## Supported gold nanoparticle catalyst for the selective oxidation of silanes to silanols in water<sup>†</sup>

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Hydroxyapatite-supported gold nanoparticles (AuHAP) can act as highly efficient and reusable catalysts for the oxidation of diverse silanes into silanols in water; this is the first catalytic methodology for the selective synthesis of aliphatic silanols using water under organic-solvent-free conditions.

Chemical reactions using water as a solvent or a nucleophile have received considerable attention in organic synthesis from both a practical and an economic standpoint.<sup>1-4</sup> The use of water in organic reactions has the following significant advantages: low cost, abundance, safety (non-explosive, non-flammable, and non-toxic), easily controlled reaction temperature due to the high heat capacity of water, and ease of phase-separation when water-insoluble products are formed.

Silanols are important chemicals that are mostly used as valuable building blocks for silicon-based polymeric materials5-8 and nucleophilic coupling partners in organic synthesis.<sup>9-12</sup> Recently, the catalytic oxidation of silanes using H<sub>2</sub>O and/or molecular oxygen as oxidants has been reported<sup>13-18</sup> (Scheme 1). The only by-products of this method are non-polluting H<sub>2</sub> and/or H<sub>2</sub>O. Therefore, this method can provide a more environmentally-friendly synthesis of silanols than conventional methods that involve toxic reagents and the production of vast amounts of environmentally damaging waste.<sup>19-26</sup> We have found that the selective oxidation of silanes into silanols with water can be achieved by using a supported silver nanoparticle catalyst; various phenyl silanes afforded the corresponding silanols in excellent yields, whereas the aliphatic silanes were hardly oxidized.<sup>13</sup> This catalyst system does not require the use of any organic solvents, which are essential for the previously reported catalyst systems, to suppress the condensation of silanols to undesired disiloxanes.

$$\begin{array}{c} R_{1} \\ R_{2} \\ Si \\ H \end{array} + H_{2}O \xrightarrow{\text{catalyst}}_{\text{solvent}} \\ R_{2} \\ Scheme 1 \\ \end{array} \xrightarrow{R_{1} \\ R_{2} \\ Si \\ OH \end{array} + H_{2}$$

Herein, we report that hydroxyapatite-supported gold nanoparticles (AuHAP) are also able to catalyze the oxidation of diverse silanes into the corresponding silanols using water under atmospheric air conditions. In particular, a wide range of aliphatic silanes can be efficiently oxidized. AuHAP is recoverable and reusable without loss of activity and selectivity. To the best of our knowledge, this is the first catalytic methodology for the synthesis of aliphatic silanols using water under organic-solvent-free conditions.

AuHAP was synthesized as follows: hydroxyapatite (HAP;  $Ca_5(PO_4)_3(OH)$ , Ca : P = 1.68) was prepared according to a previously reported procedure.<sup>27</sup> The HAP (1.0 g) was then soaked in 50 mL of an aqueous solution of HAuCl<sub>4</sub> (2 mM). After stirring for 2 min, 0.2 mL of aqueous NH<sub>3</sub> (10%) were added and the resulting mixture was stirred at room temperature for 12 h in an air atmosphere. The obtained slurry was filtered, washed with deionized water, and then dried at room temperature in vacuo. Subsequently, the HAP solid containing Au ions (0.9 g) was added to 50 mL of an aqueous solution of KBH<sub>4</sub> (18 mM) and stirred at room temperature for 1 h to yield AuHAP as a purplish red powder. The X-ray diffraction (XRD) peak positions of AuHAP were similar to those of the parent HAP, and the Au loading on AuHAP was estimated to be 1.65 wt% by elemental analysis. The  $k^3$ -weighted Au L-edge extended X-ray absorption fine structure (EXAFS) of AuHAP revealed a peak at 2.6 Å in the Fourier transform (FT), which was assigned to the Au-Au shell. Transmission electron microscopy (TEM) analysis of AuHAP revealed Au nanoparticles with a mean diameter of 3.0 nm and a narrow size distribution with a standard deviation of 0.9 nm.<sup>28</sup>

When a triphasic mixture of triethylsilane (1), water, and AuHAP was stirred at 80 °C in atmospheric air for 2 h, 1 was converted to triethylsilanol (2) in over 99% yield, without the formation of the disiloxane<sup>29</sup> (Table 1, entry 1). Moreover, 1 was quantitatively converted, even at room temperature (Table 1, entry 2). Among the various supports containing Au nanoparticles that were tested, HAP was the best support for the oxidation of 1 in water.<sup>30</sup> The use of either Au<sub>2</sub>O<sub>3</sub> or  $HAuCl_4$  for the oxidation of 1 resulted in moderate yields of 2, but with the formation of undesirable disiloxane (Table 1, entries 6 and 7). No oxidation occurred when using the parent HAP support or under blank conditions (Table 1, entries 8 and 9). HAP-supported other metal particles having catalytic potentials such as Pd, Pt, Ru, and Ag particles were prepared, and the oxidation of 1 was examined under similar reaction conditions, as shown in Fig. 1. Supported Pd nanoparticles gave a moderate yield of 2 with low selectivity and the other

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 Table 1
 Oxidation of triethylsilane in water<sup>4</sup>

| Et—            | Et<br> -<br>Si—H + H₂O<br>  Et<br>  1 | catalyst<br>water, 80 °C, air, 2 h | Et<br>Et—Si—OH<br>Et<br>2 |
|----------------|---------------------------------------|------------------------------------|---------------------------|
| Entry          | Catalyst                              | Conv. $(\%)^b$                     | Silanol : disiloxane      |
| 1              | AuHAP                                 | >99                                | >99:1                     |
| $2^c$          | AuHAP                                 | >99                                | >99:1                     |
| $3^d$          | AuHAP                                 | >99                                | >99:1                     |
| $4^e$          | AuHAP                                 | >99                                | >99:1                     |
| 5 <sup>f</sup> | AuHAP                                 | >99                                | >99:1                     |
| 6              | HAuCl <sub>4</sub>                    | >99                                | 84:16                     |
| 7              | $Au_2O_3$                             | >99                                | 81:19                     |
| 8              | HAP                                   | <1                                 | _                         |
| 9              | None                                  | <1                                 | —                         |

<sup>*a*</sup> Reaction conditions: AuHAP (0.1 g, Au: 0.83 mol%), triethylsilane (1 mmol), water (3 mL). <sup>*b*</sup> Determined by GC using internal standard technique. <sup>*c*</sup> 4 h at 27 °C. <sup>*d*</sup> reuse 1. <sup>*e*</sup> reuse 2. <sup>*f*</sup> reuse 3.



**Fig. 1** Comparison of the catalytic activity of AuHAP, PdHAP, PtHAP, RuHAP and AgHAP for the oxidation of **1** in water.

metal particles were not effective. This reveals that Au nanoparticles exhibit unique and distinct catalytic activity and selectivity for the oxidation of **1** among supported metal particles.

To determine whether the oxidation of 1 occurs on supported Au nanoparticles, AuHAP was removed from the reaction mixture by simple filtration at 50% conversion of 1. Further stirring of the filtrate under similar oxidation conditions did not provide any products. Moreover, no Au was present in the filtrate, as determined by inductively coupled plasma (ICP) analysis (detection limit: 0.10 ppm). These results show that AuHAP acts as a solid catalyst for the oxidation of 1. After the oxidation, hydrophilic AuHAP existed in aqueous phase and the product could be easily isolated by extraction using diethyl ether. The recovered aqueous phase containing AuHAP was reusable without significant loss of activity and selectivity during the recycling experiments (Table 1, entries 3-5). TEM images and the FT peak intensities of the Au-Au shell in EXAFS for the reused AuHAP were similar to those for freshly prepared AuHAP,<sup>28</sup> which indicates that the size of the Au nanoparticles is not significantly changed during oxidation. These results are

| Table 2         Oxidation of various silanes catalyzed by AuHAP in water |   |  |          |                |                         |  |  |  |
|--|---|--|----------|----------------|-------------------------|--|--|--|
| Entry  | Silane  | Silanol  | Time/h   | Conv. $(\%)^b$ | Silanol :<br>disiloxane |  |  |  |
| 1  | Et<br>Et-Si-H<br>Ét   | Et<br>Et-Si-OH<br>Et   | 2        | >99            | >99:1                   |  |  |  |
| 2 <sup><i>c</i></sup>  | Me<br>I<br>t-Bu-Si-H<br>Me                                  | Me<br>I<br>t-Bu—Si—OH<br>I<br>Me                               | 6        | 96             | >99 : 1                 |  |  |  |
| 3  | Bu<br>I<br>Bu-Si—H<br>I<br>Bu                               | Bu<br>I<br>Bu-Si-OH<br>I<br>Bu                                 | 6        | >99            | >99:1                   |  |  |  |
| 4  | Hex<br>I<br>Hex-Si—H<br>I<br>Hex                            | Hex<br>Hex-Si-OH<br>Hex  | 8        | 97             | >99 : 1                 |  |  |  |
| 5  | <i>i-</i> Bu<br>I<br><i>i</i> -Bu−Si−H<br>I<br><i>i</i> -Bu | <i>i-</i> Bu<br>I<br><i>i-</i> Bu-Si−OH<br>I<br><i>i-</i> Bu   | 8        | 97             | >99:1                   |  |  |  |
| 6  | i-Pr<br>I<br>i-Pr-Si-H<br>I<br>i-Pr                         | <i>i-</i> Pr<br>I<br><i>i</i> -Pr−Si−OH<br>!-Pr                | 24       | 96             | >99:1                   |  |  |  |
| 7  | n-Pr<br>I<br>n-Pr-Si—H<br>I<br>n-Pr                         | <i>n-</i> Pr<br><i>n-</i> Pr-Si–OH<br><i>I</i><br><i>n-</i> Pr | 6        | 96             | >99:1                   |  |  |  |
| 8 <sup>c</sup>   | Me<br>Si-H<br>Me  | Me<br>Si−OH<br>H<br>Me   | 6        | 96             | >99 : 1                 |  |  |  |
| 9  | Me<br>-Si-H<br>Me   | Me<br>−Si−OH<br>Me   | 4        | >99            | >99:1                   |  |  |  |
| 10   | Me<br>Si-H<br>Me  | Me<br>I<br>Si-OH<br>Me   | 4        | >99            | >99:1                   |  |  |  |
| 11   | Me<br>-Si-H<br>Me   | Ме<br>–Si–ОН<br>Ме   | 3        | >99            | >99:1                   |  |  |  |
| 12   | K -Si-K   | OH<br>-Si-<br>Me   | 10       | 97             | 100 : 0                 |  |  |  |
| 13<br>14 <sup>d</sup>  |   | С)-Si-OH   | 24<br>24 | <1<br>28       | >99:1                   |  |  |  |
| 15   |   | ©-si-€<br>oh   | 8        | 92             | >99:1                   |  |  |  |
| 16   | Me Me<br>H-Si-<br>Me Me                                     | HO-Si-<br>Me<br>Me<br>Me<br>Me                                 | 18       | 98             | >99:1                   |  |  |  |
| 17   | Me<br>Me-<br>Si-H<br>Me                                     | Me<br>Me-<br>Si-OH<br>Me                                       | 6        | >99            | >99:1                   |  |  |  |
| 18   | Me<br>MeO-<br>Si-H<br>Me                                    | Me<br>MeO-<br>Si-OH<br>Me                                      | 4        | >99            | >99:1                   |  |  |  |
| 19   | CI-CI-CI-H<br>Me  | Me<br>−<br>−Si−OH<br>Me  | 6        | >99            | >99:1                   |  |  |  |

<sup>*a*</sup> Silanes (1 mmol), H<sub>2</sub>O (3 mL), AuHAP (0.1 g), 80 °C, air. <sup>*b*</sup> Determined by GC and LC using internal standard technique. <sup>*c*</sup> At 40 °C. <sup>*d*</sup> Silane (1 mmol), ethyl acetate (5 mL), water (5 mmol), 80 °C, air.

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consistent with the high durability of AuHAP in the recycling experiments.

The scope of the substrate silanes using the present AuHAP catalyst system is exemplified in Table 2. In all cases, AuHAP efficiently catalyzed the oxidation of silanes to silanols without the formation of any disiloxane condensation products. Various aliphatic silanes were successfully oxidized to the silanols (Table 2, entries 1–9). Triisopropylsilane, a sterically bulky aliphatic silane, was also oxidized (Table 2, entry 6). Only the Si–H function of dimethylpropenylsilane was oxidized to a silanol, while the C=C double bond remained intact under the reaction conditions (Table 2, entry 8). Phenylsilanes were also found to be good substrates for the AuHAP catalyst, and the corresponding silanols were formed in excellent yields (Table 2, entries 10-12 and 15-19), except for triphenylsilane (Table 2, entries 13 and 14).

In conclusion, the HAP-supported gold nanoparticle (AuHAP) catalyst was developed for the oxidation of silanes in water. This catalytic methodology is a highly potential candidate for the environmentally friendly oxidation of silanes with the following advantages: (1) no requirement for organic solvents, (2) use of water as a clean oxidant, (3) simple work-up procedure, (4) high activity and selectivity for silanols, (5) a wide scope of substrate silanes, including various aliphatic silanes, and (6) reusability of the catalyst.

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- 28 See ESI<sup>†</sup>.
- 29 In a separate experiment, the AuHAP-catalyzed oxidation of **1** was conducted using isotopic  $H_2O^{18}$  and  $^{18}O$ -labeled silanol was formed in 99% selectivity, suggesting that the oxygen atom incorporated in silanol products were derived not from air (O<sub>2</sub>) but water.
- 30 In the oxidation of **1** at 80 °C for 30 min, the following yields of **2** were obtained with over 99% selectivity: AuHAP, 68%; Au/Al<sub>2</sub>O<sub>3</sub>, 62%; Au/SiO<sub>2</sub>, 51%, Au/MgO, 28%, and Au/TiO<sub>2</sub>, 27%.