CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200501414

[γ-1,2-$H_2SiV_2W_{10}O_{40}$] Immobilized on Surface-Modified SiO_2 as a Heterogeneous Catalyst for Liquid-Phase Oxidation with H_2O_2

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Abstract: An organic–inorganic hybrid support has been synthesized by covalently anchoring an *N*-octyldihydroimidazolium cation fragment onto SiO_2 (denoted as **1**-SiO_2). This modified support was characterized by solid-state ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy, IR spectroscopy, and elemental analysis. The results showed that the structure of the dihydroimidazolium skeleton is preserved on the surface of SiO_2. The modified support can act as a good anion exchanger, which allows the catalytically active polyoxometalate anion [γ-1,2-$H_2SiV_2W_{10}O_{40}$]$^{4-}$ (**I**) to be immobilized onto the support by a stoichiometric anion exchange (denoted as **I**/**1**-SiO_2). The structure of anion **I** is preserved after the anion exchange, as confirmed by IR and ^{51}V NMR spectroscopy. The catalytic performance for the oxidation of olefins and sulfides, with hydrogen peroxide (only one equivalent with respect to substrate) as the sole oxidant, was investigated with **I**/**1**-SiO_2. This supported catalyst shows a high stereospecificity, diastereoselectivity, regioselectivity, and a high efficiency of hydrogen peroxide utilization for the oxidation of various olefins and sulfides without any loss of the intrinsic catalytic nature of the corresponding homogeneous analogue of **I** (i.e., the tetra-*n*-butylammonium salt of **I**, TBA-**I**), although the rates decreased to about half that with TBA-**I**. The oxidation can be stopped immediately by removal of the solid catalyst, and vanadium and tungsten species can hardly be found in the filtrate after removal of the catalyst. These results rule out any contribution to the observed catalysis from vanadium and tungsten species that leach into the reaction solution, which means that the observed catalysis is truly heterogeneous in nature. In addition, the catalyst is reusable for both epoxidation and sulfoxidation without any loss of catalytic performance.

Keywords: green chemistry • heterogeneous catalysis • hydrogen peroxide • immobilization • oxidation • polyoxometalates

Introduction

The epoxidation of olefins is an important reaction in the chemical industry as well as in the laboratory because epoxides, with their reactive oxirane groups, are useful intermediates in various organic syntheses.[1] Although a number of epoxidation processes with various catalysts and oxidants have been developed, stoichiometric processes that use chlorine- or heavy-metal-based oxidants or catalytic processes based on expensive oxidants such as organic peroxides and peracids are still used extensively.[1] Recently, hydrogen peroxide-based catalytic epoxidation has received much attention from the viewpoint of green chemistry.[2] There are three important reasons for the use of hydrogen peroxide in oxidation reactions: 1) it generates water as the sole byproduct, 2) it has a high content of active oxygen species, and 3) it is much cheaper and safer to use than organic peroxides or peracids.[3]

Many soluble transition-metal-based catalysts have been developed for epoxidation with aqueous hydrogen peroxide.[2] Among them, tungsten-based compounds, including polyoxometalates (POMs), seem to be some of the best catalysts because their efficiency of hydrogen peroxide use and their selectivity for the epoxides are high.[4] We have reported efficient and simple routes for the highly selective and ef-

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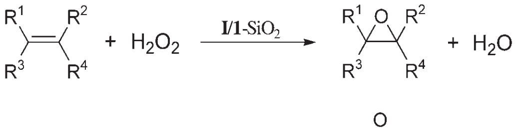
ficient epoxidation of olefins and allylic alcohols with hydrogen peroxide catalyzed by the divacant lacunary silicotungstate $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$[5] and the dinuclear peroxotungstate $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$,[6] respectively. Very recently, we also reported that the doubly hydroxo-bridged dioxovanadium-substituted polyoxotungstate $[\gamma\text{-1,2-H}_2SiV_2W_{10}O_{40}]^{4-}$ (**I**) can catalyze the epoxidation of olefins in the presence of only one equivalent of hydrogen peroxide with high epoxide yield, high efficiency of hydrogen peroxide utilization, unusual regioselectivity, and unprecedented diastereoselectivity.[7]

While many efficient epoxidation systems with hydrogen peroxide have been developed based on POMs, most of them are homogeneous and share common drawbacks such as difficult catalyst/product separation and poor catalyst reusability.[4–7] Therefore, the practical application of POM-based oxidation requires the development of easily recoverable and recyclable catalysts. One strategy in this area is the immobilization (heterogenization) of catalytically active species. The development of heterogeneous oxidations with POMs and related compounds has been attempted many times and the strategies can be classified into five groups, namely dispersion onto inert supports,[8] formation of insoluble solid ionic materials,[9] incorporation into a silica matrix using sol–gel techniques,[10] intercalation into anion-exchange materials,[11] and immobilization on surface-modified supports.[12] However, the intrinsic catalytic activities of the homogeneous catalysts are greatly decreased upon immobilization in many cases.[13] Another strategy is to use a liquid–liquid biphasic system, where the catalyst and products phases can be separated and the catalyst phase can be reused.[14–17] Many liquid–liquid biphasic systems with catalysts in aqueous,[14] fluorous,[15] supercritical fluid,[16] and ionic liquid phases[17] have recently been reported.

Herein we report the synthesis of an organic–inorganic hybrid support by covalently anchoring a dihydroimidazolium cation fragment onto SiO_2[12c] to immobilize the polyoxometalate **I**, which shows high catalytic activity and interesting selectivity for the epoxidation and is rather stable under the reaction conditions.[7] The immobilized catalyst shows high catalytic activity for the oxidation of various olefins and sulfides without any loss of its intrinsically high selectivity for the desired compounds [Eqs. (1) and (2)]. Furthermore, catalyst/product separation is very easy and the catalyst is recyclable.



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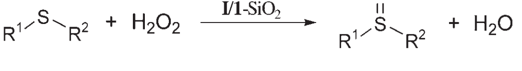

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Results and Discussion

Preparation and characterization of the catalysts: First of all we synthesized the dihydroimidazolium cation with an octyl chain at the N1 position (See Experimental Section and Figure S1 in the Supporting Information).[18] Triethoxy[3-(2-imidazolin-1-yl)propyl]silane was treated with three equivalents of 1-chlorooctane at 353 K for 24 h to give 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride. This compound was further treated with sodium hexafluorophosphate in acetonitrile at room temperature for five days to give the corresponding dihydroimidazolium cation with the PF_6^- ion (**1**). Compound **1** was isolated in almost quantitative yield (95 % total yield based on triethoxy[3-(2-imidazolin-1-yl)propyl]silane). The ^1H and ^{13}C NMR spectra of **1** and the assignments are given in Figure 1. The ^{29}Si NMR spectrum of **1** shows a signal at $\delta = -49.5$ ppm. The positive-ion ESI mass spectrum of an acetonitrile solution of **1** exhibits a peak at m/z 387 attributed to $[C_{20}H_{43}N_2O_3Si]^+$ (Figure 2). These NMR and ESI mass spectra show that compound **1** was synthesized with high purity (>95 % by NMR spectroscopy). Next, the SiO_2 surface was modified with compound **1** (see Experimental Section and Figure S1 in the Supporting Information). SiO_2 was heated at 393 K under vacuum for three hours and then the pretreated SiO_2 was refluxed (bath temperature, 353 K) for 24 h in a chloroform solution containing **1** with vigorous stirring. The resulting solid was separated by filtration, washed with *n*-heptane and acetonitrile, and dried in vacuo to afford the surface-modified SiO_2 with covalently anchored **1** (**1**-SiO_2).

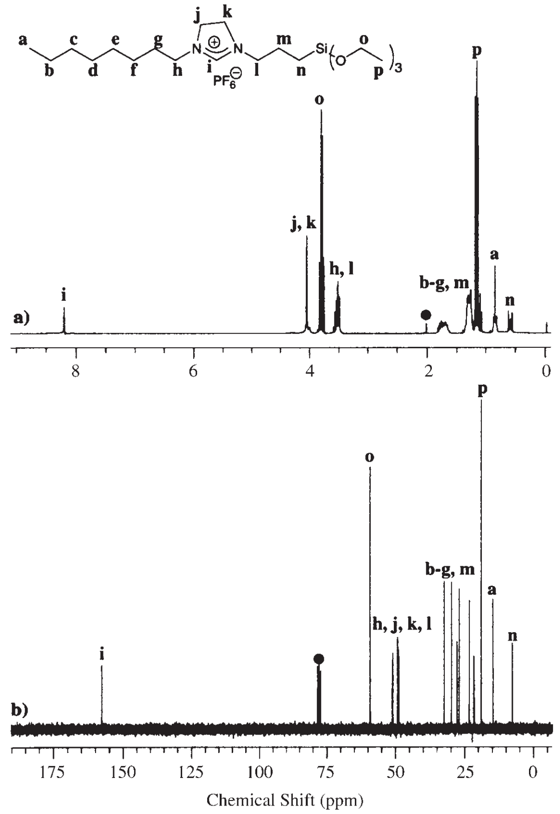


Figure 1. ^1H NMR (in [D$_6$]acetone (a)) and ^{13}C NMR (in $CDCl_3$ (b)) spectra of **1**. Circles indicate the signals corresponding to the solvents.

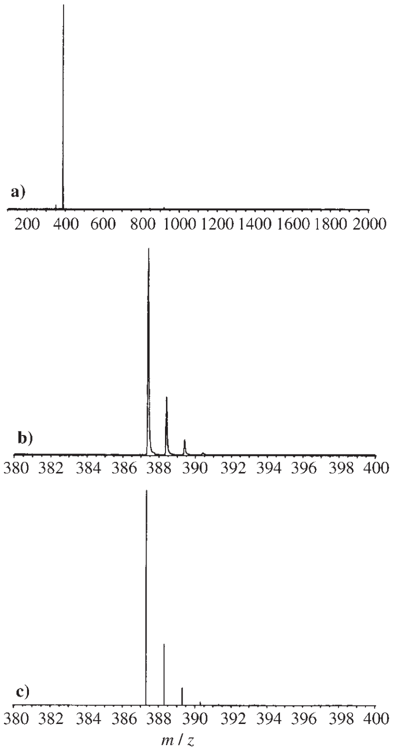


Figure 2. Positive ion ESI mass spectra of the acetonitrile solution of **1** (*m*/*z* 100–2000 (a) and *m*/*z* 380–400 (b)). The lines in (c) are the calculated pattern of $[C_{20}H_{43}N_2O_3Si]^+$.

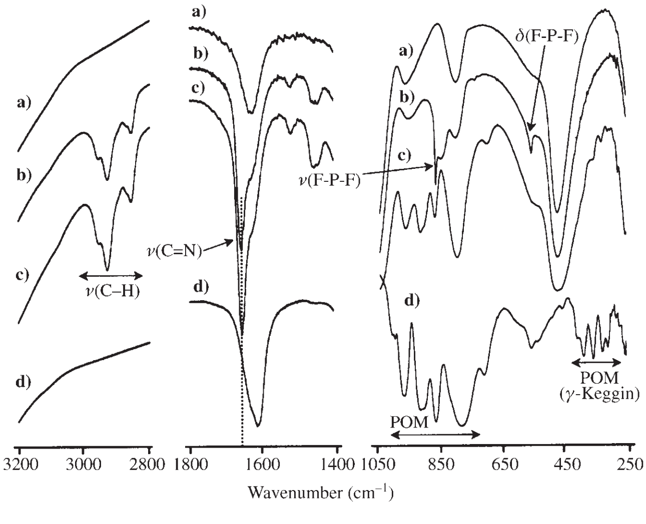


Figure 3. IR spectra of unmodified SiO_2 (a), modified silica **1**-SiO_2 (b), **I**/**1**-SiO_2 (c), and RbK-**I** (d).

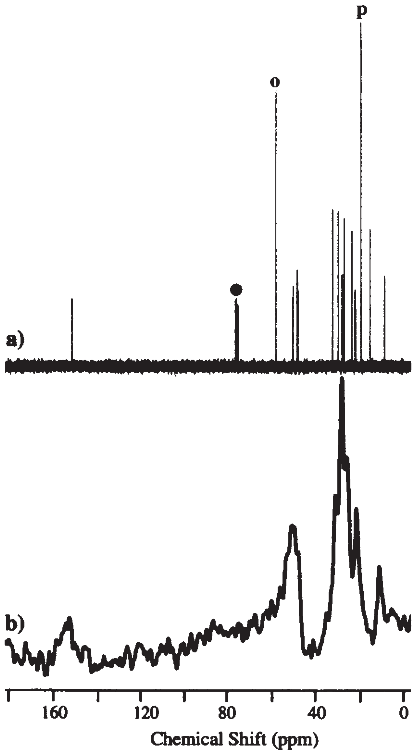


Figure 4. ^{13}C NMR spectrum of **1** in $CDCl_3$ (a) and ^{13}C CP-MAS NMR spectrum of the modified silica **1**-SiO_2 (b). The labels **o** and **p** indicate the signals corresponding to the methylene and methyl carbons of ethoxy group in **1**, respectively. A circle indicates the signals corresponding to $CDCl_3$.

The IR spectra of **1**-SiO_2 show bands characteristic of the parent **1** [ν(C=N) = 1654, ν(C–H) = 2860–2960, ν(F–P–F) = 869, and δ(F–P–F) = 560 cm^{-1}; Figure 3b]. This suggests that the main structure of the parent dihydroimidazolium skeleton of **1** is retained in **1**-SiO_2. Figure 4b shows the solid-state ^{13}C CP MAS NMR spectrum of **1**-SiO_2. The spectrum shows signals at $\delta = 152.2$, 47.0–50.0, 21.5–35.2, and 11.0 ppm assignable to the carbon between the nitrogen atoms (i), four carbons neighboring nitrogens (h, j, k, and l), methylene and methyl carbons (a–g and m), and the carbon next to silicon (n), respectively. These signal positions are similar to those of the parent **1** (Figure 4a) except that the resonances corresponding to the two carbon atoms of the ethoxy group of **1** at $\delta = 18.3$ and 58.5 ppm (o and p in Figure 4a) are much weaker. These results show that a condensation reaction between the surface silanol groups of SiO_2 and ethoxy groups of **1** occurs during the grafting process to form a covalent Si–O–Si linkage whilst maintaining the dihydroimidazolium skeleton of **1**.

The ^{29}Si MAS NMR spectrum of the unmodified SiO_2 shows two main signals at $\delta = -111$ and -101 ppm corresponding to Q^4 and Q^3 species, respectively ($Q^n = Si(OSi)_n(OH)_{4-n}$, $n = 3$, 4; Figure 5a).[19] The Q^3 sites are associated with isolated reactive silanol groups. In the ^{29}Si CP MAS NMR spectrum of **1**-SiO_2, two new signals appear at $\delta = -67$ and -58 ppm assignable to T^3 and T^2 organosilica species, respectively ($T^m = RSi(OSi)_m(OEt)_{3-m}$, $m = 2$, 3; Figure 5, inset).[19] The curve-fitting analyses show that the $Q^3/(Q^3+Q^4)$ ratio decreases from 0.25 (SiO_2) to 0.17 (**1**-SiO_2) after the immobilization. This decrease (0.08) corresponds to the reaction of 33 % of the silanol groups of the parent unmodified SiO_2 to form a covalent Si–O–Si linkage. The loading amount of the dihydroimidazolium cation on the surface of SiO_2 was found to be 353 μmol per gram of **1**-SiO_2.

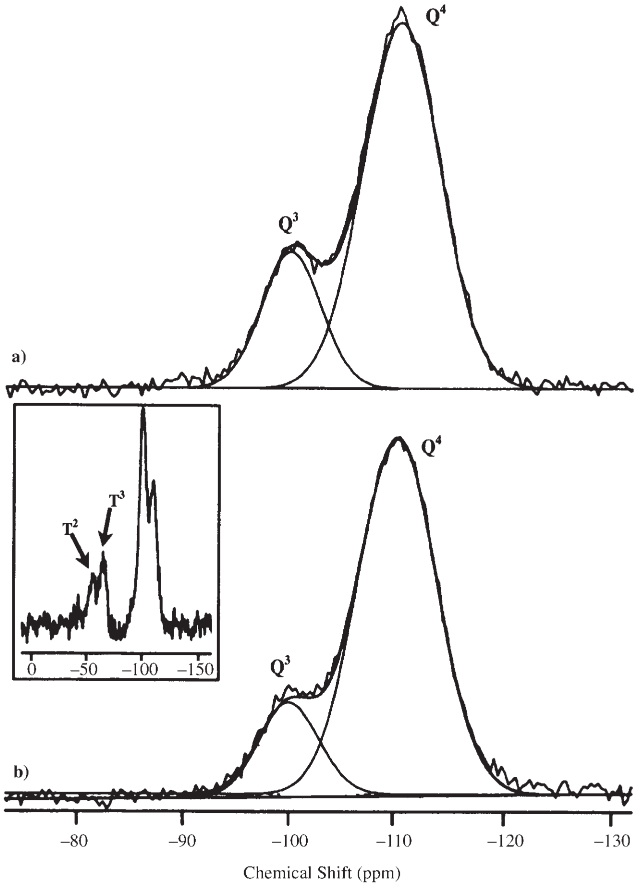


Figure 5. ^{29}Si MAS NMR spectra of unmodified SiO_2 (a) and the modified silica **1**-SiO_2 (b). Inset: ^{29}Si CP MAS NMR spectrum of **1**-SiO_2.

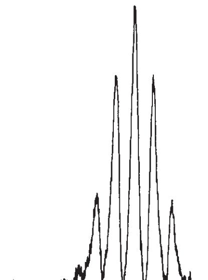


Figure 6. ^{31}P MAS NMR spectra of **1**-SiO_2 (a) and **I**/**1**-SiO_2 (b).

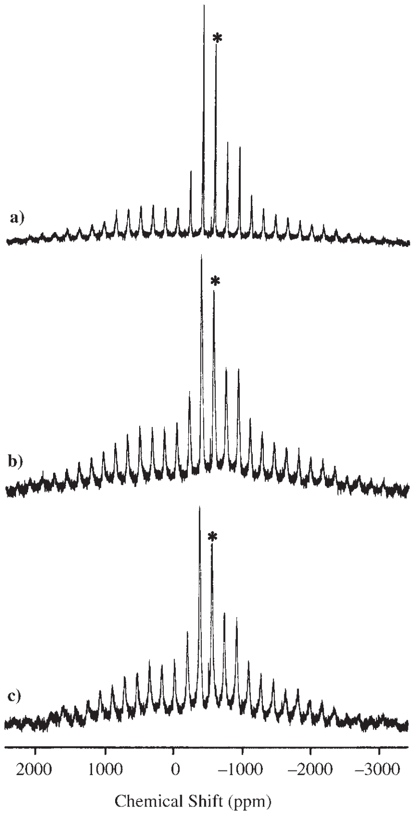


Figure 7. ^{51}V MAS NMR spectra of TBA-**I** (a), **I**/**1**-SiO_2 (b), and **I**/**1**-SiO_2 recovered after epoxidation of cyclooctene under the conditions in Table 1 (c). The center signals are indicated with asterisks.

Immobilization of **I** was then carried out according to the following procedure. The Rb^+/K^+ mixed-cation salt of **I** (RbK-**I**, >99% purity by ^{51}V NMR spectroscopy) was dissolved in an aqueous solution of HCl (1 mM). **1**-SiO_2 was then added to the solution and the suspension was vigorously stirred at room temperature for 24 h. It was then filtered and the solid was washed with a large amount of water and dried in vacuo to afford the immobilized catalyst containing **I** (**I**/**1**-SiO_2). Compound **I** could not be immobilized onto unmodified SiO_2 by a similar procedure.

The ^{31}P MAS NMR spectrum of **1**-SiO_2 shows one set of signals for the PF_6^- ion centered at $\delta = 103$ ppm (Figure 6a), whereas no ^{31}P MAS NMR signals were observed for **I**/**1**-SiO_2 (Figure 6b). The elemental analysis showed that Rb, K, and P are not detectable in **I**/**1**-SiO_2. The loading amount of **I** was found to be 91 μmol per gram of **1**-SiO_2, which is almost one-quarter of that of the dihydroimidazolium cation on the surface of **1**-SiO_2. These figures show the progress of the stoichiometric anion exchange of monovalent PF_6^- with tetravalent **I**.

The ^{51}V MAS NMR spectrum of **I**/**1**-SiO_2 shows one set of signals centered at $\delta = -561$ ppm (Figure 7b), thereby suggesting the existence of a single vanadium species. This signal was assigned to the doubly hydroxy-bridged dioxovanadium species {VO(μ-OH)$_2$VO} in **I** since the chemical shift is almost the same as that of the tetra-*n*-butylammonium salt of **I** (TBA-**I**) ($\delta = -562$ ppm, Figure 7a).[7,20] The IR spectrum of **I**/**1**-SiO_2 (in the range 450–4000 cm^{-1}) exhibits bands at 795, 871, 918, and 965 cm^{-1} in addition to the characteristic bands of **1** (Figure 3c). These bands in the range 800–1000 cm^{-1} coincide with those of the parent **I** (Figure 3d). In the range 250–450 cm^{-1}, the IR spectrum of **I**/**1**-

SiO_2 shows bands at 313, 333, 357, 389, and 408 cm^{-1} characteristic of the γ-Keggin structure of **I**.[21] These ^{51}V MAS NMR and IR results show the maintenance of the γ-Keggin structure of **I** in **I**/**1**-SiO_2.

Catalytic oxidation of olefins and sulfides with hydrogen peroxide: The catalytic activities for the epoxidation of 1-octene using one equivalent of hydrogen peroxide in an acetonitrile/*tert*-butyl alcohol solvent mixture (1/1 v/v) at 293 K were compared (Table 1). The reaction did not proceed in the absence of the catalyst or in the presence of unmodified SiO_2 (Table 1, entry 4) or modified SiO_2 (**1**-SiO_2; Table 1, entry 3). 1-Octene was epoxidized to 1,2-epoxyoctane in 82 % conversion with 98 % selectivity with **I**/**1**-SiO_2.[22,23] The epoxidation rate was 13.8 mM h^{-1}, which is lower than that of the corresponding homogeneous analogue of TBA-**I** (23.6 mM h^{-1}).[7]

Table 1. Epoxidation of olefins with one equivalent of hydrogen peroxide.[a]

Entry	Catalyst	Olefin	Conv. of olefin [%]	Select. to epoxide [%]
1	**I**/**1**-SiO_2	1-octene	82	98
2	TBA-**I**	1-octene	93	99
3[b]	**1**-SiO_2	1-octene	<1	–
4[b]	SiO_2	1-octene	<1	–
5	none	1-octene	<1	–
6	**I**/**1**-SiO_2	1-hexene	73	98
7	**I**/**1**-SiO_2	1-decene	66	96
8	**I**/**1**-SiO_2	*cis*-2-octene	78	97[c]
9	**I**/**1**-SiO_2	*cis*-3-octene	71	98[c]
10	**I**/**1**-SiO_2	*trans*-2-octene	5	99[d]
11	**I**/**1**-SiO_2	*cis*-β-methylstyrene	36	85[c,e]
12	**I**/**1**-SiO_2	cyclohexene	80	84[f]
13	**I**/**1**-SiO_2	2-norbornene	70	90 [g]
14	**I**/**1**-SiO_2	cyclooctene	81	>99
15[h]	**I**/**1**-SiO_2	cyclooctene	79	>99
16[h]	**I**/**1**-SiO_2	cyclooctene	79	>99
17[i]	**I**/**1**-SiO_2	cyclooctene	>99	>99

[a] Reaction conditions: Olefin (0.2 mmol), catalyst (**I**, 10 μmol), hydrogen peroxide (30 % aq., 0.2 mmol), acetonitrile/*tert*-butyl alcohol (3/3 mL), 293 K, 24 h. Conversions and selectivities were determined by gas chromatography or ^{1}H NMR spectroscopy using an internal standard technique and were based on olefins. [b] 100 mg. [c] The configuration of the epoxide is only *cis*. [d] The configuration of the epoxide was only *trans*. [e] Phenyl-2-propanone (4 % selectivity) was formed. [f] 1,2-Cyclohexanediol (6 % selectivity) and 2-*tert*-buthoxycyclohexanol (6 % selectivity) were formed. [g] The configuration of the epoxide was only *exo*. 2,3-Norbornanediol (3 % selectivity) was formed. [h] These experiments used a recycled catalyst; 1 st reuse (entry 15) and 2nd reuse (entry 16). Yields are the average values of two runs. The initial rates for the recycle runs were almost the same as that for the run with fresh catalyst (entry 14). [i] 1.5 equivalents of H_2O_2 were used.

The present **I**/**1**-SiO_2 system was applied to the epoxidation of various kinds of olefins using only one equivalent of hydrogen peroxide, as shown in Table 1. Unactivated aliphatic terminal olefins could be transformed into the corresponding epoxides in moderate to high yields (Table 1, entries 1, 6, and 7). Cyclic olefins such as 2-norbornene and cyclooctene were oxidized to the corresponding epoxides with high selectivity (Table 1, entries 13 and 14). When 1.5 equivalents of hydrogen peroxide was used for the epoxidation of cyclooctene the yield of the corresponding epoxide was greater than 99 % (Table 1, entry 17). In the case of cyclohexene, hydrolytic (solvolytic) decomposition of the epoxide occurred to some extent (Table 1, entry 12). *cis*-2,3- (76 % yield), *cis*-3,4- (71 % yield), and *trans*-2,3-Epoxyoctanes (5 % yield) were obtained from the epoxidation of *cis*-2-, *cis*-3-, and *trans*-2-octenes, respectively, and the configurations around the C=C double bonds were completely retained in the corresponding epoxides (Table 1, entries 8–10). Moreover, the epoxidation rate and selectivity were not changed by addition of the free-radical trap 2,6-di-*tert*-butyl-4-methylphenol. These results suggest that free-radical intermediates are not involved in the present epoxidation.

The present system also catalyzes the oxidation of various sulfides. The results are summarized in Table 2. The reaction did not proceed in the absence of the catalyst under the present reaction conditions (Table 2, entry 4). Various kinds of sulfides were selectively mono-oxygenated to the corresponding sulfoxides (ca. 90 %) along with formation of the corresponding sulfones (ca. 10 %). In the oxidation of aryl sulfides, the reaction rates were found to depend on the substituents on the aromatic rings: sulfides with electron-donating substituents were oxidized faster than those with electron-withdrawing ones (Table 2, entries 1–3 and 5–9). Both aryl and alkyl sulfides could be converted into the corresponding sulfoxides in excellent yields (Table 2, entries 10 and 11).

Table 2. Oxygenation of sulfides with one equivalent of hydrogen peroxide catalyzed by **I**/**1**-SiO_2.[a]

Entry	Sulfide	Time [h]	Conv. of sulfide [%]	Select. to sulfoxide [%]
1	thioanisole	6	92	92
2	4-methoxythioanisole	4	94	93
3[b]	4-methoxythioanisole	4	94	92
4[c]	4-methoxythioanisole	6	<1	-
5	4-methylthioanisole	5	93	91
6	4-fluorothioanisole	7	77	97
7	4-chlorothioanisole	8	81	95
8	4-(methylthio)acetophenone	8	82	92
9	4-(methylthio)benzonitrile	8	86	90
10	ethyl *n*-propyl sulfide	10	95	94
11	methyl *n*-octyl sulfide	10	95	96

[a] Reaction conditions: Sulfide (0.5 mmol), **I**/**1**-SiO_2 (**I**, 2 μmol), hydrogen peroxide (30 % aq., 0.5 mmol), acetonitrile/*tert*-butyl alcohol (1.5/1.5 mL), 293 K. Conversions and selectivities were determined by gas chromatography or ^{1}H NMR spectroscopy using an internal standard technique and were based on sulfides. The main by-products were the corresponding sulfones. [b] Recycling experiment. The initial rate for the recycle run was almost the same as that for the run with fresh catalyst (entry 2). [c] Blank experiment. The reaction was carried out without catalyst.

For the competitive epoxidation of *cis*- and *trans*-2-octenes (Figure 8), the formation rate of *cis*-2,3-epoxyoctane

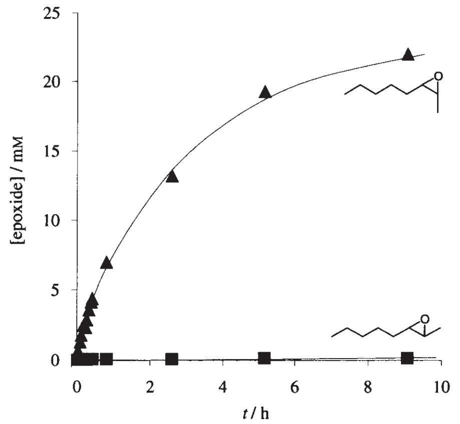
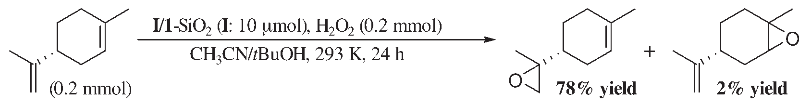


Figure 8. Competitive epoxidation of *cis*- and *trans*-2-octenes with **I**/**1**-SiO_2 catalyst. Reaction conditions: *cis*- and *trans*-2-Octenes (0.2 mmol each), **I**/**1**-SiO_2 (**I**, 10 μmol), hydrogen peroxide (30% aq., 0.2 mmol), acetonitrile/*tert*-butyl alcohol (3/3 mL), 293 K. $R_{cis} = 14.9\ mM\,h^{-1}$, $R_{trans} = 0.137\ mM\,h^{-1}$.



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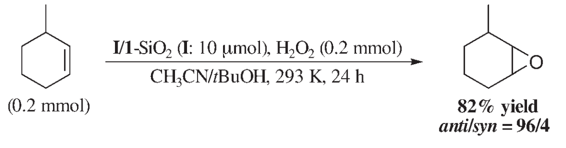
was $14.9\ mM\,h^{-1}$, much higher than that of the *trans* isomer ($0.137\ mM\,h^{-1}$, $k_{cis}/k_{trans} = 109$). The epoxidation of 3-methyl-1-cyclohexene was highly diastereoselective and gave the corresponding epoxide with the oxirane ring *trans* to the substituent (*anti* configuration) [Eq. (3)]. Further, the more accessible, but less nucleophilic, double bonds in nonconjugated dienes were highly regioselectively epoxidized. For example, *trans*-1,4-hexadiene gave only the 1,2-epoxide and the [1,2-epoxide]/[total epoxide] ratio was higher than 0.99 [Eq. (4)]. This value is much higher than those reported for the epoxidation catalyzed by sterically hindered porphyrins with NaOCl or PhIO ([Mn(TTPPP)(OAc)]/NaOCl (0.35),[24] [Mn(T(2′,6′-G1APh)P)Cl]/PhIO (0.20),[25] $[Mo(CO)_6]$/CHP (0.14),[26] [Mn(TPP)(OAc)]/NaOCl (0.03),[24] and [Mn(T(3′,5′-G2Ph)P)Cl]/PhIO (0.03)).[27] In addition, for the (+)-limonene epoxidation [Eq. (5)], the [8,9-epoxide]/[total epoxide] ratio was 0.98, which is much higher than those reported for the epoxidation with H_2O_2 and $PhCN/KHCO_3$ (0.37),[28] or Ti-β-zeolite (0.55).[29] Even the comparison with sterically hindered porphyrin catalysts with NaOCl or PhIO showed that the regioselectivity for **I**/**1**-SiO_2 is much higher than with these systems (0.62–0.75).[24,30] This unusual stereospecificity, diastereoselectivity, and regioselectivity are very similar to those for the homogeneous epoxidation by TBA-**I**,[31] which indicates that the intrinsic homogeneous catalysis has been heterogenized with retention of the catalytic performance in the present surface-modified support.



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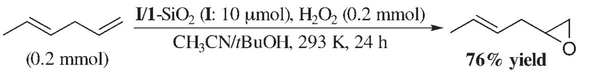

(4)

Heterogeneous nature of the catalyst: The use of solid catalysts can make the workup procedures very simple: the catalyst can easily be recovered after the reaction and can be reused without significant loss of catalytic activity or selectivity. However, leaching and/or deactivation of the heterogeneous catalyst are often responsible for severe drawbacks and are frequently observed.

To verify whether the observed catalysis is truly heterogeneous or not, the catalytic epoxidation of 1-octene was carried out with **I**/**1**-SiO_2 under the conditions in Table 1. After 1.5 h (at 30% conversion), the solid **I**/**1**-SiO_2 was removed from the reaction mixture by filtration and the reaction was allowed to proceed with the filtrate under the same conditions. As shown in Figure 9, the epoxidation was completely stopped by the removal of **I**/**1**-SiO_2. Next, the catalyst was separated by filtration after completion of the epoxidation and the leaching of vanadium and tungsten species was examined by ICP–AES analysis. These species were essentially undetectable in the filtrate (below 0.9%) in the case of **I**/**1**-SiO_2.

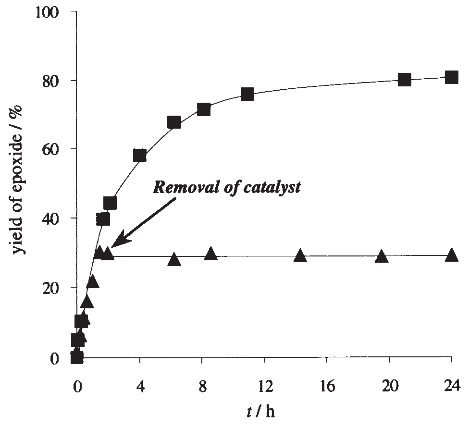

Figure 9. Effect of removal of **I**/**1**-SiO_2 on the epoxidation of 1-octene. Without removal of **I**/**1**-SiO_2 (▲); an arrow indicates the removal of **I**/**1**-SiO_2 (■). Reaction conditions were the same as those in Table 1.

Successful recovery of the catalyst can be achieved in the present system by simple decantation (or filtration) after the reaction. The IR and ^{51}V NMR spectra (Figure 7c) of the recovered catalyst are almost the same as those of the fresh catalyst, which shows the stability of the catalyst under the present conditions. It is worth noting that the recovered catalyst can be reused for both epoxidation and sulfoxidation without any loss of catalytic performance: the initial rates and final yields for the recycle runs were almost the same as that for the run with fresh catalyst (entries 15 and 16 in Table 1 and entry 3 in Table 2). Furthermore, the first-order dependence of the oxidation rate on the amount of **I**/**1**-SiO_2 was observed (Figure S2 in the Supporting Information). The above results rule out any contribution to the observed catalysis from vanadium and tungsten species that leach into the reaction solution, therefore this catalysis is truly heterogeneous.[32]

Conclusion

In conclusion, we have successfully immobilized the active polyoxometalate **I** on SiO_2 modified with the dihydroimidazolium cation by anion exchange. The catalyst is capable of heterogeneously oxidizing a broad range of olefins and sulfides with high selectivity to the desired compounds. The unique stereospecificity, diastereoselectivity, and regioselectivity of the catalyst are very similar to those of the homogeneous analogue under the same reaction conditions, which shows that the homogeneous catalysis has been heterogenized without loss of its intrinsic catalytic nature. Further, catalyst/product separation is very simple and the catalyst recovered after the reaction is reusable with retention of the catalytic performance.

Experimental Section

Instruments: GC analyses were performed with a Shimadzu GC-2014 with a FID detector equipped with a TC-WAX or TC-5 capillary column. Mass spectra were determined with a Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV. Liquid-state NMR spectra were recorded with a JEOL JNM-EX-270. The ^1H and ^{13}C NMR spectra of **1** were measured at 270 and 67.8 MHz, respectively, in [D$_6$]acetone or [D$_1$]chloroform with TMS as an internal standard. The ^{29}Si and ^{31}P NMR spectra of **1** were measured at 53.5 and 109.1 MHz, respectively, in [D$_6$]acetone with TMS and H_3PO_4 (85 %) as an external standard. The ^{51}V and ^{183}W NMR spectra of RbK-**I** were measured at 70.75 and 11.2 MHz, respectively, in D_2O. The respective external standards were $VOCl_3$ (neat) and Na_2WO_4 (2 M D_2O solution). Solid-state MAS NMR spectra (4 kHz for ^{13}C and ^{29}Si, 6 kHz for ^{31}P, 14 kHz for ^{51}V) were recorded with a Chemagnetics CMX-300 Infinity spectrometer operating at 75.6 (^{13}C), 59.7 (^{29}Si), 121.0 (^{31}P), or 79.0 MHz (^{51}V). Single-pulse-excitation ^{29}Si MAS NMR spectra were recorded with a $\pi/4$ flip angle (2.0 μs) and a repetition time of 25 s; peak deconvolutions were performed with Gaussian functions. Single-pulse-excitation ^{31}P MAS NMR spectra were recorded with a $\pi/2$ flip angle (4.0 μs) and a repetition time of 20 s. Single-pulse-excitation ^{51}V MAS NMR spectra were recorded with a $\pi/2$ flip angle (0.5 μs) and a repetition time of 1.0 s. The center signal was determined by changing the spinning speed (3–14 kHz). ^{13}C and ^{29}Si MAS NMR spectra with cross polarization (CP) were acquired with a contact time of 5 ms. Adamantane (^{13}C: $\delta = 28.5$ and 37.9 ppm), polydimethylsilane (^{29}Si: $\delta = -34.2$ ppm), $NH_4H_2PO_4$ (^{31}P: $\delta = 1.33$ ppm), and 0.16 M aq. $NaVO_3$ (^{51}V: $\delta = -574.28$ ppm) were used as external standards for the calibration of the chemical shifts. ESI mass spectra were recorded with a JMS-T100LC spectrometer. Typical settings are as follows: orifice voltage: 90 V; sample flow: 0.05 mL min^{-1}; solvent: acetonitrile; spray temp.: 523 K; ion source temp.: 353 K. IR spectra were measured with a Jasco FT/IR-460 Plus spectrometer using KBr disks.

Reagents: Olefins, sulfides, and solvents used for the oxidation reactions were purchased from Tokyo Kasei or Aldrich (reagent grade) and purified prior to use.[33] Hydrogen peroxide (30 % aqueous solution, Kanto) and triethoxy[3-(2-imidazolin-1-yl)propyl]silane (Fluka) were of analytical grade and were used without further purification. SiO_2 was obtained form Fuji Silysia (CARiACT Q-10, Lot No. C-0502007, 75–150 μm; BET surface area: 273 m^2 g^{-1}; pore volume: 1.23 cm^3 g^{-1}).

Synthesis of compound 1: All operations were performed by using Schlenk techniques under argon. A mixture of triethoxy[3-(2-imidazolin-1-yl)propyl]silane (25 mmol) and 1-chlorooctane (75 mmol) was heated at 353 K for 24 h under argon. After this time the mixture was cooled to room temperature and the volatiles were removed by evaporation under reduced pressure. An orange, viscous liquid was obtained after washing with *n*-pentane (3 × 50 mL) and evaporation to dryness. Extraction of the material into dichloromethane (ca. 50 mL) and filtration through activated carbon gave 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride (98 % yield), 25 mmol of which was dissolved in acetonitrile (80 mL) and treated with sodium hexafluorophosphate (25 mmol). The resulting mixture was vigorously stirred at room temperature for five days. After removal of the precipitate formed (NaCl) by filtration, the volatiles were evaporated under reduced pressure to give 1-octyl-3-(3-triethoxysililpropyl)-4,5-dihydroimidazolium hexafluorophosphate (**1**; 97 % yield). IR (KBr disk): $\tilde{\nu} = 2959$, 2929, 2858 (C−H), 1660 (C=N), 869 (F−P−F), 560 cm^{-1} (F−P−F); ^1H NMR (270 MHz, [D$_6$]acetone, TMS, 298 K): $\delta = 8.40$ (s, 1 H), 4.10–4.15 (m, 4 H), 3.81 (q, $^3J_{H,H} = 6.93$ Hz, 6 H), 3.58–3.64 (m, 4 H), 1.24–1.87 (m, 14 H), 1.20 (t, $^3J_{H,H} = 6.93$ Hz, 9 H), 0.87 (t, $^3J_{H,H} = 6.42$ Hz, 3 H), 0.58–0.64 ppm (m, 2 H) (see also Figure 1a); $^{13}C\{^1H\}$ NMR (67.8 MHz, $CDCl_3$, TMS, 298 K): $\delta = 156.7$, 58.5, 50.2, 48.3, 48.2, 48.0, 31.7, 29.1, 29.0, 27.1, 26.3, 22.6, 20.9, 18.3, 14.1, 7.0 ppm (see also Figure 1b); ^{29}Si NMR (53.5 MHz, [D$_6$]acetone, TMS, 298 K): $\delta = -45.9$ ppm; ^{31}P NMR (109.1 MHz, [D$_6$]acetone, 85 % H_3PO_4, 298 K): $\delta = 32.8$ ppm (7, $^1J_{P,F} = 708$ Hz); ESI-MS (positive-ion mode): *m*/*z* 387 $[C_{20}H_{43}N_2O_3Si]^+$ (see also Figure 2).

Preparation of 1-SiO_2: All operations were performed using Schlenk techniques under argon. A typical example is as follows: SiO_2 was pretreated at 393 K for 3 h under reduced pressure ($<10^{-2}$ Torr). The TG/DTA analysis revealed the presence of 3.5 silanol groups per square nanometer on the surface of this pretreated SiO_2.[34] The pretreated SiO_2 (3.0 g) was then vigorously stirred with a chloroform solution of **1** (0.24 M, 50 mL) for 24 h under reflux conditions (bath temperature: 353 K). The solid was separated by filtration, washed with *n*-heptane (50 mL) and acetonitrile (50 mL), and then dried in vacuo to afford **1**-SiO_2 as a pale yellow solid. The elemental analysis of **1**-SiO_2 (N: 1.03 %) revealed the presence of 353 μmol of the dihydroimidazolium cation per gram of **1**-SiO_2. IR (KBr disk): $\tilde{\nu} = 2960$, 2931, 2860 (C−H), 1654 cm^{-1} (C=N); ^{13}C CP MAS NMR (75.6 MHz): $\delta = 152.2$, 47.0–50.0, 21.5–35.2, 11.0 ppm; ^{29}Si CP MAS NMR (59.7 MHz): $\delta = -58$ (T^2), -67 (T^3), -101 (Q^3), -111 ppm (Q^4); ^{31}P MAS NMR (121.7 MHz): $\delta = 103.0$ ppm (7, $^1J_{P,F} = 708$ Hz); BET surface area: 199 m^2 g^{-1}. Pore volume: 0.44 cm^3 g^{-1}.

Preparation of I supported on modified SiO_2: An aqueous solution of $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ was prepared according to a literature procedure.[20] The anion was isolated as the mixed-cation salt of Rb^+ and K^+ (RbK-**I**) as it could be obtained with high purity (> 99 % by ^{51}V NMR). RbK-**I** (0.25 mmol) was dissolved in an aqueous solution of HCl (1 mM), **1**-SiO_2 was added to this solution, and the resulting mixture was vigorously stirred at room temperature for 24 h. The solid was then filtered off, washed with a large amount of water, and dried in vacuo to afford **I**/**1**-SiO_2. The loading amount of **I** was found to be 91 μmol per gram. It was proved by elemental analyses that K^+ and Rb^+ were not incorporated into **I**/**1**-SiO_2 and that all PF_6^- had been exchanged during the treatment. ^{51}V MAS NMR (79.0 MHz): $\delta = -561$ ppm. BET surface area: 146 m^2 g^{-1}. Pore volume: 0.30 cm^3 g^{-1}.

Catalytic oxidation: The catalytic oxidation was carried out in a glass tube reactor. A typical procedure for the oxidation is as follows: Catalyst **I** (10 μmol for epoxidation and 2 μmol for sulfoxidation), acetonitrile/*tert*-butyl alcohol (3/3 mL for epoxidation and 1.5/1.5 mL for sulfoxidation), substrate (0.2 mmol for epoxidation and 0.5 mmol for sulfoxidation), and hydrogen peroxide (30 % aq. solution; one equiv with respect to substrates) were added to the reaction vessel. The reaction was carried out at 293±0.2 K. The reaction solution was periodically sampled and analyzed by GC (or ^{1}H NMR). The products were identified by comparison of their mass and NMR spectra with those of authentic samples. The carbon balance in each experiment was in the range of 95–100%. After the reaction, the catalyst and reaction solution were separated by decantation (or filtration). The recovered catalyst was washed with a solvent mixture (acetonitrile/*tert*-butyl alcohol, 1/1 v/v; 2×6 mL) and then used again.

Acknowledgments

We thank Ms. C. Yoshida (The University of Tokyo) and Ms. M. Kotani (JST) for their help with experiments. This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST) and Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology.

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[23] The Arrhenius plots for the epoxidation of 1-octene with **I**/**1**-SiO_2 (plot of the pseudo-first-order rate constant, k_{obs}, vs. T^{-1} between 283 and 313 K; Figure S3) gave the following activation parameters: $E_a = 14.3\ kcal\,mol^{-1}$, $\Delta H^{\neq}_{293\,K} = 13.7\ kcal\,mol^{-1}$, $\Delta S^{\neq}_{293\,K} = -32.0$ eu, and $\Delta G^{\neq}_{293\,K} = 23.1\ kcal\,mol^{-1}$.

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Received: November 15, 2005