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Heterogeneous Catalysis

Nanostructured Materials as Catalysts: Nanoporous-Gold-Catalyzed Oxidation of Organosilanes with Water**

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Molecular transformations with a single atom/single molecular gold catalysts (**A**; Figure 1) are becoming a pressing concern to organic and catalytic chemists.[1] On the other hand, bulk gold metal (**D**) does not exhibit catalytic reactivity.

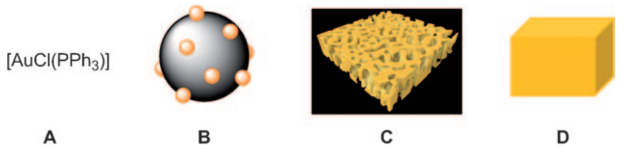

Figure 1. Examples of four types of gold: **A**) a molecule containing an atom of gold; **B**) gold nanoparticles on a support; **C**) nanoporous gold; **D**) bulk gold.

It is known that small gold particles in the range of 2 to 5 nm (**B**) on suitable oxide supports show a catalytic activity in a wide variety of molecular transformations in gas and liquid phases.[2] More recently, nanoporous gold (AuNPore) nanostructured materials (**C**) has attracted much attention as sensors[3] and actuations,[4] and furthermore, some reactions have been catalyzed by nanoporous gold.[5–7]

Silanols are useful building blocks for silicon-based polymeric materials[8] as well as nucleophilic coupling partners in organic synthesis.[9] Although a variety of preparation methods of silanols have been developed, oxidations of organosilanes with water catalyzed by heterogeneous catalysts, such as supported metal nanoparticle catalysts, would be ideal from an environmental viewpoint because the catalyst is reusable and the co-product is hydrogen gas. For example, Kaneda and co-workers reported that hydroxyapatite-supported gold nanoparticles were effective catalysts for this transformation.[10,11] However, there are some drawbacks in those cases, such as decrease of catalytic activity owing to agglomeration, limited scope to certain substrate types, formation of disiloxanes derived from the condensation of silanols, and cumbersome work-up procedures for separation of products from the catalyst.

Herein, we show how nanoporous gold exhibits a remarkable catalytic activity in the oxidation of a wide range of organosilanes. The corresponding silanols can be produced in high yields under mild conditions together with the evolution of hydrogen gas [Eq. (1)]. Furthermore, the catalyst can be recycled several times and the work-up process is quite simple.

$$\underset{\mathbf{1}}{R_{(4-n)}SiH_n} + n\,H_2O \xrightarrow{\text{AuNPore cat.}} \underset{\mathbf{2}}{R_{(4-n)}Si(OH)_n} + n\,H_2 \qquad (1)$$

The nanoporous gold catalyst used in this study was readily prepared by selective leaching of silver from an alloy foil consisting of $Au_{30}Ag_{70}$ (in atom %) with thickness of 40 μm using 70 wt % HNO_3 for 18 h at room temperature.[12] Figure 2a shows the resulting microstructure of dealloyed material; the nanopore size was measured to be around 30 nm.

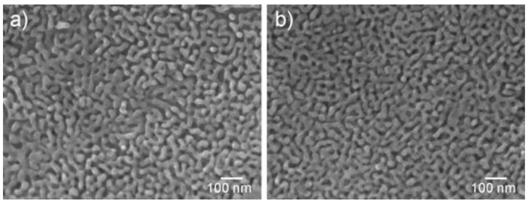

Figure 2. Scanning electron microscopy (SEM) images of dealloyed nanoporous gold leaf: a) before reaction, b) after being used five times for oxidation of $PhMe_2SiH$ (see Table 1, entry 5). Scale bars: 100 nm.

The reaction of $PhMe_2SiH$ (**1a**) with H_2O in the presence of the AuNPore catalyst was carried out and the results are summarized in Table 1. When **1a** was treated with 1 mol % of AuNPore catalyst at room temperature in aqueous acetone, hydrogen gas was evolved immediately. The gas production ceased within one hour and dimethylphenylsilanol **2a** was obtained quantitatively (entry 1). The turnover frequency (TOF) of 3.0 s^{-1} was achieved at the beginning in this catalytic system (see the Supporting Information). On the other hand, only a trace amount of **2a** was obtained in the oxidation reaction of **1a** with simple gold foil having no nanoporous structure. These results clearly indicated that the nanostruc-

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Table 1: Oxidation of organosilanes.[a]

$$\underset{\mathbf{1a}}{\mathrm{PhMe_2Si{-}H}} + \mathrm{H_2O} \xrightarrow[\text{acetone, RT, 1 h}]{\text{AuNPore (1 mol\%)}} \underset{\mathbf{2a}}{\mathrm{PhMe_2Si{-}OH}} + \mathrm{H_2}$$

Entry	Catalyst	Yield of **2a** [%][b]
1	fresh	100
2	reuse 1	98
3	reuse 2	100
4	reuse 3	99
5	reuse 4	100

[a] Reactions were performed using **1a** (1.0 mmol), H_2O (0.1 mL), and AuNPore (1 mol%) in 1.5 mL of acetone at room temperature for 1 h. [b] Yield of isolated product.

ture of the catalyst plays a crucial role for the current transformation. It is noteworthy that the formation of disiloxane, 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane, was not detected at all by GCMS. Generally, the recovery of the heterogeneous catalyst is carried out by filtration for the separation of the catalyst from the reaction mixture. In the present reaction system, we used some small pieces of the nanostructured gold foil as a catalyst with a size of around 5 × 2 mm^2. Thus, the catalyst can be recovered easily by picking up by tweezers without any cumbersome work-up procedures. After a simple washing of the catalyst with diethyl ether, it was reused without further purification. We used the catalyst repeatedly (five times), but no significant loss of activity was observed. The product **2a** was obtained nearly quantitatively every time and the turnover number (TON) reached up to 10700 (entries 1–5). Figure 2b is the SEM image of the recovered catalyst after five uses (entry 5). No significant changes were observed in comparison with Figure 2a.

The catalytic oxidation reactions with a variety of organosilanes were then carried out (Table 2). Not only aromatic silanes but also trialkylsilanes were oxidized effectively (entries 1–3). The reaction of sterically less-hindered triethylsilane **1b** proceeded smoothly in 2 h and the desired triethylsilanol **2b** was produced in 94% yield (entry 1). Even with sterically hindered trialkylsilanes, such as Bu_3SiH (**1c**) and *i*Pr_3SiH (**1d**), the corresponding silanols **2c**,**d** were obtained in high yields by increasing the catalyst loading to 3 mol% (entries 2 and 3). On the other hand, the reaction of sterically hindered Ph_3SiH proceeded with 1 mol% of the catalyst, and the corresponding silanol **2e** was obtained nearly quantitatively (entry 4). The AuNPore catalyst could also be used in the oxidations of diphenylsilane **1f** and phenylsilane **1g**, and the corresponding oxygenated products, $Ph_2Si(OH)_2$ (**2f**) and $PhSi(OH)_3$ (**2g**), were obtained in 90 and 80% yields, respectively (entries 5 and 6). Alkenyl- and alkynyl-containing silanes **1h**,**i** were suitable substrates for the current oxidation reaction, and the corresponding silanols **2h**,**i** were obtained in high yields (entries 7 and 8).

Table 2: Scope of the oxidation of organosilanes.[a]

$$\underset{\mathbf{1}}{\mathrm{R}_{(4-n)}\mathrm{SiH}_n} + n\,\mathrm{H_2O} \xrightarrow[\text{acetone, RT}]{\text{AuNPore cat.}} \underset{\mathbf{2}}{\mathrm{R}_{(4-n)}\mathrm{Si(OH)}_n} + n\,\mathrm{H_2}$$

Entry	1	$R_{(4-n)}SiH_n$	AuNPore [mol%]	t [h]	2	Yield [%][b]
1	**1b**	Et_3SiH	1	2	**2b**	94
2	**1c**	Bu_3SiH	3	3	**2c**	95
3	**1d**	*i*Pr_3SiH	3	5	**2d**	88
4	**1e**	Ph_3SiH	1	5	**2e**	99
5	**1f**	Ph_2SiH_2	1	9	**2f**	90
6	**1g**	$PhSiH_3$	5	6	**2g**	80
7	**1h**	$(H_2C{=}CH)MePhSiH$	1	1	**2h**	98
8	**1i**	$(PhC{\equiv}C)Me_2SiH$	3	1.5	**2i**	92

[a] Reactions were performed using **1** (1.0 mmol), H_2O (0.1 mL), and AuNPore (*n* mol%) in 1.5 mL of acetone at room temperature. [b] Yield of isolated product.

We then examined the reaction to clarify whether the dissolved gold species in solvents take part in the current molecular transformation or not. After the catalytic oxidation of **1a** was carried out for 10 min under the standard conditions, the nanoporous gold was removed from the reaction vessel. ^1H NMR analysis of the mixture showed that **2a** was produced in 48% yield at this time. While stirring of the mixture was continued in the absence of the catalyst for 50 min, further consumption of **1a** was not detected at all. AuNPore was then put back into the mixture. The oxidation reaction restarted immediately and finally **2a** was obtained in 99% yield within 50 min. It is also worth mentioning that leaching of the gold in the reaction of **1a** was not detected by inductively coupled plasma (ICP) analysis (< 0.0005%). These results clearly indicated that the current transformation was catalyzed by the AuNPore catalyst.

In conclusion, we have discovered that a nanoporous gold material exhibited a remarkable catalytic activity in the oxidation of organosilane compounds with water. The catalyst was easily recoverable and could be used at least five times without leaching and loss of activity. The observed excellent durability of the catalyst was also confirmed by SEM images. Indeed, the nanoporous structure of the catalyst did not change, even after five uses for the oxidation of dimethylphenylsilane **1a**. Further studies to elucidate the mechanism of this reaction and to extend the scope of synthetic utility are in progress in our laboratory.[13]

Experimental Section

The preparation of **2a** is given as a representative example. Acetone (1.5 mL), H_2O (0.1 mL), and dimethylphenylsilane **1a** (136 mg, 1 mmol) were added successively to a catalytic amount of nanoporous gold (2.0 mg, 1 mol%) in a micro reaction vial at room temperature. The mixture was stirred for 1 h and the catalyst was removed using tweezers. The reaction mixture was then concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using hexane/ether (2:1) as eluent to give **2a** (152 mg) quantitatively. The recovered catalyst was washed with ether and was reused without further purification.

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[13] The oxidation of organosilanes with water by using a different type of nanostructured materials will be reported in due course.