for the asymmetric oxidative coupling of 2-naphthol, 96% conversion, 100% selectivity to BINOL and 90% enantioselectivity, though the V-monomer is inactive for the coupling. To our knowledge, this is the first heterogeneous catalyst for the asymmetric coupling reaction.

Several V-monomer precursors with Schiff-base obtained from α-amino acids (L-valine, L-isoleucine, L-leucine, L-*tert*-leucine and L-phenylalanine) selectively reacted with surface silanols leading to a structural reconstruction of the tridentate Schiff-ligand coordination sphere characterized by ESR, XPS, UV–vis, FT-IR, XAFS and DFT calculations. The Ph–O moiety of the Schiff-base ligand transformed to Ph–OH configuration via selective reaction with surface Si-OH and the coordination number of V–O(N) single bonds analyzed by EXAFS 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 2), which can behave as an active site for the coordination of 2-naphthol.

Fig. 2 shows ESR spectra at 6 K for the L-leucine V-monomer precursor and the supported L-leucine V complex in the presence and absence of O_2. The hyperfine signals of the supported complex ($g_{\parallel} = 1.948$, $A_{\parallel} = 17.01\ cm^{-1}$; $g_{\perp} = 1.991$, $A_{\perp} = 6.49\ cm^{-1}$) 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. 2(B). The peak was accompanied with the appearance of a new peak attributed to the half-band of $|\Delta Ms| = 2$(C). 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 ($|\Delta Ms| = 2$) to the allowed transition ($|\Delta Ms| = 1$) [8]. After evacuation of the O_2-adsorbed sample, the intensity returns completely to the original one and the change in the ESR signal occurs reversibly.



Scheme 1. Structural transformations of Re species supported on HZSM-5 and the modeling of an active *N*-interstitial Re_{10} cluster inside the pore of HZSM-5 by DFT.



Scheme 2. Formation of the self-dimerized chiral assembly from vanadium-monomers on a SiO_2 surface. The modeled structures ((a) top view and (b) side view) of a chiral self-dimerized V complex were calculated by DFT.

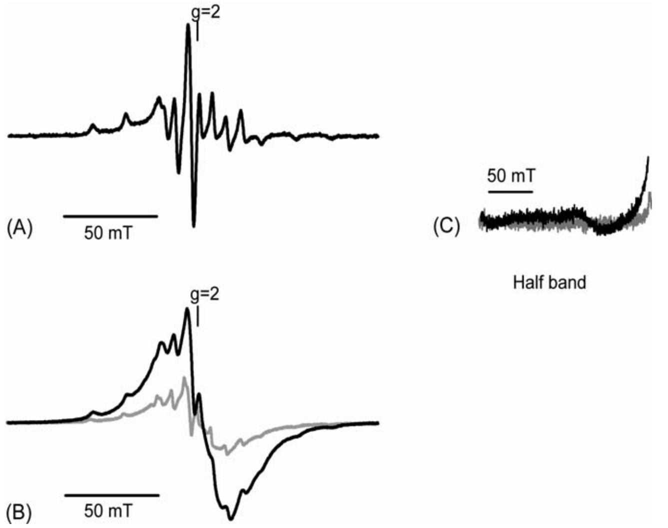


Fig. 2. ESR spectra for the SiO_2-supported V-dimer (V 3.4 wt%) in the absence (gray) and presence (black) of O_2 at 6 K. (A) Main signal of L-leucine V-monomer; (B) main signal of the supported V-dimer catalyst; (C) half-band signal of the supported V-dimer catalyst.

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. The broad ESR signal and the reversible behavior of oxygen molecules were observed similarly in the range of V loading 0.3–3.4 wt%, indicating that the chiral self-dimerization of the V precursors occurs independent of V loading on the SiO_2 surface.

The Ph–OH moiety formed by the surface reaction makes 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 $\nu_{asym(COO)}$ and $\nu_{sym(COO)}$ in 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 calculations for the self-assembled V complex based on the characterization of the V assembly on the surface, whose structure is presented in Scheme 2. Two V=O bonds are directed to the opposite sides mutually from the principal molecular plane of the V complex and molecular oxygen and 2-naphthol are activated in a chiral space between the two unsaturated V centers.

We have found that the supported V catalyst is highly active for the coupling of 2-naphthol under aerobic conditions (Table 2). On the SiO_2-supported V catalysts, the conversion reaches maximum 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 2. The homogeneous V precursor

Table 2
Catalytic performances of V-monomer precursors and oxide-supported V catalysts for the asymmetric oxidative coupling of 2-naphthol

Catalyst-V wt%	Temp. (K)	Time (day)	Solvent	Conv. (%)	Selectivity (%)	ee (*R*) (%)
Precursor[a]	293	5	$CHCl_3$	0	0	–
Precursor[a,b]	293	3	$CHCl_3$	15	73	8
Precursor[a,b]	263	9	$CHCl_3$	0	0	–
SiO_2-0.3[c]	293	2	Toluene	26	100	12
SiO_2-0.3[c]	293	5	Toluene	99	100	5
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[d]	293	2	Toluene	41	100	21
SiO_2-0.3[e]	263	5	$CHCl_3$	9	100	56
SiO_2-0.3[f]	293	2	Toluene	40	100	13
SiO_2-0.3[f]	263	6	Toluene	9	100	31
SiO_2-0.3[g]	263	5	Toluene	11	100	12
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[h]	263	5	Toluene	10	100	33
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[h]	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	–

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. Ligand: L-leucine.

[a] Homogeneous reaction.
[b] In the presence of chlorotrimethylsilane.
[c] L-valine.
[d] L-isoleucine.
[e] L-phenylalanine.
[f] Hydroxy naphthaldehyde was used instead of salicylaldehyde.
[g] L-*tert*-leucine.
[h] Reuse.

itself is inactive for the reaction. The V complexes supported on Al_2O_3 and TiO_2 are not selective for the coupling (Table 2).

The kind of the ligands gives less effect on the enantioselectivity for the oxidative coupling and thus the L-leucine-based catalysts were used for detailed investigation of the catalytic performances. Accompanied with an increase in V loading (0.3–3.4 wt%), enantioselectivity remarkably increases as shown in Table 2. The highest enantio excess (ee) 90% was achieved on the supported 3.4 wt%-V catalyst. This ee is equivalent to the highest values reported thus far for the oxidative coupling of simple 2-naphthol without functional groups on its naphthyl ring in homogeneous systems [34(c)]. From the estimation of the cross section of the V precursor, the V loading of 3.4 wt% corresponds to a 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.

4. Conclusions

We prepared and characterized metal-ensemble units on surfaces for selective oxidation. The novel *N*-interstitial Re_{10} cluster was found to be active for highly selective benzene oxidation to phenol with molecular oxygen, on which the remarkably high selectivity of 82.4% at 5.8% conversion in the steady state. There was an unsurmounted wall of 5% conversion and 50% selectivity in the direct phenol synthesis from benzene with molecular oxygen. The present performances are beyond those values. Chiral self-assembly of V Schiff-base complexes on SiO_2 was also found to provide a novel SiO_2-supported chiral V-dimer, which exhibited enantioselective catalysis for 2-naphthol oxidative coupling. The SiO_2-supported V catalyst exhibited 100% selectivity for the BINOL synthesis and the highest enantioselectivity 90% was accomplished on the full-coverage V catalyst. This is the first heterogeneous catalyst with active self-assembly structure for the asymmetric oxidative coupling of 2-naphthol.

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