

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 H₂O₂ as oxygen donor. However, these systems have disadvantages: 1) applicability to a limited number of silanes, 2) use of an excess of highly concentrated H₂O₂ or urea/H₂O₂ adduct (UHP), 3) low turnover frequencies (TOF = 1–7), and 4) significant formation of undesirable siloxanes. Therefore, catalytic systems for efficient and selective H₂O₂-based oxidation of various silanes to silanols are scarcely known.

Polyoxometalates have attracted considerable attention in the fields of structural chemistry, biological chemistry, catal-

ysis, and materials science.^[22] To date, numerous catalytic H₂O₂-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 H₂O₂ has never been reported. Here we report highly selective oxidation of organosilanes to silanols with 30–60 % aqueous H₂O₂ catalyzed by divacant lacunary polyoxotungstate (TBA)₄[γ-SiW₁₀O₃₄(H₂O)₂] [I, TBA = (n-C₄H₉)₄N⁺, Figure 1, Eq. (1)]. The present system

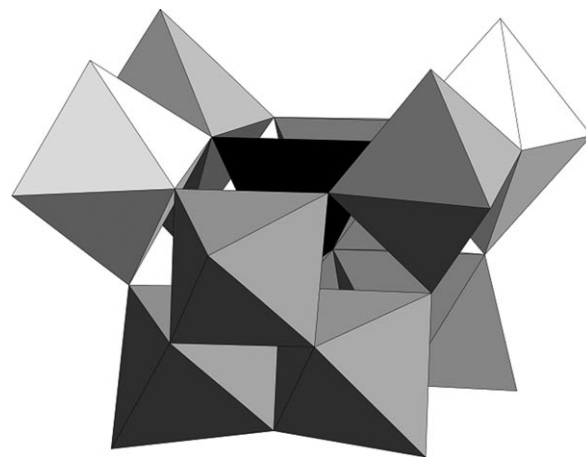
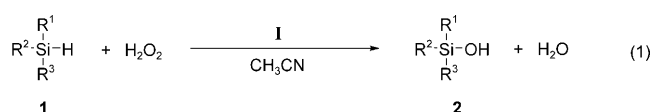


Figure 1. Polyhedral representation of the anion of (TBA)₄[γ-SiW₁₀O₃₄(H₂O)₂] (I). The {WO₆} units and {SiO₄} unit are shown as gray octahedra and a black tetrahedron, respectively. White octahedra indicate the tungsten atoms with aqua ligands.



R = aryl, alkyl, alkenyl, alkynyl, alkoxy, etc.

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 H₂O₂ with respect to the substrate instead of an excess of highly concentrated H₂O₂ 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.

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First, oxidation of dimethylphenylsilane (**1a**) to dimethylphenylsilanol (**2a**) with 30% aqueous H₂O₂ was carried out under stoichiometric conditions (substrate/H₂O₂ = 1:1). Among the solvents tested, acetonitrile gave the highest yield (78%) of **2a** (Table 1, entry 1). Formation of the

were inactive (Table 1, entries 13 and 15–18). The H₂WO₄ catalyst showed low selectivity to **2a** and significant formation of **3a** (Table 1, entry 14). Divanadium-substituted polyoxotungstate (TBA)₄[γ-H₂SiV₂W₁₀O₄₀],^[25e] selenium-containing dinuclear peroxotungstate (TBA)₂[SeO₄{WO(O₂)₂}]₂,^[23g] and

phosphorus-containing tetranuclear peroxotungstate (THA)₃-

[PO₄{WO(O₂)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 H₂WO₄, (TBA)₂[SeO₄{WO(O₂)₂}]₂, and (THA)₃[PO₄{WO(O₂)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**.

The scope of the catalytic oxidation of organosilanes with H₂O₂ was investigated for a range of structurally diverse silanes (Table 2). Various silanes could efficiently be oxidized under stoichiometric conditions (substrate/H₂O₂ = 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 hydrate 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 1: Catalytic oxidation of dimethylphenylsilane (**1a**) with H₂O₂.^[a]

Entry	Catalyst	Solvent	Yield [%]	Selectivity [%]		R ₀ [mm min ⁻¹]
				2a	3a	
1	I	CH ₃ CN	79	99	1	2.2
2	I	(CH ₂ Cl) 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 ₃ CN	80	> 99	< 1	2.9
8 ^[c]	I	CH ₃ CN	17	94	6	0.2
9 ^[d]	I	CH ₃ CN	85	96	4	0.3
10 ^[e]	I	CH ₃ CN	75	99	1	2.3
11 ^[f]	I	CH ₃ CN	< 1	–	–	–
12	none	CH ₃ CN	< 1	–	–	–
13	Na ₂ WO ₄ ·2 H ₂ O	CH ₃ CN	4	> 99	< 1	< 0.1
14	H ₂ WO ₄	CH ₃ CN	39	27	73	0.6
15	(TBA) ₄ [α-SiW ₁₂ O ₄₀]	CH ₃ CN	2	85	15	< 0.1
16	(TBA) ₄ H ₄ [α-SiW ₁₁ O ₃₉]	CH ₃ CN	3	> 99	< 1	< 0.1
17	(TBA) ₃ H ₇ [α-SiW ₉ O ₃₄]	CH ₃ CN	4	> 99	< 1	0.1
18	(TBA) ₄ [γ-SiW ₁₂ O ₄₀]	CH ₃ CN	< 1	–	–	–
19 ^[g]	(TBA) ₄ [γ-H ₂ SiV ₂ W ₁₀ O ₄₀]	CH ₃ CN	76	88	12	3.1
20	(TBA) ₂ [{WO(O ₂) ₂ }(μ-O)]	CH ₃ CN	32	91	9	1.0
21	(TBA) ₂ [SeO ₄ {WO(O ₂) ₂ }] ₂	CH ₃ CN	> 99	53	47	4.0
22 ^[h]	(THA) ₃ [PO ₄ {WO(O ₂) ₂ }] ₄	CH ₃ CN	94	86	14	2.6

[a] Reaction Conditions: Catalyst (W: 7.3 mol% with respect to **1a** and H₂O₂), **1a** (1 mmol), 30% aqueous H₂O₂ (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 H₂O₂ (1 mmol). [c] UHP (1 mmol). [d] 305 K, 24 h. [e] Under Ar (1 atm). [f] H₂O (1 mmol). [g] CH₃CN/*t*BuOH (3/3 mL). [h] THA = [(*n*-C₆H₁₃)₄N]⁺.

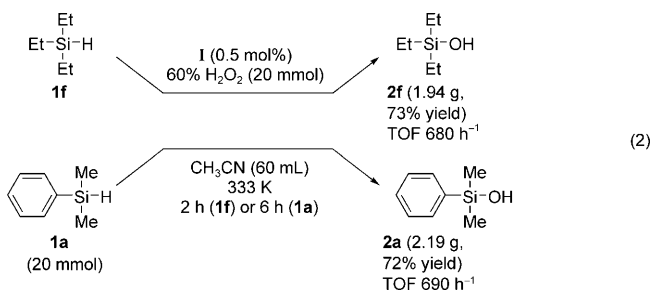
corresponding disiloxane (**3a**) by condensation of **2a** was hardly observed. 1,2-Dichloroethane, DMSO, acetone, and benzonitrile as solvents gave **2a** in 57, 50, 45, and 44% yield, respectively (Table 1, entries 2–5), while DMF was found to be a poor solvent (Table 1, entry 6). The reaction rate for the oxidation of **1a** with 60% aqueous H₂O₂ was slightly higher than that with 30% aqueous H₂O₂ (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 H₂O₂, 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 Na₂WO₄·2 H₂O and the TBA salts of fully occupied and other lacunary polyoxotungstates

Table 2: Oxidation of various silanes with aqueous H₂O₂ catalyzed by **I**.^[a]

$\begin{array}{c} \text{R}^1 \\ \\ \text{R}^2-\text{Si}-\text{H} \\ \\ \text{R}^3 \end{array} \xrightarrow[\text{CH}_3\text{CN}, 333 \text{ K}]{\text{I}, \text{H}_2\text{O}_2} \begin{array}{c} \text{R}^1 \\ \\ \text{R}^2-\text{Si}-\text{OH} \\ \\ \text{R}^3 \end{array} + \begin{array}{c} \text{R}^1 \quad \text{R}^1 \\ \quad \\ \text{R}^2-\text{Si}-\text{O}-\text{Si}-\text{R}^2 \\ \quad \\ \text{R}^3 \quad \text{R}^3 \end{array}$					
1		2		3	
Entry	Substrate	<i>t</i> [h]	Yield [%]	2 Selectivity [%]	3 Selectivity [%]
1		4	86	98	2
2		4	89	93	7
3		3	90	96	4
4		4	85	96	4
5	Ph ₂ MeSiH	5	80	> 99	
6	Et ₃ SiH	4	92	> 99	< 1
7	<i>t</i> BuMe ₂ SiH	4	92	> 99	< 1
8	<i>n</i> Bu ₃ SiH	4	80	> 99	< 1
9 ^[b, c]	(<i>n</i> -C ₆ H ₁₃)SiH	3	80	> 99	< 1
10 ^[b]	<i>i</i> Pr ₃ SiH	4	84	> 99	< 1
11		5	83	96	4
12 ^[d]		4	63	87	12
13		0.5	53	86	4
14 ^[e]	(EtO) ₃ SiH	1.5	83	93	2
15 ^[f]	(<i>n</i> BuO) ₃ SiH	2.5	68	95	< 1

[a] Reaction conditions: **I** (1 mol % with respect to substrate and H₂O₂), silane (1 mmol), 60% aqueous H₂O₂ (1 mmol), CH₃CN (6 mL), 333 K. Yield and selectivity were determined by GC and NMR spectroscopy. Yield [%] = [(silanol (mol) + disiloxane (mol) × 2)/H₂O₂ used (mol)] × 100. [b] **I** (2 mol % relative to substrate and H₂O₂). [c] CH₃CN/toluene (3/3 mL). [d] 318 K. [e] 305 K, ethanol (5% selectivity) was formed. [f] 1-Butanol (4% selectivity) was formed.

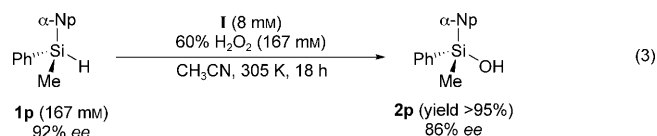
The present system was applicable to larger-scale oxidations of **1f** and **1a** with H₂O₂ (20 mmol scale), and **2f** and **2a** could be isolated in 73 and 72% yield, respectively [Eq. (2)].^[30] Their respective TOFs reached up to 680 and



690 h⁻¹. The TOF for the oxidation of **1f** is much higher than those of hydrolytic oxidation systems such as [{RuCl₂(*p*-cymene)}₂] (285 h⁻¹),^[13a] [{IrCl(C₈H₁₂)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 H₂O₂-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(C₈H₁₂)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 [{RuCl₂(*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 [{RuCl₂(*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.



The kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} = 1.15 \pm 0.15$ for oxidation of **1f** and Et₃SiD 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 H₂O₂ 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 H₂O₂ (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-SiW₁₀O₃₂(O₂)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 H₂O₂, 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: **1** (10 μ mol), **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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