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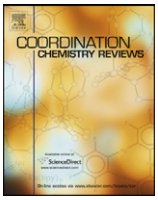

Review

Catalytic oxidation of hydrocarbons with hydrogen peroxide by vanadium-based polyoxometalates

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ABSTRACT

Vanadium compounds have attracted much attention because they have widely been used for homogeneous, heterogeneous, industrial, and biological oxidation processes with alkyl hydroperoxides, H_2O_2, and O_2. The present review summarizes recent developments for homogeneous and heterogeneous liquid-phase oxidation of hydrocarbons with H_2O_2 catalyzed by vanadium complexes and vanadium-based polyoxometalates including our recent studies on selective oxidation of hydrocarbons with H_2O_2 catalyzed by divanadium-substituted polyoxotungstates, $[\gamma\text{-SiW}_{10}O_{36}V_2(\mu\text{-OH})_2]^{4-}$ (**I**) and $[\gamma\text{-PW}_{10}O_{36}V_2(\mu\text{-OH})_2]^{3-}$ (**II**).

1. Introduction

Catalytic oxidation is an area of key technologies for converting petroleum-based feedstocks to useful chemicals such as diols, epoxides, alcohols, and carbonyl compounds [1–7]. Choice of the oxidants determines the practicability and efficiency of the oxidation reactions. While a large number of oxidants have extensively been investigated for the catalytic liquid-phase oxidation processes, some oxidants produce toxic and environmentally, politically, and economically unacceptable by-products. In addition, active oxygen contents of most oxidants are low ($\leq$30%). In these contexts, H_2O_2 and O_2 (or air) are the most attractive oxidants because of their high contents of active oxygen species (O_2: 100% for dioxygenase-type, 50% for monooxygenase-type; H_2O_2: 47%) and co-production of only water (no co-products in some cases).

Vanadium compounds have attracted much attention because they have widely been used for homogeneous, heterogeneous, industrial, and biological oxidation processes with alkyl hydroperoxides, H_2O_2, and O_2 [8–14]. Reactions of vanadium complexes with H_2O_2 have extensively been studied and several mono- [15–36], di- [37–47], and poly-nuclear [48] peroxovanadium complexes have been isolated and characterized. The isolated and/or *in situ*-generated peroxovanadium complexes catalyze H_2O_2-based

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oxidation of alkanes, alcohols, aromatic compounds, sulfides, and halides [49–68,33,69–106]. Since the oxidation of alkanes and aromatic compounds often involves a radical mechanism, electrophilic oxidation of alkenes to the corresponding epoxides with H_2O_2 has scarcely been reported because of the allylic oxidation, C=C double bond cleavage, and non-productive decomposition of H_2O_2. Therefore, the effective and selective epoxidation of alkenes by vanadium-based catalysts generally uses organic hydroperoxides such as *tert*-butyl hydroperoxide (TBHP).

Polyoxometalates (POMs) are a large family of anionic metal–oxygen clusters of early transition metals. POMs have stimulated many current research activities in broad fields of catalysis, material science, and medicine because their chemical properties such as redox potentials and acidities can finely be tuned by choosing the constituent elements and counter cations [107–120]. Therefore, well-defined single or multiple catalytically active sites can be introduced into POMs. In addition, POMs are stable under thermal and oxidative conditions. Various kinds of POMs can act as effective catalysts for oxidation reactions with H_2O_2 and O_2. Especially, multi transition metal-substituted POMs show functionalities such as cooperative activation of oxidants, simultaneous activation of oxidants and substrates, stabilization of reaction intermediates, and multielectron transfer, leading to the remarkable activities and selectivities in comparison with conventional monometallic complexes. The present review focuses on the homogeneous and heterogeneous liquid-phase oxidation of hydrocarbons with H_2O_2 catalyzed by vanadium complexes and vanadium-based POMs including our recent investigation on divanadium-substituted polyoxotungstates with the bis-μ-hydroxo core, $\{V_2(\mu\text{-OH})_2\}$ (Fig. 1) [121–124]. Recent excellent books and review articles have described structures, properties, and applications of vanadium complexes in more detail [125–131].

2. Vanadium-based polyoxometalates

Structures and properties of POMs are briefly mentioned. Isopolyoxometalates and heteropolyoxometalates are formulated as $[M_mO_y]^{p-}$ and $[X_xM_mO_y]^{q-}$ ($x < m$), respectively, where M (W^{6+}, Mo^{6+}, V^{5+}, etc.) is an addenda atom and X (P^{5+}, As^{5+}, Si^{4+}, Ge^{4+}, B^{3+}, etc.) is a heteroatom. Among various heteropolyoxometalates, the Keggin and Wells–Dawson structures, of which the respective formulas are typically represented by $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ and $[X_2{}^{n+}M_{18}O_{62}]^{(16-2n)-}$, are stable and easily available. Lacunary POMs are obtained by removal of one or more addenda atoms from the corresponding fully occupied POMs. For example, hydrolytic cleavages of W–O bonds in dodecatungstosilicates occur and well-defined lacunary POMs with eleven, ten, and nine tungsten atoms are formed upon increase in pH. Mono-, di-, and tri-nuclear transition metal-substituted POMs are synthesized by reactions of transition metals with the corresponding lacunary POMs.

Representative molecular structures of vanadium-based POM catalysts for homogeneous oxidation with H_2O_2 are shown in Fig. 2. Various kinds of isopolyoxovanadates are formed in solutions depending on the synthetic conditions such as pH and concentration [115]. The decavanadate, $[V_{10}O_{28}]^{6-}$, has 10 vanadium atoms assembled in a compact structure. Biological activities of decavanadate have well been investigated [128]. Some mixed-addenda isopolyoxometalates such as hexametalates $[V_xW_{6-x}O_{19}]^{(2+x)-}$ ($x = 1–3$) are also isolated. Di- and tetra-nuclear peroxovanadates with a $PO_4{}^{3-}$ ligand have structurally been characterized. Mixed-addenda heteropolyoxometalates are usually synthesized by changing the molar ratios of the starting materials, and the products are mixtures of several vanadium-substituted species and their positional isomers [119,120]. In contrast to the mixed-addenda heteropolyoxometalates, well-defined active

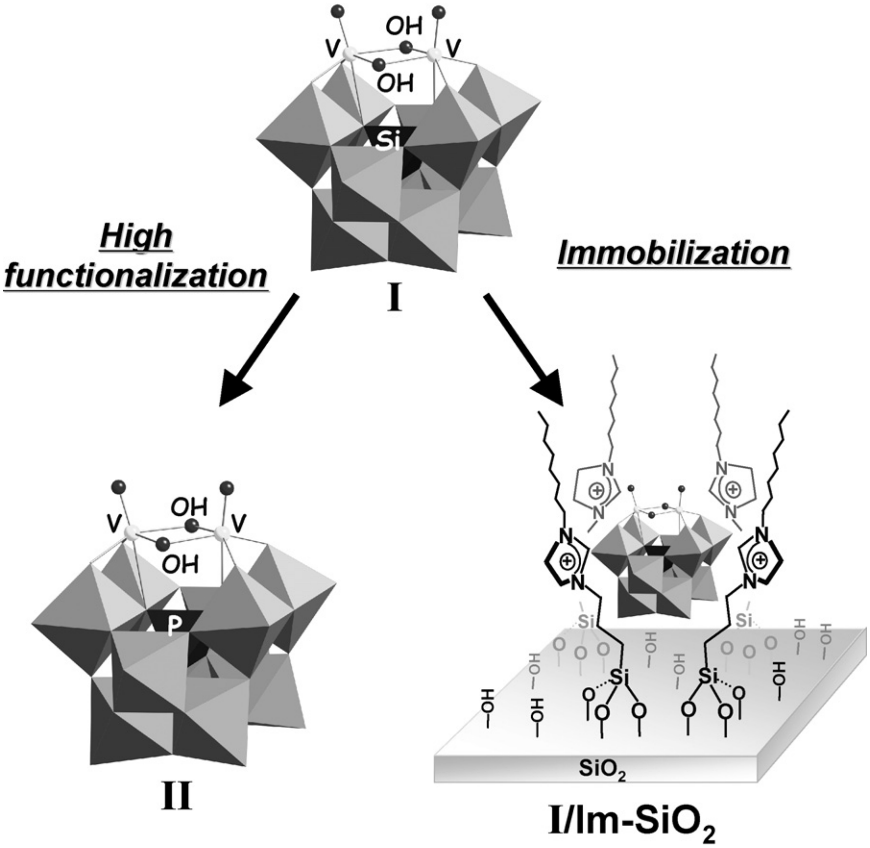


Fig. 1. Design of divanadium-substituted polyoxotungstate catalysts [121–124].

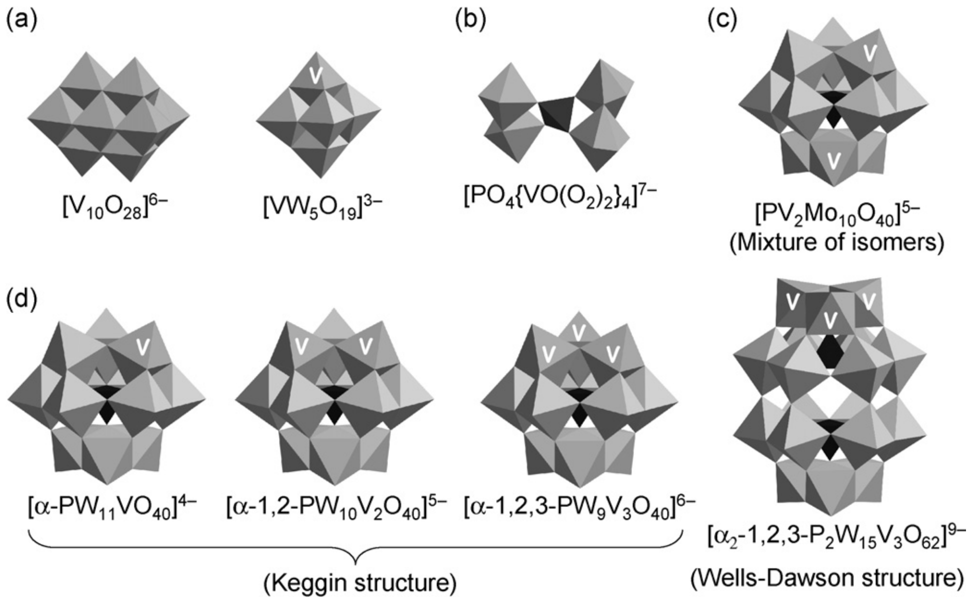


Fig. 2. Polyhedral representations of various kinds of vanadium-based POMs. (a) Isopolyoxometalates, (b) peroxometalate, (c) mixed-addenda heteropolyoxometalate, and (d) transition metal-substituted heteropolyoxometalates.

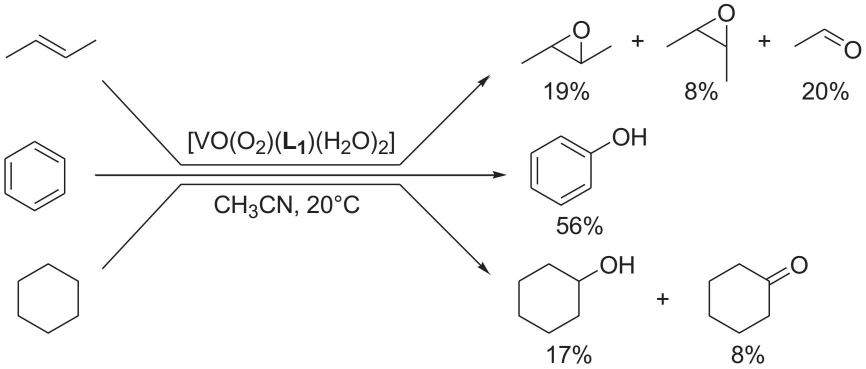
sites of vanadium can be introduced for vanadium-substituted heteropolyoxometalates. Catalytic oxidation with H_2O_2 by the mixed-addenda heteropolyoxometalates of vanadium and molybdenum, $H_{3+x}[PMo_{12-x}V_xO_{40}]$, and Keggin- and Wells–Dawson-type vanadium-substituted heteropolyoxometalates has well been investigated, while stoichiometric and catalytic oxidation activities of isopolyoxo- and peroxo-vanadates have not been reported [39,48].

3. Oxidation with H_2O_2 by vanadium complexes and vanadium-based polyoxometalates

3.1. Homogeneous stoichiometric oxidation

Activation of H_2O_2 by vanadium complexes leads to generation of a large number of peroxovanadium complexes with various coordination modes (η^2-O_2, μ-η^1:η^1-O_2, μ-η^1:η^2-O_2, μ-η^2:η^2-O_2, OOH, etc.), and their solution-states have been investigated by using ^{51}V NMR spectroscopy [131]. Among them, several mono- [15–36], di- [37–47], and tetra-nuclear [48] peroxovanadium complexes have structurally been characterized. The structures are strongly dependent on the synthetic procedures, kinds of ligands, and reaction conditions (solvent, ratio of H_2O_2 to vanadium atom, reaction temperature, etc.). While structures of metal-coordinated active oxygen species play an important role in oxidative transformation of organic substrates, there are only a few reports on stoichiometric reactivities of the structurally characterized peroxovanadium complexes with organic substrates (Table 1). There are only two examples of peroxovanadium POMs [39,48] and the reactivities have never been reported.

Mononuclear oxoperoxovanadium complexes reacted with the sulfur atom in $[Co(en)_2\{S(CH_2)_2NH_2\}]^{2+}$, bromide, triphenylphosphine, and hydroquinone to produce the corresponding sulfoxide [20,35], tribromide [26], triphenylphosphine oxide [21,23,24], and benzoquinone [23], respectively. Oxidative bromination of 1,3,5-trimethoxybenzene to 1-bromo-2,4,6-trimethoxybenzene also proceeded [21]. In contrast, stoichiometric reactions of the mononuclear oxoperoxovanadium complexes with hydrocarbons such as alkanes, alkenes, and aromatic compounds have scarcely been reported [27,44]: $[VO(O_2)(\mathbf{L_1})(H_2O)_2]$ ($H{\cdot}\mathbf{L_1}$ = picolinic acid, Fig. 3) reacted with *cis*-2-butene to give a mixture of *cis*- and *trans*-epoxides with acetaldehyde formed by oxidative cleavage of the C=C double bond (Eq. (1)). Benzene and cyclohexane were also oxidized to phenol and a mixture of cyclohexanol and cyclohexanone, respectively. Radical intermediates such as V(IV)–OO$^\bullet$ diradical [27] and radical anion [49] have been proposed for the reactions. A dinuclear oxoperoxovanadium complex, $(n\text{-}Bu_4N)_2[V_2O_2(O_2)_2(C_2H_2O_3)_2]{\cdot}H_2O$, could oxidize benzene to phenol under mild conditions, while the phenol yield was 12% (based on the peroxo oxygen content) and lower than that with a monomer (see Eq. (1)) [27,44]:



(1)

Table 1
Physical data for peroxovanadium complexes and stoichiometric reactivities.

Entry	Compound	O–O (Å)	ν(O–O) (cm^{-1})	λ_{max} (nm)	Substrate for stoichiometric reaction[a]	Ref.
1[b]	$K[VO(O_2)(omeida)]\cdot H_2O$	1.431(3)	928	439	$[Co(en)_2\{S(CH_2)_2NH_2\}]^{2-}$ (–) *N*-Acetyl-L-cysteine (–)	[20]
2[c]	$[VO(O_2)HSalhyhb(H_2O)]$	1.429(4)	921	–	1,3,5-Trimethoxybenzene (90) Thioanisole (75) Triphenylphosphine (quantitative)	[21]
3[d]	$[VO(O_2)(^tBu_2bpy)_2]BF_4$	1.402(10)	927	475	Triphenylphosphine (170) Stilbene (0) Hydroquinone (150)	[23]
4[e]	$Tp^{Pri2}VO(O_2)(Pz^{Pri2}H)\cdot THF$	1.379(6)	960	495	Triphenylphosphine (31)	[24]
5[f]	$K[VO(O_2)Hheida]\cdot H_2O$	1.432(2)	961	430	Halide (quantitative)	[26]
6	$VO(O_2)(\mathbf{L_1})(H_2O)_2$	1.435(3)	935	–	Alkanes (cyclohexane (25), isobutane (20), *cis*-decalin (17), *n*-octane (11)) Alkenes (*cis*-2-butene (47), *trans*-2-butene (17), 2-norbornene (22), *trans*-β-methylstyrene (91), 2-methyl-2-pentene (60)) Aromatic compounds (benzene (56), toluene (52), 1,3,5-trimethylbenzene (31))	[27]
7[g]	$K[VO(O_2)ceida]\cdot 2H_2O$	1.436(3)	927	438	$[Co(en)_2\{S(CH_2)_2NH_2\}]^{2-}$ (–)	[35]
8	$(^nBu_4N)_2[V_2O_2(O_2)_2(C_2H_2O_3)_2]$	1.436(12), 1.36(5)	920	420	Benzene (12)	[44]

[a] Numbers in parentheses were yields (%) of the products.

[b] Omeida = *N*-[2-(2-oxomorpholine-4-yl)ethyl]iminodiacetato(2−).

[c] H_2Salhyhb = γ-hydroxybutanoic acid hydrazide.

[d] $^tBu_2$bpy = 4,4′-di-*tert*-butylbipyridine.

[e] Tp^{Pri2} = hydrotris(3,5-diisopropylpyrazol-1-yl)borate. $Pz^{Pri2}H$ = 3,5-diisopropylpyrazole.

[f] H_3heida = *N*-(2-hydroxyethy1)iminodiacetic acid.

[g] H_2ceida = *N*-(carbamoylethyl)iminodiacetatic acid.

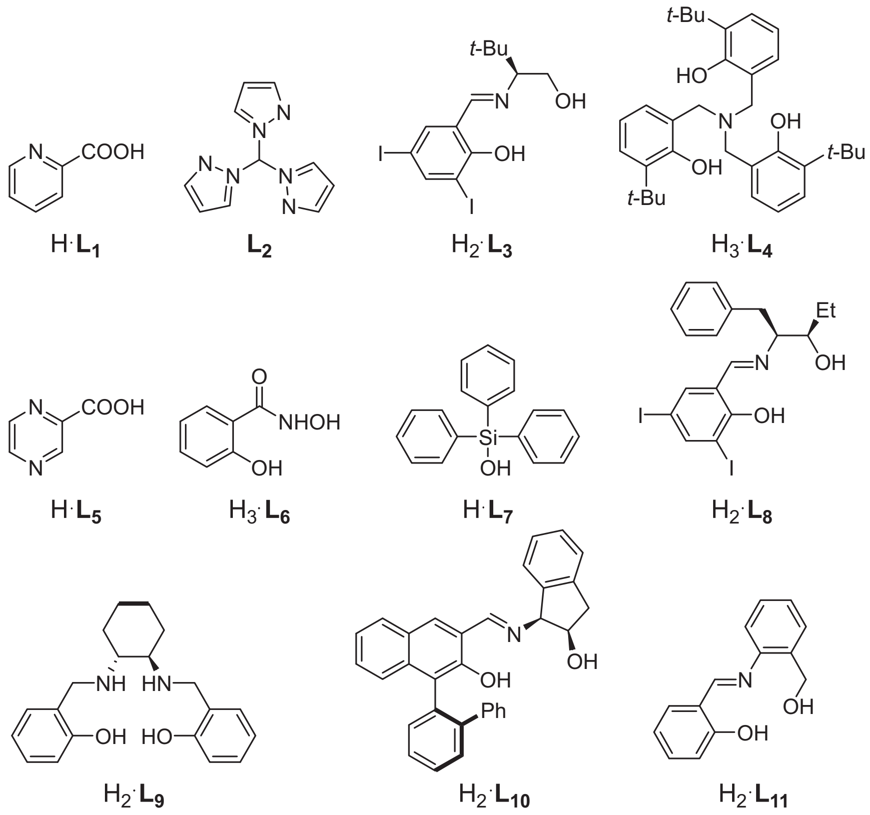


Fig. 3. Ligands of vanadium complexes for homogeneous oxidation with H_2O_2 [16,63–68,33,69–72].

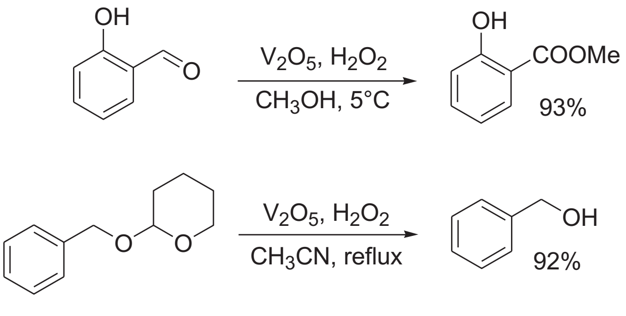
Peroxovanadium complexes are generally less reactive than those of molybdenum or tungsten. Oxygen transfer reactivities of peroxovanadium, -molybdenum, and -tungsten complexes correlate with both the peroxo O–O bond lengths (ν(O–O) band positions) and λ_{max} values of the peroxide-to-metal charge transfer bands [50]. In accord with this idea, among entries 2–4 in Table 1, the lowest yield of triphenylphosphine oxide was observed upon use of $Tp^{Pri2}VO(O_2)(Pz^{Pri2}H)\cdot THF$, which showed the highest ν(O–O) band position and λ_{max}.

3.2. Homogeneous catalytic oxidation

3.2.1. Vanadium complexes

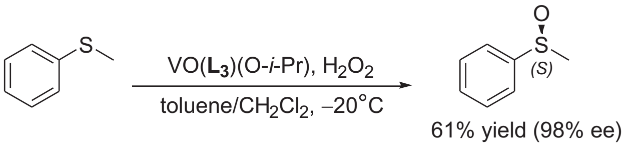
Vanadium complexes such as simple vanadium (III, IV, and V) salts (VCl_3, $VO(acac)_2$, $NaVO_3$, V_2O_5, etc.) [52–62], isolated or *in situ*-generated vanadium complexes with polydentate ligands (picolinate $\mathbf{L_1}$ [69], hydrotris(1-pyrazolyl)methane $\mathbf{L_2}$ [63], Schiff bases $\mathbf{L_3}$, $\mathbf{L_9}$, and $\mathbf{L_{10}}$ [64,71,72], amine triphenolate $\mathbf{L_4}$ [65], pyrazine-2-carboxylate $\mathbf{L_5}$ [66–68], salicylhydroximate $\mathbf{L_6}$ [33], triphenylsiloxane $\mathbf{L_7}$ [16], and *N*,*N*′-alkyl bis(salicylamine) $\mathbf{L_8}$ [70] (Fig. 3)), and vanadium-based POMs [132–145] have been used for homogeneous catalytic oxidation with H_2O_2. Oxygenation of sulfides to sulfoxides [20,35] and alkenes to epoxides [27], oxidative cleavage of C=C double bonds of alkenes to aldehydes or ketones [27], allylic oxidation of alkenes to alcohols/ketones [27], hydroxylation of aromatic compounds [27,44], and oxidation of alkanes to alcohols and ketones [27] are the examples as is expected according to reactivities of peroxovanadium complexes (see Section 3.1). The oxidation of hydrocarbons such as alkanes, alkenes, and aromatic compounds proceeds via radical mechanisms possibly involving both *C*- and *O*-centered radicals and metal-based oxidants. Oxidation of ethanol and 2-propanol also involves radical processes [51], while oxidation of benzyl alcohols and sulfides involves non-radical nucleophilic addition of $VO(O_2)_2^-$ to benzyl alcohols [61] and sulfides to $VO(O_2)(OCH_3)$ [9,13,130], respectively.

Interestingly, V_2O_5 was an effective catalyst for oxidative transformation such as esterification of aldehydes or diols to esters [54,55], oxidation of acetals to esters [56], and deprotection of tetrahydropyranyl or *tert*-butyldimethylsilyl ethers to alcohols (Eq. (2)) [56]. It is proposed that peroxovanadium species are formed by the reaction of V_2O_5 with H_2O_2 and act as homogeneous catalysts [55]. A wide variety of 1,3-oxathiolanes could chemoselectively be deprotected to the corresponding carbonyl compounds in good yields in the presence of V_2O_5 and NH_4Br, and the following reaction mechanism is proposed [62]: reactive peroxovanadium intermediates, which are formed by the reaction of V_2O_5 with H_2O_2, oxidize Br^- to Br^+. Then, Br^+ reacts with sulfur to form a bromosulfonium complex, which is finally hydrolyzed by water to yield the carbonyl compounds:



(2)

The catalytic activities of the peroxovanadium complexes and product selectivities can be controlled by the presence of the polydentate ligands. More interestingly, asymmetric oxidation of thioanisole catalyzed by an oxovanadium(V) complex with a tridentate Schiff base of a β-amino alcohol, $[VO(\mathbf{L_3})(O\text{-}i\text{-}Pr)]$, efficiently proceeded to afford the chiral sulfoxide (Eq. (3)) [64]. High ee values were also reported for catalytic systems of $VO(acac)_2$-Schiff base or $VO(acac)_2$-*N*,*N*′-alkyl bis(salicylamine) ligands $\mathbf{L_8}$–$\mathbf{L_{10}}$ (Fig. 3) [70–72]. A C_3 vanadium amine triphenolate complex, $[VO(\mathbf{L_4})]$, efficiently catalyzed oxidation of thioanisole. The turnover frequency (TOF) was 8000 h^{-1} and turnover number (TON) reached up to 9900 [65]. Oxidation of 2-methylcyclohexanone in the presence of $[PPh_4][(\mathbf{L_7})_2VO_2]_x[(\mathbf{L_7})_2VO(O_2)]_{1-x}$ ($x = 0.57$) gave 6-oxoheptanoic acid in moderate yield (Eq. (4)) [16]. Oxidation of cyclohexane in the presence of $[(n\text{-}C_4H_9)_4N][VO_2(\mathbf{L_5})_2]$ and 2 equiv. of $H\cdot\mathbf{L_5}$ gave cyclohexanol and cyclohexanone in 18% and 2% yields, respectively [25]. Similar systems with vanadium complexes, $H\cdot\mathbf{L_5}$, air, and H_2O_2 were also highly efficient for oxidation of various kinds of alkanes and aromatic compounds [66–68]. On the basis of the kinetic, spectroscopic, and computational results, the proposed catalytic cycle involves formation of hydroperoxyl and hydroxyl radicals as well as peroxovanadium (IV and V) complexes [68]. It has also been proposed that the co-catalyst $\mathbf{L_5}$ acts as a stabilizer for the transition state of the H-transfer reaction (i.e., an H-transfer from the vanadium (IV) complex–H_2O_2 adduct to the hydroxo ligand) [68]:



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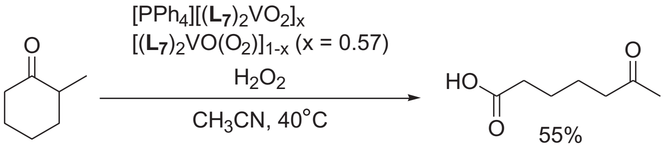

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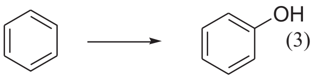
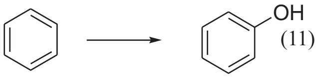
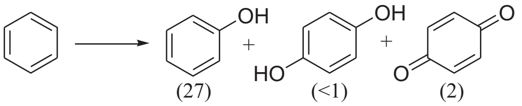
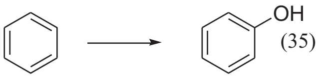
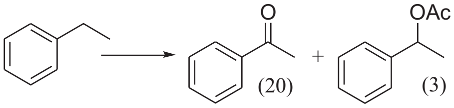
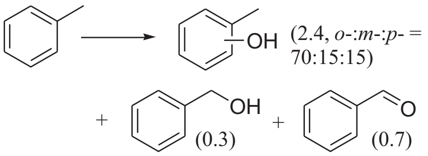
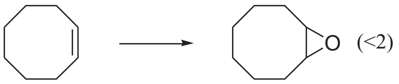
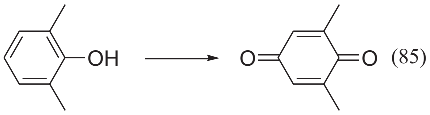
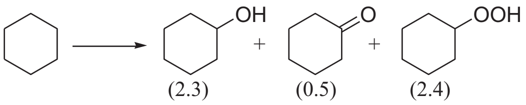
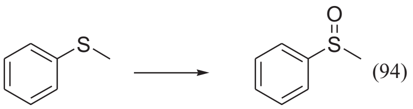
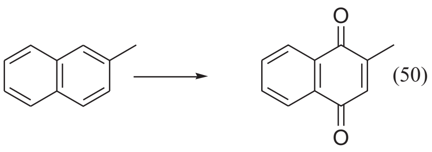
3.2.2. Vanadium-based polyoxometalates

Typical examples for homogeneously catalyzed oxidation reactions by vanadium-based POMs are listed in Table 2 [132–143]. Mixed addenda POMs of vanadium and molybdenum, $H_{3+x}[PMo_{12-x}V_xO_{40}]$, showed catalytic activities for oxidation of aromatic compounds [132,133,135,137,139,142–144], alkanes [134,140,145], alkenes [136], phenols [138], and sulfides [141] with H_2O_2. Among these reactions, the hydroxylation of benzene has often been studied [133,135,139,142], and was hardly catalyzed by $[PMo_{12}O_{40}]^{3-}$, suggesting that the presence of vanadium is essential for the reaction. The TON (based on vanadium atom) of the monovanadium-substituted polyoxomolybdate, $H_4[PMo_{11}VO_{40}]$, was higher than those of the di- and tri-substituted ones, and the monosubstituted POM was the most stable during the reaction [133,139]. On the other hand, monovanadium-substituted Keggin-type and Dawson-type polyoxotungstates, $[\alpha\text{-}PW_{11}VO_{40}]^{4-}$ and $[\alpha_2\text{-}P_2W_{17}VO_{62}]^{7-}$, were almost inactive, while di- and tri-vanadium-substituted Keggin-type polyoxotungstates, $[\alpha\text{-}1,2\text{-}PW_{10}V_2O_{40}]^{5-}$ and $[\alpha\text{-}1,2,3\text{-}PW_9V_3O_{40}]^{6-}$, showed catalytic activities [144]. The ^{31}P and ^{51}V NMR spectra after the reaction showed that $[\alpha\text{-}1,2\text{-}PW_{10}V_2O_{40}]^{5-}$ was stable, while $[\alpha\text{-}1,2,3\text{-}PW_9V_3O_{40}]^{6-}$ completely decomposed.

Oxidation of methane with H_2O_2 also efficiently proceeded in the presence of an $H_4[PMo_{11}VO_{40}]$ catalyst precursor in trifluoroacetic anhydride [134]. It is proposed that catalytically active $[VO(O_2)]^+$ and $[PMo_{11}O_{39}]^{7-}$ are formed by the reaction of $H_4[PMo_{11}VO_{40}]$ with H_2O_2 and that the catalytic oxidation includes a radical path [145]. In the case

Table 2
Homogeneous oxidation with H_2O_2 catalyzed by vanadium-based POMs.

Catalyst	Reaction (Yield[a] (%))	Solvent	Temp. (°C)	Ref.
$H_6[PV_3Mo_9O_{40}]$		CH_3CN	25	[133]
$H_4[PVMo_{11}O_{40}]$		CH_3CN	65	[135]
$H_6[PV_3Mo_9O_{40}]$		AcOH	rt	[139]
$H_6[PV_3Mo_9O_{40}]$		CH_3CN/AcOH	65	[142]
$H_4[PVMo_{11}O_{40}]$[b]	$CH_4 \longrightarrow CH_3OH$ (<1) + HCO_2H (11) + HCO_2CH_3 (24) + $CF_3CO_2CH_3$ (4) + COx (2)	$(CF_3CO)_2O$	80	[134]
$H_5[PV_2Mo_{10}O_{40}]$		AcOH	80	[132]
$K_5[PV_2W_{10}O_{40}]$		CH_3CN	rt	[137]
$Q_q[(VO)H_2F_6NaW_{11}O_{55}]$[c]		$ClCH_2CH_2Cl$	rt	[136]
$H_4[PVMo_{11}O_{40}]$		$(CH_3)CO$	20	[138]
$H_9[P_2V_3Mo_{15}O_{62}]$		$(CH_3)_2CO$	40	[140]
$H_5[PV_{0.5}Al_{0.5}Mo_{11}O_{40}]$		CH_3CN	20	[141]
$H_5[PV_2Mo_{10}O_{40}]$		CH3CN	60	[143]

[a] Yield was based on substrate.
[b] Yield was based on H_2O_2.
[c] Q = tricaprylmethylammonium.

of oxidation of various kinds of alkylaromatic compounds with H_2O_2, divanadium-substituted $H_5[PMo_{10}V_2O_{40}]$ was an effective catalyst [132]. Catalytic activities for oxidation of ethylbenzene to acetophenone decreased in the order of $H_5[PMo_{10}V_2O_{40}] > H_5[PW_{10}V_2O_{40}] \gg H_3[PMo_{12}O_{40}] > H_3[PW_{12}O_{40}]$, and kinds of the central heteroatoms (i.e., $H_5[PMo_{10}V_2O_{40}]$ vs. $H_6[SiMo_{10}V_2O_{40}]$) and numbers of vanadium atoms (i.e., $H_5[PMo_{10}V_2O_{40}]$ vs. $H_4[PMo_{11}VO_{40}]$) did not much change the yields of acetophenone. The proposed reaction includes hydroxyl and hydroperoxyl radicals generated by homolytic cleavage of H_2O_2 at the vanadium centers.

As mentioned above, the catalytic oxidation of hydrocarbons with H_2O_2 catalyzed by vanadium complexes and vanadium-based POMs often involves a radical mechanism. Therefore, highly efficient and selective production of epoxides has not been established because of simultaneous progress of allylic oxidation and

Table 3
Comparison of regioselectivity for epoxidation of *trans*-1,4-hexadiene.

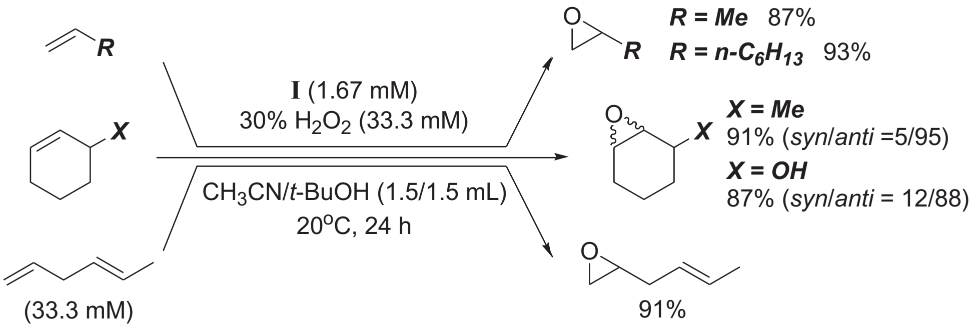
System	[Terminal epoxide]/[total epoxide]	Ref.
I/H_2O_2	0.99	[121]
[(dppe)Pt(C_6F_5)(H_2O)]OTf/H_2O_2[a]	≥0.99	[149]
[γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$/H_2O_2	0.61	[147]
[{$WO(O_2)_2$}$_2$(μ-O)]$^{2-}$/H_2O_2	0.28	[147]
[$PO_4(WO(O_2)_2)_4$]$^{3-}$/H_2O_2	0.17	[147]
Mo(CO)$_6$/cumene hydroperoxide	0.14	[150]
Mn(TTPPP)(OAc)/NaOCl/4′-(imidazol-1-yl)acetophenone[b]	0.35	[151]
Mn(TTMPP)(OAc)/NaOCl/4′-(imidazol-1-yl)acetophenone[b]	0.04	[151]
Mn(TPP)(OAc)/NaOCl/4′-(imidazol-1-yl)acetophenone[b]	0.02	[151]
m-CPBA	0.02	[151]
[MnT(3′,5′-G2Ph)P]Cl/PhIO[c]	0.03	[152,153]
[MnT(3′,5′-G1Ph)P]Cl/PhIO[c]	0.03	[152,153]

[a] dppe = 1,2-bis(diphenylphosphino)ethane.

[b] TPP = 5,10,15,20-tetrakis(phenyl)porphinato. TTMPP = 5,10,15,20-tetrakis(2,4,6-trimethoxyphenyl)porphinato. TTPPP = 5,10,15,20-tetrakis(2,4,6-triphenylphenyl)porphinato.

[c] Dendrimer-porphyrins, T(3′,5′-G1Ph)P and T(3′,5′-G2Ph)P, were synthesized by the reaction of 5,10,15,20-tetrakis(3′,5′-hydroxyphenyl)-porphyrin with the first generation (G1) and second generation (G2) dendrimers, respectively.

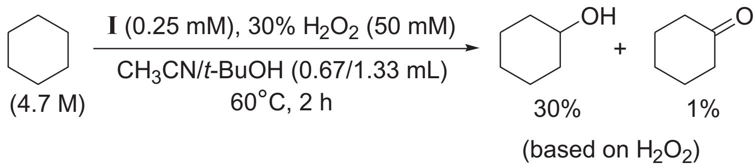
C=C double bond cleavage. While various efficient catalytic systems for H_2O_2-based epoxidation by peroxotungstates, lacunary POMs, and iron-, manganese-, cobalt-, zinc-, nickel-substituted POMs have been developed [113], these systems require either an excess amount of H_2O_2 with respect to an alkene or an excess amount of an alkene with respect to H_2O_2 to attain high yields of an epoxide or efficiency of H_2O_2 utilization. Therefore, there is still room for their improvements [113]. We have found that a γ-Keggin-type divanadium-substituted silicotungstate, [γ-$SiW_{10}O_{38}V_2(\mu\text{-}OH)_2$]$^{4-}$ (**I**), could catalyze epoxidation of various kinds of alkenes with 1 equiv. H_2O_2 under very mild reaction conditions (Eq. (5)) [121,123]. Notably, more accessible, but less nucleophilic C=C double bonds in non-conjugated dienes such as *trans*-1,4-hexadiene, *R*-(+)-limonene, 7-methyl-1,6-octadiene, and 1-methyl-1,4-cyclohexadiene were regioselectively epoxidized in high yields. The [less substituted epoxide]/[total epoxides] values (≥0.88) were much higher than those reported for the stoichiometric oxidant of *m*-chloroperoxybenzoic acid (*m*-CPBA) and catalytic oxidation systems including sterically hindered metalloporphyrins and [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$, and comparable to those of an electron-poor Pt(II) complex, [(dppe)Pt(C_6F_5)(H_2O)]OTf [146–153] (Table 3). Such unique stereospecificity, diastereoselectivity, and regioselectivity with **I** have scarcely been reported:



(5)

Direct functionalization of alkanes by oxidation of the C–H bonds to form alcohols under mild conditions is a challenge for synthetic chemistry. Since it is expected that an electrophilic oxidant formed by the reaction of **I** with H_2O_2 can activate alkane C–H bonds, oxidation of cyclohexane with H_2O_2 was attempted in the presence of **I** (Eq. (6)). Cyclohexanol and cyclohexanone were obtained in 30% and 1% yields based on H_2O_2, respectively, and the TOF was 90 h^{-1}.

The catalytic activity of **I** was much improved by changing the central heteroatom from Si^{4+} to P^{5+}. Under the same conditions as those of Eq. (6), oxidation of cyclohexane catalyzed by [γ-$PW_{10}O_{38}V_2(\mu\text{-}OH)_2$]$^{3-}$ (**II**) gave cyclohexanol and cyclohexanone in 76% and 2% yields based on H_2O_2, respectively, with the TOF of 710 h^{-1} [124]. The value was higher than those reported for H_2O_2-based catalytic systems [60,67,154–157]:



(6)

Compound **II** catalyzed stereo- and regio-selective hydroxylation of various kinds of alkanes with H_2O_2 [124]. Both cyclic and acyclic alkanes were oxidized to alcohols with ≥96% selectivity. The catalyst also avoided wasteful decomposition of H_2O_2, which can result in production of hydroxyl radicals and lead to non-selective oxidation and overoxidation of the desired products. Most alkanes contain a large number of C–H bonds that present difficulties for selectivity, and the oxidants employed often result in overoxidation. The bulky framework of **II** resulted in the unusual selectivity that can lead to the oxidation of secondary rather than the weaker tertiary C–H bonds (Eq. (7)). For the oxidation of *trans*-1,2-dimethylcyclohexane, the total selectivity to the secondary

Table 4
Comparison of regioselectivity for oxidation of *trans*-1,2-dimethylcyclohexane.

System	[2° alcohols]/[3° alcohols][a]	Ref.
I/H_2O_2	90/10	[124]
Mn(II)(TPFPP)(ClO_4)/*m*-CPBA[b]	80/20	[158]
(*n*-Bu_4N)[Os(VIII)(N)O_3]/$FeCl_3$/Cl_2PyO[c]	69/31	[159]
[Mn(IV)$_2$(TMTACN)$_2$(μ-O)](PF_6)$_2$/peracetic acid[d]	67/33	[160]
[Mn(II)(BQEN)(CF_3SO_3)$_2$]/peracetic acid[e]	62/38	[161]
Fe(III)(TPFPP)Cl/PhI(OAc)$_2$[b]	63/37	[162]
[Fe(II)(TPA)(MeCN)$_2$](ClO_4)$_2$/H_2O_2[f]	50/50	[154]
Co(III)(TPFPP)(CF_3SO_3)/*m*-CPBA[b]	16/84	[163]
Methyl(trifluoromethyl)dioxirane/TFP[g]	10/90	[164]
CH_3ReO_3/H_2O_2	0/>99	[165]
[(N4Py)Fe(III)(MeCN)](ClO_4)$_2$/H_2O_2[h]	0/>99	[155]
Cr(VI)O_2(OAc)$_2$/H_5IO_6	0/>99	[166]
Dimethyldioxirane	0/>99	[167]
Perfluoro *cis*-2-*n*-butyl-3-*n*-propyloxaziridine	0/>99	[168]

[a] [2° alcohols]/[3° alcohols] was the ratio of the total amount of the secondary alcohols and corresponding ketones to the amount of the tertiary alcohols.
[b] TPFPP = *meso*-tetrakis(pentafluorophenyl)porphinato.
[c] Cl_2PyO = 2,6-dichloropyridine *N*-oxide.
[d] TMTACN = 1,4,7-trimethyl-1,4,7-triazacyclononane.
[e] BQEN = *N*,*N*′-dimethyl-*N*,*N*′-bis(8-quinolyl)ethane-1,2-diamine.
[f] TPA = tris(2-pyridylmethyl)amine.
[g] TFP = 1,1,1-trifluoropropanone.
[h] N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine.

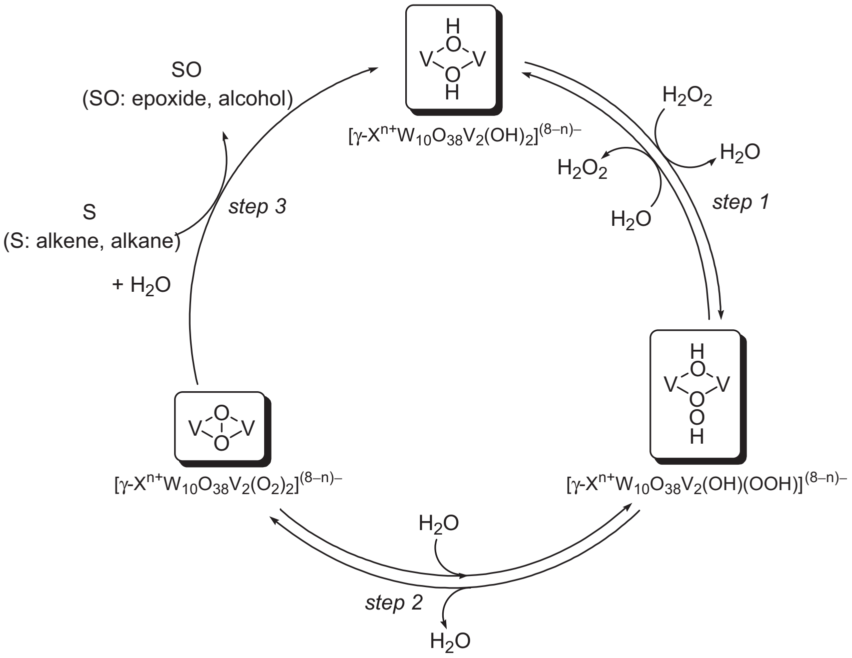
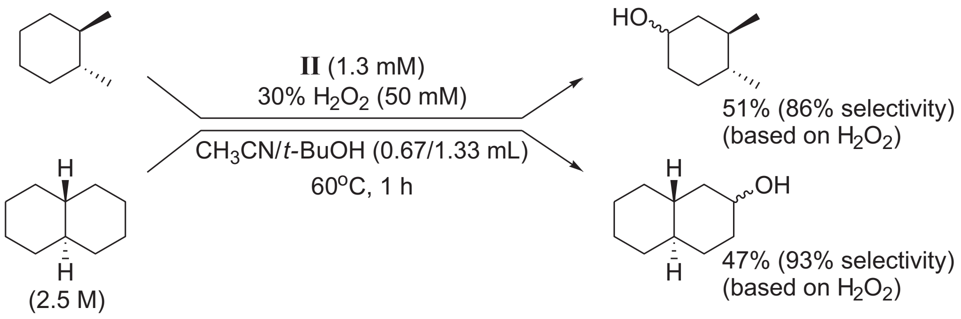


Fig. 4. Proposed mechanism for oxidation of hydrocarbons with H_2O_2 catalyzed by divanadium-substituted polyoxotungstates $[\gamma\text{-}X^{n+}W_{10}O_{38}V_2(\mu\text{-}OH)_2]^{(8-n)-}$ (X = Si^{4+} (**I**) and P^{5+} (**II**)) [123,124].

alcohols was 90% and the value was higher than those of the sterically hindered metalloporphyrin system and much higher than those of stoichiometric oxidants and iron-based catalytic oxidation systems [154,155,158–168] (Table 4):



(7)

A possible reaction mechanism for the **I**- and **II**-catalyzed oxidation with H_2O_2 is shown in Fig. 4 [121,123,124]. The ^1H, ^{51}V, and ^{183}W NMR spectroscopies and cold spray ion-

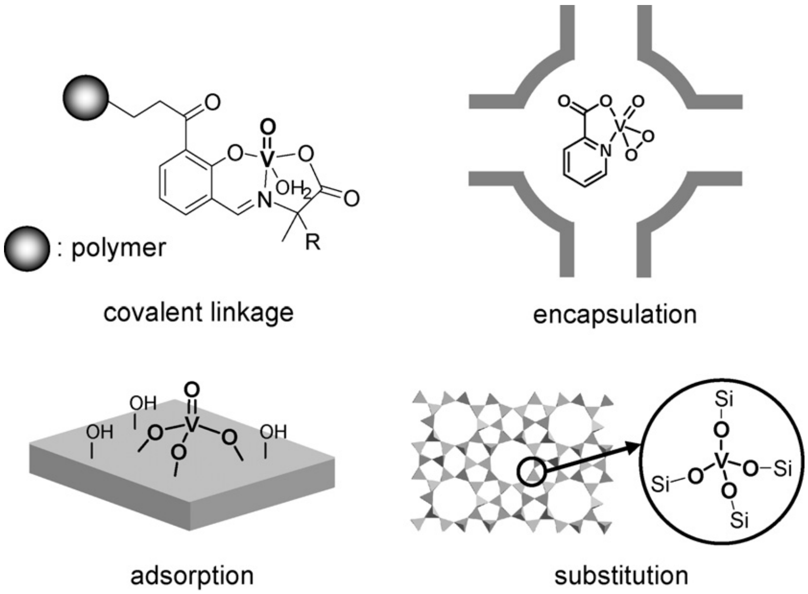


Fig. 5. Schematic representation of strategies for heterogenization of vanadium complexes.

ization mass spectrometry show that reactions of **I** and **II** with H_2O_2 lead to reversible formation of the hydroperoxo species $[\gamma\text{-}X^{n+}W_{10}O_{38}V_2(OH)(OOH)]^{(8-n)-}$ (X = Si^{4+}, P^{5+}). The successive dehydration of $[\gamma\text{-}X^{n+}W_{10}O_{38}V_2(OH)(OOH)]^{(8-n)-}$ forms $[\gamma\text{-}X^{n+}W_{10}O_{38}V_2(O_2)]^{(8-n)-}$, which possibly has an active oxygen species of a μ-η^2:η^2-peroxo group. On the basis of the spectroscopic, kinetic, and computational data, the μ-η^2:η^2-peroxo species $[\gamma\text{-}X^{n+}W_{10}O_{38}V_2(O_2)]^{(8-n)-}$ has been proposed to be possible active species for the **I**-catalyzed epoxidation and **II**-catalyzed hydroxylation. Such a unique active species could act as a non-radical electrophilic oxidant in a different way from those of typical vanadium-based POMs and vanadium complexes with η^2-peroxo groups. In addition, the steric effect of the all-inorganic, rigid, and bulky POM frameworks in **I** and **II** leads to a specific regioselectivity for the epoxidation of non-conjugated dienes and hydroxylation of alkyl-substituted cycloalkanes, respectively.

3.3. *Heterogeneous catalytic oxidation*

While many efficient catalytic oxidation reactions by vanadium complexes and vanadium-based POMs have been developed as above mentioned, most of them are homogeneous and share common drawbacks of the complicated procedure for catalyst/product(s) separation (i.e., problem of product contamination) and difficulty of the reuse of expensive catalysts [169]. The practical application would need developments of easily recoverable and recyclable heterogeneous catalysts through covalent linkage, encapsulation, adsorption, and substitution (Fig. 5).

3.3.1. *Vanadium complexes*

Vanadium complexes have been immobilized on modified polystyrene (PS) and silica or in nano-cavity of zeolites. Schiff-bases covalently bound to chloromethylated PS cross-linked with 5% divinylbenzene [90,91] and aminopropyl-functionalized MCM-41 [92] were synthesized. Upon treatment of these surface-modified supports with $VO(acac)_2$ or $VOSO_4$ in organic solvents, the oxovanadium species could be immobilized. These heterogeneous catalysts showed catalytic activities for oxidation of *p*-chlorotoluene [90], sulfides [91,92], and alkenes [90] with H_2O_2. A polymer-bound oxovanadium(IV) complex, PS–[VO(fsal–D,L-Ala)(H_2O)] (H_2fsal–D,L-Ala = Schiff base derived from 3-formylsalicylic acid and D,L-alanine, Fig. 5), could be a recyclable heterogeneous catalyst for oxidation of cyclohexene, while the selectivity to the corresponding epoxide was low due to significant formation of the allylic oxidation products and triol (Eq. (8)) [90]. Polymeric oxovanadium complexes were isolated with polymeric Schiff bases derived from 5,5′-methylenebis(salicylaldehyde) and 1,2-diaminoethene, 1,2-diaminopropane, or 1,3-diaminopropane [94]. All these complexes were insoluble in common solvents, and showed catalytic activities for oxidative bromination of salicylaldehyde and hydroxylation of phenol:

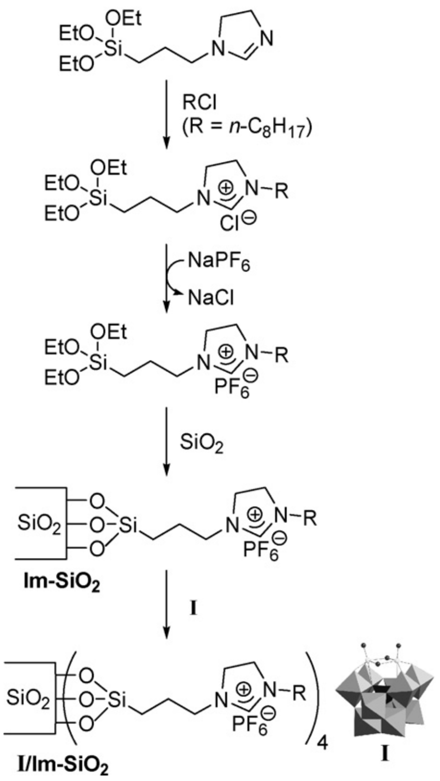
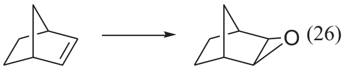
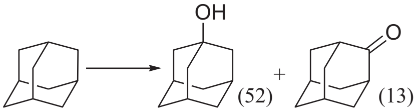
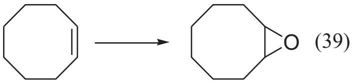
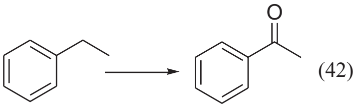
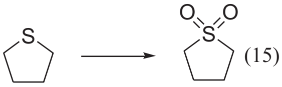
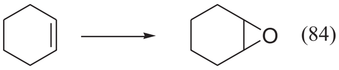
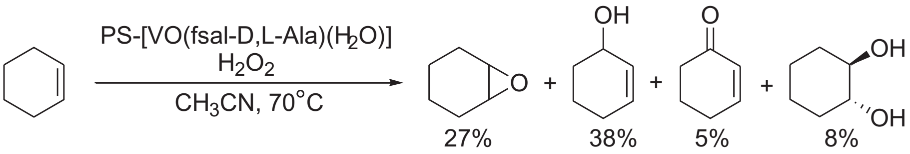


Fig. 6. Preparation of **I/Im-SiO₂** catalysts [122].

Table 5
Heterogeneous oxidation with H_2O_2 catalyzed by vanadium-based POMs.

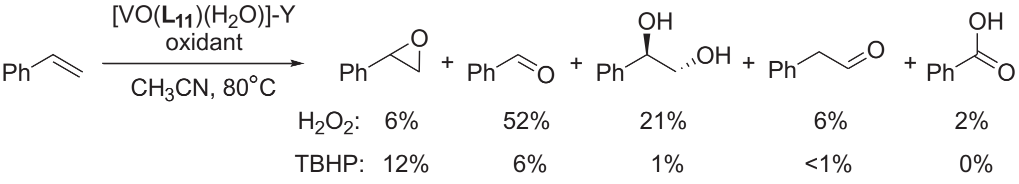
Catalyst	Reaction (Yield[a] (%))	Solvent	Temp. (°C)	Ref.
$H_5[PV_2Mo_{10}O_{40}]$ /NH_2-SBA-15[b]		CH_3CN	60	[170]
$H_5[PV_2Mo_{10}O_{40}]$ /NH_2-SBA-15[b]		C_3H_7CN	85	[171]
$Na_5[PV_2Mo_{10}O_{40}]$ /MCM-41		$ClCH_2CH_2Cl$	Ultrasonic irradiation	[173]
$Na_5[PV_2Mo_{10}O_{40}]$ /MCM-41		$ClCH_2CH_2Cl$	Ultrasonic irradiation	[173]
V Isopolyoxometalates /LDH[c]		CH3CN	25	[172]
$Na_5[PV_2Mo_{10}O_{40}]$ /CNT[d]		CH_3CN	Ultrasonic irradiation	[174]

[a] Yield was based on substrate.
[b] NH_2-SBA-15 = amine-functionalized SBA-15.
[c] LDH = layered double hydroxide.
[d] CNT = carbon nanotube.



(8)

Encapsulated vanadium complexes with H·**L₁** [102] and Schiff bases [103–106] in super cages of the zeolite Y showed catalytic activity for oxidation of alkanes [102,106], phenol [103], isosafrol [105], and sulfide [106], and oxidative bromination of salicylaldehyde [104]. The selectivity was dependent on the oxidants in the case of oxidation of styrene catalyzed by an encapsulated oxovanadium(IV) complex of Schiff base $\mathbf{L_{11}}$ in the zeolite Y, [VO($\mathbf{L_{11}}$)(H_2O)]-Y [106]. Use of H_2O_2 produced benzaldehye with 59% selectivity, while use of TBHP produced styrene oxide with 60% selectivity and the overall conversion decreased to 20% (Eq. (9)):



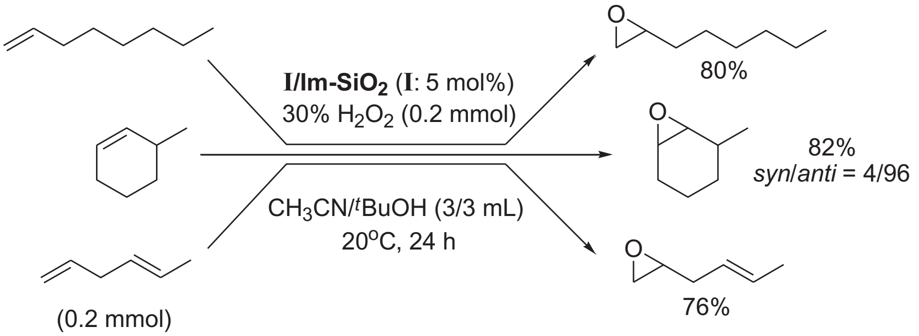
(9)

3.3.2. *Vanadium-based polyoxometalates*

Recently, developments of heterogeneous oxidation catalysts based on POMs and the related compounds have been attempted and would be classified into the following two categories; "solidification" of POMs (formation of insoluble solid ionic materials with appropriate counter cations) and "immobilization" of POMs through adsorption, covalent linkage, and ion-exchange [118]. Typical examples for the heterogeneously catalyzed oxidation by vanadium-based POMs are listed in Table 5 [170–174]. Vanadium-based POMs were immobilized onto surface-modified SBA-15 and MCM-41 with amino-functional groups [170,171,173] and intercalated into layered double hydroxides (LDHs) via anion-exchange [172]. Mixed-addenda heteropolyoxometalates, $H_{3+x}[PMo_{12-x}V_xO_{40}]$, immobilized onto amino-functionalized SBA-15 and MCM-41 catalyzed oxidation of alkanes [171] and alkenes [170,173] with H_2O_2. $Mg_2Al(OH)_6NO_3$ (MgAl-LDH) underwent facile and complete intercalation with $[V_{10}O_{28}]^{6-}$ by anion-exchange. This V-LDH catalyzed oxidation of tetrahydrothiophene with H_2O_2, while the catalytic activity was much lower than that of tungstate-exchanged LDH [172].

While some heterogenized vanadium complex and vanadium-based POM catalysts can be reused several times without significant loss of the activity and selectivity, they have some disadvantages; leaching of the catalytically active species [74,85,88,102], low yield and selectivity, and need of microwave irradiation [173,174]. At present, only a few successful examples, in which the catalytic activities and selectivities of heterogeneous vanadium catalysts are comparable to (or even higher than) those of the corresponding homogeneous analogues, have been developed.

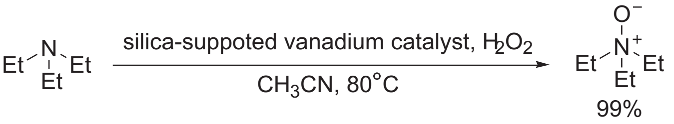
We have synthesized an organic–inorganic hybrid support by covalently anchoring an *N*-octyldihydroimidazolium cation fragment (**Im**) onto SiO_2 (denoted as **Im-SiO$_2$**) [122,175,176]. The synthetic procedure is shown in Fig. 6. By using **Im-SiO$_2$** as an anion-exchanger, catalytically active **I** could be immobilized. The **I/Im-SiO$_2$** catalyst could be applied to epoxidation of various kinds of structurally diverse alkenes with only 1 equiv. H_2O_2 (Eq. (10)). The unusual stereospecificity, diastereoselectivity, and regioselectivity were very close to those for the homogeneous epoxidation by **I** [121,123], indicating that the intrinsic homogeneous catalysis can be heterogenized with retention of the catalytic performance by use of the present surface modified support **Im-SiO$_2$**. The epoxidation was completely stopped by removal of **I/Im-SiO$_2$**. The catalyst was separated by filtration after completion of epoxidation, and vanadium and tungsten species could hardly be detected in the filtrate. The recovered catalyst could be reused for the epoxidation without any loss of the catalytic performance; the initial rates and final yields for the recycle runs were almost the same as that for the run with the fresh catalyst. The above results can rule out any contribution to the observed catalysis from vanadium and tungsten species that leached into the reaction solution and the observed catalysis is truly heterogeneous [122]:



(10)

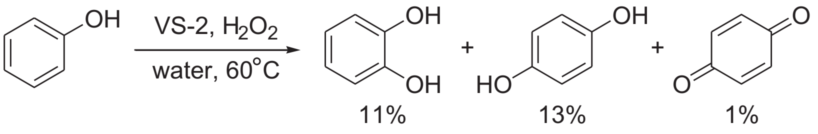
3.3.3. Others

The vanadium salts supported on oxide supports, vanadium-substituted molecular sieves, and vanadium-containing mixed oxides are other examples. The incipient wetness is an often used impregnation method to support $VO(acac)_2$, NH_4VO_3, $VO(SO_4)$, and V_2O_5 on various kinds of supports such as SiO_2 [73–76], Al_2O_3 [74–76], TiO_2 [76,77], ZrO_2 [77], CeO_2 [76,77], nitrogen-doped carbon sphere [78], and mesoporous materials [79,80]. These supported vanadium catalysts were active for H_2O_2-based oxidation of tertiary amines to *N*-oxides [73], aromatic compounds to phenols [74,77,79,80], sulfides to sulfoxides (or sulfones) [75,76], and styrene to benzaldehyde [78]. The silica-supported vanadium catalyst could be recovered by filtration and reused three times without significant loss of catalytic activity for oxidation of triethylamine to the corresponding *N*-oxide (Eq. (11)) [73]:

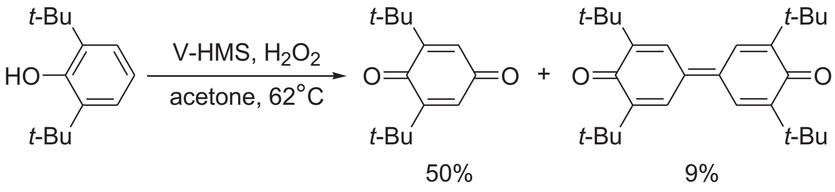


(11)

The isomorphous substitution of silicon in the framework of molecular sieves by various active transition metals leads to formation of isolated metal sites, which show remarkable catalytic activities. Vanadium-containing molecular sieves such as VS-1 [81–84] and VS-2 [85] have attracted considerable attention due to their high catalytic activities for oxidation of alkanes [81,84], aromatic compounds [85], sulfides [85], alcohols [85], and amines [82,83] (Eq. (12)). Since accessibility of the substrates to the active vanadium sites is limited because of the pore sizes, vanadium-containing mesoporous materials such as V-MCM-41 [86–88] and V-HMS [89] were utilized for oxidation of larger substrates of 1-naphthol [86], cyclododecene [86], styrene [87], ethyl benzene [88], diphenyl methane [88], 2,6-di-*tert*-butyl phenol [89], naphthalene [89], and cyclododecanol [89] (Eq. (13)). Significant leaching of metal species was observed for some reactions [88]. The electron paramagnetic resonance spectroscopy shows that a reactive superoxo-vanadium(V) species is generated by the reaction of microporous VS-1 and mesoporous V-MCM-41 with H_2O_2. The cleavage manner of O–O bonds in H_2O_2 and TBHP influenced chemoselectivities for oxidation of *n*-hexane [84]:

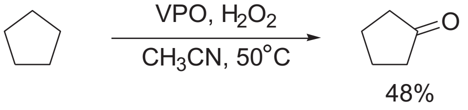


(12)



(13)

Mixed oxides such as vanadium phosphorus oxide (VPO) [95,96], manganese–vanadium ternary oxide [97], V_2O_5–SiO_2 and –TiO_2 composite xerogels prepared by sol–gel methods [98–101] were used for heterogeneous oxidation of alcohols [95,97–99], alkanes [96,100], phenol [97–99], alkenes [98,99], and sulfides [101]. While VPO is an efficient catalyst for vapor phase oxidation of *n*-butane to maleic anhydride, the liquid-phase oxidation has scarcely been known. Vanadyl hydrogen phosphate hemihydrate, $(VO)HPO_4{\cdot}0.5H_2O$, was prepared by reduction of V(V) to V(IV) in 2-methylpropan-1-ol with benzyl alcohol as a reducing agent followed by calcination in air at 400 °C. Calcined VPO was an effective catalyst for oxidation of various cyclic and linear alkanes (Eq. (14)), while the VPO catalyst was soluble in the reaction mixture and could not be recovered [96]:



(14)

4. Conclusion

Structurally characterized peroxovanadium complexes showed activities for stoichiometric oxidation of hydrocarbons such as alkanes, alkenes, and aromatic compounds and radical intermediates are proposed. While various kinds of vanadium complexes and vanadium-based POMs homogeneously catalyzed liquid-phase oxidation with H_2O_2, oxidation of hydrocarbons often involve a radical mechanism. Therefore, electrophilic oxidation of alkenes to the corresponding epoxides with H_2O_2 by vanadium catalysts has scarcely been reported. Our recent studies on a divanadium-substituted-silicotungstate could establish the epoxidation of various kinds of alkenes with H_2O_2 under mild conditions. The system could be applied to hydroxylation of alkanes by changing the central heteroatom from Si^{4+} to P^{5+}. A unique μ-η^2:η^2-peroxo species formed by the reaction of the bis-μ-hydroxo core, $\{V_2(\mu\text{-}OH)_2\}$, with H_2O_2 could act as a non-radical electrophilic oxidant in a different way from those of typical vanadium-based POMs and vanadium complexes with η^2-peroxo groups. Vanadium-based heterogeneous oxidation catalysts were developed through covalent linkage, encapsulation, adsorption, and substitution. Vanadium-based POMs could also be immobilized onto surface-modified supports and intercalated into LDHs. Some heterogenized vanadium complex and vanadium-based POM catalysts could be reused several times without significant loss of the activity and selectivity.

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