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Heterogeneous Catalysis

Heterogeneously Catalyzed Aerobic Cross-Dehydrogenative Coupling of Terminal Alkynes and Monohydrosilanes by Gold Supported on OMS-2**

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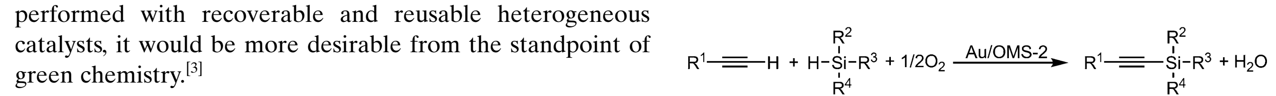
Alkynylsilane derivatives are an important class of compounds and have been used not only as versatile alkynyl nucleophiles for common organic synthesis but also as silicon-protected intermediates for olygo-yne polymers, silylene–acetylene copolymers, and acetylene-bridged organometallic complexes.[1] Up to the present, the vast majority have commonly used metal–acetylides and halosilanes (or pseudohalosilanes) for synthesis of alkynylsilanes; that is, silylation has been performed by pre-functionalization of terminal alkynes with alkyl lithium or Grignard reagents to form metal–acetylide species, followed by coupling with halosilanes.[2] However, this antiquated silylation has shortcomings of 1) multi-step procedures with stoichiometric reagents, 2) inevitable formation of large amounts of byproducts during the pre-functionalization step as well as the coupling, and 3) use of toxic halosilanes and moisture-sensitive reagents. Thus, the development of efficient catalytic procedures instead of the above-mentioned stoichiometric ones, that is, the direct use of terminal alkynes without pre-activation and the replacement of halosilanes with hydrosilanes, is an important subject. If the coupling could be performed with recoverable and reusable heterogeneous catalysts, it would be more desirable from the standpoint of green chemistry.[3]

Metal-catalyzed cross-dehydrogenative coupling represents the next generation of cross-coupling and is now emerging as an important reaction in organic synthesis.[4] Cross-dehydrogenative coupling can construct C−C, C−X, and X−X bonds (X = heteroatoms) through direct activation of C−H and/or X−H bonds, which can avoid pre-functionalization of substrates and formation of vast amounts of byproducts.[4] With regard to cross-dehydrogenative coupling of terminal alkynes and hydrosilanes, to date there have been several homogeneously catalyzed procedures using metal salts and complexes such as H_2PtCl_6/I_2,[5a] CuCl/TMEDA (TMEDA = *N*,*N*,*N*′,*N*′-tetraethylenediamine),[5b] M(η^2-Ph_2CNPh)$(hmpa)_3$ (M = Yb[5c] or Ca,[5d] hmpa = hexamethylphosphoramide), $LiAlH_4$,[5e] and $Zn(OTf)_2$/pyridine (Tf = SO_2CF_3).[5f] These procedures typically require additives to attain high yields of desired alkynylsilanes, and the recovery and reuse of the catalysts are very difficult.[5] Although MgO[6a] and KNH_2/Al_2O_3[6b] can catalyze the cross-dehydrogenative coupling, the scope of both terminal alkynes and hydrosilanes is quite limited; for example, the reaction of ethynylbenzene hardly proceeds with KNH_2/Al_2O_3.[6b] Therefore, efficient catalytic systems with widely usable and reusable heterogeneous catalysts have never been reported to date, to the best of our knowledge.

Herein, we demonstrate for the first time that gold supported on a cryptomelane-type manganese oxide-based octahedral molecular sieve OMS-2[7] (Au/OMS-2, average particle size of gold: 4.5 nm, Figure S1, see the Supporting Information for the preparation) can act as an efficient reusable heterogeneous catalyst for cross-dehydrogenative coupling of terminal alkynes and monohydrosilanes using O_2 as a terminal oxidant [Eq. (1)]. Various kinds of structurally diverse terminal alkynes (including acetylene) and monohydrosilanes can be applied to the present coupling, affording the corresponding alkynylsilanes in moderate to high yields.



$$R^1{-}{\equiv}{-}H + H{-}\underset{R^4}{\overset{R^2}{Si}}{-}R^3 + 1/2O_2 \xrightarrow{Au/OMS\text{-}2} R^1{-}{\equiv}{-}\underset{R^4}{\overset{R^2}{Si}}{-}R^3 + H_2O \quad (1)$$

Initially, the cross-dehydrogenative coupling of ethynylbenzene (**1a**) and triethylsilane (**2a**, 1.1 equivalents with respect to **1a**) was carried out in the presence of catalytic amounts of various kinds of supported metal catalysts (e.g., gold, palladium, platinum, ruthenium, rhodium, and copper, approximately 2 mol% with respect to **1a**; Table S1). The reaction was performed at 80 °C under 1 atm of O_2 with slow addition of **2a** (see the Experimental Section in the Supporting Information). Under the present conditions, the reaction did not proceed at all in the absence of the catalysts or the presence of OMS-2 alone. Only the gold catalyst gave the desired alkynylsilane, triethyl(phenylethynyl)silane (**3aa**). No reaction proceeded in the presence of platinum, ruthenium, and rhodium catalysts. When using the copper catalyst, only the alkyne–alkyne homocoupling product of 1,4-diphenylbutadiyne was obtained.[8] Among catalyst supports examined, OMS-2 showed the highest selectivity to **3aa** (Table S2, see the latter part). Thus, gold supported on OMS-2 (Au/OMS-2) was the best catalyst; for example, when the cross-dehydrogenative coupling was carried out under the conditions

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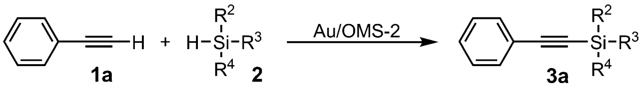
described in Table S2 with Au/OMS-2, **3aa** was obtained in 93 % yield with small amounts of a mixture of hydrosilylation products (mainly the *E* isomer).

To verify whether the observed catalysis is derived from solid Au/OMS-2 or leached metal species (gold and/or manganese), the cross-dehydrogenative coupling of **1a** and **2a** was carried out, and Au/OMS-2 was removed from the reaction mixture by hot filtration at about 25 % conversion of **1a**. Then, the filtrate was again heated at 80 °C in 1 atm of O_2 with slow addition of **2a**. In this case, no further production of **3aa** was observed (Figure S2). It was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis that no gold and manganese species were detected in the filtrate (Au: below 0.001 %, Mn: below 0.003 %). These results can rule out any contribution to the observed catalysis from metal species that leached into the reaction solution, and the observed catalysis for the present cross-dehydrogenative coupling is truly heterogeneous.[9]

After the cross-dehydrogenative coupling was completed, Au/OMS-2 was easily retrieved from the reaction mixture by simple filtration with > 95 % recovery. The retrieved catalyst could be reused at least ten times for the cross-dehydrogenative coupling of **1a** and **2a**; even for the tenth reuse experiment, 80 % yield of **3aa** was still obtained, although the selectivities to **3aa** were gradually decreased by repeating reuse experiments (Figure S3).[10]

Various kinds of monohydrosilanes could be used for the present Au/OMS-2-catalyzed cross-dehydrogenative coupling (Table 1).[11] The reaction with dimethylphenylsilane (**2b**) afforded the corresponding alkynylsilane in a high yield. Triisopropylsilyl (TIPS), *tert*-butyldimethylsilyl (TBDMS), *tert*-butyldiphenylsilyl (TBDPS) groups are very useful protecting groups for many organic syntheses because of their high stabilities under acidic and basic conditions. By using **2c**–**2e**, TIPS-, TBDMS-, and TBDPS-protected alkynes could be synthesized in high yields. In these cases, no slow addition of monohydrosilanes was required. Notably, an alkoxysilyl-substituted alkyne could be obtained by the cross-dehydrogenative coupling of **1a** and **2f**.

Table 1: Cross-dehydrogenative coupling of **1a** and various monohydrosilanes.[a]

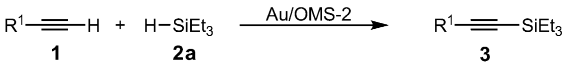


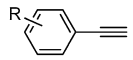
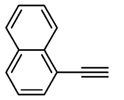
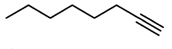
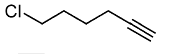
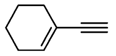
Entry	Monohydrosilane		Method	Yield [%][b]		
				3a		Others
1	Et_3Si–H	(**2a**)	A	93	(91)	6
2	$PhMe_2Si$–H	(**2b**)	A	88		11
3	*i*Pr_3Si–H	(**2c**)	B	87	(85)	12
4	*t*$BuMe_2Si$–H	(**2d**)	B	92		8
5	*t*$BuPh_2Si$–H	(**2e**)	B	91	(90)	9
6[c]	$(EtO)_3Si$–H	(**2f**)	A	74		11

[a] Method A: Into a Pyrex glass reactor were successively placed Au/OMS-2 (1.9 mol%, 40 mg), **1a** (0.5 mmol), and toluene (1 mL), and then a toluene solution of **2** (0.55 M, 1 mL) was added to the reaction mixture over 1 h by a syringe pump at 80 °C under 1 atm of O_2. Method B: Into a Pyrex glass reactor were successively placed Au/OMS-2 (1.9 mol%, 40 mg), **1a** (0.5 mmol), **2** (0.55 mmol), and toluene (2 mL) in a single step, and then the mixture was heated at 100 °C for 2 h under 1 atm of O_2. [b] Yields were based on **1a** and determined by GC analysis. The hydrosilylation was a major side reaction. Values in the parentheses were the isolated yields. [c] Au/OMS-2 (3.8 mol%, 80 mg), a toluene solution of **2f** (0.75 M, 1 mL) was added over 4 h.

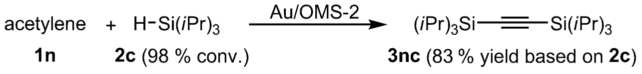
Next, the cross-dehydrogenative coupling of various terminal alkynes and **2a** was carried out (Table 2). Ethynylbenzene derivatives (**1a**–**i**) with electron-donating as well as electron-withdrawing substituents on different positions were all good coupling partners for **2a**. Reactions of 2-, 3-, and 4-ethynyltoluenes (**1b**–**d**) well proceeded, and the yields were almost equal, suggesting that a steric effect of substituents on aromatic rings is negligible. In the case of halo-substituted aromatic alkynes (**1e** and **1f**), the desired alkynylsilanes were obtained in high yields without dehalogenation. Thus, it would be possible to use these halo-functionalities for further modification of the alkynylsilane molecules (in particular the alkynylsilane from **1f**). The reaction of 1-ethynylnaphthalene (**1j**) also efficiently proceeded. Not only aromatic alkynes but also aliphatic ones (**1k** and **1l**) could act as good coupling partners for **2a**. The reaction of an enyne (**1m**) and **2a** also

Table 2: Cross-dehydrogenative coupling of various terminal alkynes and **2a**.[a]



Entry	Alkyne			Yield [%][b]		
				3		Others
1		R = H	(**1a**)	93	(91)	6
2		R = 2-Me	(**1b**)	90		9
3		R = 3-Me	(**1c**)	86		13
4		R = 4-Me	(**1d**)	95	(92)	5
5		R = 4-F	(**1e**)	94	(90)	6
6		R = 4-Br	(**1f**)	81	(77)	19
7		R = 4-CF_3	(**1g**)	90	(83)	9
8[c]		R = 4-NO_2	(**1h**)	85	(80)	14
9[c]		R = 4-NH_2	(**1i**)	54	(51)	33[d]
10			(**1j**)	85	(78)	14
11			(**1k**)	98		1
12			(**1l**)	95	(89)	4
13			(**1m**)	58		35

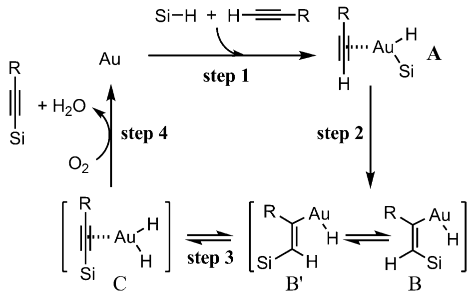
[a] Reaction conditions: Into a Pyrex glass reactor were successively placed Au/OMS-2 (1.9 mol%, 40 mg), **1** (0.5 mmol), and toluene (1 mL), and then a toluene solution of **2a** (0.55 M, 1 mL) was added to the reaction mixture over 1 h by a syringe pump at 80 °C under 1 atm of O_2. [b] Yields were based on **1** and determined by GC analysis. Values in parentheses were the isolated yields. The hydrosilylation was a major side reaction. [c] Reaction conditions: Into a Pyrex glass reactor were successively placed Au/OMS-2 (1.9 mol%, 40 mg), **1** (0.5 mmol), **2a** (0.75 mmol), and toluene (2 mL) in a single step, and then the mixture was heated at 100 °C under 1 atm of O_2. 2 h for entry 8, 12 h for entry 9. [d] The *N*-silylation of the alkynylsilane product was also proceeded (13 %).



Scheme 1. Cross-dehydrogenative coupling of acetylene (**1n**) and **2c**. Into a Pyrex glass reactor were successively placed Au/OMS-2 (1.9 mol%, 20 mg), **2c** (0.25 mmol), and toluene (1 mL) in a single step, and then the mixture was heated at 80°C for 7 h in 1 atm of acetylene/air (ca. 20 mL/50 mL). The monosilylated (4%) and hydrosilylation (7%) products were also formed.

proceeded to give the corresponding alkynylsilane in a moderate yield. Notably, the present system could be applied to acetylene (gaseous), giving the corresponding disilylated product in 83% yield (Scheme 1).

The reaction of **1a** and **2a** under 1 atm of Ar (instead of O_2) mainly gave the hydrosilylation products (87% total yield) with a small amount of **3aa** (7% yield; Table S2, entry 2).[12] This result suggests that the formation of gold–alkenyl species (species B and B′ in Scheme 2) is involved in the present cross-dehydrogenative coupling and that O_2 plays a crucial role to attain high yields of the desired alkynylsilanes (step 4 in Scheme 2). The H/D-exchange reaction of monodeuterated ethynylbenzene (**1a′**) hardly proceeded with Au/OMS-2, suggesting that a gold–acetylide species is not involved in the present catalytic cycle.[13,14] When the reaction of **2c** with **1a** or **1a′** was carried out at 80°C, a kinetic isotope effect (k_H/k_D) of 0.70 was observed. This inverse kinetic isotope effect (secondary isotope effect) suggests that the rehybridization step (sp→sp^2) is included in the rate-limiting step (step 2 in Scheme 2).



Scheme 2. Possible reaction mechanism for the present Au/OMS-2-catalyzed cross-dehydrogenative coupling of terminal alkynes and monohydrosilanes (Si−H ≡ monohydrosilane, Au ≡ Au/OMS-2).

Here, we propose a possible reaction mechanism for the present Au/OMS-2-catalyzed cross-dehydrogenative coupling (Scheme 2). Initially, the Si−H bond of **2** is activated by Au/OMS-2, and then an electrophilic silicon species is possibly formed (step 1 in Scheme 2). We confirmed that Au/OMS-2 could also act as an efficient heterogeneous catalyst for hydrolytic oxidation of monohydrosilanes to the corresponding silanols (Figure S4). In this case, water acts as a nucleophile for electrophilically activated monohydrosilanes. Thus, this result also suggests the formation of an electrophilic silicon species on Au/OMS-2. Next, the electophilic attack of the silicon species to an alkyne proceeds in a common Markovnikov way to form a gold–alkenyl species B (and B′). (step 2 in Scheme 2). This is likely the rate-limiting step, as above-mentioned. Finally, the hydride elimination takes place to form a species C (step 3 in Scheme 2), followed by oxidation with O_2 to give the corresponding alkynylsilane and H_2O (step 4 in Scheme 2). In the absence of O_2, the gold–alkenyl species B and B′ give the hydrosilylation products (Table S2, entry 2).

In the presence of Au/Al$_2$O$_3$ (with a average particle size of gold similar to that of Au/OMS-2: 3.7 nm, Figure S5), the reaction of **1a** and **2a** showed a relatively lower selectivity to the desired **3aa** and gave a mixture of the cross-dehydrogenative coupling and the hydrosilylation products (1.9:1; Table S3).[15] The use of a physical mixture of Au/Al$_2$O$_3$ and OMS-2 significantly increased the cross-dehydrogenative coupling/hydrosilylation ratio from 1.9 to 14.8 (Table S3), suggesting that the oxidation of the species C (step 4 in Scheme 2) is efficiently promoted by the presence of OMS-2.

In summary, we have successfully developed an efficient heterogeneous catalytic system for aerobic cross-dehydrogenative coupling of terminal alkynes and monohydrosilanes. Various kinds of structurally diverse terminal alkynes and monohydrosilanes could be applied to the present cross-coupling, affording the corresponding alkynylsilanes in moderate to high yields (54–98% yields). In the present system, acetylene could be used. The observed catalysis was truly heterogeneous, and the catalyst could be reused without a significant loss of its high catalytic performance. This convenient procedure with Au/OMS-2 demonstrated herein will provide a new green route to alkynylsilanes, which can completely avoid use of stoichiometric reagents and formation of vast amounts of byproducts, and will be one of the choices for green alkynylsilane synthesis.

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Keywords: alkynylsilanes · cross-dehydrogenative coupling · gold · heterogeneous catalysis · terminal alkynes

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[10] The average particle size of gold was increased from 4.5 nm (fresh Au/OMS-2) to 8.7 nm after the tenth reuse experiment (Figure S1). The consumption rates of substrates in reuse experiments were almost the same as those of the reaction with the fresh catalyst. On the other hand, the selectivities to **3aa** were gradually decreased by repeating reuse experiments. When the eleventh reuse experiment was carried out with a mixture of the used Au/OMS-2 (average particle size of gold: 8.7 nm) and OMS-2, 89% yield of **3aa** was obtained (Figure S3). Thus, the decrease in the selectivities to **3aa** during the repeating reuse experiments is likely caused by the deactivation of OMS-2 (rather than an increase in the particle size of gold).

[11] We attempted the cross-dehydrogenative coupling of diphenylsilane (dihydrosilane) and phenylsilane (trihydrosilane). However, the desired alkynylsilanes were hardly obtained, and the corresponding siloxanes were mainly formed under the present conditions using Au/OMS-2.

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[13] The reaction of **1a**′ was performed as follows: Into a Pyrex glass reactor (volume: ca. 20 mL) were successively placed Au/OMS-2 (2.5 mol%), **1a**′ (0.48 mmol, deuterium content at the terminal position: 98%), $CDCl_3$ (1.5 mL), and a Teflon-coated magnetic stirring bar, and then the mixture was stirred at room temperature for 5 h. The ^1H NMR and GC-MS analyses of the solution showed that the H/D-exchange reaction of **1a**′ hardly proceeded with Au/OMS-2. We have reported that supported copper catalysts showed high catalytic activity for homocoupling of terminal alkynes[8] and 1,3-dipolar cycloaddition of terminal alkynes and azides.[14] It has been confirmed by UV/Vis analysis that copper–acetylide species are involved in these reactions. In the case of copper catalysts, the H/D-exchange reaction of **1a**′ proceeded under the above-mentioned conditions (e.g., the deuterium content in **1a**′ was decreased from 98% to 51% by the presence of a supported copper catalyst on Al_2O_3).[14]

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[15] It was confirmed that hydrosilylation and hydrogenation of alkynylsilanes hardly proceeded with supported gold catalysts under the present reaction conditions.