Cross-Coupling

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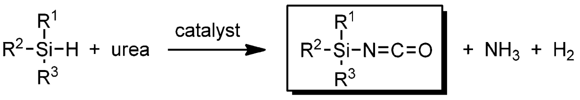
Heterogeneous-Gold-Catalyzed Acceptorless Cross-Dehydrogenative Coupling of Hydrosilanes and Isocyanic Acid Generated in situ from Urea**

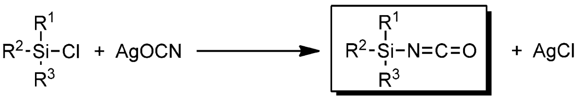
*Kento Taniguchi, Shintaro Itagaki, Kazuya Yamaguchi, and Noritaka Mizuno**

Cross-coupling reactions (e.g., Suzuki, Negishi, Heck, Stille, Kumada, and Buchwald-Hartwig reactions) are of paramount importance and have proven useful for the design of molecules.[1] Although cross-coupling reactions can precisely construct new C–C, C–X, and X–X bonds (X = heteroatom), they usually utilize preactivated substrates (e.g., halides, tosylates, and triflates) and require transmetalation steps, which concurrently generate at least stoichiometric amounts of metal salts as waste.[1] Recently, cross-dehydrogenative coupling reactions by direct activation of C–H or X–H bonds have been emerging as synthetic tools because they are more atom efficient and environmentally benign than classical cross-coupling reactions.[2] To date, several efficient cross-dehydrogenative coupling reactions using hydrogen acceptors (oxidants) such as *tert*-butyl hydroperoxide,[3] hydrogen peroxide,[4] and molecular oxygen[5] have been developed. Acceptorless cross-dehydrogenative coupling reactions have also been developed.[6] Quite recently, we have also reported C–N (terminal alkynes and amides),[7] P–N (*H*-phosphonates and amides),[8] Si–N (hydrosilanes and indoles),[9] and Si–C (hydrosilanes and terminal alkynes)[10] bond-forming reactions by cross-dehydrogenative coupling strategy. Herein, we successfully developed a novel green synthetic route to silyl isocyanates through heterogeneous-gold-catalyzed, acceptorless cross-dehydrogenative coupling of hydrosilanes and isocyanic acid (generated by in situ thermolysis of urea[11]) [Eq. (1)].



$$R^1R^2R^3Si\text{–}H + \text{urea} \xrightarrow{\text{catalyst}} \boxed{R^1R^2R^3Si\text{–}N{=}C{=}O} + NH_3 + H_2 \qquad (1)$$

Silyl isocyanates have been utilized as silane coupling and surface finishing agents,[12] and are potentially useful as carbamoyl synthons for organic synthesis.[12,13] Up to the present, the vast majority of silyl isocyanates have been synthesized using chlorosilanes and metal cyanates (e.g., silver cyanate) [Eq. (2)].[14]



$$R^1R^2R^3Si\text{–}Cl + AgOCN \longrightarrow \boxed{R^1R^2R^3Si\text{–}N{=}C{=}O} + AgCl \qquad (2)$$

However, toxic and moisture-sensitive chlorosilanes and expensive metal cyanates are required in this antiquated procedure. In addition, the atom efficiency is low because of the inevitable formation of stoichiometric amounts of metal salts as waste. For example, the atom efficiency of the reaction of dimethylphenylchlorosilane (R^1, $R^2 = CH_3$, $R^3 = Ph$) with silver cyanate to form dimethylphenylsilyl isocyanate is 55% [Eq. (2)]. Thus, the development of efficient catalytic synthetic procedures using alternative starting materials is very important for green silyl isocyanate synthesis. The use of hydrosilanes and urea as starting materials would be more desirable because 1) they are readily available, inexpensive, and less-toxic, 2) coproducts are NH_3 and H_2, and 3) the atom efficiency reaches up to 90% (for R^1, $R^2 = CH_3$, $R^3 = Ph$) [Eq. (1)].

To realize the reaction in Equation (1), hydrosilanes should electrophilically be activated with appropriate catalysts. With regard to activation of hydrosilanes, several hydrolytic oxidation systems using gold,[15] ruthenium,[16] rhenium,[17] platinum,[18] iridium,[19] and silver catalysts[20] have been reported where electrophilic silicon species are possibly generated. If the efficient synthetic procedures for silyl isocyanates using recoverable and reusable heterogeneous catalysts could be developed, they would be more desirable from the standpoint of green chemistry.[21]

Therefore, we initially prepared various kinds of supported metal catalysts (gold, silver, copper, ruthenium, rhodium, palladium, and platinum on Al_2O_3; see the Supporting Information for the preparation), and their catalytic performances were evaluated by the reaction of dimethylphenylsilane (**1a**) with urea (1.1 equivalents with respect to **1a**) to form dimethylphenylsilyl isocyanate (**2a**; Table 1). The reactions were carried out under reflux conditions in toluene using 0.2 mol% of catalyst with respect to **1a** (see also Table S1 in the Supporting Information).[22] The catalysts and urea were carefully dried before use for the transformation (to avoid the undesirable hydrolysis of urea and in situ formed isocyanic acid, see the Supporting Information). Under the present reaction conditions, the reaction did not proceed at all

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[*] K. Taniguchi, S. Itagaki, Dr. K. Yamaguchi, Prof. Dr. N. Mizuno
Department of Applied Chemistry, School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp

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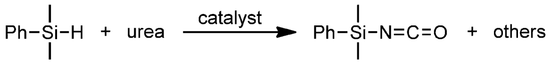
Table 1: Synthesis of dimethylphenylsilyl isocyanate (**2a**) by the reaction of dimethylphenylsilane (**1a**) with urea in the presence of various catalysts.[a]



1a **2a**

Entry	Catalyst	Conv. [%]	Yield [%] **2a**	Others[b]
1	Au/Al_2O_3	66	60	6
2[c]	Au/Al_2O_3	>99	91	9
3	Pd/Al_2O_3	54	48	6
4	Rh/Al_2O_3	5	4	1
5	Ag/Al_2O_3	4	4	<1
6	Pt/Al_2O_3	2	2	<1
7	Ru/Al_2O_3	<1	<1	<1
8	Cu/Al_2O_3	<1	<1	<1
9	Au/SiO_2	55	52	3
10	Au/TiO_2	47	45	2
11	Au/CeO_2	6	4	2
12[d]	$Au/CeO_2 + Al_2O_3$	53	46	7
13[d]	$Au/CeO_2 + SiO_2$	26	22	4
14[d]	$Au/CeO_2 + MgO$	12	3	9
15[d]	Al_2O_3	<1	<1	<1
16	None	<1	<1	<1

[a] Reaction conditions: Catalyst (metal: ca. 0.2 mol%), **1a** (0.5 mmol), urea (0.55 mmol), toluene (2 mL), reflux (bath temperature: 135 °C), Ar (1 atm), 1 h. Conversions and yields were determined by GC analyses. [b] Silanols, disiloxanes, and disilazanes were formed as byproducts (see also Table S1 in the Supporting Information). [c] 3 h. [d] Metal oxide additives (40 mg).

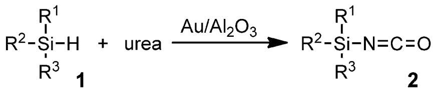
in the absence of the catalysts or the presence of Al_2O_3 alone (Table 1, entries 15 and 16). The supported gold catalyst was the most effective for the transformation among the catalysts examined (Table 1, entries 1 and 2), and the supported palladium catalyst also showed a good performance (Table 1, entry 3). The reaction hardly proceeded in the presence of supported rhodium, silver, platinum, ruthenium, and copper catalysts (Table 1, entries 4–8). Al_2O_3 was the best support (Table 1, entry 1), and SiO_2 and TiO_2 were also good supports for the transformation (Table 1, entries 9 and 10). In contrast, the reaction hardly proceeded with gold on relatively basic CeO_2 (Table 1, entry 11). Thus, gold supported on Al_2O_3, Au/Al_2O_3,[23] was the best catalyst. For example, when the reaction of **1a** with urea was carried out in the presence of Au/Al_2O_3 for 3 hours, the desired silyl isocyanate **2a** was obtained in 91 % yield (Table 1, entry 2).

To verify whether the observed catalysis is truly caused by solid Au/Al_2O_3 or leached gold species, the following control experiment was carried out. The reaction of **1a** with urea was carried out under the reaction conditions described in Table 1, and the Au/Al_2O_3 was removed from the reaction mixture by filtration; the yield of **2a** was 70 %. Urea (0.55 mmol) was then added to the filtrate, and the resulting mixture was again heated at 135 °C (bath temperature) under 1 atm of Ar. In this case, no further production of **2a** was observed (see Figure S1 in the Supporting Information). In addition, we confirmed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis that no gold species was detected in the filtrate (below the detection limit of 3.0 ppb). These results can rule out any contribution to the observed catalysis from gold species which leached into the reaction solution, and the observed catalysis for the present transformation is truly heterogeneous in nature.[24]

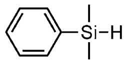
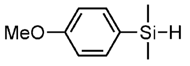
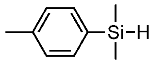
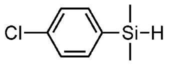
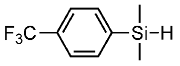
After the reaction of **1a** with urea was completed, Au/Al_2O_3 could easily be retrieved from the reaction mixture by simple filtration with greater than 95 % recovery. The retrieved Au/Al_2O_3 catalyst could be reused at least six times for the same reaction without significant loss of its high catalytic performance. Even for the sixth reuse experiment, 95 % yield of **2a** was still obtained (see Figure S2 in the Supporting Information), though the formation rate of **2a** for the sixth reuse experiment (2.2 mM min^{-1}, determined by the yield for 1 h) was somewhat smaller than that of the first run with fresh Au/Al_2O_3 (2.6 mM min^{-1}; Figure S3 in the Supporting Information).[23] The average turnover number (TON; TON = **2a** produced [mol]/Au used [mol]) for one run was 474, and the total TON reached up to 3320 after the sixth reuse experiment.

Next, the scope of the present Au/Al_2O_3-catalyzed synthesis of silyl isocyanates was examined. As shown in Table 2, various kinds of hydrosilanes could be converted into the corresponding silyl isocyanates. The reaction of dimethylphenylsilane (**1a**) and its derivatives with electron-donating (**1b** and **1c**) as well as electron-withdrawing (**1d** and **1e**) substituents at the *para*-position of the phenyl rings efficiently

Table 2: Scope of the present Au/Al_2O_3-catalyzed synthesis of silyl isocyanates.[a]



1 **2**

Entry	Hydrosilane		*t* [h]	Yield [%]
1		**1a**	3	91
2		**1b**	3	94
3		**1c**	3	91
4		**1d**	3	87
5		**1e**	3	97
6	Ph_2MeSi-H	**1f**	3	93
7	Ph_3Si-H	**1g**	4.5	97
8	Et_3Si-H	**1h**	6	99
9	$(nPr)_3Si$-H	**1i**	15	69
10	$(EtO)_3Si$-H	**1j**	9	56
11	$(nBuO)_3Si$-H	**1k**	24	43

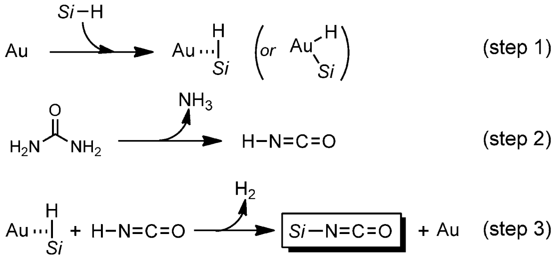
[a] Reaction conditions: Au/Al_2O_3 (Au: 0.2 mol%), hydrosilane (0.5 mmol), urea (0.55 mmol), [D_8]toluene (2 mL), reflux (bath temperature: 135 °C), Ar (1 atm), 1 h. Yields were determined by ^1H NMR and GC analyses. Conversions of **1a–h** were greater than 99 %. Conversions of **1i**, **1j**, and **1k** were 72 %, 87 %, and 65 % respectively. The major byproducts were the corresponding silanols, disiloxanes, and disilazanes. As for entry 10, tetraethoxysilane (23 %) was also formed as a byproduct. As for entry 11, tetra(*n*-butoxy)silane (18 %) was also formed as a byproduct.

proceeded to afford the corresponding substituted dimethylphenylsilyl isocyanate derivatives in high yields (Table 2, entries 1–5). The reactions of sterically more hindered diphenylmethylsilane (**1f**) and triphenylsilane (**1g**) also efficiently proceeded (Table 2, entries 6 and 7). Besides hydrosilanes having phenyl groups, trialkylsilanes (**1h** and **1i**) could be converted into the corresponding trialkylsilyl isocyanates, though the steric effect was significant (Table 2, entries 8 and 9). Notably, alkoxysilyl isocyanates could be obtained in moderate yields by the reaction of alkoxysilanes (**1j** and **1k**) with urea (Table 2, entries 10 and 11). In these cases, tetraalkoxysilanes were formed as by products.

We confirmed in separate experiments that Au/Al_2O_3 could also act as an efficient heterogeneous catalyst for hydrolytic oxidation of hydrosilanes, silylation of alkynes, and hydrosilylation of alkynes and ketones (see Figure S4 in the Supporting Information). It is well known that hydrolytic silane oxidation,[15–20] silylation,[6b,10] and hydrosilylation[25] proceed through formation of electrophilically activated hydrosilanes. Thus, in the present case, the formation of electrophilic silicon species on Au/Al_2O_3 is suggested. The MS analyses of the gas phase for the reaction of **1a** with urea showed formation of NH_3 and H_2 during the transformation. In the absence of **1a**, isocyanic acid and NH_3 were detected.[11]

As mentioned in Table 1, Au/CeO_2[26] showed lower catalytic performance than that of Au/Al_2O_3 (Table 1, entries 1 and 11). Interestingly, the use of a physical mixture of Au/CeO_2 and Al_2O_3 significantly increased the yield of **2a** from 4 % (Au/CeO_2 alone) to 46 % (Table 1, entry 12), thus suggesting that Al_2O_3 plays an important role in the present transformation. SiO_2 also promoted the reaction (Table 1, entry 13), while the effect of MgO (basic oxide) was almost negligible (Table 1, entry 14). It is known that the thermolysis of urea to isocyanic acid and NH_3 can be promoted by the presence of zeolites (e.g., H-Y, H-β, and H-ZSM-5) and that the acidic sites are the active sites for the thermolysis.[27,28]

Here, we propose a possible reaction mechanism for the present Au/Al_2O_3-catalyzed synthesis of silyl isocyanates (Scheme 1). The Si–H bond of a hydrosilane is activated by Au/Al_2O_3, and then an electrophilic silicon species is possibly formed (step 1). During the reaction, the thermolysis of urea also takes place to form isocyanic acid and NH_3, and is possibly promoted by acidic sites on Al_2O_3 (step 2).[27,28] Finally, the cross-dehydrogenative coupling reaction of the electrophilic silicon species and isocyanic acid (nucleophile) proceeds, thus giving the corresponding silyl isocyanate with the concurrent formation of H_2 (step 3) to complete the catalytic cycle.



Scheme 1. Possible reaction mechanism for the present Au/Al_2O_3-catalyzed synthesis of silyl isocyanates by the reaction of hydrosilanes with urea. *Si*-H ≡ hydrosilane, Au ≡ Au/Al_2O_3.

In summary, we have successfully developed for the first time an efficient heterogeneous catalytic system for synthesis of silyl isocyanates through acceptorless cross-dehydrogenative coupling of hydrosilanes and isocyanic acid obtained by the in situ thermolysis of urea. This novel synthetic procedure with the heterogeneous Au/Al_2O_3 catalyst could completely avoid utilization of stoichiometric reagents (e.g., metal cyanates) and formation of vast amounts of byproducts (e.g., metal halides).

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[11] It is well known that the thermolysis of urea produces equimolar amounts of isocyanic acid and NH_3 at temperatures from 133 °C to about 300 °C (see the following references). In the present system, the bath (reactor wall) temperature was set at 135 °C.

Thus, the thermolysis possibly proceeds. Indeed, urea decomposed to some extent under the standard reaction conditions even in the absence of hydrosilanes. Furthermore, we confirmed by the thermogravimetric and online MS (TG-MS) analysis of the evolved gas that the thermolysis of urea proceeded at 135 °C, thus giving isocyanic acid and NH_3 (see Figures S5 and S6 in the Supporting Information): a) M. U. Alzueta, R. Bilbao, A. Millera, M. Oliva, J. C. Ibanez, *Energy Fuels* **1998**, *12*, 1001; b) M. Koebel, M. Elsener, M. Kleemann, *Catal. Today* **2000**, *59*, 335.

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[22] The Au/Al_2O_3-catalyzed reaction of **1a** with urea efficiently proceeded even with one equivalent of urea (see Table S2 in the Supporting Information). Toluene and mesitylene were good solvents, while DMF, DMSO, and diglyme were poor solvents for the present transformation (see Table S3 in the Supporting Information). The reaction efficiently proceeded at temperatures over 120 °C, but hardly proceeded at temperatures below 100 °C (see Table S4 in the Supporting Information). When the reaction of **1a** was carried out without pretreatment of the catalysts (see the Supporting Information), the selectivity to **2a** decreased by about 10 % and is likely due to the hydrolytic decomposition of **2a** and/or isocyanic acid (see Table S5 in the Supporting Information).

[23] We confirmed by the TEM analysis that the average particle size of gold in the fresh Au/Al_2O_3 catalyst was 2.7 nm (standard deviation: 0.7 nm; Figure S7a in the Supporting Information). The average particle size increased up to 5.1 nm (standard deviation: 2.5 nm) after the fifth reuse experiment (Figure S7b).

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[26] We confirmed by the TEM analysis that the average particle size of gold in Au/CeO_2 was 4.6 nm (standard deviation: 1.3 nm).

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[28] We confirmed by the TG-MS analysis that Al_2O_3 could promote the thermolysis of urea; the rate of the thermolysis in the presence Al_2O_3 at 135 °C (estimated form the TG curve, Figure S6) was approximately three times larger than that in the absence of Al_2O_3. In contrast, in the case of MgO, the evolution of isocyanic acid was not observed because MgO likely promoted the condensation of urea to polymeric compounds such as biuret and cyanuric acid.