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Selective hydrosilylation of alkynes with a nanoporous gold catalyst†

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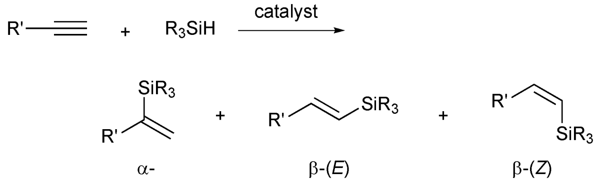
The hydrosilylation of acetylenic compounds proceeded smoothly in the presence of a reusable nanoporous gold catalyst under mild conditions and the β-(*E*)-*cis*-addition products were obtained in good to high yields regio- and stereoselectively.

Introduction

The hydrosilylation of acetylenic compounds is a powerful synthetic method for vinylsilane compounds,[1] which are synthetically versatile organosilicon reagents in organic synthesis.[2] Since three isomeric products, α-, β-(*E*)-, and β-(*Z*)-isomers, can possibly be formed with terminal alkynes (Scheme 1), the control of regio- and stereoselectivity in this process is highly desirable for selective preparation of these vinylsilane compounds. Generally, the selectivity is mainly affected by the nature of catalysts, alkynes, hydrosilanes, and reaction conditions. We have previously reported the selective *trans*-hydrosilylation with Lewis acid catalysts, such as $AlCl_3$ and $EtAlCl_2$, leading to the β-(*Z*)-product exclusively.[3] On the other hand, most of the reactions with homogeneous and heterogeneous transition metal catalysts, such as Pt, Co, Ni, and Pd, proceed in a *cis*-fashion stereoselectively.[4] But they often gave low regioselectivity between α- and β-(*E*)-products. We are particularly focusing on the development of heterogeneous green catalysis because a heterogeneous catalytic system has many advantages compared to the homogeneous one, such as easy separation of catalysts from the reaction mixture, easy recycling, and enhanced stability.[5,6] Recently, supported-gold nanoparticles have emerged as efficient catalysts with considerable synthetic potential for many types of molecular transformations.[7] The hydrosilylation also proceeded with these catalysts, but they often have some drawbacks, such as formation of side-products, low substrate generality, and low selectivity.[8] A thin gold film on the surface of glass capillaries also exhibits the activity for this reaction in a continuous-flow reactor, for which cumbersome microwave irradiation is necessary.[9] Recently, we were successful in using a monolithic nanoporous gold material (AuNPore) as an effective unsupported catalyst for some molecular transformations.[10,11] In this communication, we report that the AuNPore, fabricated from an Au–Al alloy, is an effective green catalyst for hydrosilylation of terminal alkynes, leading to β-(*E*)-products with high regio- and stereoselectivities.[12]



Scheme 1 Hydrosilylation of alkynes giving three possible isomeric vinylsilane compounds.

Results and discussion

The requisite nanoporous gold materials were fabricated from two kinds of alloys, AuAl and AuAg. The selective removal of aluminum from an $Au_{20}Al_{80}$ alloy ribbon was conducted with 20% NaOH to obtain AuNPore-1.[13] On the other hand, the silver from a $Au_{30}Ag_{70}$ alloy thin film was dissolved in 70% HNO_3 (AuNPore-2).[14] The scanning electron microscopy (SEM) study revealed that both materials exhibited an open bicontinuous interpenetrating ligament-channel structure with a length scale of 10–30 nm. The energy dispersive X-ray (EDX) spectra showed that small amounts of less noble metals, aluminum (4 at%) and silver (2 at%), remained, respectively.

The hydrosilylation of phenylacetylene **1a** with triethylsilane **2a** was carried out with these catalysts and the results are

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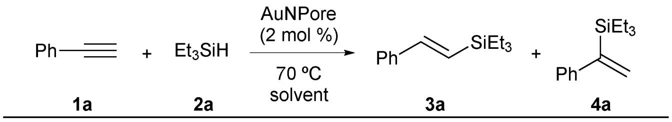
Table 1 Hydrosilylation of phenylacetylene with Et_3SiH with a AuNPore catalyst[a]



Entry	Solvent	Time (h)	Yield[b] (%) 3a	Yield[b] (%) 4a
1	AcOEt	1	74	1
2[c]	AcOEt	1	21	2
3[d]	AcOEt	1	50	1
4	Dioxane	1	66	1
5	CH_3CN	1	55	1
6	$(CH_2Cl)_2$	1	48	1
7	Toluene	1	43	1
8	AcOEt	3	98	1

[a] Reactions were carried out with **1a** (1 mmol) and **2a** (1.5 mmol) in the presence of 2 mol% of AuNPore-1 catalyst at 70 °C. [b] Determined by ^1H NMR analysis with *p*-xylene as an internal standard. [c] Reaction was conducted with AuNPore-2 derived from an AuAg alloy. [d] Reaction was conducted in the presence of 10 mol% of BHT.

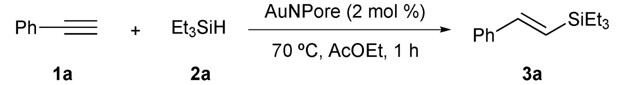
summarized in Table 1. The reaction proceeded smoothly with a catalytic amount of AuNPore-1, derived from the AuAl alloy, at 70 °C for 1 h, and gave the β-(*E*)-product **3a** in 74% yield selectively and small amounts of α-isomer **4a** was produced (1%, entry 1). In contrast, the chemical yield of **3a** dramatically decreased to 21% when AuNPore-2 was used, which was fabricated from the AuAg alloy (entry 2). The reaction proceeded even in the presence of 10 mol% of BHT as a radical inhibitor and **3a** was obtained in 50% yield (entry 3). This result suggested that the reaction is not likely to proceed through the radical mechanism. Besides AcOEt, 1,4-dioxane and CH_3CN are suitable solvents for this reaction (entries 4 and 5), but less polar solvents, such as $(CH_2Cl)_2$ and toluene, were less effective (entries 6 and 7). Finally, optimization experiments revealed that the chemical yield of **3a** increased up to 98% when the reaction was conducted in AcOEt for 3 h (entry 8).

Further studies were conducted focusing on the difference in the catalytic activity between AuNPore-1 and 2. The specific surface area (SSA) was electrochemically measured and the catalytic turnover frequencies (TOFs, number of converted molecules per surface site and hour) are shown in Table 2. Obviously, AuNPore-1 has a higher TOF than AuNPore-2 (entries 1 and 2). One might think that the fabrication process of AuNPore-2 with HNO_3 would deactivate the materials. However, the catalytic activity of AuNPore-1 did not change upon treatment with 70% HNO_3 although the surface area of the resulting AuNPore-3 slightly decreased as reported previously (entry 3).[15] These results suggested that two plausible synergistic effects generated by the residual metals should be considered. One is the activation effect by aluminum, and the other is the deactivation effect by silver.

Then, we next fabricated a new nanoporous gold catalyst, including both Al and Ag, from the $Au_{19}Ag_1Al_{80}$ alloy ribbon. The chemical etching was carried out with 20% NaOH for the selective removal of aluminum to obtain $Au_{93}Ag_3Al_4$ (AuNPore-4). We found that the catalytic activity of AuNPore-4 was quite low and **3a** was produced in only 2% yield (entry 4). In comparison with the activity of AuNPore-1 in entry 1, this result revealed that the residual silver has the inhibition effect in this process. Indeed, after immersion of AuNPore-4 in HNO_3, the resulting AuNPore-5, having a lower amount of silver, exhibited comparable catalytic activity with that of AuNPore-2 (entries 2 and 5). At the same time, this result also indicated that aluminum had no special activation effect on this reaction. As a blank test, the reaction was conducted with Au powder, the average diameter of particles of which is 3 μm, but it was ineffective (entry 6).

The substrate generality was examined and the results are summarized in Table 3. In every case, the reactions gave the desired products **3** in high yields together with less than 3% of **4**. Compared to the phenylacetylene **1a** (entry 1), *p*-fluorophenylacetylene **1b** was more reactive and **3b** was obtained in 97% yield in 2 h (entry 2). On the other hand, the reaction of *p*-methoxy-phenylacetylene **1c** needed longer reaction times (entry 3). These results clearly showed that electron-withdrawing

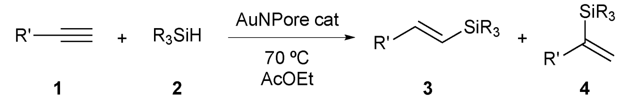
Table 2 Catalytic activity of AuNPores in the hydrosilylation[a]



Entry	Catalyst	Composition	SSA ($m^2\ g^{-1}$)	Yield[b,c] (%)	TOF (h^{-1})
1	AuNPore-1	$Au_{96}Al_4$	10.5	74	757
2	AuNPore-2	$Au_{98}Ag_2$	12.0	21	189
3	AuNPore-3	$Au_{98}Al_2$	8.4	62	789
4	AuNPore-4	$Au_{93}Ag_3Al_4$	11.3	2	19
5	AuNPore-5	$Au_{96}Ag_1Al_3$	8.3	16	207
6[d]	Au powder		0.1	1	22

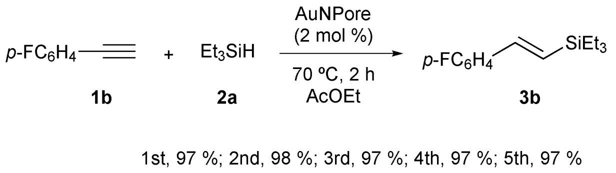
[a] Reactions were carried out with **1a** (1 mmol) and **2a** (1.5 mmol) in the presence of 2 mol% of AuNPore catalyst at 70 °C for 1 h unless otherwise noted. [b] Determined by ^1H NMR analysis with *p*-xylene as an internal standard. [c] α-Isomer **4a** was produced in less than 1% yield in each case. [d] Reaction was conducted with 2 mol% of Au powder at 70 °C for 2 d.

Table 3 AuNPore-catalyzed hydrosilylation with a variety of alkynes and hydrosilanes[a]



Entry	R′		R_3SiH		Cat (mol%)	Time (h)	Yield[b] (%) 3	Yield[b] (%) 4
1	C_6H_5	**1a**	Et_3SiH	**2a**	2	3	98	1
2	*p*-FC_6H_4	**1b**	Et_3SiH	**2a**	2	2	97	2
3	*p*-$MeOC_6H_4$	**1c**	Et_3SiH	**2a**	2	6	97	2
4	C_6H_{13}	**1d**	Et_3SiH	**2a**	2	3	99	2
5	$PhCH_2$	**1e**	Et_3SiH	**2a**	2	3	97	1
6	*c*-C_6H_{11}	**1f**	Et_3SiH	**2a**	2	3	97	1
7	C_6H_5	**1a**	$PhMe_2SiH$	**2b**	2	6	96	3
8	C_6H_5	**1a**	$(EtO)_3SiH$	**2c**	5	12	85	3
9	C_6H_5	**1a**	Bu_3SiH	**2d**	10	12	98	2
10	C_6H_5	**1a**	$(i\text{-}Pr)_3SiH$	**2e**	20	18	80	2

[a] Reactions were carried out with **1** (1 mmol) and **2** (1.5 mmol) in the presence of AuNPore catalyst at 70 °C. [b] Determined by ^1H NMR analysis with *p*-xylene as an internal standard.



Scheme 2 Hydrosilylation with the recovered catalyst.

groups on the phenyl group promoted the present reaction. Not only aromatic alkynes but also aliphatic alkynes are suitable substrates (entries 4–6). Besides Et_3SiH **2a**, other hydrosilanes **2b–d** were available (entries 7–9). Even with sterically bulky $(i\text{-}Pr)_3SiH$ **2e**, the reaction proceeded to give the corresponding vinylsilane **3j** in 80% yield although increased loading amounts of catalyst and longer reaction time were required (entry 10).

The catalyst can be recovered easily by tweezers and any cumbersome separation procedures, such as filtration and centrifugation, are not required. We conducted the reaction of **1b** several times with the recovered catalyst, but no significant loss of the catalytic activity was observed even after 5 times (Scheme 2). The SEM image of the recovered catalyst after five uses has no differences compared to that of the fresh one and these results clearly demonstrate that the catalyst has high reusability and stability due to its robust nanoporous structure.

We next investigated the leaching test. The hydrosilylation of triethylsilane **2a** to phenylacetylene **1a** was carried out for 15 min under the standard conditions, and **3a** was produced in 22% yield at this time. Then, the catalyst was removed from the reaction vessel. Even after stirring for 2 h in the absence of the catalyst, further generation of **3a** was not detected at all. The reaction restarted when the removed catalyst was put back into the mixture, and finally **3a** was obtained in 96% yield. Furthermore, leaching of the gold into the reaction mixture was not detected by inductively coupled plasma (ICP) analysis (<1 ppm). These results clearly indicated that the current transformation was really heterogeneous.

Conclusions

In conclusion, we have disclosed that the AuNPore exhibited a remarkable catalytic activity in the hydrosilylation of alkynes as a non-supported nanostructured catalyst. The reaction does not need any additives, such as bases, stabilizers, and ligands, as well as any cumbersome work-up procedures like filtration or centrifugation. Further applications of the AuNPore catalyst in other transformations are currently under investigation in our laboratory.

Acknowledgements

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