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Gold Catalysis

Highly Efficient Dehydrogenative Coupling of Hydrosilanes with Amines or Amides Using Supported Gold Nanoparticles

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Abstract: Hydroxyapatite-supported gold nanoparticles (Au/HAP) can act as a highly active and reusable catalyst for the coupling of hydrosilanes with amines under mild conditions. Various silylamines can be selectively obtained from diverse combinations of equimolar amounts of hydrosilanes with amines including less reactive bulky hydrosilanes. This study also highlights the applicability of Au/HAP to the selective synthesis of silylamides through the coupling of hydrosilanes with amides, demonstrating the first example of an efficient heterogeneous catalyst. Moreover, Au/HAP shows high reusability and applicability for gram-scale synthesis.

Si–N bond-containing compounds, such as silylamines and silylamides, are important materials for silylation reagents, ligands, and valuable building blocks of silicone polymers.[1] Conventionally, silylamines or silylamides have been synthesized through stoichiometric reactions of chlorosilanes with amines or amides in the presence of bases.[1d] However, chlorosilanes are toxic and unstable in air moisture, and a large amount of the HCl salt is formed as the by-product, which restricts the applicability of these transformations. In this context, the cross-coupling reaction of hydrosilanes with amines or amides is an alternative and attractive synthetic method of silylamines or silylamides. The easy-handling and availability of hydrosilanes under neutral conditions enable efficient synthesis of diverse Si–N bond-containing compounds to produce H_2 as the sole co-product. To date, several catalysts for the cross-coupling reaction of hydrosilanes with amines have been developed and some improvements have been made in catalytic performance.[2] However, these catalysts still have suffered from problems in low activities,[2b–d,h–j,m] limitations of substrate applicability[2a–l] and necessity of excess amounts of hydrosilanes or amines for the high-yielding coupling. With regard to the coupling reaction of hydrosilanes with amides, only one catalytic method has been reported despite the utility of silylamides.[3] Furthermore, these above-reported methods are difficult to recover and reuse.[4] Therefore, it is evident that the development of an environmentally benign and highly efficient catalytic system for the selective coupling of hydrosilanes with amines or amides is still an important research target.

Recently, we first disclosed that hydroxyapatite-supported gold nanoparticles (Au/HAP) catalyzed the oxidation of hydrosilanes with water to the corresponding silanols associated with the formation of H_2.[5] This transformation method by using gold NPs has since been explored by other researchers with respect to size and shape of gold NPs.[6] The activity of Au/HAP for hydrosilanes was also applicable to the dehydrogenative coupling of hydrosilanes with alcohols[7] and the deoxygenation of amides, sulfoxides, and pyridine *N*-oxides by using hydrosilanes as reductants.[8]

In the course of our study on the interaction between gold nanoparticles and hydrosilanes, we herein demonstrate a green protocol for the selective coupling of hydrosilanes with amines or amides by using gold nanoparticle catalysts. Hydroxyapatite-supported gold nanoparticles with a mean diameter of 3.0 nm (Au/HAP) can act as an efficient heterogeneous catalyst for the selective coupling of various kinds of hydrosilanes with amines or amides.

This catalyst system requires only equimolar amounts of hydrosilanes and amines or amides to achieve high-yielding synthesis of the desired Si–N bond-containing compounds. The catalytic activity is significantly higher than the previously reported catalysts. Furthermore, the Au/HAP catalyst is recoverable and reusable while maintaining its high catalytic performance.

The synthesis of Au/HAP followed our previous report.[5] The characterization was performed by X-ray absorption fine structure and transmission electron microscope analyses. The highly dispersed gold nanoparticles with a mean diameter of 3.0 nm formed on the surface of HAP were confirmed.[9]

Various HAP-supported metal nanoparticles were synthesized, and the catalytic activities were investigated in the coupling reaction of an equimolar amount of dimethylphenylsilane (**1**) and *n*-butylamine (**2**) in THF solvent. Among the metal nanoparticles tested, Au/HAP exhibited the best activity to give *N*-(*n*-butyl)dimethylphenylsilylamine (**3**) in 99% yield accompanied by the generation of equimolar amounts of H_2 (Table 1, entry 1).[10] Ag/HAP and Pd/HAP were also active, but

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Table 1. Dehydrogenative coupling of **1** with **2** using various catalysts.[a]

$$\underset{\mathbf{1}}{PhMe_2SiH} + \underset{\mathbf{2}}{n\text{-}BuNH_2} \xrightarrow[\text{THF, Ar, 60 °C, 4 h}]{\text{catalyst}} \underset{\mathbf{3}}{PhMe_2SiNH(n\text{-}Bu)}$$

Entry	Catalyst	*d* [nm]	Conv. (yield) [%][b]
1	Au/HAP	3.0	99
2[c]	Au/HAP	3.0	99
3[d]	Au/HAP	3.0	99
4	Ag/HAP	5.4	54
5	Pd/HAP	3.2	48
6	Cu/HAP	4.0	0
7	Ru/HAP	2.4	0
8	Rh/HAP	3.3	0
9	Pt/HAP	4.8	0
10	Au/TiO_2	3.6	72
11	AuAl_2O_3	3.6	63
12	Au/SiO_2	2.2	29
13	Au/MgO	3.1	15
14	Au/HAP	5.7	83
15	Au/HAP	6.5	33

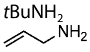
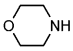
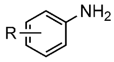
[a] Reaction conditions: Catalyst (metal: 0.83 mol%), **1** (1 mmol), **2** (1 mmol), THF (3 mL). [b] Determined by GC using an internal standard technique. [c] Reuse **1**. [d] Reuse **2**.

the yields of **3** were much lower than that obtained by Au/HAP (Table 1, entries 4 and 5). Other metal nanoparticles, such as Cu, Ru, Rh, and Pt, did not show any activities (Table 1, entries 6–9), revealing that gold nanoparticles had uniquely high catalytic activity. We then investigated the support effect of different kinds of inorganic materials to immobilize the gold nanoparticles, and found that HAP was an effective support compared to other supports, such as TiO_2, Al_2O_3, SiO_2, and MgO (Table 1, entries 1 vs. 10–13).[11] The size effect of gold nanoparticles was also studied by using Au/HAP having different gold-particle sizes, confirming that smaller gold nanoparticles provided higher catalytic activities (Table 1, entries 1 vs. 14 and 15).

With the optimized Au/HAP catalyst having a mean diameter of 3.0 nm in hand, the scope of hydrosilanes and amines was explored in this transformation. The results summarized in Table 2 demonstrate that Au/HAP showed broad applicability for diverse combinations of hydrosilanes with amines in an equimolar ratio of hydrosilanes to amines. Compound **1** was efficiently coupled with aliphatic (entries 1–6) and aromatic (entries 7–9) amines, providing the corresponding silylamines in high yields. Functionalized amines, such as allylamine (entry 3), morpholine (entry 4), and 4-bromoaniline (entry 8), were also tolerated. It is said that ammonia often causes low selectivity[12] and low yields[2i] of the corresponding monosilylamines due to the production of disilazane by-products and poisoning by strong coordination of ammonia to active metal species, respectively. In contrast, Au/HAP worked well, giving the monosilylamine in high yields (entries 6 and 13). The high-yielding coupling reaction of other tertiary hydrosilanes with **2** was also successful (entries 10–12 and 14). Although sterically hindered hydrosilanes, such as triethylsilane and benzyldimethylsilane, are known to be only slightly reactive,[2i] these were quantitatively coupled with **2** to afford the corresponding silylamines (entries 12 and 14).

Table 2. Dehydrogenative coupling of hydrosilanes with amines using Au/HAP.[a]

$$R^1R^2R^3SiH + R'R''NH \xrightarrow[\text{THF (3 mL), Ar}]{\text{Au/HAP (Au: 0.83 mol\%)}} R^1R^2R^3SiNR'R'' + H_2$$

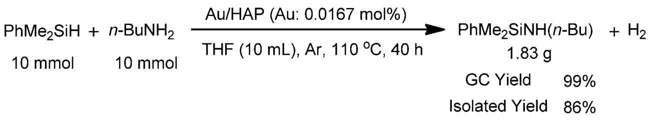
Entry	Hydrosilane	Amine	*T* [°C]	*t* [h]	Yield [%][b]
1	$PhMe_2SiH$	*n*-$BuNH_2$	60	4	99 (87)
2		*t*$BuNH_2$	100	10	96 (88)
3			60	3	99 (86)
4			60	8	99 (86)
5		Et_2NH	100	10	92 (83)
6		NH_3	100	1	(90)
7		R = H	40	1	99 (88)
8		4-Br	40	2	97 (82)
9		4-MeO	40	2	99 (88)
10	Ph_2MeSiH	*n*-$BuNH_2$	60	16	95 (87)
11[c]	Ph_3SiH	*n*-$BuNH_2$	100	20	96 (85)
12	Et_3SiH	*n*-$BuNH_2$	100	12	99 (86)
13		NH_3	100	20	(86)
14	$BnMe_2SiH$	*n*-$BuNH_2$	60	12	99 (83)
15	Ph_2SiH_2	*n*-$BuNH_2$	60	2	99 (84)
16		$PhNH_2$	25	0.5	99 (86)
17	$PhMeSiH_2$	*n*-$BuNH_2$	60	2	95 (84)
18		$PhNH_2$	25	1	89 (78)
19	*t*Bu_2SiH_2	*n*-$BuNH_2$	60	0.5	98 (88)
20		$PhNH_2$	25	1	99 (85)
21[d]	Ph_2SiH_2	$PhNH_2$	60	1	99[e]
22	Ph_2SiH_2	$PhNH_2$	60	1	0

[a] Reaction conditions: Au/HAP (Au: 0.83 mol%), hydrosilane (1 mmol), amine (1 mmol), THF (3 mL), Ar. [b] Determined by GC using an internal standard technique; values in parenthesis are the yield of the isolated products. [c] Au/HAP (Au: 1.6 mol%), hydrosilane (0.5 mmol), amine (0.5 mmol), THF (2 mL), Ar. [d] Aniline (2 mmol). [e] Yield of the monoaminosilane.

Selective synthesis of monoaminosilanes from hydrosilanes containing multiple Si–H bonds is a challenging issue due to the easy formation of the undesired silazane by-product. Notably, the present Au/HAP catalyst system was found to be useful for the synthesis of monoaminosilanes from dihydrosilanes. The selective coupling of dihydrosilanes with simple amines in an equimolar ratio successfully proceeded, giving the desired monoaminosilanes in excellent yields (entries 15–20). This result is in sharp contrast with previous reports, in which the delicate modulation of the ratio of silane/amine or use of bulky amines was required to achieve high selectivity of monoaminosilanes.[2d,i,k]

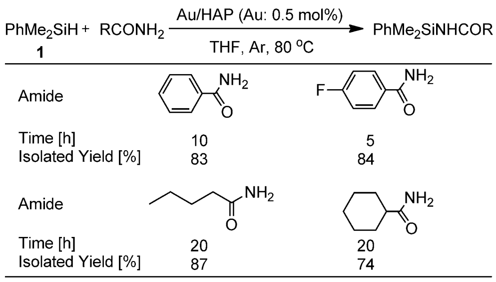
To elucidate the high selectivity toward monoaminosilanes, the following control experiments were investigated. 1) Monoaminohydrosilane was solely produced when using two equivalents of amine with hydrosilane (entry 21). 2) When the monoaminohydrosilane diphenylsilylaniline was employed as a starting material, no reaction occurred, and diphenylsilylaniline was quantitatively recovered (entry 22). These results clearly demonstrated that the reason for the high selectivity is due to no reactivity of the monoaminohydrosilanes under our reaction conditions.

We also checked the possibility of the participation of homogeneous gold species leaching from Au/HAP. The coupling processes were abruptly and completely terminated by the removal of Au/HAP from the reaction mixtures by filtration, and no leaching of gold species could be detected by inductively coupled plasma (ICP) analysis of the filtrate, thus proving that the observed catalysis of Au/HAP was intrinsically heterogeneous. In addition, Au/HAP showed excellent reusability in the recycling experiments (Table 1, entries 2 and 3). Furthermore, the practical applicability of Au/HAP for the gram-scale synthesis of silylamines was demonstrated in the coupling of **1** with **2** (Scheme 1). The transformation proceeded efficiently, giving 1.83 g of the silylamine (86 % isolated yield), in which the turnover number reached 5180. This value is the best among reported catalysts.[13]



Scheme 1. Gram-scale synthesis of silylamine.

Next, the catalytic potential of Au/HAP to the selective synthesis of silylamides was investigated in the coupling of **1** with several amides. The results exemplified in Scheme 2 revealed that Au/HAP showed high efficiency in this transformation. The activity of Au/HAP was 15-fold higher than that of the reported homogeneous Ni catalyst, demonstrating the first example of a highly active heterogeneous catalyst.[3]



Scheme 2. Dehydrogenative coupling of **1** with amides using Au/HAP. Reaction conditions: Au/HAP (0.3 g, Au: 0.5 mol %), hydrosilane (5 mmol), amide (5 mmol), and THF (15 mL).

To gain insights into the catalytic features of Au/HAP in the coupling of hydrosilanes with amines, the dependency of reaction rates using **1** and **2** were investigated under Ar atmosphere at 60 °C.[9] The initial rate was proportional to the amount of **1** and independent of the concentration of **2**. When using $PhMe_2SiD$, a kinetic isotope effect (kH/kD = 1.5) and generation of HD were observed, suggesting that the rate-determining step is the activation step of the Si–H bond of **1** by Au nanoparticles. In a separate experiment, the treatment of an equimolar mixture of $PhMe_2SiD$ and n-Bu_3SiH in the presence of Au/HAP in THF under Ar at 60 °C provided HD-scrambled $PhMe_2SiH$ and n-Bu_3SiD, clearly showing that Si–H cleavage occurred on the gold nanoparticles.[14] The activation of the Si–H bond of **1** by gold nanoparticles was also confirmed by a Fourier transform infrared study.[15] From these results, the coupling reaction may occur as follows. First, a cleavage of Si–H bond of a hydrosilane adsorbed on Au/HAP by a gold atom occurs. Next, nucleophilic attack of an amine to the electrophilic Si atom bound on the gold atom gives the corresponding silylamine together with generation of H_2.

In conclusion, we disclosed that hydroxyapatite-supported gold nanoparticles act as a highly efficient catalyst for the selective coupling of hydrosilanes with amines or amides. A wide range of silylamines and silylamides can be obtained in good to excellent yields, in which only an equimolar ratio of hydrosilanes to amines or amides could be utilized. This catalyst system provides a simple, efficient, and sustainable protocol for the synthesis of various silylamines and silylamides.

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Keywords: amides · amines · coupling · gold · nanoparticles · silanes

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[9] See the Supporting Information for detailed results.

[10] In Table 1, no by-products other than H_2 were observed.

[11] Prominent catalytic activity of Au/HAP may be due to the strong adsorption ability of the HAP support for hydrosilanes. The highly condensed hydrosilanes on the HAP surface efficiently interact with active sites on gold nanoparticles, leading to the high catalytic activity of Au/HAP; see Ref. [7].

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[13] Pd/C (TON = 174) [**2a**], $[(Et_2N)_3U][BPh_4]$ (118) [**2f**], tethered ruthenium complex (100) [**2l**], $Ru_3(CO)_{12}$ (100) [**2j**], $[Cp(i\text{Pr}_3P)Ru(NCMe)_2]^+BAF$ (33) [**2h**], $[Yb(\eta^2\text{-}Ph_2CNAr)(hmpa)_4]$ (33) [**2e**], $[areneCr(CO)_2(\eta^2\text{-}HsiHPh_2)]$ (20) [**2c**], $[(NHC)Yb(SiMe_3)_2]$ (20) [**2k**], $To^MMg\text{–}NR_2$ (20) [**2i**], $[M\{N(SiMe_3)_2\}_2]_2$ (20) [**2m**] and CuCl (15) [**2d**].

[14] No formation of the HD-scrambled hydrosilanes was confirmed in the absence of Au/HAP; see the Supporting Information for detailed results.

[15] We previously reported that the redshift of an absorption band assigned to a Si–H bond stretching vibration of **1** occurred after the treatment of **1** with Au/HAP, indicating the activation of the Si–H bond of **1** by gold nanoparticles; see Ref. [7].

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