Communication

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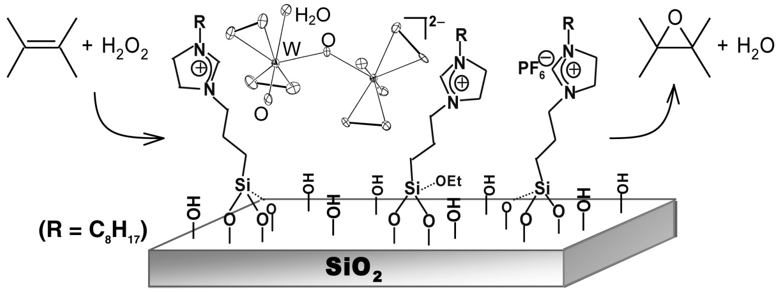

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Peroxotungstate Immobilized on Ionic Liquid-Modified Silica as a Heterogeneous Epoxidation Catalyst with Hydrogen Peroxide

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H_2O_2-based catalytic epoxidation has received much attention from an economic and environmental point of view.[1] Soluble transition metal-based catalysts such as tungsten, manganese, molybdenum, and rhenium have been developed for the oxidation with an aqueous H_2O_2.[1] Among them, tungsten-based catalysts including polyoxometalates show the high efficiency of H_2O_2 utilization and the high selectivity to the epoxides.[2−6] The significant development in tungsten-based catalysts is the Ishii−Venturello system,[3,4] followed by the Noyori's halide-free method for the oxidation of various substrates including olefins, alcohols, and sulfides with sodium tungstate and alkylammonium hydrogen sulfate.[5] We also reported efficient routes for epoxidation of olefins and allylic alcohols with H_2O_2 catalyzed by the divacant lacunary silicotungstate $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$[6a] and the dinuclear peroxotungstate $[\{W({=}O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$ (**W2**),[6b,c] respectively.

Although many efficient procedures based on the tungsten catalysts for the oxidation with H_2O_2 have been developed, most of them are homogeneous systems and share common drawbacks, that is, catalyst/product separation and catalyst reuse are difficult. The immobilization (heterogenization) of catalytically active species onto solid supports can solve the catalyst recovery and recycle.[7−11] For the development, insoluble bulk materials,[8] impregnation of homogeneous catalysts onto inert solid supports such as metal hydroxides[9] and polymers,[10] and attachment of active species through covalent or ionic bonds with supports[11] have been utilized. With regard to the immobilized tungsten-based catalysts for epoxidation with H_2O_2, various supports such as anion-exchange resins,[11a,b] surface-modified metal oxides,[11b−g] and layered double hydroxide[9a,b] have been used. However, these systems have the disadvantages: (i) some extent of tungsten leaching, (ii) low accessibility of organic substrates and H_2O_2 because of the hydrophilicity and/or the low surface area of the catalysts, (iii) decomposition of H_2O_2 by the basic sites of the supports, and/or (iv) the decrease in activities by the immobilization.[12,13]

Here, we synthesized peroxotungstate (**W2**) immobilized on dihydroimidazolium-based ionic liquid-modifed SiO_2 as an efficient heterogeneous epoxidation catalyst with H_2O_2 to overcome disadvantages i−iv, especially iv. *To our knowledge, this type of ionic liquid-modifed supports have never been used to immobilize polyoxometalates and peroxometalates.*[14]

1-Octyl-3-(3-triethoxysililpropyl)-4,5-dihydroimidazolium chloride was synthesized by the reaction of 3-(2-imidazolin-1-yl)-propyltriethoxysilane with 1-chlorooctane. The resulting compound was further treated with sodium hexafluorophosphate in acetonitrile, giving the corresponding ionic liquid **1** (Figure S1). Then, SiO_2 (BET surface area 259 $m^2 \cdot g^{-1}$, 4.7 silanol groups/nm^2) was vigorously stirred with a chloroform solution of the ionic liquid **1** for 24 h under reflux conditions to anchor covalently the ionic liquid fragments to the SiO_2 surface (**1**−SiO_2). The IR spectrum of **1**−SiO_2 showed the bands characteristic of the parent ionic liquid **1**, for example, ν(C═N) (1654 cm^{-1}) and ν(C−H) (2860, 2931, and 2960 cm^{-1}). The solid-state ^{13}C CP MAS NMR spectrum of **1**−SiO_2 showed similar signals to those of **1**, except for the near disappearance of the resonances corresponding to the two carbon atoms of the ethoxy group of **1** at 18.3 and 58.5 ppm (Figure S2). These suggest that a condensation reaction between the surface silanol groups of SiO_2 and ethoxy group of **1** to form the covalent Si−O−Si linkage occurred during the grafting process with the maintenance of the main structure of **1**. The ^{29}Si MAS NMR spectrum of SiO_2 showed two signals at −111 and −101 ppm corresponding to Q^4 and Q^3 species of the silica framework, respectively ($Q^m = \mathit{Si}(OSi)_m(OH)_{4-m}$, Figure S3). For **1**−$SiO_2$, additional signals appeared at −67 and −58 ppm assignable to T^3 and T^2 organosilica species, respectively ($T^n = R\mathit{Si}(OSi)_n(OEt)_{3-n}$, Figure S4). The $Q^3/(Q^3 + Q^4)$ ratio was decreased from 0.24 to 0.11 by the grafting. The decrease of 0.13 corresponds to the reaction of 54% of silanol groups. Elemental analysis of **1**−SiO_2 revealed that 365 μmol of ionic liquid fragments per gram of **1**−SiO_2 (0.85 ionic liquid fragments/nm^2) existed and that 2.7 ethoxy groups of **1** reacted with 49% of silanol groups to form covalent Si−O−Si linkage. The reacted amount of silanol groups estimated with the elemental analysis data was in good agreement with that by ^{29}Si MAS NMR. The BET surface area of **1**−SiO_2 was 184 $m^2 \cdot g^{-1}$.

Next, **1**−SiO_2 (1 g) was vigorously stirred with 10 mL of an aqueous solution of potassium salt of **W2** (0.1 M) at room temperature (ca. 298 K) for 12 h. It was proved by elemental analyses and ^{31}P MAS NMR spectroscopy that K^+ was not incorporated into **1**−SiO_2 and that PF_6^- was leached during the treatment, showing that the anion exchange between PF_6^- and **W2** occurs during the treatment. The loading amount of **W2** anion was 105 $\mu mol \cdot g^{-1}$. The Raman bands of the **W2**/**1**−SiO_2 agreed well with those of the parent potassium salt of **W2**, showing the maintenance of the **W2** structure during the anion exchange process. Further, the IR, ^{13}C, and ^{29}Si MAS NMR spectra of **W2**/**1**−SiO_2 reveal that the structure of ionic liquid fragments is also preserved during the immobilization process. The BET surface area of **W2**/**1**−SiO_2 was 203 $m^2 \cdot g^{-1}$.

The present **W2**/**1**−SiO_2 could be applied to the epoxidation of various olefins using H_2O_2 as shown in Table 1.[15] For the epoxidation of *cis*- and *trans*-olefins, the configuration around the C═C double bonds was completely retained in the corresponding epoxides, suggesting that the free-radical intermediates are not involved in the present epoxidation. The regioselective epoxidation of geraniol took place at the electron-deficient 2,3-allylic double bond to afford 2,3-epoxy alcohol in high yield. The epoxidation of secondary β,β-disubstituted allylic alcohol of 4-methyl-3-penten-2-ol proceeded diastereoselectively to form the *threo*-epoxy alcohol (*threo*/*erythro* = 90/10). In addition, the epoxidation of (*Z*)-3-

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Table 1. Epoxidation of Olefins with H_2O_2 Catalyzed by **W2**/**1**−SiO_2[a]

entry	olefin	time (h)	yield of epoxide (%)
1	*cis*-2-octene	3	>99[b]
2	*trans*-2-octene	7	73[c]
3	*cis*-β-methylstyrene	2	>99[b]
4	cyclohexene	3	80
5	2-norbornene	2.5	80[d]
6	cycloheptene	2	>99
7	cyclooctene	1	>99
8	geraniol	4	95[e]
9	4-methyl-3-penten-2-ol	4	90[f]
10	(*Z*)-3-methyl-3-penten-2-ol	4	90[g]

[a] Reaction conditions: Olefin (1 mmol), catalyst (**W2**: 1 mol % with respect to olefin), H_2O_2 (30% aq solution, 0.2 mmol), CH_3CN (0.5 mL), 333 K. Yields and selectivities were determined by GC or ^1H NMR with an internal standard technique. Selectivities to the corresponding epoxides were >95% in all cases. Yield (%) = epoxide (mmol) per initial H_2O_2 (mmol) × 100. [b] Only cis. [c] Only trans. [d] Only exo. [e] Only 2,3-epoxide. [f] threo/erythro = 90/10. [g] threo/erythro = 40/60.

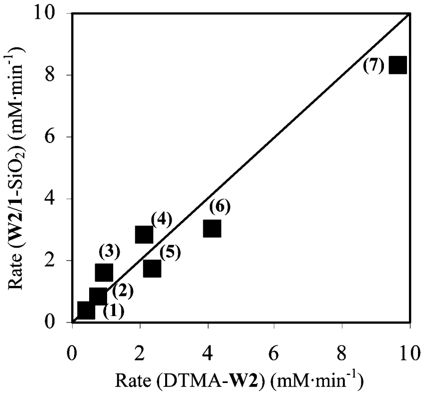

Figure 1. Comparison of the reaction rates obtained by the use of **W2**/**1**−SiO_2 catalyst (heterogeneous) with those of $[n\text{-}C_{12}H_{25}N(CH_3)_3]_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$ (DTMA-**W2**, homogeneous) for the epoxidation of olefins under the same reaction conditions. The reactions were carried out under the conditions in Table 1. (1) 1-Octene, (2) *trans*-2-octene, (3) 2-norbornene, (4) 1-methyl-1-cyclohexene, (5) cyclohexene, (6) *cis*-2-octene, and (7) cyclooctene.

methyl-3-penten-2-ol, in which 1,3- and 1,2-allylic strains compete with each other, was more erthro-selective (threo/erythro = 40/60). A similar regio- and diastereoselectivity for allylic alcohols was also observed for the homogeneous **W2**-catalyzed epoxidation.[6b,c]

The epoxidation was completely stopped by the catalyst removal (Figure S5). It was confirmed by ICP-AES analysis that no tungsten species could be detected in the filtrate (below detection limit of 16 ppb). Further, **W2**/**1**−SiO_2 could be easily recovered by the filtration and reused at least three times for the epoxidation of cyclooctene without the loss of the catalytic activity and selectivity (99% yield, >99% selectivity under the conditions in Table 1 after the third recycle). The above results can rule out any contribution to the observed catalysis from the tungsten species that leached into the reaction solution, and the observed catalysis is truly heterogeneous in nature.

The catalytic activity of **W2**/**1**−SiO_2 was compared with that of the corresponding homogeneous analogue of $[n\text{-}C_{12}H_{25}N(CH_3)_3]_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$ (DTMA-**W2**) under the same conditions. As shown in Figure 1, the reaction rates by the use of **W2**/**1**−SiO_2 were comparable to those of DTMA-**W2**. This fact indicates that *the homogeneous catalysis can be heterogenized with retention of the **W2** catalyst performance by the support on ionic liquid-modified SiO_2.*

In conclusion, **W2**/**1**−SiO_2 was capable of heterogeneously epoxidizing a broad range of olefins with high selectivity. The activity and selectivity were comparable to those of the homogeneous analogue, showing that the homogeneous catalysis could be heterogenized.

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Supporting Information Available: Experimental section, effect of alkyl chain length on the N1 position of dihydroimidazolium cation on the epoxidation of cyclooctene, and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) A tungstate-exchanged layered double hydroxide, WO_4^{2-}(MgAl)LDH, was more than 100 times more active for oxidative bromination and bromide-assisted epoxidation than the homogeneous analogue of $NaWO_4$. See refs 9a and b.

(13) The sandwich-type polyoxometalate, $[(Fe(OH_2)_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$, electrostatically immobilized on cationic silica/alumina nanoparticles was more active than the same quantity of the parent polyoxometalate for the aerobic oxygenation of sulfides and autoxidation of aldehyde. See: (a) Okun, N. M.; Anderson, T. M.; Hill, C. L. *J. Am. Chem. Soc.* **2003**, *125*, 3194. (b) Okun, N. M.; Anderson, T. M.; Hill, C. L. *J. Mol. Catal.* **2003**, *197*, 283.

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(15) We synthesized **W2** supported on triethylammonium cation-grafted SiO_2. The yield of cyclooctene oxide under the conditions in Table 1 was 14% and much lower than that with **W2**/**1**−SiO_2.

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