Silicon Chemistry

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Highly Selective Oxidation of Organosilanes to Silanols with Hydrogen Peroxide Catalyzed by a Lacunary Polyoxotungstate**

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Organosilicon compounds have attracted much attention, and silanols are widely utilized as building blocks for the production of silicon-based polymer materials and organic donors in metal-catalyzed cross-coupling reactions.[1,2] Silanols are conventionally synthesized by hydrolysis of chlorosilanes[3] and treatment of siloxanes with alkaline reagents.[4] Strictly controlled reaction conditions are needed and it is difficult to synthesize sterically exposed silanols that readily condense to form disiloxanes. Oxidation with stoichiometric oxidants such as silver salts,[5] peracids,[6] permanganate,[7] dioxiranes,[8] osmium tetroxide,[9] oxaziridines,[10] and ozone[11] has also been reported. However, most of them lead to undesired production of the corresponding siloxanes instead of silanols. In contrast to these approaches, transition-metal-catalyzed oxidation of silanes to silanols is a promising synthetic method. Hydrolytic oxidation systems based on Ir,[12] Ru,[13] Ag,[14] Cu,[15] Cr,[16] Re,[17] Pt,[18] and Au[19] catalysts with water as oxygen donor have been reported, and some of them show broad substrate scope and high catalytic activity. Another approach is oxidation of silanes by Re[20] and Ti-zeolite[21] catalysts with H_2O_2 as oxygen donor. However, these systems have disadvantages: 1) applicability to a limited number of silanes, 2) use of an excess of highly concentrated H_2O_2 or urea/H_2O_2 adduct (UHP), 3) low turnover frequencies (TOF = 1–7), and 4) significant formation of undesirable siloxanes. Therefore, catalytic systems for efficient and selective H_2O_2-based oxidation of various silanes to silanols are scarcely known.

Polyoxometalates have attracted considerable attention in the fields of structural chemistry, biological chemistry, catalysis, and materials science.[22] To date, numerous catalytic H_2O_2-based oxidations by polyoxometalates such as peroxometalates,[23] lacunary polyoxometalates,[24] and transition metal substituted polyoxometalates[25] have been developed. However, application of polyoxometalate catalysts to the oxidation of silanes with H_2O_2 has never been reported. Here we report highly selective oxidation of organosilanes to silanols with 30–60% aqueous H_2O_2 catalyzed by divacant lacunary polyoxotungstate $(TBA)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ [**I**, TBA = $(n\text{-}C_4H_9)_4N^+$, Figure 1, Eq. (1)]. The present system has the following significant advantages: 1) high yields and selectivities to silanols without significant formation of undesired disiloxanes, 2) use of one equivalent of aqueous H_2O_2 with respect to the substrate instead of an excess of highly concentrated H_2O_2 or UHP, and 3) broad substrate scope including the production of sterically exposed silanols. To the best of our knowledge, this study provides the first example of catalytic oxidation of alkoxy silanes to the corresponding silanols.

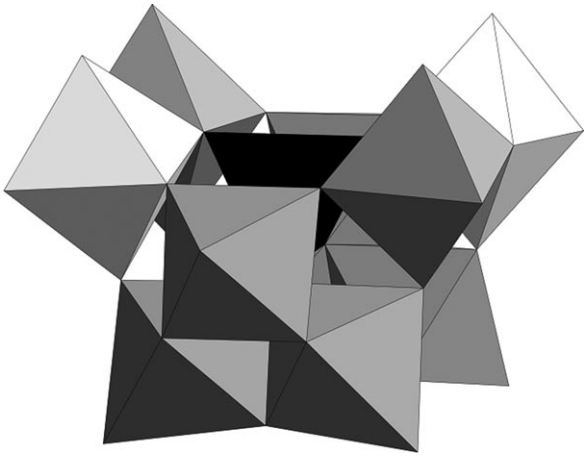
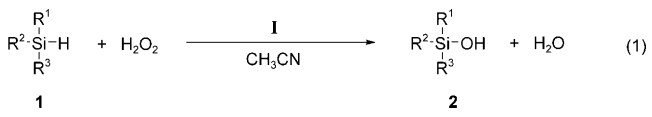


Figure 1. Polyhedral representation of the anion of $(TBA)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ (**I**). The $\{WO_6\}$ units and $\{SiO_4\}$ unit are shown as gray octahedra and a black tetrahedron, respectively. White octahedra indicate the tungsten atoms with aqua ligands.



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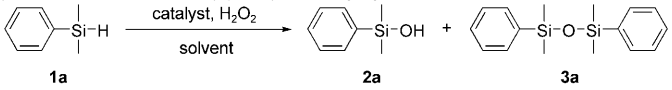
First, oxidation of dimethylphenylsilane (**1a**) to dimethylphenylsilanol (**2a**) with 30% aqueous H_2O_2 was carried out under stoichiometric conditions (substrate/H_2O_2 = 1:1). Among the solvents tested, acetonitrile gave the highest yield (78%) of **2a** (Table 1, entry 1). Formation of the corresponding disiloxane (**3a**) by condensation of **2a** was hardly observed. 1,2-Dichloroethane, DMSO, acetone, and benzonitrile as solvents gave **2a** in 57, 50, 45, and 44% yield, respectively (Table 1, entries 2–5), while DMF was found to be a poor solvent (Table 1, entry 6). The reaction rate for the oxidation of **1a** with 60% aqueous H_2O_2 was slightly higher than that with 30% aqueous H_2O_2 (Table 1, entries 1 and 7). On the other hand, UHP was not an effective oxidant in the present system (Table 1, entry 8). The reaction proceeded efficiently even at 305 K without significant changes in yield and selectivity (Table 1, entries 1 and 9). The yield, selectivity, and reaction rate for oxidation under argon were almost the same as those for oxidation under air (Table 1, entries 1 and 10). With water instead of H_2O_2, oxidation did not proceed at all (Table 1, entry 11). All these results suggest that participation of molecular oxygen in air and water can be excluded. Oxidation did not proceed in the absence of **I** (Table 1, entry 12). The catalyst precursor $Na_2WO_4 \cdot 2H_2O$ and the TBA salts of fully occupied and other lacunary polyoxotungstates were inactive (Table 1, entries 13 and 15–18). The H_2WO_4 catalyst showed low selectivity to **2a** and significant formation of **3a** (Table 1, entry 14). Divanadium-substituted polyoxotungstate $(TBA)_4[\gamma\text{-}H_2SiV_2W_{10}O_{40}]$,[25e] selenium-containing dinuclear peroxotungstate $(TBA)_2[SeO_4\{WO(O_2)_2\}_2]$,[23g] and phosphorus-containing tetranuclear peroxotungstate $(THA)_3[PO_4\{WO(O_2)_2\}_4]$[23b] showed low selectivity to **2a**, while the reaction rates were comparable to or higher than that of **I** (Table 1, entries 19, 21, and 22). To investigate the high selectivity to **2a** in the present system, condensation of **2a** to give **3a** was carried out in the presence of various catalysts (Table S1, Supporting Information). The H_2WO_4, $(TBA)_2[SeO_4\{WO(O_2)_2\}_2]$, and $(THA)_3[PO_4\{WO(O_2)_2\}_4]$ catalysts gave **3a** in 83, 80, and 43% yield, respectively. On the other hand, condensation hardly proceeded in the presence of **I**. Thus the low activity for condensation in the present system results in high selectivity to **2a**.

Table 1: Catalytic oxidation of dimethylphenylsilane (**1a**) with H_2O_2.[a]



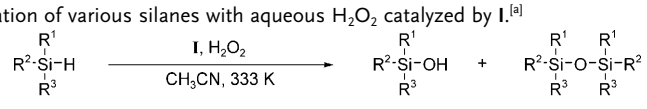
1a **2a** **3a**

Entry	Catalyst	Solvent	Yield [%]	Selectivity [%]		R_0 [mM min^{-1}]
				2a	**3a**	
1	I	CH_3CN	79	99	1	2.2
2	I	$(CH_2Cl)_2$	59	97	3	1.7
3	I	DMSO	50	99	1	0.9
4	I	acetone	46	98	2	0.7
5	I	benzonitrile	45	98	2	1.6
6	I	DMF	3	92	8	< 0.1
7[b]	I	CH_3CN	80	> 99	< 1	2.9
8[c]	I	CH_3CN	17	94	6	0.2
9[d]	I	CH_3CN	85	96	4	0.3
10[e]	I	CH_3CN	75	99	1	2.3
11[f]	I	CH_3CN	< 1	–	–	–
12	none	CH_3CN	< 1	–	–	–
13	$Na_2WO_4 \cdot 2H_2O$	CH_3CN	4	> 99	< 1	< 0.1
14	H_2WO_4	CH_3CN	39	27	73	0.6
15	$(TBA)_4[\alpha\text{-}SiW_{12}O_{40}]$	CH_3CN	2	85	15	< 0.1
16	$(TBA)_4H_4[\alpha\text{-}SiW_{11}O_{39}]$	CH_3CN	3	> 99	< 1	< 0.1
17	$(TBA)_3H_7[\alpha\text{-}SiW_9O_{34}]$	CH_3CN	4	> 99	< 1	0.1
18	$(TBA)_4[\gamma\text{-}SiW_{12}O_{40}]$	CH_3CN	< 1	–	–	–
19[g]	$(TBA)_4[\gamma\text{-}H_2SiV_2W_{10}O_{40}]$	CH_3CN	76	88	12	3.1
20	$(TBA)_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$	CH_3CN	32	91	9	1.0
21	$(TBA)_2[SeO_4\{WO(O_2)_2\}_2]$	CH_3CN	> 99	53	47	4.0
22[h]	$(THA)_3[PO_4\{WO(O_2)_2\}_4]$	CH_3CN	94	86	14	2.6

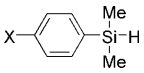
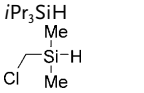
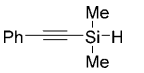
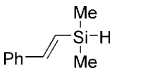
[a] Reaction Conditions: Catalyst (W: 7.3 mol% with respect to **1a** and H_2O_2), **1a** (1 mmol), 30% aqueous H_2O_2 (1 mmol), solvent (6 mL), 333 K, 2 h, under air (1 atm). Yield was determined by GC analysis. Yield = {[**2a** (mol) + **3a** (mol) × 2]/(**1a** used (mol))} × 100. Selectivity to **2a** [%] = {(**2a** (mol)/[**2a** (mol) + **3a** (mol) × 2]} × 100. Selectivity to **3a** [%] = {**3a** (mol) × 2/[**2a** (mol) + **3a** (mol) × 2]} × 100. [b] 60% aqueous H_2O_2 (1 mmol). [c] UHP (1 mmol). [d] 305 K, 24 h. [e] Under Ar (1 atm). [f] H_2O (1 mmol). [g] CH_3CN/*t*BuOH (3/3 mL). [h] THA = $[(n\text{-}C_6H_{13})_4N]^+$.

The scope of the catalytic oxidation of organosilanes with H_2O_2 was investigated for a range of structurally diverse silanes (Table 2). Various silanes could efficiently be oxidized under stoichiometric conditions (substrate/H_2O_2 = 1:1), and the corresponding silanols were obtained in high yields and selectivities. Catalytic oxidation of dimethylphenylsilanes **1a–1d**, which contain electron-donating or electron-withdrawing *para* substituents, proceeded selectively to afford the corresponding silanols **2a–2d** in high yields (Table 2, entries 1–4). Not only aryl silanes **1a–1e** but also alkyl silanes **1f–1j** were efficiently oxidized to the corresponding silanols (Table 2, entries 1–10). Sterically exposed silanes were smoothly oxidized to silanols in high yields, and the selectivity to silanols was not sensitive to the type of substituents. Compound **I** could be recovered quantitatively by the addition of an excess of diethyl ether (precipitation method) to the reaction solution. Recovered **I** could be reused at least three times without loss of catalytic activity and selectivity (see Supporting Information). Reactions of chloro-, alkenyl-, and alkynyl-containing silanes **1k–1m** also proceeded selectively to form the corresponding silanols **2k–2m** (Table 2, entries 11–13). Notably, triethoxysilane (**1n**) and tri-*n*-butoxysilane (**1o**) were also selectively oxidized to the corresponding silanols **2n** and **2o** without significant formation of the hydrative by-products (Table 2, entries 14 and 15).[26,27] To the best of our knowledge, catalytic conversion of alkoxy silanes to alkoxy silanols has not been reported to date.[28,29]

Table 2: Oxidation of various silanes with aqueous H_2O_2 catalyzed by **I**.[a]

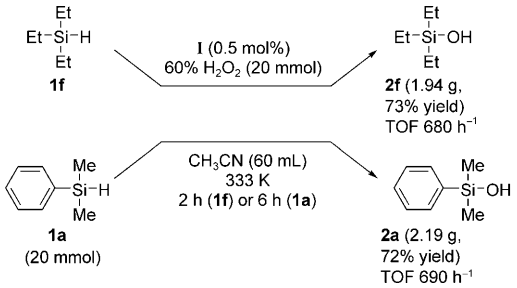


1 **2** **3**

Entry	Substrate		t [h]	Yield [%]	Selectivity [%]	
					2	**3**
1		X = H: **1a**	4	86	98	2
2		X = OMe: **1b**	4	89	93	7
3		X = Me: **1c**	3	90	96	4
4		X = CF_3: **1d**	4	85	96	4
5	Ph_2MeSiH	**1e**	5	80	> 99	
6	Et_3SiH	**1f**	4	92	> 99	< 1
7	$tBuMe_2SiH$	**1g**	4	92	> 99	< 1
8	nBu_3SiH	**1h**	4	80	> 99	< 1
9[b,c]	$(n\text{-}C_6H_{13})SiH$	**1i**	3	80	> 99	< 1
10[b]	iPr_3SiH	**1j**	4	84	> 99	< 1
11		**1k**	5	83	96	4
12[d]		**1l**	4	63	87	12
13		**1m**	0.5	53	86	4
14[e]	$(EtO)_3SiH$	**1n**	1.5	83	93	2
15[f]	$(n\text{BuO})_3SiH$	**1o**	2.5	68	95	< 1

[a] Reaction conditions: **I** (1 mol% with respect to substrate and H_2O_2), silane (1 mmol), 60% aqueous H_2O_2 (1 mmol), CH_3CN (6 mL), 333 K. Yield and selectivity were determined by GC and NMR spectroscopy. Yield [%] = {[silanol (mol) + disiloxane (mol) × 2]/H_2O_2 used (mol)} × 100. [b] **I** (2 mol% relative to substrate and H_2O_2). [c] CH_3CN/toluene (3/3 mL). [d] 318 K. [e] 305 K, ethanol (5% selectivity) was formed. [f] 1-Butanol (4% selectivity) was formed.

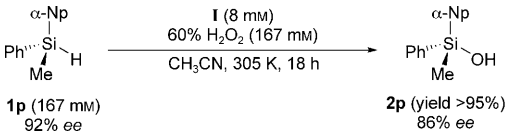
The present system was applicable to larger-scale oxidations of **1f** and **1a** with H_2O_2 (20 mmol scale), and **2f** and **2a** could be isolated in 73 and 72% yield, respectively [Eq. (2)].[30] Their respective TOFs reached up to 680 and



(2)

690 h^{-1}. The TOF for the oxidation of **1f** is much higher than those of hydrolytic oxidation systems such as [{$RuCl_2$(*p*-cymene)}$_2$] (285 h^{-1}),[13a] [{IrCl(C_8H_{12})}$_2$] (80 h^{-1}),[12] Ru–hydroxyapatite (HAP; 3 h^{-1}),[13b] Au–HAP (60 h^{-1}),[19] Ag–HAP (< 1 h^{-1}),[14,19] and Pt nanoclusters (125 h^{-1})[18] and H_2O_2-based oxidation systems such as methyltrioxorhenium (MTO)/zeolite NaY[20] (2 h^{-1}) and Ti-β (< 1 h^{-1}).[21] The TOF for the oxidation of **1a** is much higher than those of [{IrCl(C_8H_{12})}$_2$] (85 h^{-1}),[12] Ru–HAP (78 h^{-1}),[13b] Au–HAP (40 h^{-1}),[19] Ag–HAP (178 h^{-1}),[14] Pt nanoclusters (200 h^{-1}),[18] MTO/zeolite NaY (2 h^{-1}),[20] and Ti-β (< 1 h^{-1}),[21] while the value is lower than that of [{$RuCl_2$(*p*-cymene)}$_2$] (5460 h^{-1}).[13a]

Oxidation of optically active silane (+)-(*S*)-methyl-(α-naphthyl)phenylsilane (**1p**, *ee* = 92%) proceeded selectively to afford the corresponding silanol (+)-(*R*)-methyl-(α-naphthyl)phenylsilanol (**2p**) in greater than 95% yield with 86% *ee* [Eq. (3); α-Np = α-naphthyl]. Such a high retention of configuration is also observed with stoichiometric oxidants such as *m*-chloroperbenzoic acid (*m*-CPBA, 86% *ee*),[6a] dimethyldioxirane (98% *ee*),[8] and oxaziridines (99% *ee*),[10] as well as catalytic MTO/UHP (94% *ee*),[20a] for which concerted transition-state structures are proposed. On the other hand, oxidation of **1p** proceeds with inversion of configuration at the silicon center in hydrolytic oxidation with [{$RuCl_2$(*p*-cymene)}$_2$] (67% *ee*)[13a] and Ru-HAP (97% *ee*),[13b] for which nucleophilic attack of water on a silyl metal hydride intermediate has been proposed.



(3)

The kinetic isotope effect of $k_H/k_D = 1.15 \pm 0.15$ for oxidation of **1f** and Et_3SiD under the conditions in Table 2 is comparable to those of 1.23–1.40 for hydrolysis and alcoholysis of **1f**,[17b] alkaline cleavage of triphenylsilane,[31a] and dichlorocarbene insertion into tri-*n*-butylsilane.[31b] Kinetic studies on the catalytic oxidation of **1f** with H_2O_2 showed first-order dependences of the reaction rates on the concentrations of **I** (0.29–2.29 mM), **1f** (0.04–0.29 M), and H_2O_2 (0.04–0.29 M); see Figures S2 and S3 in the Supporting Information. These kinetic results are consistent with those of the **I**-catalyzed epoxidation of olefins, for which a hydroperoxo species (**III**) formed by protonation of diperoxo species (TBA)$_4$[γ-$SiW_{10}O_{32}(O_2)_2$] (**II**) has been proposed as catalytically active species.[24c,32] Therefore, all these results suggest that the reaction of **III** with an organosilane is the rate-determining step in the present system (Scheme S1, Supporting Information).

In conclusion, the divacant lacunary polyoxotungstate **I** is an effective homogeneous catalyst for oxidation of silanes with H_2O_2, and various kinds of silanes can be selectively converted to the corresponding silanols in high yields.

Experimental Section

The catalytic oxidation of various silanes was carried out in a 30 mL glass vessel containing a magnetic stir bar. A typical procedure for catalytic oxidation was as follows: **I** (10 μmol), **1a** (1 mmol), and acetonitrile (6 mL) were charged to the reaction vessel. The reaction was initiated by addition of 30 or 60% aqueous H_2O_2 (1 mmol), and the reaction solution was periodically analyzed. The silanols were identified by comparison of their GC retention time, mass spectra, and ^1H and ^{13}C NMR spectra with the literature data (see Supporting Information).

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[26] Oxidation of trimethoxysilane gave unknown hydrative by-products. Oxidation of triisopropoxysilane hardly proceeded, probably due to the steric hindrance of the isopropoxyl groups.

[27] Triethoxysilanol (**2n**) is a starting material for the synthesis of hyperbranched polyalkoxysiloxanes: M. Jaumann, E. A. Rebrov, V. V. Kazakova, A. M. Muzafarov, W. A. Goedel, M. Möller, *Macromol. Chem. Phys.* **2003**, *204*, 1014.

[28] The stoichiometric synthesis of **2n** requires the following two steps: 1) synthesis of chloro(triethoxy)silane by chlorination of tetraethoxysilane with $SOCl_2$, and 2) hydrolysis of chloro(triethoxy)silane in the presence of a base. V. V. Kazakova, O. B. Gorbatsevich, S. A. Skvortsova, N. V. Demchenko, A. M. Muzafarov, *Russ. Chem. Bull.* **2005**, *54*, 1350.

[29] Catalytic oxidation of **1n** with MTO/UHP and [{$RuCl_2$(*p*-cymene)}$_2$]/H_2O systems was carried out according to the literature procedures.[13a,20] Complex mixtures were formed and **2n** could not be obtained.

[30] In the larger-scale oxidations of **1f** and **1a**, the selectivities to **3f** and **3a** were 7 and 1%, respectively.

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[32] The **I**-catalyzed oxidation of organosilanes proceeded with an induction period that disappeared on treatment of **I** with H_2O_2, and the induction period was still observed for oxidation catalyzed by isolated **II** with H_2O_2. Therefore, **II** is inactive for the present oxidation.

