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Development of a Method for Preparing a Highly Reactive and Stable, Recyclable and Environmentally Benign Organopalladium Catalyst Supported on Sulfur-Terminated Gallium Arsenide(001): A Three-Component Catalyst, {Pd}-S-GaAs(001), and its Properties

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Abstract: We have developed a method for preparing a recyclable and environmentally benign organopalladium catalyst for the Heck reaction supported on sulfur-terminated gallium arsenide(001). This three-component catalyst, {Pd}-S-GaAs(001), exhibited high stability and activity, furthermore, it tolerated reuse in 10 runs of the Heck reaction (average yield, 97%) under aerobic conditions. The sulfur layer was very important to stabilize this catalyst. Only trace amounts of Pd were leached from this catalyst to the reaction mixture, as measured by ICP-mass. The valence of immobilized Pd was zero by XPS spectrometry.

Keywords: Heck reaction; heterogeneous catalysis; immobilization; palladium; semiconductors; sulfur

Introduction

Organopalladium catalysts are very important in organic chemistry and widely used in the synthesis of biologically active compounds.[1] The Heck reaction has received considerable attention because it offers a reliable method for carbon-carbon bond formation.[2] Like many organic reactions using organometallic reagents and catalysts, the standard procedure under homogeneous conditions suffers from wasted noble metals or catalytically active metals which are difficult to recover and lost in aqueous work-up. With regard to green chemistry, heterogeneous organometallic catalysts are favored and currently being extensively studied.[3] However, most of these systems do not give as high a level of activity as homogeneous catalysts. Recently, it has reported that some heterogeneous catalysts showed a higher activity than homogeneous ones, and the mechanism was studied in detail.[4]

We have been interested in the development of more practical heterogeneous catalysts, which should be active, leach-free and easy to handle, and have reported an entirely novel organopalladium catalyst supported on a semiconductor surface, GaAs(001), terminated by elemental sulfur evaporation using molecular beam epitaxy (MBE)[5] or ammonium sulfide solution (Figure 1).[6] As far as we know, the ability of a semi-conductor to support an organometallic catalyst has not been reported previously. We expected this new material to amplify the recyclability or to activate differently the aryl halides. In these reports, we have presented the following findings: 1) a {Pd}-S-GaAs(001) plate catalyzed the Heck reaction more efficiently than $Pd(PPh_3)_4$, which is widely used as a

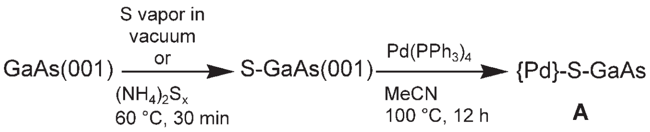


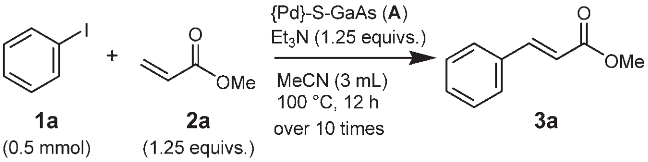
Figure 1. Preparation of three-phase catalyst, {Pd}-S-GaAs(001), catalyst **A**.

homogeneous catalyst, and could be reused at least 10 times, 2) inactivated {Pd}-S-GaAs(001) could be revitalized by further treatment with $Pd(PPh_3)_4$, 3) sulfur termination in this catalyst was important for stability of this catalyst.[5,6]

In this paper, we present a method for preparing {Pd}-S-GaAs(001), which is drastically improved in both catalytic activity and stability. Some chemical and physical properties of the catalyst were elucidated using X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Furthermore, experiments were carried out in order to attempt identification of the real active Pd species.

Results and Discussion

As we have previously reported,[6] {Pd}-S-GaAs(001), which is named catalyst **A**, was prepared by a three-step procedure, $(NH_4)_2S_x$ treatment (aqueous solution, 60 °C, 30 min.), and Pd adsorption [$Pd(PPh_3)_4$, 7.2 mM in MeCN, 100 °C, 12 h] followed by washing at room temperature with acetonitrile (MeCN). This catalyst **A** could be used for the Heck reaction of iodobenzene (**1a**) and methyl acrylate (**2a**) over 10 times (Scheme 1). The chemical yield of the 10th run, however, was only 24 % and the average chemical yield of 10 runs was 56 % (Table 1, entry 1). To identify a more reactive catalyst, we surveyed the sources of Pd. Catalysts **B** – **F** were prepared by the same method as catalyst **A** except for the source of Pd, and then repeatedly subjected to the Heck reaction as shown in Scheme 1. The results are summarized in Table 1. Catalyst **B**, prepared with $PdCl_2$, showed almost no activity (entry 2). Catalysts **C** and **D**, prepared with $Pd(acac)_2$ and $Pd(MeCN)_2Cl_2$, respectively, were unstable and lost most of their catalytic activity before the 7th run (entries 3 and 4). Catalyst **E**, prepared with $Pd(dba)_2$, retained its activity until the 10th run, although its activity was lower than that of catalyst **A** (entry 5). In contrast, catalyst **F**, prepared with $Pd(OAc)_2$, had a much higher activity than catalyst **A** and the coupling product was obtained in 79 % yield in the 10th run (entry 6). Therefore, $Pd(OAc)_2$ is the best source of Pd among those tested for preparing {Pd}-S-GaAs(001).



Scheme 1. Heck reaction.

Next, we examined heated-washing conditions after Pd adsorption, since it is possible that excess Pd on surface, which is not bound to sulfur, could deactivate {Pd}-S-GaAs(001) by forming a less active or inactive colloidal Pd species.[7] Hence, catalysts **G** and **H** were prepared by a new three-step procedure, which consisted of $(NH_4)_2S_x$ treatment (60 °C, 30 min.), Pd adsorption [$Pd(PPh_3)_4$ or $Pd(OAc)_2$, 100 °C, 12 h], and heated-washing in refluxing MeCN for 12 h. The catalysts were subjected to the same Heck reaction (Scheme 1) over 10 times, respectively. As shown in Table 2, the activity of catalyst **G**, which was prepared

Table 1. Effect of Pd sources in Pd adsorption.

Entry	Cat.	Pd source	Yield of **3a** [%][a]										
			1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	ave.
1	**A**	$Pd(PPh_3)_4$	93	87	71	72	57	54	35	37	25	24	56
2	**B**	$PdCl_2$	1	1	0	-	-	-	-	-	-	-	-
3	**C**	$Pd(acac)_2$	51	31	14	15	10	12	1	-	-	-	-
4	**D**	$Pd(CH_3CN)_2Cl_2$	43	8	1	0	1	-	-	-	-	-	-
5	**E**	$Pd(dba)_2$	74	66	31	46	12	9	5	1	1	4	25
6	**F**	$Pd(OAc)_2$	100	99	91	98	97	88	81	72	71	79	88

[a] Yields of isolated products.

Table 2. Effects of washing conditions after Pd adsorption.

Entry	Cat.	Pd source	Heated-washing	Yield of **3a** [%][a]										
				1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	ave.
1	**A**	$Pd(PPh_3)_4$	No	93	87	71	72	57	54	35	37	25	24	56
2	**G**	$Pd(PPh_3)_4$	Yes	90	55	67	66	57	54	46	43	43	39	56
3	**F**	$Pd(OAc)_2$	No	100	99	91	98	97	88	81	72	71	79	88
4	**H**	$Pd(OAc)_2$	Yes	96	100	91	93	98	100	96	99	98	95	97

[a] The yields were determined by NMR analysis.

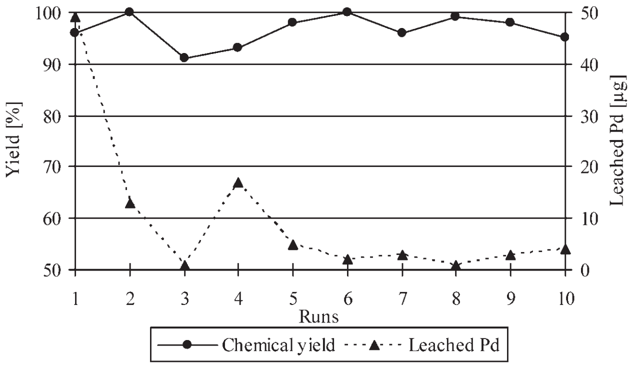


Figure 2. Chemical yield and amount of leached Pd using catalyst **H**.

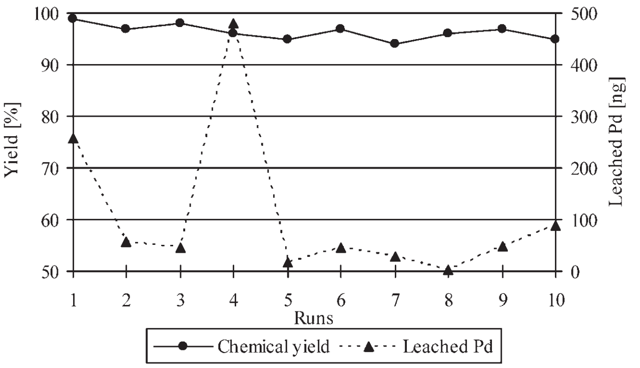


Figure 3. Chemical yield and amount of leached Pd using catalyst **N**. Unit of leached Pd is ng not µg.

with $Pd(PPh_3)_4$ followed by heated-washing, was the same as that of catalyst **A**, which was not treated by heated-washing. In contrast, catalyst **H**, which was prepared with $Pd(OAc)_2$, had a higher activity than catalyst **F**, that is, the catalytic activity of **H** did not decrease over 10 runs (95%, entry 4), and the average chemical yield over 10 runs was 97%.

We measured the amount of leached Pd into the reaction solution after the Heck reaction using catalyst **H** by inductively coupled plasma mass spectrometry (ICP-mass). Figure 2 summarizes the chemical yield of the product and the amount of leached Pd in each run. While the chemical yield was almost quantitative through 10 runs, the amount of leached Pd decreased after 4 uses. The amount of Pd leached after the 5th run is a few µg, less than 1.7 ppm. Considering that the amount of immobilized Pd after the 10th run is 125 µg, only trace amounts of Pd were leached after 5th run.

Unfortunately, after several experiments, we found that the reproducibility of the catalytic activity for catalyst **H** was poor. Hence, we optimized the heated-washing conditions. First, we carried out the heated-washing using some solvents at 100 °C (Table 3, entries 1 – 4). Among the solvents we examined, catalyst **H**, which has been washed in MeCN at 100 °C (bath temperature), had the best catalytic activity. Next, we continued to examine the effect of solvent in heated-washing at higher temperature (135 °C, bath temperature). As the result, we found that toluene can be another candidate for heated-washing, but its catalytic activity was lower than that of catalyst **H** (entry 6). In entry 7, we carried out heated-washing in xylene at 135 °C. The activity of catalyst **N** was as high as that of catalyst **H** with good reproducibility and catalyst **N** kept its high activity through 10 runs (entry 7). When the heated-washing was carried out in xylene at 150 °C, the activity of catalyst **O** decreased slightly (entry 8).

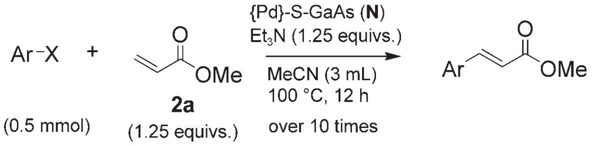
When catalyst **N** was employed, ICP-mass analysis indicated that the amount of Pd leached into the reaction mixture was extremely low in each run (0.04 – 0.26 ppm, Figure 3). These results suggested that heated-washing in a non-coordinating solvent can prepare highly reactive and stable catalysts with good reproducibility and lower leaching, although further experiments are required to explain why these differences in catalytic activities come about, merely by changing solvent and temperature in heated-washing.

Table 3. Optimization of heated-washing conditions.

Entry	Cat.	Heated-washing		Yield of **3a** [%][a]										
		Solvent	T [°C][b]	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	ave.
1	**H**	MeCN	100	96	100	91	93	98	100	96	99	98	95	97
2	**I**	toluene	100	98	96	92	82	82	63	55	48	62	63	74
3	**J**	DMF	100	98	86	95	89	80	84	75	77	69	70	82
4	**K**	DMSO	100	88	78	64	38	21	17	16	12	13	14	36
5	**L**	DMF	135	70	80	78	58	52	49	43	32	31	31	52
6	**M**	toluene	135	95	93	93	97	94	91	91	90	90	85	92
7	**N**	xylene	135	96	100	99	98	100	91	96	97	92	91	96
8	**O**	xylene	150	99	99	100	97	99	91	97	94	92	86	95

[a] The yields in entry 1 were determined by NMR analysis. The yields in entries 2 to 8 were determined by HPLC analysis.
[b] Bath temperature.

Table 4. Heck reaction of various aryl halides.



Entry	Substrate [Ar-X]			Product	Yield of **3a** [%][a]										
	No.	Ar	X		1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	ave.
1	**1b**	C_6H_5	Br	**3a**[b]	0	0	0[c]	0[d]	0[e]	-	-	-	-	-	0[f]
2	**1c**	C_6H_5	OTf	**3a**[b]	0	0	0[c]	0[d]	0[e]	-	-	-	-	-	0[f]
3	**1d**	2-MeC_6H_4	I	**3b**	98	90	94	81	72	63	52	49	43	36	68
4	**1e**	3-MeC_6H_4	I	**3c**	100	100	100	72	62	56	59	47	46	38	68
5	**1f**	4-MeC_6H_4	I	**3d**	100	100	100	100	100	100	100	100	98	96	99
6	**1g**	4-MeOC_6H_4	I	**3e**	100	92	100	87	75	89	68	48	50	54	76
7	**1h**	2-BrC_6H_4	I	**3f**	92	71	80	57	65	58	36	28	28	25	54
8	**1i**	3-BrC_6H_4	I	**3g**	100	100	81	57	47	39	40	38	25	29	56
9	**1j**	4-BrC_6H_4	I	**3h**	98	81	67	56	65	49	42	41	38	42	58
10	**1k**	4-$NO_2C_6H_4$	I	**3i**	82	34	10	4	0	-	-	-	-	-	26[f]
11	**1l**	4-MeC(O)C_6H_4	I	**3j**[h]	91	59	51	44	38	-	-	-	-	-	57[f]
12	**4**	xylene	I	**5**	99	100	100	99	94	100	83	92	91	83	94

[a] Yields were determined by ^{1}H NMR spectra; $PhNO_2$ (0.25 mmol) was employed as an internal standard.
[b] Yields were determined by HPLC analysis.
[c] Reaction time was 24 h.
[d] Reaction was carried out in toluene at 135 °C (bath temperature) for 12 h.
[e] Reaction was carried out in toluene at 135 °C (bath temperature) for 24 h.
[f] Average yield through 1 to 5 runs.
[g] 0.50 mmol of acetophenone was used as an internal standard.

Next, to probe the scope and limitations of catalyst **N**, it was subjected to the Heck reaction of other substrates. The results are summarized in Tables 4 and 5. Bromobenzene (**1b**) and phenyl trifluoromethanesulfonate (**1c**), which are widely used as a substrate for Heck reaction,[8] were inactive under our conditions (Table 4, entries 1 and 2). In these cases, catalyst **N**, which was used over 5 runs, still possessed catalytic activity for the Heck reaction between **1a** and **2a**, therefore, we assume that our catalyst could not have undergone oxidative addition with **1b** and **1c** under these reaction conditions. When 2-, 3-, and 4-iodotoluene were used as substrates, chemical yields of the corresponding product were varied depending on the position of the methyl group on the aromatic ring (entries 3 – 5). When 4-iodoanisole (**1g**) was used as a substrate, the reaction proceeded, although the yields decreased gradually (entry 6). When bromo-1-iodobenzene (**1h–j**) was used, the reaction proceeded chemoselectively to give the corresponding bromocinnamate, but the reactivity also gradually decreased (entries 7–9). In entries 10 and 11, aryl iodides with electron-withdrawing groups at the *para*-position were used to yield the corresponding products at the 1st run, however, after the 2nd run, the chemical yields decreased drastically, and no reactivity remained after the 5th run. In entry 12, 1-iodonaphthalene, which was sometimes known for its low activity,[9] was used as a substrate and gave the corresponding product in excellent yield over 10 runs and the average yield was 94%. The fact that non- or de-activated aryl iodides react better than activated ones (entries 3 – 6 versus

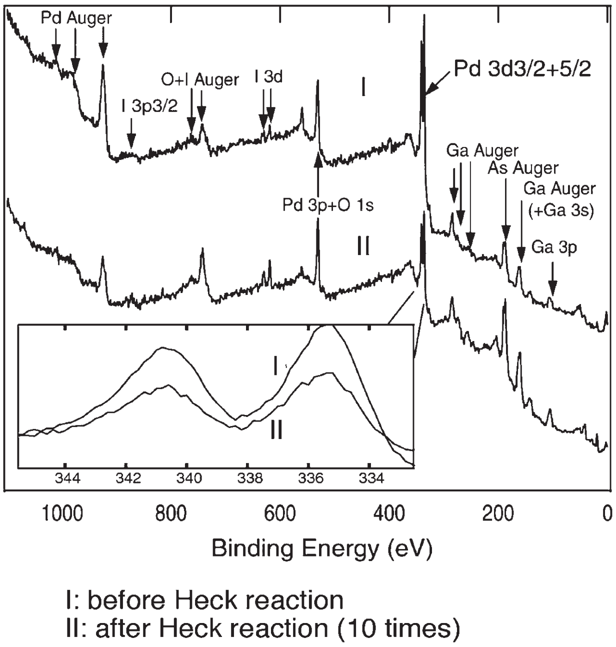
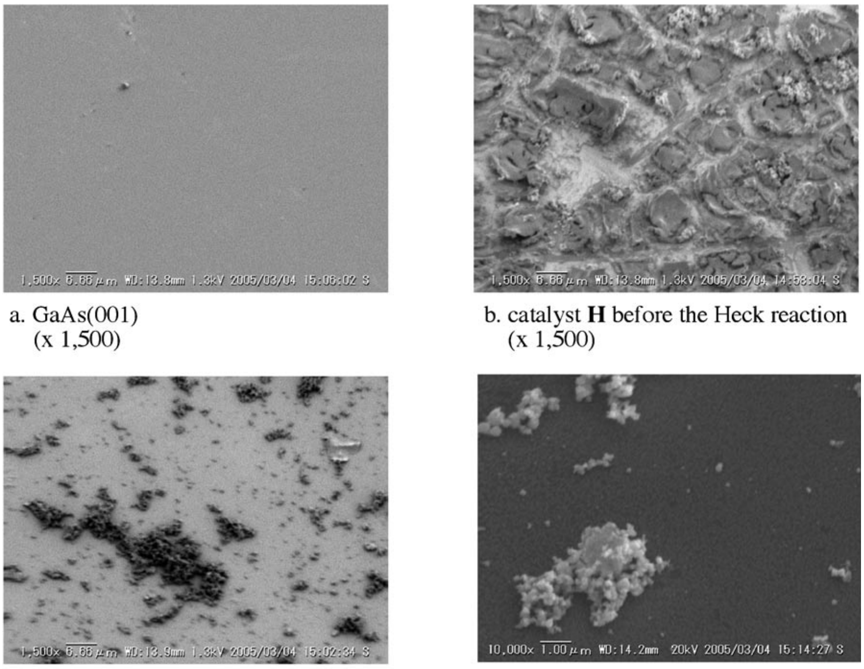


Figure 4. XPS spectra of catalyst **H**.



a. GaAs(001) (x 1,500)

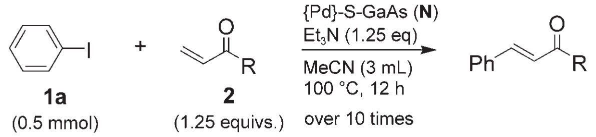
b. catalyst **H** before the Heck reaction (x 1,500)

c. catalyst **H** after the Heck reaction (x 1,500)

d. catalyst **H** after the Heck reaction (x 10,000)

Figure 5. SEM observation of catalyst **H**.

Table 5. Heck reaction of methyl vinyl ketone.



Entry	Substrate [**2**]		Product	Yield of **3a** [%][a]										
		R		1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	ave.
1	**2a**	OMe	**3a**	96	100	99	98	100	91	96	97	92	91	96
2	**2b**	Me	**3k**	76	80	79	78	77	76	72	75	74	71	76

[a] Yields were determined by ^{1}H NMR spectra; $PhNO_2$ (0.25 mmol) was employed as an internal standard.

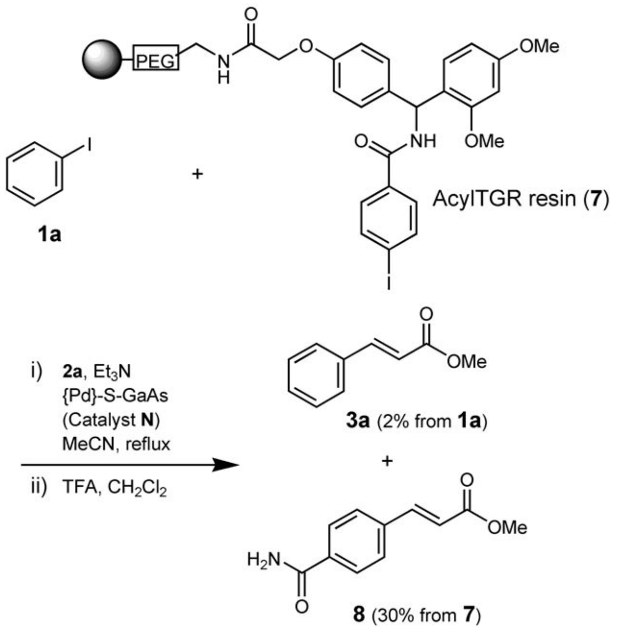
8 – 9) might suggest that the use of the support modifies slightly the reaction mechanism, or displaces the limiting step of the reaction from the oxidative addition of the aryl halide to Pd(0) to the reductive elimination to give the expected compound, although we do not have enough data to discuss this matter in detail at this stage.

When methyl vinyl ketone (**2b**) was used instead of **2a**, the chemical yield of the 1st run was 76%,[10] but almost the same chemical yields were maintained through 10 runs (Table 5).

From these results, we found that our catalyst could catalyze only aryl iodides, and the catalytic activities were also influenced by the substituent on aryl iodides.

Catalysis Properties

Based on above discoveries, we investigated the characteristics of catalyst **H** in detail. First, the status of Pd on the surface both before and after these reactions, was examined by XPS measurement[11] of catalyst **H** using Mg Kα radiation (K.E. = 1253 eV) in a separate ultrahigh vacuum chamber. The energy shift due to sample charging was corrected as the C 1s peak is located at 285.0 eV. The XPS spectrum of catalyst **H** before the Heck reaction exhibited clear peaks of Pd 3d core-level photoemission, indicating that the organopalladium was definitely immobilized as expected (spectrum I in Figure 4). The peak width is slightly wider than that of metal Pd (not shown),



Scheme 2. Three-phase test.

suggesting a complex chemical environment and/or partial oxidation of Pd. The binding energy of the Pd $3d_{5/2}$ peak, 335.9 eV, is close to that of metal Pd, 335.0 eV, indicating that the valence of Pd is zero,[12] while that of the Pd source, $Pd(OAc)_2$, is 2. Even after repeated cycles of the Heck reaction, catalyst **H** showed almost the same Pd 3d peaks (spectrum II in Figure 4), suggesting that the oxidation state of the immobilized Pd did not changed in repeated the Heck reactions.

Second, to obtain further information about the surface both before and after 10 runs of the Heck reaction, catalyst **H** was directly surveyed by SEM and compared to the GaAs(001) substrate. As shown in Figure 5, catalyst **H** before the Heck reaction had a characteristic structure on GaAs(001) (Figure 5 b) and after 10 runs of the Heck reaction, the surface structure was obviously changed (Figures 5 c and d), although the catalytic activity showed no significant difference between the 1 st run and the 10th run of the Heck reaction.

Mechanistic Study

For the development of a novel heterogeneous catalyst, to identify the real catalyst is one of the important problems.[4] First, we examined a three-phase test.[13] This test can clarify which soluble or insoluble species is the real active catalyst by running a metal-catalyzed reaction at the presence of a substrate immobilized on a polymer. We prepared immobilized iodobenzene (**7**) according to the Davies' protocol,[14] and carried out the Heck reactions of **1a** and **7** with **2a** in the presence of {Pd}-S-GaAs, catalyst **N** (Scheme 2). After the reaction mixture had been refluxed for 12 h, the catalyst was removed. Then the reaction mixture was filtered. From the filtrate, 2% of coupling product **3a** was obtained, while the resin was treated with an excess amount of trifluoroacetic acid (TFA) at room temperature for 2 h to give **8** in 30% yield. As a control, we ran the Heck reaction of only **7** using {Pd}-S-GaAs. In this case, the coupling product **8** was not obtained. Furthermore, using the homogeneous catalyst, $Pd(OAc)_2$, the Heck reaction proceeded to give **8** in 62% yield.

Next, we examined hot and cold filtration tests to see whether leached Pd species have catalytic activity for the Heck reaction.[15] A mixture of **1a**, **2a**, Et_3N, and {Pd}-S-GaAs in MeCN was refluxed for 6 h without stirring, and then the catalyst was removed from the 'hot' mixture. The yield of **3a** was 13% in this step. The 'hot' solution was continuously refluxed without {Pd}-S-GaAs. After 24 h (total time 30 h), the yield of **3a** was 35%. In addition, a mixture of **1a**, **2a**, Et_3N, and {Pd}-S-GaAs in MeCN was refluxed for 6 h without stirring. After the mixture was cooled to room temperature, the catalyst was removed from the 'cold' mixture. The yield of **3a** was 13% in this step. The 'cold' clear solution was refluxed for 24 h (total time 30 h) without {Pd}-S-GaAs to give **3a** in 28% yield. In both cases, the amount of product increased, even when the catalyst was removed from the reaction mixture. However, these chemical yields were much lower than that of the reaction in which {Pd}-S-GaAs was employed from the beginning to the end (Figure 6).

Considering that there is no relationship between chemical yield and amount of leached Pd (Figures 2 and 3) for the Heck reaction, these results indicate that: 1) During the Heck reaction, a trace of Pd species was leached from {Pd}-S-GaAs into the reaction mixture. 2) The leached Pd species has some activity in the Heck reaction. 3) The catalytic activity of leached Pd is lower than that of {Pd}-S-GaAs. 4) For a highly efficient Heck reaction, the presence of {Pd}-S-GaAs is critical, although we do not know whether {Pd}-S-GaAs works as the actual active species or as the pre-catalyst.

Conclusions

We have successfully developed a method for preparing {Pd}-S-GaAs(001), the catalytic activity of which for the Heck reaction does not decrease after 10 uses and which shows only trace amounts of Pd leached into the reaction mixture after the 5th run. In addition, it was clear that the immobilized Pd on S-

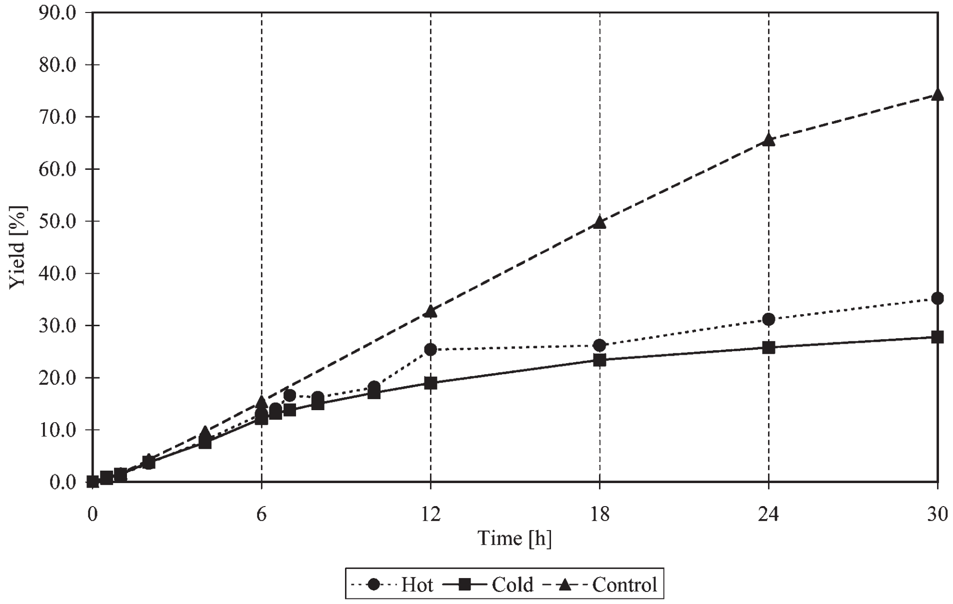


Figure 6. Hot and cold filtration tests.

GaAs(001) is in the oxidation state Pd(0). This catalyst is easy to recover and transfer under air using a pair of tweezers. We hope that this catalyst might lead to new opportunities in environmentally benign immobilized catalysts and microreactors.

Experimental Section

^{1}H NMR spectra were obtained on JEOL JNM-GSX 400α and ecp400 spectrometers with tetramethylsilane as the internal standard. HPLC was carried out using a Cica Mightysil RP-18 and the HPLC spectra were detected by a Hitachi variable wavelength UV monitor 638–41 (254 nm) and recorded by a Hitachi D-2500. ICP-mass spectra were obtained on Hewlett Packard 4500 series and 7500 series instruments. XPS was carried out using a VG ESCALAB Mk-II. All air- and moisture-sensitive reactions were carried out under an argon atmosphere. Heck reactions were carried out with Eyela ChemiStation^{TM} PPS-1510. MeCN (Kokusan Chemicals) and DMF (Kanto Chemicals) were distilled with CaH_2 (Wako Chemicals) before use.

Preparation of {Pd}-S-GaAs(001)

*Catalysts **A** – **F** (non-heated-washing conditions):* A 13×11×0.6 mm^3 sample of GaAs(001) [(Sumitomo Electric Industries, Ltd. for catalysts **A** – **I** and **K**, (Dowa Mining Co., Ltd.) for catalysts **J** and **L** – **O**, there are no differences between suppliers in catalytic activity in our system] was placed in $(NH_4)_2Sx$ (ammonium sulfide solution, yellow, sulfur content: 5 – 7%, 3 mL, Kishida Chemical Co., Ltd.) at 60 °C for 30 min and then rinsed in succession with H_2O (3 mL × 10) and MeCN (3 mL × 5). The sample was placed in a flask and dried at room temperature for 10 min, then the sample was heated at 250 – 300 °C using 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 source (see Table 1) in MeCN (3 mL) and stirred at 100 °C (bath temperature) for 12 h under an argon atmosphere. The plate was rinsed with MeCN (3 mL ×100) until the washings showed no activity in the Heck reaction, as shown in Scheme 1 and dried under vacuum to give {Pd}-S-GaAs.

*Catalysts **G** – **O** (heated-washing conditions):* After sulfur-terminating on GaAs by the same procedure as for catalysts **A** – **F**, the S-GaAs plate were placed in $Pd(PPh_3)_4$ or $Pd(OAc)_2$ (0.022 mmol) in degassed MeCN (3 mL) and stirred at 100 °C (bath temperature) for 12 h under an argon atmosphere. The plate was rinsed with MeCN (3 mL × 100) until the washings showed no activity in the Heck reaction shown in Scheme 1, and dried under vacuum. The plate was placed in the solvent (3 mL) shown in Tables 2 and 3, and kept at an appropriate temperature (see Tables 2 and 3) for 12 h under an argon atmosphere. The plate was rinsed with MeCN (3 mL × 50) until the washings showed no activity in the Heck reaction, as shown in Scheme 1 and dried under vacuum to prepare {Pd}-S-GaAs. ICP-mass (Hewlett Packard 4500 or 7500 series) revealed that 104 μg to 209 μg of Pd were adsorbed on the surface.

Heck Reaction

A mixture of iodobenzene (**1a**; 56.0 μL, 0.50 mmol), methyl acrylate (**2a**; 56.2 μL, 0.63 mmol), and Et_3N (87.1 μL, 0.63 mmol) in MeCN (3 mL) 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 mixture had been cooled to room temperature, the {Pd}-S-GaAs plate was removed from the reaction solution and rinsed several times with MeCN. Yields of methyl *trans*-cinnamate (**3a**) were determined by isolated weight, ^{1}H NMR analysis (0.25 mmol of nitrobenzene was used as an internal standard), or HPLC analysis (0.05 mmol of nitrobenzene was used as an internal standard). In addition, the amount of Pd species in the reaction mixture was examined by ICP-mass after treatment with concentrated nitric acid for a few weeks. The recovered {Pd}-S-GaAs plate was again subjected to the above reaction conditions as a 2nd run. This procedure was repeated for a total of 10 runs.

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