Heterogeneous Catalysis

DOI: 10.1002/anie.200802761

Supported Silver-Nanoparticle-Catalyzed Highly Efficient Aqueous Oxidation of Phenylsilanes to Silanols**

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Metal nanoparticles have attracted a great deal of attention in various areas of materials science, such as catalysis, optoelectronics, and drug delivery owing to their unique physical and chemical properties.[1] Recently, some metal nanoparticles have been revealed to have unprecedented catalytic performances that far exceed those of conventional homogeneous catalysts.[2] Of all metal nanoparticles, silver-nanoparticle catalysts are generally considered to have low activities for many liquid-phase organic reactions and, consequently, investigations into their catalytic properties have been scarce.[3] We recently discovered that hydrotalcite-supported Ag nanoparticles exhibit high catalytic activity for the oxidant-free dehydrogenation of alcohols into carbonyl compounds under liquid-phase conditions, where the combination of Ag with hydrotalcite plays a crucial role in the dehydrogenation.[4] Further applications of the unique catalytic behavior obtained by combining Ag nanoparticles with inorganic supports have been explored.

Silanols are useful as building blocks for silicon-based polymeric materials[5] and nucleophilic coupling partners in organic synthesis.[6] However, they are generally synthesized using toxic reagents and their synthesis generates vast amounts of environmentally damaging waste.[7] Some promising alternative catalytic transformations of silanes into silanols, using H_2O as a green oxidant, have been reported in the presence of organic solvents.[8–10] By using highly efficient and reusable heterogeneous catalysts, it should be possible to find more environmentally benign and practical processes for synthesizing silanols, that do not require the use of organic solvents. However, reported synthetic methods, in the absence of organic solvents, are unfortunately precluded by the main production of disiloxanes.[9]

Herein, we report that Ag nanoparticles supported on hydroxyapatite (Ag-HAp) exhibit high catalytic activities for the selective oxidation of silanes into silanols using water as an oxidant without the use of organic solvents. To our knowledge, this is the first catalytic system that uses water as a solvent for the selective oxidation of silanes into the corresponding silanols.

Hydroxyapatites (HAps), a phosphate mineral species found in teeth and bones, are of considerable interest owing to their potential usefulness as biomaterials,[11] adsorbents,[12] and ion-exchangers.[13] We have reported the benefit of utilizing HAp as a support for high-performance heterogeneous catalysts in various organic syntheses.[14] Ag-HAp was synthesized as follows: Ca-HAp ($Ca_5(PO_4)_3(OH)$, Ca/P = 1.68, 2.0 g), was soaked in an aqueous solution of $AgNO_3$ (6.7×10^{-3} M, 150 mL) and stirred at room temperature for 6 h. The resultant solid was collected by filtration, washed, and dried at room temperature in vacuo. Reduction with an aqueous solution of potassium borohydride under an argon atmosphere gave HAp-supported Ag nanoparticles (Ag-HAp).

The XRD peak positions of Ag-HAp were similar to those of the parent HAp. Elemental analysis showed that the Ca/P ratio of Ag-HAp remained at 1.68 and the Ag loading on Ag-HAp was 3.3 wt %. Ag k^3-weighted K-edge extended X-ray absorption fine structure (EXAFS) study of Ag-HAp revealed that a peak around 2.8 Å of the Fourier transformation was assignable to the Ag–Ag shell. UV/Vis analysis gave a plasmon peak at 414 nm, indicating that the diameter of the Ag nanoparticles is 6.0–8.0 nm.[15] Transmission electron microscopy showed that Ag nanoparticles with a mean diameter of 7.6 nm, with a narrow size distribution with a standard deviation of 1.8 nm, were formed on the surface of the HAp substrate.[16]

When a triphasic mixture of dimethylphenylsilane (**1**), water, and Ag-HAp was heated at 80 °C under an argon atmosphere for 15 min, oxidation of **1** occurred quantitatively to afford dimethylphenylsilanol (**2**) with coproduction of the equivalent molar amount of H_2 (Table 1, entry 1). The use of Ag salts, such as $AgNO_3$, Ag_2O, $AgPF_6$, and AgOTf, instead of Ag-HAp resulted in poor yields of **2**. A blank experiment and Ag-free HAp did not provide oxidized products under the above conditions (Table 1, Entries 13–16).[17] Other immobilized forms of Ag, such as Ag-Al_2O_3, Ag-TiO_2, Ag-SiO_2, and Ag-hydrotalcite (Ag-HT), gave moderate yields of **2** (Table 1, Entries 9–12). The combination of Ag with HAp is

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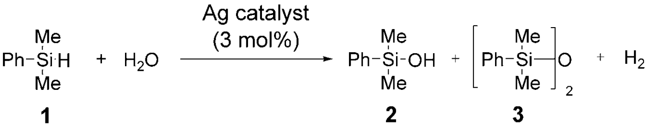
[**] The work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan and by a Grant-in-Aid for Scientific Research on Priority Areas (No. 18065016, "Chemistry of Concerto Catalysis") from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Some of the work was carried out at the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802761.

Table 1: Oxidation of dimethylphenylsilane using Ag-catalysts.[a]



$$\mathrm{PhSiMe_2H} + \mathrm{H_2O} \xrightarrow[\text{(3 mol\%)}]{\text{Ag catalyst}} \mathrm{PhSiMe_2OH} + [\mathrm{PhSiMe_2}]_2\mathrm{O} + \mathrm{H_2}$$

Entry	Catalyst	t [min]	Conv. [%][b]	Selectivity (**2**:**3**)[b]	V_m [mL m^{-2}][c]
1	Ag-HAp	15	99	> 99:1	0.311
2	reuse1	15	99	> 99:1	–
3	reuse2	15	99	> 99:1	–
4	reuse3	15	99	> 99:1	–
5	reuse4	15	99	> 99:1	–
6[d]	Ag-HAp	90	97	> 99:1	–
7[e]	Ag-HAp	600	98	> 99:1	–
8[f]	Ag-HAp	15	99	> 99:1	–
9	Ag-Al_2O_3	15	79	> 99:1	0.271
10	Ag-TiO_2	15	71	> 99:1	0.246
11	Ag-SiO_2	15	29	> 99:1	0.157
12	Ag-TC	15	25	> 99:1	–
13	$AgNO_3$	15	24	> 99:1	–
14	Ag_2O	15	27	> 99:1	–
15	$AgPF_6$	15	23	82:18	–
16	AgOTf	15	30	88:12	–

[a] Conditions unless otherwise stated: dimethylphenylsilane (1.0 mmol), H_2O (2.0 mL), catalyst (Ag: 0.03 mmol), 80 °C, Ar flow. [b] Determined by GC using internal standard technique. [c] H_2O monolayer adsorption capacity. [d] Room Temperature. [e] Ethyl acetate (5.0 mL) was added into reaction mixture, −40 °C. [f] Air atmosphere.

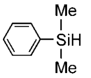
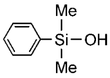
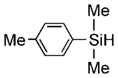
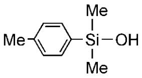
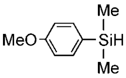
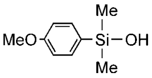
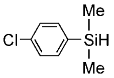
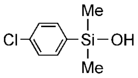
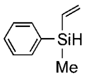
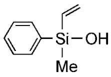
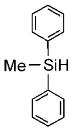
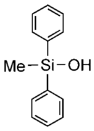
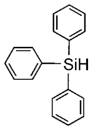
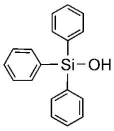
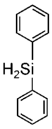
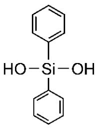
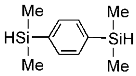
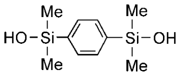
the most efficient for achieving a high catalytic activity for the selective oxidation of **1** into **2**. The Ag-HAp catalyst was also found to exhibit extremely high activity in the oxidation of **1** at room temperature (Table 1, entry 6) and moreover, **1** was converted quantitatively even at −40 °C (Table 1, entry 7). Interestingly, Ag-HAp also catalyzed the quantitative formation of **2** and the concerted formation of an equimolar amount of H_2 in an air atmosphere (Table 1, entry 8).

To check whether the oxidation takes place on Ag nanoparticles immobilized by HAp, the reaction mixture was hot-filtered at 40 % conversion of **1**. Further stirring of the filtrate under the above reaction conditions did not yield any additional product. An inductively coupled plasma method (detection limit: 0.007 ppm) was used to confirm that no Ag leached into the filtrate. These results demonstrate that the present oxidation occurred exclusively on the surface of Ag-HAp. Solid Ag-HAp could be easily retrieved from the reaction mixture by simple filtration and was found to be reusable without any reduction in its activity or selectivity; the yield of **2** from the oxidation of **1** could be maintained at over 99 % during four recycles of the catalyst (Table 1, Entries 2–5).

100 mmol of **1** was also smoothly converted by Ag-HAp, to give **2** at a yield of 98 % after 9 h, and a turnover number (TON) of up to 1600 was achieved. This value is superior to those obtained using other catalyst systems, for example, [{$RuCl_2$(*p*-cymene)}$_2$] (TON = 455),[8a] [IrCl(C_8H_{12})]$_2$ (85),[8b] oxorhenium (880),[9] Ru-HAp (TON = 470),[10] and [{$RuCl_2$(*p*-cymene)}$_2$]/C (9).[8d]

Ag-HAp exhibited high specific activities for the oxidation of various aromatic silanes (Table 2). A range of phenylsilanes was oxidized in high yields with over 99 % selectivity for the silanols (Table 2, Entries 1–9). Methylphenylvinylsilane was selectively oxidized to the corresponding unsaturated silanol while retaining the olefinic group (Table 2, entry 5). Triphenylsilane and 1,4-bis(dimethylsilylbenzene) are known to be less reactive than the majority of the investigated phenylsilanes, as a result of their greater steric bulk.[10] However, Ag-HAp smoothly catalyzed the selective oxidations of these silanes in high yields (Table 2, Entries 7 and 9).

Table 2: Oxidation of various silanes catalyzed by Ag-HAp in water.[a]

Entry	Silane	Silanol	t [min]	Conv. [%][b]	Silanol:Disiloxane[b]
1			15	99	> 99:1
2			180	99	> 99:1
3			30	97	> 99:1
4			30	97	> 99:1
5			60	97	> 99:1
6			60	97	> 99:1
7[c]			5	99	> 99:1
8			15	99	> 99:1
9			240	96	> 99:1
10	(nBu)$_3$SiH	(nBu)$_3$SiOH	1440	trace	–
11	tBuMe$_2$SiH	tBuMe$_2$SiOH	1440	trace	–

[a] Conditions unless otherwise stated: Silane (1.0 mmol), H_2O (2.0 mL), Ag-HAp (Ag: 0.03 mmol), 80 °C, Ar flow. [b] Determined by GC using internal standard technique. [c] Silanes (1.0 mmol), ethyl acetate (5.0 mL), H_2O (5.0 mmol), Ag-HAp (Ag: 0.03 mmol), 80 °C, Ar flow.

The interaction between the Ag-HAp surface and silanes was examined using IR spectroscopy. Following the adsorption of **1** onto Ag-HAp, a band at 1257 cm^{-1}, assigned to the aromatic ring vibration, was shifted to 1263 and 1253 cm^{-1}. The attempted adsorption of tributylsilane (**4**) onto Ag-HAp gave rise to no corresponding peaks in the IR spectrum, indicating no adsorption had taken place.[16] This finding revealed the strong adsorption of **1** through an aromatic group interaction onto the surface of Ag-HAp. Measurement of water vapor adsorption onto HAp exhibited the highest hydrophilicity among tested supports for the oxidations. The yield of **2** increased with increasing the water adsorption capacity (V_m) of Ag-HAp, Ag-Al_2O_3, Ag-TiO_2, and Ag-SiO_2 (Table 1, Entries 1, 9–11). Moreover, microwave dielectric studies on the dynamics of water[16] demonstrated the relaxation peak of water in Ag-HAp appeared at a lower frequency than that in HAp, suggesting that H_2O interacts strongly with the surface of the Ag nanoparticles to generate a nucleophilic OH^- species.[18]

The above results indicate that the cooperative action between Ag nanoparticles and HAp plays an important role in the specific activity for phenylsilanes in this aqueous catalytic system. A possible mechanism is as follows: A phenylsilane dispersed in H_2O is adsorbed onto the surface of Ag nanoparticles by a strong aryl-ring–Ag interaction. A nucleophilic OH^- species from H_2O, activated on Ag surface,[19] attacks the adsorbed phenylsilane to form the phenylsilanol through a pentacoordinate silicon intermediate.[20] This hydrophilic environment for the Ag-HAp surface increases the concentration of nucleophiles (OH^- or H_2O) and promotes formation of the silanol by suppressing condensation to the disiloxane.[21]

In conclusion, Ag nanoparticles supported on HAp showed a high catalytic activity for the selective oxidation of various phenylsilanes into phenylsilanols in water, as a result of the cooperative behavior between hydrophilic HAp and Ag nanoparticles that interact strongly with both H_2O and phenylsilanes. Moreover, Ag-HAp was reusable without any appreciable loss in activity or selectivity.

Received: June 11, 2008

Keywords: heterogeneous catalysis · nanoparticles · silanes · silver · water chemistry

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[16] See Supporting Information for details.

[17] Ru-HAp, $[\{RuCl_2(p\text{-cymene})\}_2]$[8a] and $[\{IrCl(C_8H_{12})\}_2]$[8b], which have been reported to show high catalytic performances for selective oxidation of silanes into silanols in organic solvents, were used under solvent-free conditions. The conversions of **1**/selectivities of **2** obtained using the above three catalysts were 20/99, 95/21 and 99/3, respectively.

[18] Membrane-bound water acts as a nucleophile for hydration of lipids. See A. Ghosh, M. Smits, J. Bredenbeck, M. Bonn, *J. Am. Chem. Soc.* **2007**, *129*, 9608.

[19] There are three possibilities from where the nucleophilic OH^- species might come: from the solution, the support, or the Ag nanoparticles. The results of the microwave dielectric studies on the dynamics of water, suggest that the OH^- species comes from the surface of Ag nanoparticles in this instance.

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[21] The biphasic nature of the organosilane/H_2O system reduced the effective concentration of water in the organosilane phase, resulting in condensation of silanols into disiloxanes.[9]