Novel Palladium Catalyst Supported on GaAs(001) Passivated by Ammonium Sulfide

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A more reactive palladium catalyst than homogeneous $Pd(PPh_3)_4$ catalyst for the Heck reaction supported on a sulfur-terminated GaAs(001) plate was developed. Sulfur termination using $(NH_4)_2S_x$ at 60 °C and Pd absorption in acetonitrile at 100 °C is essential for the preparation of an active and stable catalyst. The catalyst could be reused in this reaction up to ten times.

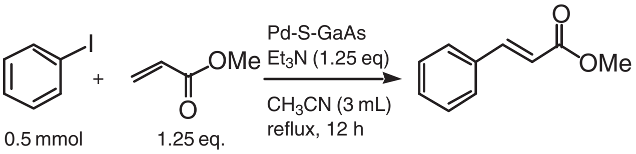
Immobilized and reusable transition-metal catalysts are needed to overcome problems regarding transition-metal chemistry, such as difficulties in separating the catalyst from the product and economic considerations. Over the past 10 years, this issue has been extensively studied and immobilized transition-metal catalysts have been developed using organic and inorganic supports. A recently developed ionic solvent is also a promising candidate.[1–3]

We have been interested in the reactivity of transition metals on a GaAs surface and started to study the preparation of a palladium catalyst supported on a GaAs surface: a typical compound semiconductor consists of Ga(III) and As(V). Its single-crystal has a zincblende structure that is strong enough for handling. Since the fresh surface of GaAs is quite reactive and easily oxidized upon exposure to air, surface passivation is necessary to produce a chemically stable surface. Sulfur-termination is an efficient method for passivating a GaAs surface.

We previously reported methods for fabricating sulfur-terminated GaAs(001) surfaces by direct exposure to sulfur vapor and subsequent annealing in a molecular beam epitaxy (MBE) system,[4,5] and we examined these surfaces by X-ray photoelectron spectroscopy (XPS).[6] Recently, we found that a sulfur-terminated GaAs(001) plate adsorbed $Pd(PPh_3)_4$ in benzene at room temperature, resulting in a new palladium catalyst which catalyzes the Heck reaction and Suzuki coupling.[7] Although this catalyst was easily handled in air, its catalytic activity and stability were insufficient for repeated use. Since the catalytic activity and stability of this catalyst must be enhanced for practical use, different conditions for surface passivation and palladium adsorption were investigated. In this paper, we report an improved method for preparing a more active palladium catalyst on sulfur-terminated GaAs, which can be reused up to ten times in the Heck reaction.

Although direct exposure to sulfur vapor is a more sophisticated method for sulfur-termination and is suitable for basic studies on the surface, this method is inefficient for preparing many samples with limited experimental resources. Therefore, we used the more common method of dipping into an aqueous solution of $(NH_4)_2S_x$. However, the surface becomes atomically rough and oxidized compared to that obtained by the termination technique in vacuum.[4]

Preparation of Pd–S–GaAs(001): A $13 \times 11 \times 0.6\,mm^3$ sample of GaAs(001) (Sumitomo Electric Industries, Ltd.) was placed in 3 mL of $(NH_4)_2S_x$ (ammonium sulfide solution, yellow, sulfur content: 5–7%, KISHIDA CHEMICAL CO., LTD.) at 60 °C for 30 min and then rinsed with H_2O and acetonitrile in succession. After being rinsed, the sample was dried at room temperature for 10 min and then heated with a heat-gun for 20 min under reduced pressure (ca. 6 mmHg). The resulting sulfur-terminated GaAs plate [S–GaAs] was placed in a solution of $Pd(PPh_3)_4$ (25 mg) in acetonitrile (3.0 mL) and kept at 100 °C (bath temperature) for 12 h under an argon atmosphere with stirring to prepare palladium-adsorbed S–GaAs [Pd–S–GaAs].[8] The Pd–S–GaAs plate was then rinsed with acetonitrile (3.0 mL, 100 times) until the washings showed no activity in the Heck reaction shown in Scheme 1. Measurements of the sample weight using balance and ICP-Mass revealed that less than 277 and 267 µg of palladium species was adsorbed on the surface, respectively.



Scheme 1.

Table 1. Heck reaction using Pd–S–GaAs(001)

Run	Yield /%	Pd in the Mixture/µg	Run	Yield /%	Pd in the Mixture/µg
1	93	49	6	54	1
2	87	3	7	35	1
3	71	4	8	37	1
4	72	1	9	25	1
5	57	1	10	24	1

Heck reaction: A mixture of iodobenzene (0.5 mmol), methyl acrylate (1.25 equiv.) in 3 mL of acetonitrile, and triethylamine (1.25 equiv.) was heated in the presence of Pd–S–GaAs at 100 °C (bath temperature) for 12 h under an argon atmosphere without stirring. After the Pd–S–GaAs plate was removed from the solution and rinsed several times with acetonitrile, the reaction mixture was concentrated in vacuo to give a residue that was subjected to column chromatography. Yields of methyl *trans*-cinnamate were determined using isolated weight or NMR spectroscopy. In addition, the amount of Pd species in the reaction mixture was examined by ICP-Mass. The recovered plate was again subjected to the above reaction conditions as a 2nd run.

This procedure was repeated for a total of 10 runs and the results are shown in Table 1. Even in the 10th run the plate showed catalytic activity and gave the product in 24% yield.

Table 2. Heck reaction using homogeneous catalyst

Entry	$Pd(PPh_3)_4$/mg	Pd/μg	mol %	Yield/%
1	29	2900	5	53
2	2.9	290	0.5	70
3	0.58	58	0.1	65
4	0.058	5.8	0.01	60
5	0.0058	0.58	0.001	9

In the same reaction using a homogeneous catalyst, $Pd(PPh_3)_4$, the yield of the product was only 53 to 70% (Table 2). These results reflect higher catalytic activity of the Pd–S–GaAs plate, although its activation mechanism is not yet clear.

A sample of GaAs itself and S–GaAs showed no reactivity in the Heck reaction (Table 3, Entries 1 and 2). A Pd–GaAs plate, on which $Pd(PPh_3)_4$ was adsorbed without sulfur termination, showed moderate catalytic activity in the Heck reaction, and the yield of the product decreased faster than with Pd–S–GaAs (Entries 3–12). These findings suggest that sulfur termination of the GaAs surface plays an important role in the catalytic activity.

Table 3. Heck reaction using GaAs(001), S–GaAs(001), and Pd–GaAs(001)

Entry	Catalyst	Run	Yield /%	Entry	Catalyst	Run	Yield /%
1	GaAs		0	7	Pd–GaAs	5	33
2	S–GaAs		0	8	Pd–GaAs	6	29
3	Pd–GaAs	1	77	9	Pd–GaAs	7	12
4	Pd–GaAs	2	70	10	Pd–GaAs	8	5
5	Pd–GaAs	3	71	11	Pd–GaAs	9	5
6	Pd–GaAs	4	43	12	Pd–GaAs	10	6

Table 4. Heck reaction using revitalized Pd–S–GaAs(001)

Run	Yield/%	Run	Yield/%
1	89	6	54
2	88	7	58
3	85	8	41
4	84	9	32
5	68	10	30

Even though repeated use of Pd–S–GaAs degrades its catalytic activity, the activity was restored by further treatment with $Pd(PPh_3)_4$ solution. The results are shown in Table 4.

Both of before and after the reaction, we performed XPS measurements. The spectrum for the surface before it was subjected to the above reactions revealed clear signals of Pd and P core-level photoemissions and no signals from the GaAs substrate, indicating that the surface is completely covered by layers of $Pd(PPh_3)_4$ (Figure 1A). After repeated cycles of the Heck reaction, signals from Pd still appeared for the surface with sulfur-termination (Figure 1B), while no detectable signals were observed for the surface without sulfuration (Figure 1C). These results suggest that sulfur-termination is essential for stabilizing the $Pd(PPh_3)_4$ molecule on the surface.

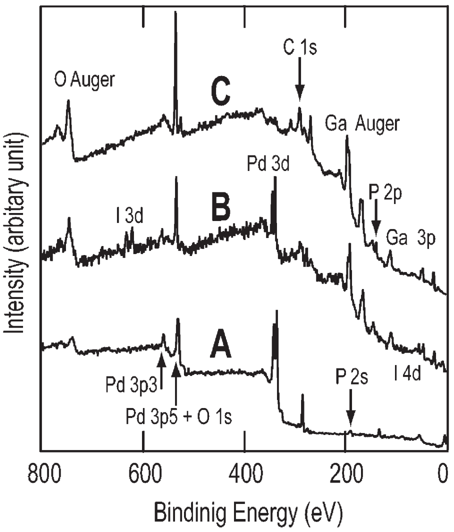


Figure 1. XPS spectrum of Pd–S–GaAs(001) before use (A), Pd–S–GaAs (B) and Pd–GaAs (C) after the repeated reactions (ten times).

In conclusion, we have prepared a highly active Pd–S–GaAs catalyst using sulfur-termination with aq. $(NH_4)_2S_x$ followed by the adsorption of $Pd(PPh_3)_4$ at 100 °C. The Pd–S–GaAs plate more efficiently catalyzed the Heck reaction than homogeneous $Pd(PPh_3)_4$ catalyst and could be reused at least 10 times. Inactivated catalyst could be revitalized by further treatment with $Pd(PPh_3)_4$. The importance of sulfur-termination was clearly demonstrated by XPS.

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8 In the case of sulfur-terminated GaAs(001) using sulfur vapor (Ref. 7), Pd absorption at 100 °C (bath temperature) in MeCN gave better results than that at RT in benzene. Even using sulfur-termination with $(NH_4)_2S_x$, a Pd–S–GaAs plate that was prepared by palladium absorption in benzene at RT did not show any catalytic activity.