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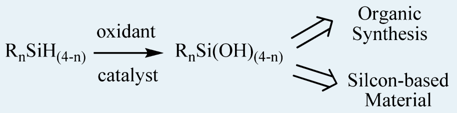
Catalytic Synthesis of Silanols from Hydrosilanes and Applications

Mina Jeon, Junghoon Han, and Jaiwook Park*

Pohang University of Science and Technology (POSTECH), San 31 Hyoja-dong, Pohang, Gyeongbuk 790-784, Republic of Korea



ABSTRACT: In recent years reusable and highly active metal-nanoparticle catalysts were developed for the selective transformation of hydrosilanes into the corresponding silanols using water as the oxidant. The catalysts are much more active than conventional homogeneous ones under ambient conditions. In this perspective, we summarize known catalyst systems as well as stoichiometric methods for the synthesis of silanols from hydrosilanes. Plausible pathways for the hydrolytic oxidation of hydrosilanes on metal nanoparticles are described on the basis of the observations of mechanistic studies, including Si−H bond activation, nucleophilic attack of water (or silanol) at the silicon bonded to metal, and the liberation of silanol (or disiloxane) products. The applications of silanols are classified into usages in organic synthesis and silicon-based materials. Silanols were employed as nucleophilic partners in transition-metal catalyzed carbon−carbon cross-coupling reactions, organocatalysts for activating carbonyl compounds, intramolecular guiding groups for C−H bond activation reactions, inhibitors of enzymes, and isosteres of bioactive compounds. Various polymeric silicon-based materials were synthesized by the activation of Si−H bonds in bis-trihydrosilanes, bis-hydrosilanes, and polyhedral oligomeric silsesquioxanes (POSS).

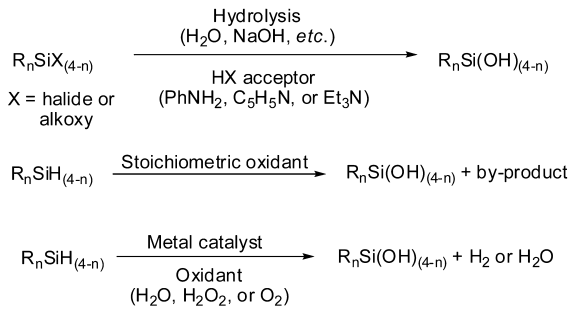
KEYWORDS: *silanol, heterogeneous catalysis, homogeneous catalysis, silane, oxidation*

1. INTRODUCTION

Silanols are compounds having Si−OH groups and are receiving great attention in the synthesis of silicon-based polymeric materials as well as in organic synthesis.[1−4] Particularly, in organic synthesis, silanols are employed as nucleophilic partners in transition-metal catalyzed carbon−carbon cross-coupling reactions,[5−7] organocatalysts for activating carbonyl compounds,[8−10] intramolecular guiding groups for C−H bond activation reactions,[11−14] inhibitors of enzymes,[15] and isosteres of pheromones.[16]

Silanols can be prepared from chlorosilanes,[17,18] siloxanes,[19] and hydrosilanes[20−25] through hydrolysis, nucleophilic substitution, and oxidation,[26] respectively (Scheme 1). Chlorosilanes are widely available and frequently used as the precursors of silanols. However, strictly buffered conditions are required to avoid condensation of silanol products into siloxanes. While various catalytic oxidation methods for the synthesis of silanols from hydrosilanes are known,[27−32] recent reports are focusing on the catalytic oxidation using water because of its economical and environmental benefits.[33−39] In particular, several reusable heterogeneous catalysts show attractive properties in their substrate scope as well as in their reactivity and selectivity for silanols under neutral and mild conditions.[40−49]

Scheme 1. Synthetic Methods for Silanols



$$R_nSiX_{(4-n)} \xrightarrow[\text{HX acceptor (PhNH}_2\text{, C}_5\text{H}_5\text{N, or Et}_3\text{N)}]{\text{Hydrolysis (H}_2\text{O, NaOH, } etc.\text{)}} R_nSi(OH)_{(4-n)}$$

X = halide or alkoxy

$$R_nSiH_{(4-n)} \xrightarrow{\text{Stoichiometric oxidant}} R_nSi(OH)_{(4-n)} + \text{by-product}$$

$$R_nSiH_{(4-n)} \xrightarrow[\text{Oxidant (H}_2\text{O, H}_2\text{O}_2\text{, or O}_2\text{)}]{\text{Metal catalyst}} R_nSi(OH)_{(4-n)} + H_2 \text{ or } H_2O$$

This perspective highlights the catalyst systems for the synthesis of silanols from hydrosilanes using water as the oxidant. For comparison, those using oxidants other than water and noncatalytic methods are summarized with their benefits and limitations. Plausible pathways for the catalytic oxidation are discussed on the basis of the reported results from mechanistic studies. Then the applications of silanols in organic synthesis are classified according to their characteristic reaction types. And silicon-based materials prepared from hydrosilanes are briefly described.

2. OXIDATION OF HYDROSILANES INTO SILANOLS

Various hydrosilanes are available commercially and can be prepared by (1) reduction of Si−X (X = halide) or Si−OR (R = alkyl) groups,[15,50,51] (2) nucleophilic substitution reaction of chlorohydrosilanes with organometallic reagents,[35] (3) nucleophilic substitution reaction of hexacoordinated silicon species with organomagnesium and organolithium reagents,[52] and (4) catalytic Si−C coupling reaction of dihydrosilanes with aryl halides (Scheme 2).[53−56]

For the transformation of hydrosilanes into silanols, water is an ideal oxidant because the side-product is only molecular hydrogen in contrast to other stoichiometric oxidants producing toxic wastes. However, in general, catalysts are needed for the transformation with water as the oxidant. Heterogeneous catalysts based on metal nanoparticles are attracting considerable attention because of their excellent activities and reusability,[40−49]

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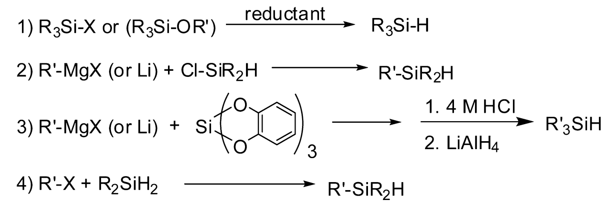
Scheme 2. Synthetic Methods for Hydrosilanes



while several homogeneous catalysts also have useful properties in hydrolytic oxidation of hydrosilanes.[53−56]

2.1. Catalyst Systems with Water As the Oxidant.

2.1.1. Heterogeneous Catalysts. Metal nanoparticle catalysts were prepared with varying metal sources and supports for the hydrolytic oxidation of hydrosilanes (Table 1). Although, early in 1966, Norman and co-workers reported metals on charcoal or alumina support as the heterogeneous catalysts for the hydrolytic oxidation of hydrosilanes (entries 4, 13, and 15),[40] recent catalysts are much more active under mild conditions and reusable. For example, the turnover frequency (TOF) and the turnover number (TON) are greater than 10,000 h^{-1} and 70,000, respectively, at room temperature for the oxidation of dimethylphenylsilane with a Pd or a Au catalyst (entries 1 and 8). Furthermore, some catalysts are reusable at least 10 times (entries 2 and 5).

Recently, Park and co-workers reported the use of metal nanoparticles embedded in aluminum oxyhydroxide support [M/AlO(OH), M = Pd, Au, Rh, Ru, and Cu] for the catalytic oxidation of hydrosilanes,[49] which were prepared from readily available reagents through simple synthetic procedures. Among the catalysts, Pd/AlO(OH) showed the highest activity for a wide range of hydrosilanes. It was reusable at least for 10 times and applicable for large-scale reactions. Calculated TON (99,000) and TOF (20,000 h^{-1}) were the highest among those reported so far (entry 1). However, partial hydrogenation of the alkynyl group was observed in the oxidation of some alkynylsilanes; the hydrogenation could be suppressed by changing reaction atmosphere with an oxygen balloon. Meanwhile, Au/AlO(OH) showed a much better selectivity for alkynylsilanols with an activity comparable to that of Pd/AlO(OH) in the hydrolytic oxidation (entry 5).

Shimizu and co-workers also reported Pd-catalyzed hydrolytic oxidation of hydrosilanes.[48] Interestingly, they showed the critical effect of oxygen absorbed on the surface of palladium nanoparticles. Pd/C-500H prepared by treating commercial Pd/C catalyst with H_2 at 500 °C was significantly less active than Pd/C-500Hox obtained by exposing Pd/C-500H to air at room temperature. The activity of Pd/C-100Hox was about 2 times higher than that of Pd/C-500Hox in the oxidation of dimethylphenylsilane (entry 3). They insisted that the high activity comes from the water dissociation on oxygen-absorbed Pd surfaces.

A nanoporous gold catalyst (Au NPore) was introduced for the hydrolytic oxidation by Yamamoto and co-workers (entry 6), which was prepared from Au/Ag alloy (5 mm × 2 mm × 0.04 mm) by selective leaching with 70 wt % nitric acid.[46] The gold pieces recovered using tweezers were reused at least five times without loss of activity. Various kinds of hydrosilanes including dihydrosilane, trihydrosilane, and alkynylsilanes were selectively transformed into the corresponding silanols.

Doris and co-workers developed a layer-by-layer assembly of gold nanoparticles on a carbon nanotube (CNT) to make a gold nanohybrid catalyst and demonstrated its efficient catalytic activity in the oxidation of hydrosilanes (entries 7 and 8).[47] Its activity was comparable with that of Au/AlO(OH) in the 0.20 mmol-scale oxidation of dimethylphenylsilane (entries 5 and 7).

Metal nanoparticles embedded in hydroxyapatite (HAP) were employed in the hydrolytic oxidation of hydrosilanes by Kaneda and co-workers (entries 9−11).[42,43,45] Molecular oxygen was an indispensable component for the transformation with the ruthenium catalyst (RuHAP) (entry 11), while that with AgHAP did not require molecular oxygen with liberating an equimolar amount of H_2. The silver catalyst showed a much higher activity than that of the ruthenium catalyst in water (entry 10). However, the silver catalyst was effective only for aromatic silanes which can interact strongly with silver nanoparticles. This limitation for substrate scope was overcome in the oxidation with AuHAP (entry 9). They carried out the oxidations with AgHAP and AuHAP in water under organic-solvent-free conditions. They explained the good results with increased concentration of nucleophiles (OH^- or H_2O) on the Ag-HAP surface, which

Table 1. Heterogeneous Catalyst Systems for the Oxidation of Dimethylphenylsilane with Water

$$PhMe_2SiH \xrightarrow[H_2O(Oxidant)]{Catalyst} PhMe_2SiOH$$

entry	catalyst (mol % of metal)	scale (mmol)	t (°C)	time (h)	solvent	yield (%)	TOF (h^{-1})	TON	reuse (times)	ref.
1	Pd/AlO(OH) (0.0010)	10	RT	5	EtOAc	99	20,000	99,000	0	49
2	Pd/AlO(OH) (0.10)	0.5	RT	10 (min)	EtOAc	98	5,900	980	10	49
3	Pd/C-100Hox (0.005)	20	35	3.5	glyme	99	5,700	20,000	3	48
4	Pd/Al_2O_3 (0.5)	100	30−35	11	dioxane-buffered H_2O	95	17	190	0	40
5	Au/AlO(OH) (0.10)	0.5	RT	0.5	EtOAc	98	1,960	980	10	49
6	Au NPore (1)	1	RT	1	H_2O	100	100	100	5	46
7	AuCNT (0.1)	0.2	RT	45 (min)	THF-H_2O	98	1,300	980	5	47
8	AuCNT (0.001)	1	RT	6	THF-H_2O	72	12,000	72,000	0	47
9	AuHAP (0.83)	1	80	3	H_2O	>99	40	120	4	45
10	AgHAP (3)	1	80	15 (min)	H_2O	99	132	33	5	43
11	RuHAP (5)	1	80	3	EtOAc	99	6.6	20	5	42
12	$[RuCl_2(p\text{-cymene})]_2/C$ (9.8)	1	RT	10 (min)	CH_3CN	96	59	9.8	6	41
13	Ru/C (1)	100	25−31	23.5	dioxane-buffered H_2O	92	3.9	92	0	40
14	Pt/PMHS (0.1)	1	RT	5	THF	95	190	950	4	44
15	Ni powder (0.66)	100	110	20	dioxane-buffered H_2O	85	6.4	130	0	40
16	Ni/AlO(OH) (3.0)	0.5	60	7	EtOAc	93	4.4	31		57

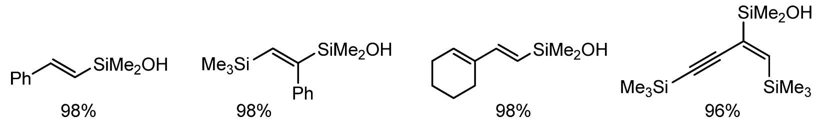


Figure 1. Selective synthesis of functional silanols using Pt-nanocluster catalyst.

promotes formation of silanols by suppressing condensation to disiloxane byproducts,[43] although biphasic nature of the organosilane/H_2O system reduces the effective concentration of water in the organosilane phase.[37]

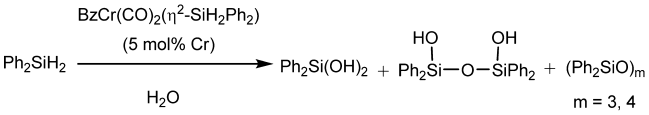
A heterogeneous ruthenium catalyst was prepared by a simple adsorption of $[RuCl_2(p\text{-cymene})]_2$ on active carbon by Chang and co-workers.[41] They demonstrated its utility in aerobic oxidation of alcohols, dehydration of aldoximes into nitriles, and hydrolytic oxidation of silanes into silanols. Recovery and reuse of the heterogeneous catalyst was carried out in the reaction of diphenylmethylsilane in tetrahydrofuran (THF), although the reaction times were longer over the cycles.

Chauhan and co-workers reported a platinum nanoparticle catalyst for the hydrolytic oxidation, which was prepared by reduction of $Me_2Pt(COD)$ (COD: 1,5-cyclooxtadiene) with poly(methylhydro)siloxane (PMHS) (entry 14).[44] The catalyst could be recovered by centrifugation and reused four times without significant loss of activity and selectivity. Notably, synthetically useful silanols possessing alkynyl or alkenyl functional groups were obtained in almost quantitative yields (Figure 1).

Nickel catalysts such as nickel powder and Ni/AlO(OH) were tested as the catalysts for the hydrolytic oxidation (entries 15 and 16). The activities are much lower than those of other metal catalysts, and heating (60−110 °C) was needed to complete the oxidation.

2.1.2. Homogenous Catalysts. Homogeneous catalysts were also used for the hydrolytic oxidation of hydrosilanes. However, as shown in the reaction with $BzCr(CO)_2(\eta^2\text{-HSiHPh}_2)$, it was not easy to control the selectivity for silanols:[33] the corresponding silanol, disiloxane, and oligomers were formed in the oxidation of diphenylsilane (Scheme 3). Dehydrogenative coupling reaction was dominant in the oxidation of dimethylphenylsilane with a copper catalyst, $[Ph_3PCuH]_6$: $(Me_2PhSi)_2O$ was formed as the major product in 89% yield.[34]

Scheme 3. Catalytic Oxidation of Dihydrosilanes by $BzCr(CO)_2(\eta^2\text{-SiH}_2Ph_2)$



In Table 2, the homogeneous catalyst systems selective for the production of silanols in the hydrolytic oxidation of hydrosilanes are summarized.

Very recently, Mizuno and co-workers reported the hydrolytic oxidation of hydrosilanes using a polyoxometalate (POM) containing the diamond-shaped $[Ag_4]^{4+}$ core, which was synthesized by reaction of $TBA_4H_4[\eta\text{-SiW}_{10}O_{36}]$ (SiW10, TBA = tetra-*n*-butylammonium) with silver acetate (entry 1 of Table 2).[39] The catalyst prepared in situ by mixing SiW10 and AgOAc showed a similar activity (88% yield). Generally, the oxidations of aromatic silanes with this catalyst were very fast at 50 °C under 1 atm of air: the oxidation of dimethylphenylsilane was completed in 4 min. However, those of aliphatic silanes were significantly slow: the oxidation of triethylsilane took 8 h even at 70 °C.

Chang and co-workers used commercially available $[RuCl_2(p\text{-cymene})]_2$ for the hydrolytic oxidation (entry 2).[35] A wide range of silanols were obtained selectively in high yields. Particularly, this catalyst system was effective for the synthesis of silanols possessing aryl, alkynyl, or alkenyl groups, which have potential utilities as nucleophilic partners transferring the unsaturated moieties in metal-catalyzed carbon−carbon cross coupling reactions (Figure 2). A commercially available iridium complex, $[IrCl(C_8H_{12})]_2$, was also active for the hydrolytic oxidation of hydrosilanes at room temperature under neutral conditions (entry 3), although its efficiency for the preparation of alkenylsilanols and alkynylsilanols was not satisfactory.[36]

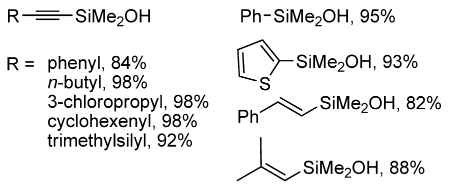


Figure 2. Synthesis of functional silanols using $[RuCl_2(p\text{-cymene})]_2$.

The hydrolytic oxidation of silanes was studied for producing hydrogen by Abu-Omar and co-workers with a cationic oxorhenium(V) catalyst (entry 4).[37] This was the first example of dehydrogenative oxidation of hydrosilanes with water using high-valent metal complexes.

2.2. Catalyst Systems with Oxidants Other than Water.

While water is an ideal oxidant for the oxidation of hydrosilanes, hydrogen peroxide and molecular oxygen are also cheap and environmentally benign in comparison to other stoichiometric ones. The catalyst systems using hydrogen peroxide or oxygen are summarized in Table 3.

Weichold and co-workers tested a Ti-doped zeolite for the catalytic oxidation of hydrosilanes on the basis of the fact that Ti-beta is known to catalyze a variety of oxidations with H_2O_2.[27,28] With this catalyst system, small- and medium-sized hydrosilanes such as dimethylethylsilane, dimethylphenylsilane, and triethylsilane could be transformed into the corresponding silanols with high conversion and excellent selectivity using 30% of aqueous H_2O_2 as the oxidant (entry 1 of Table 3).

Table 2. Oxidation of Dimethylphenylsilane Using Homogeneous Catalysts with Water

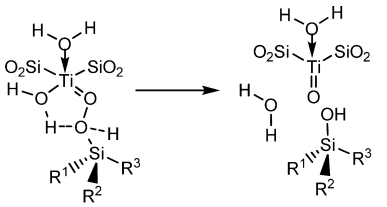
entry	catalyst (mol %)	scale (mmol)	*t* (°C)	time	solvent	yield (%)	TOF (h^{-1})	TON	ref.
1	$TBA_8[Ag_4(\gamma\text{-H}_2SiW_{10}O_{36})_2]$ (0.5)	0.5	50	4 min	CH_3CN	96	2900	190	39
2	$[RuCl_2(p\text{-cymene})]_2$ (0.20)	100	25	5 min	CH_3CN	91	5500	460	35
3	$[IrCl(C_8H_{12})]_2$ (1)	2	25	1 h	CH_3CN	88	88	88	36
4	Re(V) complex (1)	6.53	20	1.5 h	CH_3CN	84	56	84	37, 38

Table 3. Catalyst Systems Using H_2O_2 or O_2 for the Oxidation of Dimethylphenylsilane

entry	catalyst	scale (mmol)	oxidant	*t* (°C)	time (h)	solvent	yield (%)	TOF (h^{-1})	TON	ref.
1	Ti-*β* zeolite (9 mol %)	0.33	H_2O_2	20	24	CH_3CN	99	0.46	11	27, 28
2	CH_3ReO_3 (1 mol %)	0.33	H_2O_2-urea	20	13	CH_2Cl_2	87	6.7	87	29
3	CH_3ReO_3−NaY (2 mol %)	0.33	H_2O_2	20	24	CH_2Cl_2	99	2.1	50	30
4	Mes_2Te (10 mol %)	2	air (O_2)	50 with light	4	pyridine	87	2.2	8.7	31
5	$(TBA)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ (1 mol %)	20	H_2O_2	60	6	CH_3CN	72	690	4,100	32

They suggested that the catalytic oxidation takes place inside the zeolite channels through a peracid-type transition state (Scheme 4).

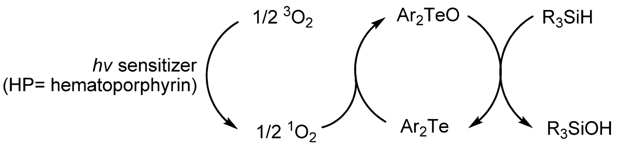
Scheme 4. Transition State for the Ti-Catalyzed Oxidation of Hydrosilanes



Methyltrioxorhenium(MTO) was used for the catalytic oxidation of hydrosilanes with hydrogen peroxide as the oxidant (entry 2). Urea was an essential additive to form the urea/hydrogen peroxide adduct (UHP) for this catalyst system. The presence of urea was beneficial not only for the product selectivity but also for making the Si−H insertion highly stereoselective with a high degree of retention of configuration:[29] (+)-(*R*)-(*α*-Naphthyl)-phenylmethylsilanol (91% *ee*) was obtained selectively (silanol/disiloxane = 96:4) from the oxidation of (+)-(*S*)-(*α*-Np)PhMeSiH (>98% *ee*). It was proposed that the urea acts as a host and that the reactions take place inside the urea channels. Instead of urea, NaY zeolite was employed for MTO-catalyzed oxidation of hydrosilanes into silanols in a mixture of 85% aqueous H_2O_2 and CH_2Cl_2 (entry 3).[30] The role of the zeolite was suggested as absorbent for the aqueous phase and preventer of the MTO catalyst from decomposition.

Diorganotelluride is an rare example that can activate atmospheric oxygen under photosensitized conditions for the oxidation of hydrosilanes.[31] Dimethylphenylsilane (0.1 M) in pyridine was transformed selectively into dimethylphenylsilanol in 87% in the reaction with 10 mol % of bis(2,4,5-trimethylphenyl)telluride (Mes_2Te) in the presence of hematoporphyrin (entry 4). A catalytic cycle was proposed to involve singlet oxygen and diaryl telluroxide (Scheme 5). This catalyst system was applied successfully for the stereoselective oxidation of (+)-(*R*)-(*α*-Np)PhMeSiH (96% *ee*) into (+)-(*S*)-(*α*-Np)PhMeSiOH (89% *ee*) in 79% isolated yield.

Scheme 5. Catalytic Oxidation Hydrosilane with Ar_2Te



Recently, a divalent lacunary polyoxotungstate has been reported by Mizuno and co-workers for the catalytic oxidation of hydrosilanes with aqueous hydrogen peroxide (30−60%) (entry 5).[32] This catalyst system was applicable for a wide range of hydrosilanes possessing aryl, alkyl, alkynyl, alkenyl, or alkoxy group. The oxidation of optically active silane (+)-(*S*)-(*α*-Np)PhMeSiH (*ee* = 92%) was highly selectively to give (+)-(*R*)-(*α*-Np)PhMeSiOH (*ee* = 86%) in greater than 95% yield. Such a high retention of configuration is comparable with those observed in the oxidation with stoichiometric oxidants: *m*-chloroperbenzoic acid (86% *ee*),[21] dimethyldioxirane (98% *ee*),[22] and oxaziridines (99% *ee*).[23]

2.3. Noncatalytic Oxidation of Hydrosilanes.

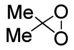
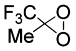
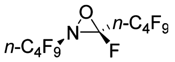
Stoichiometric oxidants such as $KMnO_4$, $AgNO_3$, Ag_2O, O_3, osmium tetroxide, oxaziridines, and dioxiranes are known for the oxidation of hydrosilanes. Among them dioxiranes are useful for stereospecific conversion of hydrosilanes into silanols with more than 95% retention of configuration (entries 1 and 2 of Table 4).[22] On the basis of the stereospecificity and the H/D kinetic isotope effect (k_H/k_D = 2.6), an oxene mechanism was proposed for the activation of Si−H bonds. Perfluoro oxaziridine was also used to oxidize simple hydrosilanes at room temperature (entry 3).[23] However, the epoxidation of carbon−carbon double bond was faster than the oxyfunctionalization at silicon in the case of allyldimethylsilane. Lickiss and co-worker used potassium permanganate for the preparation of sterically hindered silanols containing *t*-Bu, Ph, or Tsi ($(Me_3Si)_3C$) group (entry 4).[24] Mayer and co-workers studied the oxidation of hydrosilanes with OsO_4 to get mechanistic insight into *σ*-bond oxidations. Besides its toxicity and high price, deactivation by over-reduction of osmium species limited the general utility of OsO_4 for preparing silanols (entry 5).[25]

3. MECHANISTIC STUDIES FOR THE CATALYTIC OXIDATION OF HYDROSILANES WITH WATER

The major pathway for the hydrolytic oxidation of hydrosilanes with catalysts leads to the inversion of configuration at the silicon center,[35,42] while that of the oxidation with peracids, peroxides, or oxiranes generally results in the retention of configuration.[21−23,29,32] Abu-Omar and co-workers showed that the −OH of silanols comes from water by exclusive transfer of oxygen to the silicon atom of hydrosilanes in the rate determining step in the experiments with $^{18}OH_2$ and D_2O.[37,38] They observed quantitative ^{18}O-enrichment in the cationic oxorhenium catalyzed oxidation of hydrosilanes with $^{18}OH_2$, confirming water as the oxygen donor (Scheme 6). They also carried out the reaction of Et_3Si−D with H_2O and that of Et_3Si−H with D_2O to show that the dihydrogen product is composed of one hydrogen atom from hydrosilane and the other from water. Meanwhile, the rate of silyl ether (disiloxane) formation was first-order in [silanol] and [catalyst], but inhibited by water.[37] In fact, disiloxane was observed as the major product when they used only 1 equiv of water.

In some reports, the formation of disiloxanes during the hydrolytic oxidation of hydrosilanes was explained by the condensation reaction between two silanols. Park and co-workers,

Table 4. Oxidation of Dimethylphenylsilane with Stoichiometric Oxidants

entry	Silane	oxidant	*t* (°C)	Time	solvent	yield (%)	ref
1	(+)-(*R*)-α-(Np)(Ph)(Me)SiH		0	18 min	CH_2Cl_2	>98	22
2	(+)-(*R*)-α-(Np)(Ph)(Me)SiH		-20	<1 min	CH_2Cl_2	>98	22
3	Et_3SiH		RT	<1 min	$CFCl_3$	>95	23
4	$TsiSiMe_2H$	$KMnO_4$	RT	6 h	THF	84	24
5	Et_3SiH	OsO_4	RT	2 h	CH_2Cl_2	>98	25

Scheme 6. Isotope Labeling Experiments

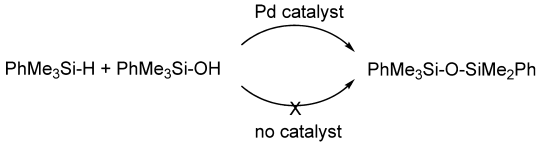
$$Et_3Si\text{-}H + H_2{}^{18}O \xrightarrow{\text{1 mol\% Re cat.}} H_2 + Et_3Si({}^{18}OH)$$

$$Et_3Si\text{-}D + H_2O \xrightarrow{\text{1 mol\% Re cat.}} Et_3SiOH + HD \quad (HD : H_2 : D_2 = 94.2 : 5.6 : 0.2)$$

$$Et_3Si\text{-}H + D_2O \xrightarrow{\text{1 mol\% Re cat.}} Et_3SiOD + HD \quad (HD : H_2 : D_2 = 97.6 : 2.0 : 0.4)$$

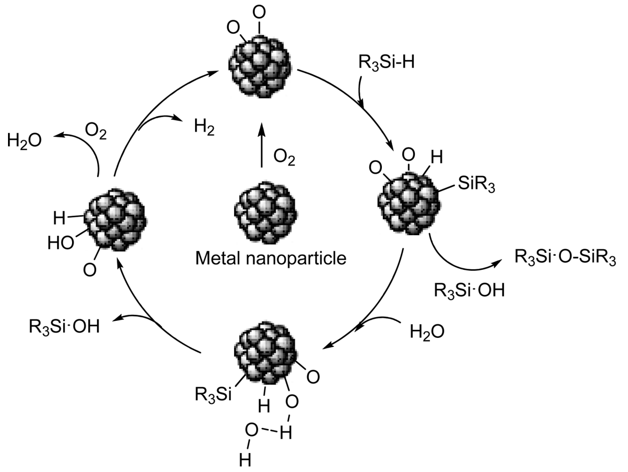
however, showed that a disiloxane is formed from the coupling reaction between a hydrosilane and a silanol under hydrolytic oxidation conditions using palladium nanoparticle catalysts (Scheme 7).[49] The rate of the coupling reaction appeared to depend on the Pd catalyst employed, implicating the essential effect of the matrix of Pd nanoparticles. This type of catalytic dehydrogenative coupling reaction was reported in the synthesis of oligomeric organosilanes and silicon-based polymeric materials.[58,59]

Scheme 7. Pd-Catalyzed Dehydrogenative Coupling Reaction between Hydrosilane and Silanol



Partial hydrogenation of the alkynyl group was observed as a side reaction in the hydrolytic oxidation of alkynylhydrosilanes with Pd/AlO(OH). However, the hydrogenation was suppressed by increasing the pressure of molecular oxygen, implicating that the Pd−H species responsible for the hydrogenation could be removed by the reaction with molecular oxygen.[49] In contrast to the molecular oxygen effect in the case of Pd/AlO(OH), the reaction rate in the absence of O_2 (under flowing N_2) was nearly the same as those in the presence of O_2 when oxygen-absorbed Pd catalysts were used by Shimizu and co-workers.[48] Pt/PMHS and AgHAP are also known to be active under anaerobic conditions,[43,44] while RuHAP and AuCNT require both water and oxygen in the hydrolytic oxidation.[42,47]

Scheme 8. Hydrolytic Oxidation of Hydrosilanes to Silanols on the Surface of Metal Nanoparticles



The results of mechanistic studies for the hydrolytic oxidation of hydrosilanes on the surface of metal nanoparticles with the aid of oxygen can be summarized as shown in Scheme 8. At first, molecular oxygen is activated on the surface of metal nanoparticles, although a detailed structure of the oxygen-adsorbed metal nanoparticle is not clear yet. The Si−H bond of hydrosilane is activated to make M-H and M-Si bonds on the surface. The silyl groups on the surface react with water (or silanol) which is activated by the metal oxide moiety. Backside approach of OH (or $OSiR_3$) species toward the silyl group leads to the configuration inversion at the Si center. Liberation of silanol product and molecular hydrogen regenerates the starting oxygen-adsorbed metal nanoparticle. Meanwhile, external molecular oxygen can participate in the regeneration of active surface by the reaction with Pd−H species.

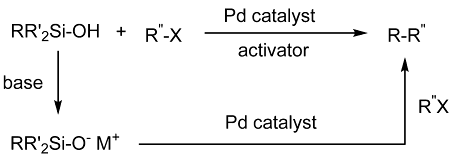
4. APPLICATIONS OF SILANOLS

Silanols are frequently used as synthons of polysiloxanes, metallosiloxanes, and ceramics in material science. In this perspective, however, the examples for the usages are limited to those related to hydrosilanes because there are excellent reviews covering the silanols for material science.[26,60−64] Meanwhile, silanols are attracting attention of various fields of organic synthesis because of their unique and beneficial properties: nucleophilic partners in carbon−carbon cross coupling reactions, directing groups in C−H bond activation, H-bond donors in organocatalysis, and isosteres of bioactive compounds.

4.1. Organic Synthesis.

4.1.1. Metal-Catalyzed Carbon−Carbon Cross-Coupling Reactions. Transition-metal-catalyzed cross-coupling reactions of organometallic reagents with organic halides have become a powerful method for carbon−carbon bond formation.[65−68] Organotin,[69−71] organoboron,[72−76] and organozinc[77] reagents are well-known nucleophilic partners for Pd-catalyzed cross-coupling reactions, but they have inherent

Scheme 9. Pd-Catalyzed Cross-Coupling Reactions Using Silanols or Silanolates



Scheme 10. Preparation of Silanols for Pd-Catalyzed Cross-Coupling Reactions

1) $\text{R-X} \xrightarrow[\text{2.}(\text{Me}_2\text{SiO})_3]{\text{1. BuLi}} \text{RMe}_2\text{Si-OH}$

2) $\text{RMe}_2\text{Si-X} \xrightarrow[\text{buffered}]{\text{H}_2\text{O}} \text{RMe}_2\text{Si-OH}$

3) $\text{RMe}_2\text{Si-H} \xrightarrow[\text{catalyst}]{\text{H}_2\text{O}} \text{RMe}_2\text{Si-OH}$

4) $\text{RMe}_2\text{Si-H} \xrightarrow[\text{Bu}_4\text{NOH}]{\text{H}_2\text{O}} \text{RMe}_2\text{Si-OH}$

5) $\text{Ar-X} \xrightarrow[\text{2. hydrolysis at pH 5}]{\text{1. Pd catalyst, (EtO)Me}_2\text{Si-SiMe}_2\text{(OEt)}} \text{ArMe}_2\text{Si-OH}$

drawbacks such as toxicity, low atom-economy, moisture and oxygen sensitivity, and difficulty of purification. With the extensive works initiated by Hiyama and Denmark, organosilanes have emerged as competitive alternatives with advantages, including lack of toxicity, high chemical stability, and low molecular weight. Particularly, silanols are suitable for coupling reactions with electrophilic partners that possess silyl protecting groups. In contrast to other silane reagents generally requiring a fluoride-promoter, silanols can be activated under fluoride-free conditions. Thus, various silanols were employed successfully in Pd-catalyzed coupling reactions with organic halides and pseudohalides.[78−89] Aryl, alkenyl, heteroaryl, and isoxazolinyl groups of silanols were transferred preferentially to form carbon−carbon bonds (Scheme 9). Furthermore, this protocol was used as the key step for the total synthesis of natural products.[90,91] Notably, isolable silanolate salts prepared from corresponding silanols by treating with Brønsted bases such as $KOSiMe_3$, Cs_2CO_3, NaOt-Bu, KO^tBu, NaH, KH, and NaHMDS do not require activators in the cross-coupling reactions.[92−97]

Most of the silanol substrates for the cross-coupling reaction were prepared by one of the following methods (Scheme 10):[5] (1) reactions of organolithium reagents with hexamethylcyclotrisiloxane; (2) hydrolysis of chlorosilanes or alkoxysilanes under buffered conditions; (3) metal-catalyzed hydrolytic oxidation of hydrosilanes; (4) hydrolysis of hydrosilanes under basic conditions; and (5) Pd-catalyzed silylation of aryl halides; hydrolysis of hydrosilanes under basic conditions.

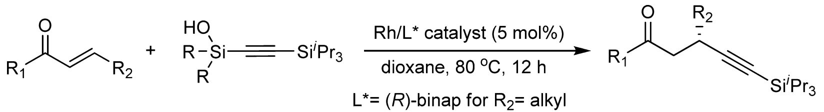
Another example of carbon−carbon cross-coupling reaction employing silanol is conjugate alkynylation of α,β-unsaturated ketones with (triisopropylsilyl)ethynylsilanols (Scheme 11).[98] Hayashi and co-workers developed a rhodium-catalyzed asymmetric reaction of enones with alkynylsilanols giving β-alkynylketones with high enantioselectivity. They prepared the alkynylsilanols by hydrolytic oxidation of the corresponding hydrosilanes and optimized the reactions with varying chiral ligands to extend the scope of enone substrates.[35]

4.1.2. C−H Bond Activation. In the view of green chemistry, Pd-catalyzed alkenylation of unfunctionalized arenes through C−H activation is ideal in comparison to the Mizoroki−Heck reaction that requires prefunctionalized arenes. Recently, silanol-directed C−H bond activation reaction was reported.[11] Ge and co-workers used the silanol substrate whose Si atom is attached to the benzylic position of arenes, which was prepared by the reaction of Grignard reagents with dichlorosilane and the hydrolysis of the resulting chlorosilanes. (Scheme 12).[12] The silanol-directed activation led to selective *ortho*-alkenylation, while hydroxyl-directed alkenylation suffered from subsequent cyclization as a side reaction. The silanol group could be removed by the treatment with tetrabutylammonium fluoride (TBAF) after the alkenylation.

Gevorgyan and co-workers demonstrated that di-*tert*-butylsilanol group can serve as an efficient directing group for the Pd-catalyzed *ortho*-alkenylation of phenols (Scheme 13).[13] Substituted catechols could be also prepared from the silanols through *ortho*-acetoxylation and the subsequent hydrolysis.[14] The silanol substrates were prepared by the reaction of phenols with $t\text{-Bu}_2\text{SiClH}$, bromination, and hydrolysis of the resulting bromosilanes.

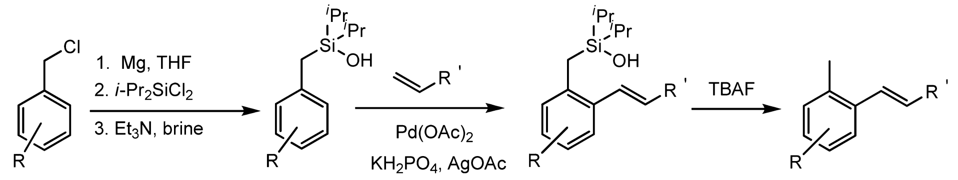
4.1.3. Organocatalysts. Silanediols are receiving attention as a new class of hydrogen bond donor (HBD) catalysts. Kondo and co-workers reported a silanediol-based receptor to recognize anions. The silanediols showed the anion recognition ability by forming hydrogen bonds between Si−OH groups and anions.[99] Franz and co-workers investigated the possibility of silanols and silanediols as models mimicking reactive sites of catalytic silica materials. Indeed, they demonstrated that silanols and silanediols activate carbonyl dienophiles in the Diels−Alder

Scheme 11. Rh-Catalyzed Cross-Coupling Reaction between Enone and Alkynylsilanol

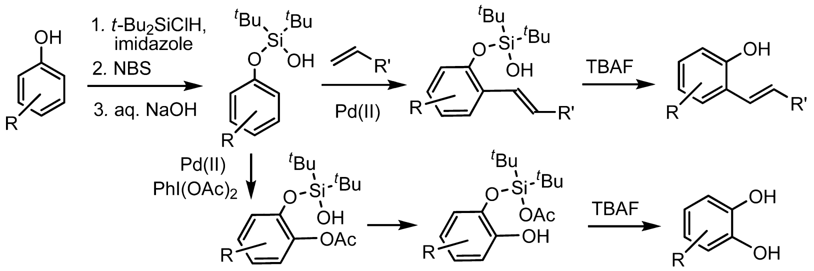


L*= (*R*)-binap for R_2= alkyl
L*= (*R*)-DTBM-segphos for R_2= aryl
L*= (*R,R*)-Bn-bod for cyclic enones

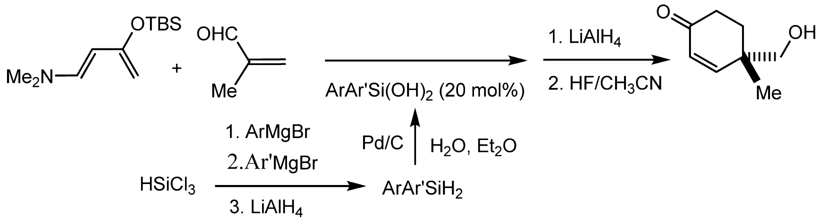
Scheme 12. Silanol as a Directing Group for C−H Activation of Arenes



Scheme 13. Silanol as a Directing Group for C−H Activation of Phenols



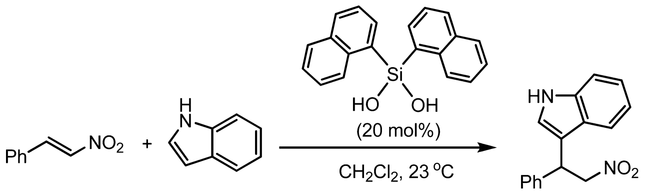
Scheme 14. Silanols and Silanediols as Organocatalysts in Diels−Alder Reaction



reaction (Scheme 14).[8] They synthesized the silanediols by Pd/C-catalyzed hydrolytic oxidation of dihydrosilanes.

Mattson and co-workers developed silanediol catalysts for the activation of nitroalkenes toward nucleophilic attack (Scheme 15).[9]

Scheme 15. Silanediol as Organocatalysts for the Reaction of Nitroalkenes with Indole



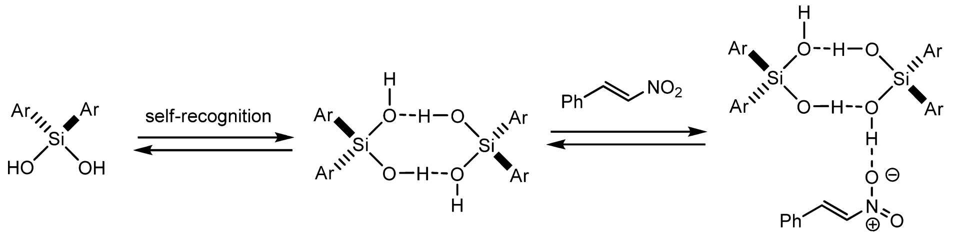
Using a silanediol possessing two naphthyl groups, the Friedel−Crafts addition of indole to β-nitrostyrene was achieved with an excellent yield. The silanediol was prepared by hydrolysis of dichlorodinaphthylsilane which was formed in the reaction of naphthyllithium with silicon tetrachloride.

Recently, Franz and co-workers reported the importance of cooperative H-bonding effect and SiOH-acidification to form unique dimeric structure for silanediol catalysis. They proposed that the cyclic dimer is the predominant catalytic species activating the nitro group in the Friedel−Crafts addition of indole or anisidine to β-nitrostyrene (Scheme 16).[10] The catalytic ability was dependent on the acidity as well as the solubility of the silanediol.

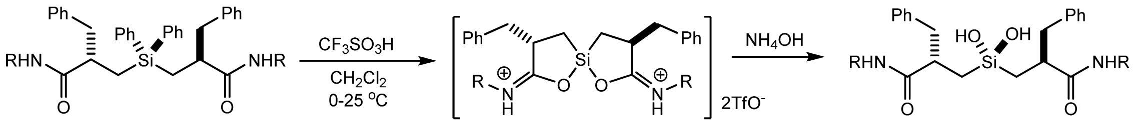
4.1.4. Bioactive Compounds Possessing Silanol Groups. Bioactive organosilicon compounds attract great attention because of the chemical and physical properties related but distinctive to their carbon analogues.[100−107] Recent studies demonstrated that silanols can function as isosteres and transition-state analogues in biochemistry.[108] Sieburth and co-workers extensively investigated silanediols and silanetriols as inhibitors of various hydrolase enzymes.[109] In 2001, they synthesized silanediol analogues of a carbinol-based inhibitor of the HIV protease. The critical step for the synthesis was the transformation of Si−Ph into Si−OH (Scheme 17). The transformation was achieved by the use of excess trifluoromethanesulfonic acid (CF_3SO_3H). A symmetric and spirocyclic intermediate was formed. The intermediate was hydrolytically unstable, and readily hydrolyzed by the treatment with ammonium hydroxide to give the silanediol product. They also synthesized a silanediol as a silicon-based thermolysin inhibitor (Scheme 18).[110,111] The key intermediate was a diphenylsilane again, but the silanediol was obtained by hydrolysis of a difluorosilane intermediate prepared from the diphenylsilane. They also reported polypeptide mimics with a central methylsilanol or a silanediol group, which were tested as transition-state analogue inhibitors of angiotensin-converting enzyme (ACE).[108] The key hydrolysis reaction to remove the phenyl group was achieved by the use of triflic acid in methylene chloride for 10 min at 0 °C (Scheme 19).

Linalool is an attractant to males of a vernal solitary bee species. Tacke and co-workers synthesized a sila-linalool as a pheromone analogue.[15] *rac*-Sila-linalool was prepared by a three-step synthesis (Scheme 20), starting from dimethoxy(methyl)-vinylsilane. The intermediate hydrosilane was obtained by nucleophilic substitution of a methoxy group with a Grignard

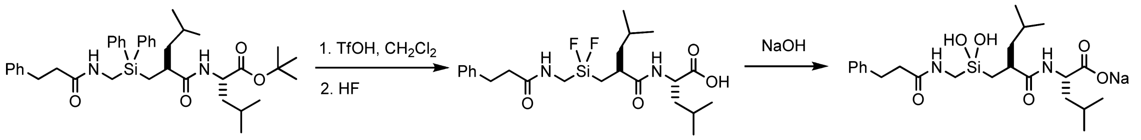
Scheme 16. Dimeric Species Active for the Silanediol-Catalyzed Friedel−Crafts Reaction



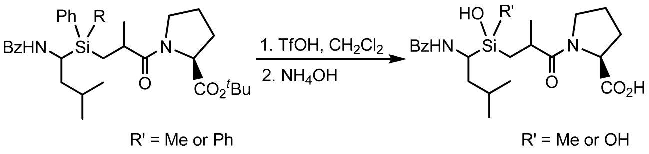
Scheme 17. Synthesis of Silanediol Analogues of HIV Protease Inhibitor



Scheme 18. Synthesis of a Silanediol Analogue of Thermolysin Inhibitor



Scheme 19. Synthesis of Silanediol Analogues of ACE Inhibitor



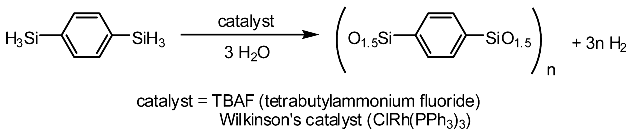
reagent and reduction of another methoxy group with lithium aluminum hydride ($LiAlH_4$). The hydrosilane was hydrolyzed to methyl(4-methylpent-3-enyl)vinylsilanol (*rac*-sila-linalool) by treatment with potassium hydroxide in *tert*-butanol.

In 2012, Sieburth and co-workers reported the synthesis and properties of a sterically unencumbered δ-silanediol amino acid.[16] An enantiomerically pure amino acid carrying a 1-(4-dihydroxymethylsilyl)butyl side chain was synthesized as a potential inhibitor of the enzyme arginase. The silanediol was prepared by hydrosilylation of an optically active alkene with diethoxymethylhydrosilane in the presence of Karstedt's Pt-catalyst and then hydrolysis of the Si−OEt groups into silanols (Scheme 21). Belokon's nickel complex was employed as a glycine enolate for diastereoselective introduction of the 3-butenyl group.

4.2. Silicon-Based Materials Prepared by Hydrolytic Oxidation of Hydrosilanes. Chlorosilanes are conventional starting materials and hydrolyzed with the aid of hydrogen chloride acceptor such as aniline or triethylamine to give the silanol synthons of silicon-based materials, while various silicon compounds possessing Si−X bonds (X = alkoxy, F, Cl, Br, I, H, carboxylate, perchlorate, sulfate) can be also used as starting materials.[26] The second general synthetic method for silanols is the oxidation of hydrosilanes with stoichiometric oxidants such as perbenzoic acid, $KMnO_4$, Ag salts, ozone, and dioxiranes ($(O_2)CMe_2$ and $(O_2)CMe(CF_3)$). In particular, dioxiranes are preferred oxidants because they are active under neutral and mild conditions. Furthermore, acetone and triflouoroacetone formed as the byproducts are not interfering with silanol products and are easy to remove.

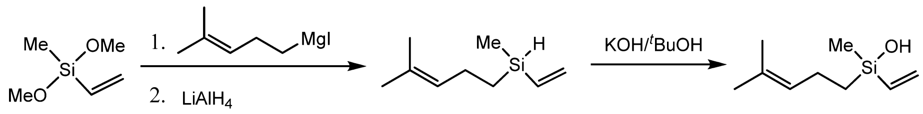
Polyorganosiloxanes are useful materials, and various synthetic methods were developed.[112,113] However, hydrosilanes received less attention as starting monomers, although the reactions of silanols with hydrosilanes are well-known in the presence of amines, alkali metal fluorides, or various transition metal catalysts. Side reactions limit the efficiency of the polymerization, which include homocondensation of silanols and reactions of hydrosilanes with water. Michalska investigated Rh-catalyzed reactions of silanols with hydrosilanes to give oligomeric organosiloxanes.[59] As a route to organosilsesquioxanes, Corriu and co-workers investigated the hydrolytic oxidation of trihydrosilanes and the condensation of the resulting silanols.[114] The Si−H bonds of a bis-trihydrosilane were hydrolyzed in the presence of Wilkinson's rhodium catalyst or tetrabutylammonium fluoride (TBAF) (Scheme 22). The fluoride ion catalysis produced a highly condensed hybrid siloxane network, while the rhodium catalysis gave partially cross-linked materials containing residual Si−H bonds.

Scheme 22. Hydrolytic Oxidation of Bis-Trihydrosilanes

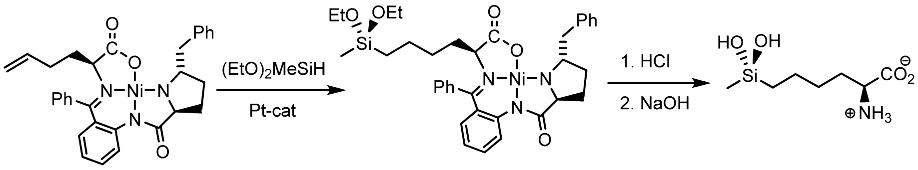


Mark and co-workers reported dehydrocoupling polymerization of bis-silanes and disilanols to give poly(silphenylenesiloxane)

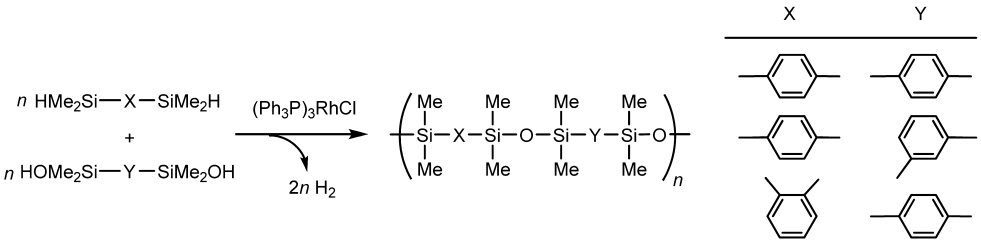
Scheme 20. Synthesis of Sila-linalool



Scheme 21. Synthesis of δ-Silanediol Amino Acid



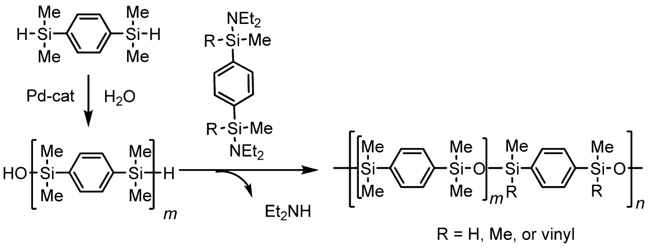
Scheme 23. Dehydrocoupling Polymerization of Bis-Silanes and Silanediols



(Scheme 23).[58] In contrast to the Michalska's results,[59] in which no polymer was produced, they obtained polymers of high molecular weights. For example, poly(tetramethyl-*p*-silphenylenesiloxane) was obtained as a white crystalline material with an M_n of 17,200 g/mol and M_w/M_n of 1.58 in quantitative yield.

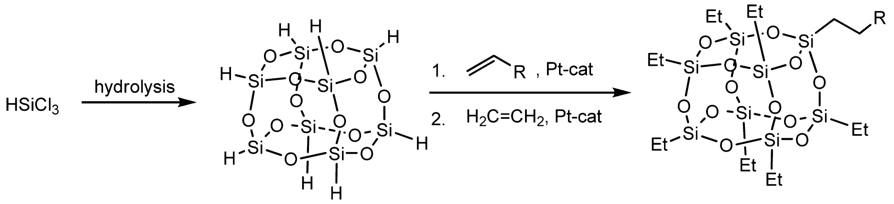
Kawakami and co-workers synthesized poly(silphenylenesiloxane)s containing hydride or vinyl functional groups by deaminative polycondensation of bis(aminosilane)s having the functional groups with monomeric or polymeric bis-silanol.[115] The bis-silanol prepolymer was prepared by palladium-catalyzed dehydrocoupling polymerization of 1,4-bis(dimethylsilyl)benzene with water. Then, the bis(aminosilane)s were coupled with the bis-silanol prepolymers to give a polysiloxane block-copolymer (Scheme 24). The poly(silphenylenesiloxane)s had low glass transition temperatures (T_g) ranging from −23 to −40 °C, and exhibited good thermal stability in both nitrogen and air atmosphere.

Scheme 24. Synthesis of Polysiloxanes by Coupling of Bis-Silanol Prepolymer with Bis(aminosilane)



In recent years polyhedral oligomeric silsequioxanes (POSS) received great attention as organic−inorganic hybrid materials, and various POSS materials were prepared by condensation of $XSi(OH)_3$.[116,117] Generally, monomers of the POSS structure are $XSiY_3$ type, where X is a chemically stable substituent (such as CH_3, phenyl, or vinyl), and Y is a highly reactive substituent (such as Cl, OH, or OR). Frey and co-workers prepared several copolymers containing POSS as side groups.[118] The POSS (H_8T_8), which has eight Si−H bonds, was synthesized from $HSiCl_3$ by hydrolysis and condensation process. H_8T_8 was functionalized to have a 9-decenyl group (Scheme 25). The functionalized POSS monomer was polymerized to give homopolymer, or incorporated into copolymers with ethene and propene via metallocene catalysis.

Scheme 25. Synthesis of POSS Monomer Possessing Si−H Bonds



5. SUMMARY AND OUTLOOK

The catalytic oxidation of hydrosilanes with water into silanols under neutral conditions is much more convenient and efficient in comparison to the conventional methods such as hydrolysis of chlorosilanes, nucleophilic substitution of siloxanes, and oxidation of hydrosilanes with stoichiometric oxidants. Reusable heterogeneous catalysts make the hydrolytic oxidation more attractive from the viewpoint of green chemistry. Among various catalyst systems for the hydrolytic oxidation of hydrosilanes, those based on palladium nanoparticles, gold nanoparticles, and nanoporous gold are particularly noticeable with their high activity and selectivity for silanols. For example, dimethylphenylsilane can be transformed into dimethylphenylsilanol selectively under ambient conditions with a reusable palladium catalyst (TON = 99,000; TOF = 20,000 h^{-1}).

Silanols are used not only in material science but also in organic synthesis and biochemistry. Furthermore, new applications will be developed on the basis of the structural diversity of silanols. To meet diverse needs, new catalyst systems will be required for the preparation of silanols from hydrosilanes possessing various functionalities, although simple silanols can be readily prepared with present ones.

The formation of siloxanes during the preparation of silanols is an undesirable side reaction. However, the dehydrocoupling reactions between Si−H and Si−OH bonds are desirable for polysiloxane synthesis. Thus detailed mechanistic studies for selective transformations of hydrosilanes are needed for the development of efficient catalyst systems not only for the synthesis of silanols but also for that of silicon-based materials.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pjw@postech.ac.kr.

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Notes

The authors declare no competing financial interest.

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