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Sulfur Modification of Au via Treatment with Piranha Solution Provides Low-Pd Releasing and Recyclable Pd Material, SAPd

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Research involving self-assembled monolayers (SAMs) of alkylthiols (RSH) on metal (especially gold) surfaces has rapidly expanded due to the potential applications of these materials, the ease of their preparation, and their facile connection between organic moieties and metal surfaces.[1−5] However, since studies on the thermal stability of SAMs are limited, and the role of the solvent in the formation of SAMs is not yet well understood, questions still remain concerning the mechanism of monolayer formation.[6,7] Prior to the emergence of SAMs, Piranha solution (**Danger!** A strong oxidizer.) had been traditionally used to clean gold surfaces.[5,8−12]

In an effort to create reusable, Pd-leach-free catalysts, many heterogeneous catalysts have been developed with Pd immobilized on supports such as activated carbon, inorganic solids, and polymers.[13,14] Yet few of these immobilized Pd catalysts for C−C bond formations can claim both high recyclability (>10 times) and low Pd-leaching (<1 ppm). People purify the product several times and sometimes they use commercially available Pd scavengers, which increase the cost.

In this report, we offer new insight into the treatment of Au with Piranha solution to induce sulfur modification. In addition, we show the application of this process to the development of novel Pd materials that exhibited both high recyclability and remarkably low Pd-leaching in the Suzuki−Miyaura coupling.

In the course of our research to develop an environmentally benign catalyst,[15] we unexpectedly found in an SR-HXPS (Synchrotron radiation hard X-ray photoelectron spectroscopy) analysis that Piranha treatment can place a sulfur atom on the gold surface. The sulfur is expected to be located under the $Pd(dba)_2$/Pd overlayers. The usual laboratory-XPS is disadvantageous in observing the underlying sulfur because of its short observation depth. SR-HXPS with the long observation depth up to 20 nm enables the high sensitivity detection of the underlying sulfur.[16] SR-HXPS measurements were performed at the beamline BL15XU in the synchrotron radiation facility SPring-8.[17] We measured the SR-HXPS spectrum of Piranha-treated Au(111)/mica and found, to our surprise, that the S 1s peak appeared near 2478 eV in the spectrum (Figure 1 Red line), although no S 1s peak was observed on Au(111)/mica before the Piranha treatment. These results indicated that the surface of Au(111)/mica had been modified by a sulfur species upon Piranha treatment. Although Piranha treatment has been frequently used to remove impurities from the gold surface,[5,8−12] our results show that this treatment could also be employed for sulfur modification of the gold surface. To the best of our knowledge, this is the first report that Piranha treatment attaches S atoms to the gold surface. Since the binding energy of the S 1s peak for Piranha-treated Au(111)/mica is close to that of Na_2SO_3,

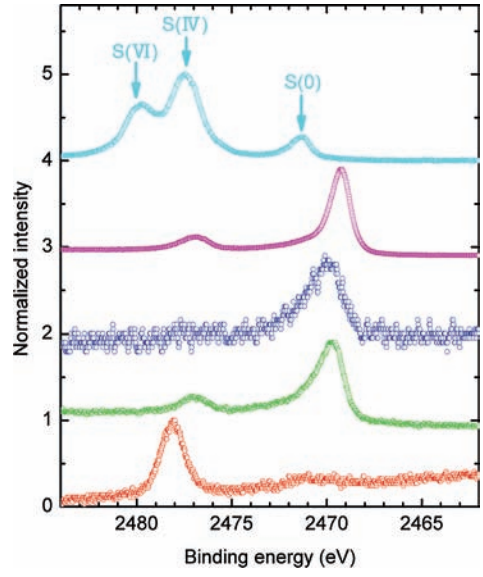

Figure 1. Sulfur 1s core-level photoemission spectra. Light blue, Na_2SO_3; Pink, PdS; Blue, **A** after 10 times of Suzuki−Miyaura coupling; Green, **A** before Suzuki−Miyaura coupling; Red, Piranha-treated Au(111)/mica.

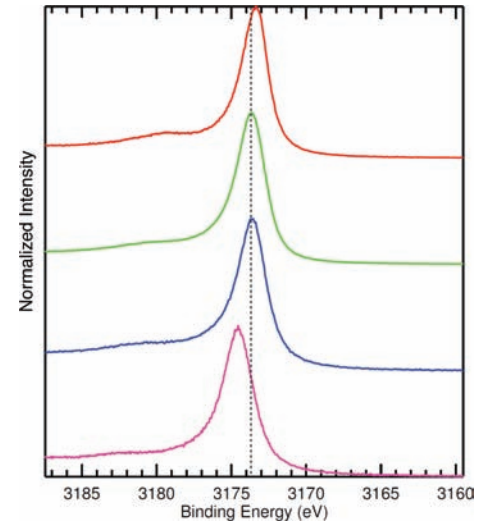

Figure 2. Palladium $2p_{3/2}$ core-level photoemission spectra. Red, Pd(meal); Green, **A** before Suzuki−Miyaura coupling; Blue, **A** after 10 times of Suzuki−Miyaura coupling; Pink, PdS.

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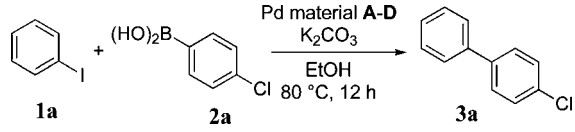
Table 1. Yields of the Suzuki−Miyaura Coupling Using Pd Materials **A**−**D**[a]



				Yield of **3a** (%)[b]									
Entry	Pd material	Support	Pd source	first	second	third	fourth	fifth	sixth	seventh	eighth	ninth	10th
1	**A**	Au(111)/mica	$Pd(dba)_2$	96	95	97	96	98	99	>99	96	96	99
2	**B**	Au(foil)	$Pd(dba)_2$	97	96	92	89	97	97	97	99	98	95
3	**C**	Au(mesh)	$Pd(dba)_2$	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
4	**D** (SAPd)	Au(mesh)	$Pd(OAc)_2$	>99	98	>99	>99	>99	96	>99	97	99	>99

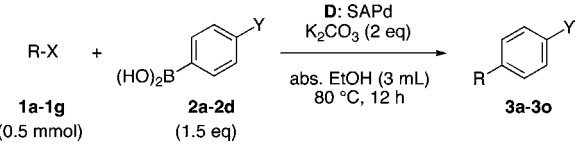
[b] Determined by HPLC. [a] Conditions of Suzuki−Miyaura coupling: **1a** (102 mg, 0.5 mmol), **2a** (1.5 equiv), K_2CO_3 (2 equiv), EtOH (3 mL), Pd material, 80 °C, 12 h.

Table 2. Amount of Released Pd into Reaction Mixture in the Suzuki−Miyaura Coupling of **1a** and **2a**

			Amount of Releasing Pd (ng)[b]										
Entry	Pd material	Pd (μg)[a]	first	second	third	fourth	fifth	sixth	seventh	eighth	ninth	10th	Total
1	**B**	95	90	60	50	50	40	40	30	110	50	30	550
2	**C**	80	60	80	70	70	30	60	20	50	30	10	480
3	**D** (SAPd)	38 ± 9[c]	36 ± 15	26 ± 9	25 ± 11	28 ± 23	24 ± 15	28 ± 14	19 ± 8	30 ± 8	25 ± 12	23 ± 13	260 ± 110

[a] Amount of absorbed Pd on Au substrate. The standard deviation was calculated from 4 sets of samples. [b] The whole reaction mixture was directly subjected to ICP-Mass measurement. The standard deviation was calculated from 4 sets of samples. [c] Pd (%) based on the amount of starting material is 7.0×10^{-2}.

Table 3. Suzuki−Miyaura Coupling of Various Substrates Using Pd Material **D**



	Substrate [Ar-X]		Boronic acid				Yield of **3** (%)[a,c]									
Entry		Ar	X	Y			first	second	third	fourth	fifth	sixth	seventh	eighth	ninth	10th
1[b]	**1a**	C_6HM_5	I	**2a**	Cl	**3a**	>99 (36)	98 (26)	>99 (25)	>99 (28)	>99 (24)	97 (28)	>99 (19)	97 (30)	99 (25)	>99 (23)
2			I	**2b**	Me	**3b**	94 (55)	>99	92	97	99	94	90	92	>99	94 (47)
3			I	**2c**	H	**3c**	92 (43)	92	92	90	91	91	85	87	91	89 (36)
4			I	**2d**	Ac	**3d**	99	98	>99	98	97	99	99	98	97	99
5	**1b**	4-$NO_2C_6H_4$	I	**2a**	Cl	**3e**	96 (1307)	96	90	93	>99	96	94	>99	99	>99 (295)
6			I	**2b**	Me	**3f**	93	96	99	96	88	99	94	95	>99	95
7			I	**2c**	H	**3g**	97	99	90	>99	98	96	96	98	99	95
8			I	**2d**	Ac	**3h**	96	>99	89	87	95	92	98	98	94	98
9[b]	**1c**	4-$MeOC_6H_4$	I	**2a**	Cl	**3i**	96 (641)	97	98	96	93	97	95	97	96	92 (54)
10			I	**2b**	Me	**3j**	>99	>99	>99	>99	95	>99	>99	>99	>99	96
11			I	**2c**	H	**3k**	99	99	96	91	98	95	>99	98	96	93
12[b]			I	**2d**	Ac	**3l**	97	94	99	99	99	95	94	96	97	92
13	**1d**	4-$NO_2C_6H_4$	Br	**2a**	Cl	**3e**	>99 (482)	94	>99	>99	>99	>99	>99	>99	>99	99 (116)
14	**1e**	4-Ac-C_6H_4	Br	**2a**	Cl	**3m**	95	97	99	99	99	93	81	95	86	80
15	**1f**	2-Me-C_6H_4	I	**2b**	Me	**3n**	96	97	93	94	92	92	91	99	95	89
16	**1g**	2-HO-C_6H_4	I	**2a**	Cl	**3o**	96	97	93	94	92	92	91	99	95	89

[a] Isolated yields. [b] Yields were determined by HPLC. [c] Numbers in parentheses indicate the amount of releasing Pd(ng) in the solution.

which was used as a reference sample (Light blue line), *the sulfur on Au appears to be oxidized sulfur*.

Given that sulfur has a high affinity for Pd, $Pd(dba)_2$ was adsorbed on this sulfur modified Au(111)/mica in xylene (100 °C, 12 h). After the Pd adsorption, the S 1s peak appears at 2470 eV (Green line), which is almost identical to the binding energy of the S 1s peak from the S-modified GaAs.[15] Significant changes in S 1s binding energies between those in the Piranha-treated Au(111)/mica and those in the sample **A** indicate that the sulfur on Au was reduced and had chemically bonded with Pd during Pd adsorption.[18] In Pd 2p core-level photoemission spectra, the peaks from **A** appear close to the metallic palladium peak. These results suggest that, in the case of **A**, $Pd(dba)_2$ molecules react with the substrate, yielding zerovalent molecules or metallic palladium (Figure 2).[19]

Single crystal Au(111)/mica is very expensive and not versatile. Consequently, we used Au foil and mesh instead of Au(111)/mica

to prepare **B** and **C** according to the Pd-adsorption procedure for **A**. When **A**, **B**, or **C** was subjected to the Suzuki−Miyaura coupling of iodobenzene and 4-chlorophenylboronic acid, the yields for runs 1 to 10 were excellent to quantitative in all cases (Table 1, entries 1−3). **D**, prepared from Au(mesh) with $Pd(OAc)_2$ as a Pd source, was also highly active for the Suzuki−Miyaura coupling (entry 4). These results showed that the Pd materials **A**, **B**, **C**, and **D** are highly recyclable.[20]

We next measured the amount of Pd adsorbed on the Pd materials **B**−**D** with inductively coupled plasma mass spectrometry (ICP-MS) analysis. These analyses revealed that **B**, **C**, and **D** included 95, 80, and 38 μg of Pd, respectively.[21] We subsequently measured the amount of Pd released into the reaction mixtures of each Suzuki−Miyaura coupling run by ICP-MS. Table 2 shows that the amount of released Pd in each run was extremely low. The amount of Pd in the reaction mixture using **B**−**D** is far lower than the U.S. government-required value of <5 ppm residual metal in product streams.[22] In particular, in the case of **D**, the leached Pd into the reaction mixture was only 76−38 ng for 1 mmol scale preparation (12.7−6.3 ppb in 3 mL of solvent, 0.2−0.1% of Pd from **D**), the average being 26 ng for 10 runs. The Crudden group reported an excellent Pd material supported on mercaptopropyl-modified mesoporous silica, which has been recognized as one of the best catalytic Pd materials from the point of view of leaching: 720−30 ng for 1 mmol scale preparation (72−3 ppb in 2.5 mL of solvent, 0.006−0.13% of Pd from the Pd material), the average being 242 ng for 4 runs.[23,24] The amount of the leached Pd in the reaction of our Pd material **D** is similar or less, compared with that of Crudden's material. Furthermore, since Crudden's material can only be recycled 5 times, **D** would be considered highly recyclable, making it one of the lowest releasing Pd materials with high recyclability. Due to its extremely low Pd leaching levels, we employed **D**, i.e., SAPd (Sulfur-modified Au supported Pd material) for further studies.

We then investigated the scope and limitation of SAPd in the Suzuki−Miyaura coupling using aryl iodides and arylboronic acids. The corresponding products were obtained in excellent yields as summarized in Table 3. It is noteworthy that isolated yields (%) of **3i** between the first run to fourth run were 54, 46, 8, and 5 respectively, when the control experiment of entry 9 was carried out using SAPd without Piranha treatment. These control experiments indicate Piranha treatment is necessary and sulfur is needed to create an active catalyst or retain Pd on the surface.

In summary, we have found in the SR-HXPS measurement of Piranha-treated Au(111)/mica that the gold surface underwent sulfur modification during this treatment, which was believed to have only removed impurities from the gold surface. We also successfully developed a practical Pd material, SAPd, whose Pd was immobilized on sulfur-modified Au. With the lowest Pd-releasing levels and high recyclability, this is one of the best Pd materials thus far developed. Because it leaches extremely low levels of Pd into reaction mixtures, removal of the residual Pd is unnecessary using SAPd, even in syntheses involving pharmaceutical ingredients.

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Supporting Information Available: Experimental procedures and full characterizations of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) This does not mean a sulfur atom is embedded at an ~20 nm depth, and it is unclear whether the sulfur atoms are embedded at the interface between gold and Pd adlayers or not.
(17) Proposal No. 2007B4600 and No. 2008A4605. For the measurements, the incident X-ray energy was 5.95 KeV and a total energy resolution of 240 meV was employed.
(18) It should be noted that the sulfur for sample **A** remained in almost the same chemical state before (Figure 1, Green line) and after (Figure 1, Blue line) the Suzuki−Miyaura coupling. Pd-XPS was shown in Figure 2.
(19) We did not use Pd 3d peaks but Pd 2p peaks, since the peaks of Pd $3d_{5/2}$ or $3d_{3/2}$ overlap with that of Au $4d_{5/2}$ of substrates in the energy region.
(20) **D** could be recycled at least 20 times.
(21) Au(foil) in **B** is $13 \times 11 \times 0.127$ mm^3 (325 mg). Au(mesh) in **C** and **D** is 12×12 mm^3 (100 mesh, 99 mg). **D** included 14 ± 9 μg of S ($n = 4$).
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