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ARTICLE TYPE

Hydroxylated surface of GaAs as a scaffold for heterogeneous Pd catalyst

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A novel use of GaAs, namely, as a scaffold for a heterogeneous palladium catalyst, is proposed. Hydroxy groups on the GaAs surface play important roles. During the adsorption of Pd(OAc)₂ on the GaAs surface, the hydroxy groups attract Pd(II) species by anion exchange. A subsequent redox reaction proceeds to
10 generate Pd(0) nanoparticles, which are stabilized on the GaAs surface. This process is confirmed by surface-sensitive measurements: diffuse reflection IR spectroscopy and X-ray photoelectron spectroscopy. Moreover, a more bulk-sensitive measurement, hard X-ray photoemission spectroscopy with synchrotron radiation, also supported our considerations. The amounts of Pd(0) nanoparticles on the surface were evaluated by catalytic activity, yield, and recyclability in the Heck reaction, in addition to deposit test.

15 Introduction

Palladium-catalyzed C-C bond forming reactions have various potential applications in organic synthesis. The coupling reactions are efficiently catalyzed by soluble Pd(0) species (homogeneous catalysts).^{1,2} However, the major disadvantage of the
20 homogeneous catalysts is the difficulty of catalyst/product separation, resulting in a considerable loss of the noble metal during catalyst recovery and regeneration. In addition, air-sensitive and moisture-sensitive phosphine ligands are necessary in most cases, which considerably restricts large-scale use. On the
25 other hand, solid-supported catalysts (heterogeneous catalysts)³⁻⁵ are advantageous from environmental and industrial viewpoints because they are inexpensive, easily recovered, and reusable. There are several strategies for preparing effective heterogeneous catalyst systems. Palladium complexes anchored on solid
30 supports⁶⁻¹² or encapsulated in polystyrenes¹³ have been successfully synthesized and used in a variety of reactions. Recently, solid-supported Pd(0) nanoparticles have gained
35 importance¹⁴⁻²⁴ because of their size effect²²⁻²⁵ as well as air and moisture stability. Another advantage of these catalysts is that they can be synthesized using inexpensive ligands. Numerous solid-supported ligand-free Pd(0) catalysts have also been synthesized, and several of them are commercially available. In solid-supported palladium catalysts, Pd(0) nanoparticles tend to aggregate to form large inactive clusters, which eventually
40 form palladium black.^{2,26} When Pd(0) nanoparticles are prepared from easily available, treatable and stable Pd(II) reagents by reduction, aggregation is the major cause for the loss of catalytic activity. Another serious problem with these catalysts is the leaching of palladium species during the catalytic reaction.^{9,20}
45 However, it has been suggested that the leached palladium particles are the actual active species that accelerate the cross-

coupling reactions.^{9,15,16} A small amount of palladium dissolves in a solution by complex formation with the aryl halide used in the coupling reaction and re-deposits on the surface of the solid
50 support after the aryl halide is completely consumed. This implies that solid-supported palladium catalysts serve as reservoirs of catalytically active species to effect the C-C bond formations homogeneously. Hence, it is desirable to develop a suitable scaffold that has a moderate affinity for Pd(0) nanoparticles^{15-21,27}
55 and is strong enough to retain and stabilize them without aggregation, but weak enough to release them slowly. Recently, suitable scaffolds with moderate affinity have been developed for surface stabilization of Pd(0) nanoparticles, in which multiple hydroxy groups on the surface serve as ligands to
60 prevent the aggregation of nanoparticles while preserving the catalytic activity.²⁷ Moreover, it is preferable to reduce the Pd(II) species into Pd(0) on the surface of the scaffold rather than in solution to avoid aggregation of the Pd(0) nanoparticles. From this viewpoint, our attention was focused on the GaAs surface
65 covered with hydroxy groups, which is able to have higher oxidation state. In the present paper, we demonstrate the preparation of a new catalytic system, Pd(0)-GaAs (abbreviated hereafter as GaAs-Pd). The surface structure was analyzed by diffuse reflection infrared spectroscopy (DRIR) and by X-ray
70 photoelectron spectroscopy (XPS), both of which are surface-sensitive. In addition, hard X-ray photoemission spectroscopy (HX-PES) with synchrotron radiation was applied to analyze the details of the palladium catalyst. Since high-energy photon radiation can excite photoelectrons with high kinetic energies,
75 HX-PES provides more bulk-sensitive measurements than laboratory XPS; observations with high resolution from deeper areas of the surfaces are enabled. The amounts of catalytically active Pd(0) species were evaluated by the Heck reaction using iodobenzene and methyl acrylate.

Experimental

General

All of reagents including GaAs powder and solvents were commercially available, and used as received. The size of GaAs particles is 10–150 μm , and their surface area is $7.5 \times 10^{-2} \text{ m}^2/\text{g}$. DRIR spectra were recorded on JASCO FT/IR-4200 spectrometer without dilution by KBr under dry N_2 flow. Although the surface area of GaAs particles is small, enough absorption was observed because only GaAs particles were subjected to the DRIR measurement without dilution by KBr. Figures 1, 2, and 4 show raw data without Kubelka-Munk conversion. XPS spectra were observed with a VG ESCALAB MkII spectrometer using Al $K\alpha$ radiation ($h\nu = 1486.7 \text{ eV}$). HX-PES measurements were performed at the synchrotron radiation facility BL15XU in SPring-8 by using a VG Scienta R4000 analyzer. The photon energy was set at 5945 eV. Peak fitting with Voigt function was applied to decompose multi-peak spectra. ^1H NMR spectra were measured on a Bruker Avance III at 400 MHz with tetramethylsilane as an internal standard.

Preparation of GaAs-Pd (series A)

To a solution of palladium acetate ($\text{Pd}(\text{OAc})_2$, 10 mg, 0.04 mmol) in acetonitrile (MeCN, 6.0 mL), GaAs powder (A-0, 200 mg) was added. The resultant mixture was heated at 80 $^\circ\text{C}$. GaAs-Pd was collected by filtration, and was dried in a desiccator under reduced pressure for 30 min. to give GaAs-Pd. GaAs-Pd was named A-1 and A-24, respectively, according to the heating time 1 h and 24 h.

Preparation of GaAs-Pd (series B)

GaAs powder (200 mg) was treated with 10% HCl (2.0 mL) at room temperature for 1 min. After collection by filtration, GaAs powder was washed with MeCN (5 mL \times 3) to afford B-0 powder. The following adsorption of $\text{Pd}(\text{OAc})_2$ on B-0 was performed in the same way to the series A. GaAs-Pd was named B-0.5, B-1, B-6, B-12, B-24, and B-48, respectively, according to the heating time.

Preparation of GaAs-Pd (series C)

After GaAs powder (200 mg) was treated with 10% HCl (2.0 mL) at room temperature for 1 min, the aqueous solution was decanted off, and then the powder was washed with H_2O (5 mL \times 3). The collected powder was heated with aqueous 30% H_2O_2 (2.0 mL) at 60 $^\circ\text{C}$ for 15 min, which was collected by filtration, and washed with MeCN (5 mL \times 3) to afford C-0 powder. The following adsorption of $\text{Pd}(\text{OAc})_2$ on C-0 was performed in the same way to the series A with 24 h heating.

Preparation of GaAs(100)-Pd (series D)

A piece of GaAs(100) plate (D-0) was immersed in a solution of $\text{Pd}(\text{OAc})_2$ (5 mg) in MeCN (3.0 mL) and heated at 80 $^\circ\text{C}$ for 12 h. Subsequently, the plate was washed with MeCN (3.0 mL) and then dried by air.

Evaluation of catalytic activity the by the Heck reaction (in the presence of GaAs-Pd)

To a mixture of GaAs-Pd powder (30 mg) and MeCN (2.0 mL), were added iodobenzene (Ph-I, 23 μL , 0.20 mmol), methyl

acrylate **2** (MA-H, 23 μL , 0.25 mmol) and NEt_3 (35 μL , 0.25 mmol). The resultant mixture was heated at 120 $^\circ\text{C}$ for 6 h in a screw capped test tube ($\phi = 20 \text{ mm}$, $H = 150 \text{ mm}$). After GaAs-Pd was filtered off, the filtrate was concentrated under reduced pressure. The amount of the coupling product, methyl cinnamate (Ph-MA), in the residue, was determined by ^1H NMR using $\text{Cl}_2\text{CHCHCl}_2$ as an internal standard. The recovered GaAs-Pd was subjected to the next Heck reaction.

Deposit test (in the absence of GaAs-Pd)

After the Heck reaction, the used test tube was washed with MeCN (5 mL \times 3), and dried in an oven at 60 $^\circ\text{C}$ for 1 h. To the test tube, a solution of Ph-I (23 μL , 0.20 mmol), MA-H (23 μL , 0.25 mmol) and NEt_3 (35 μL , 0.25 mmol) in MeCN (2.0 mL) was added and then heated at 120 $^\circ\text{C}$ for 6 h. After removal of the solvent, the amount of a coupling product, Ph-MA, was determined by ^1H NMR using $\text{Cl}_2\text{CHCHCl}_2$ as an internal standard.

Results and discussion

The DRIR spectra (Fig. 1) provide useful information about hydroxy groups on the GaAs surface by exhibiting a broad absorption between 3200 and 3600 cm^{-1} . This absorption was observed when commercially available GaAs powder (A-0) was subjected to the measurement. Since the absorption was intact upon heating the GaAs powder at 80 $^\circ\text{C}$ for 0.5 h in MeCN, it is likely that multilayer of water were strongly adsorbed on the surface by hydrogen bonding, perturbing the stretching modes. This confirmed that the hydroxy groups are chemically fixed on the surface through covalent bonding besides water molecules strongly adsorbed on the hydroxy groups through hydrogen bonding. On the other hand, the broad absorption disappeared after heating with $\text{Pd}(\text{OAc})_2$ in MeCN for 1 h (A-1), which implies that $\text{Pd}(\text{OAc})_2$ reacted with the hydroxy groups on the GaAs surface.²⁸ Moreover, two new absorptions appeared at 1560 and 1450 cm^{-1} with prolonged heating time (A-24), which are presumably due to acetate ion (AcO).²⁹⁻³⁰

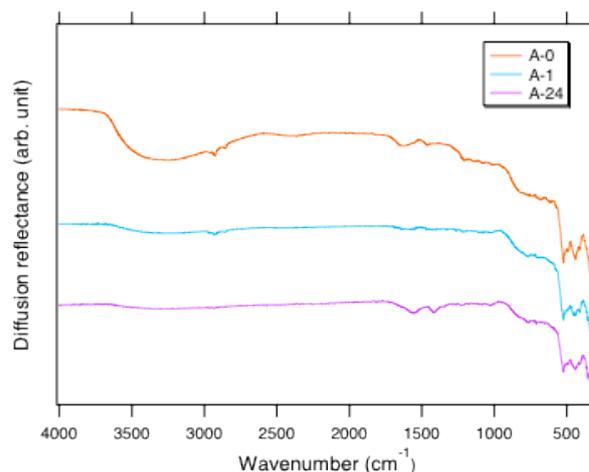


Fig. 1 DRIR spectra of GaAs-Pd powder (series A).

These intriguing results prompted us to monitor surface changes with respect to the heating time by DRIR measurement (Fig. 2).

In order to exclude the effect of originally presenting GaAs oxide layer, etching by hydrochloric acid was performed before heating with Pd(OAc)₂ (series B). In series B, similar changes as a consequence of the heating time were observed. The absorption of hydroxy groups observed for B-0 disappeared upon heating with Pd(OAc)₂ for 0.5 h (B-0.5), and absorptions of AcO⁻ were clearly observed in the case of B-24. The intensity of these AcO⁻ absorptions increased after heating for 48 h (B-48).

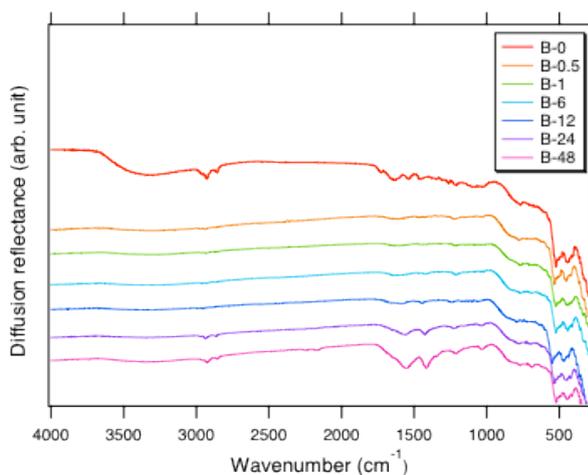
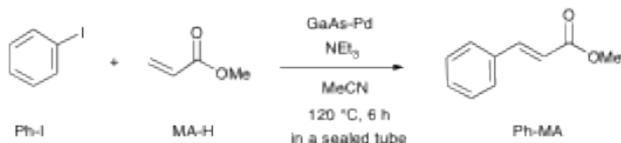


Fig. 2 DRIR spectra of GaAs-Pd powder (series B).



Scheme 1. The Heck reaction for estimating catalytic activity of the GaAs-Pd powders.

Prepared GaAs-Pd powders were employed as the catalyst for the Heck reaction using Ph-I and MA-H. In order to estimate catalytic activity, the yield of Ph-MA was compared in the early stage of the reaction (Scheme 1 and Table 1). Although both catalysts A-24 and B-24 catalyzed the Heck reaction to afford cross-coupling product in high yields, the yields decreased in the second to fourth runs. These results are consistent with the observation that most heterogeneous catalysts serve as reservoirs of catalytically active species.^{9,15,16} Indeed, the Heck reaction proceeded in the used test tube even in the absence of GaAs powder. This is proof of the role of GaAs-Pd as a scaffold (reservoir). Active palladium species are dissolved into the solution and deposited on the internal wall of the test tube after working as a homogeneous catalyst. On the basis of these results, B-24 was found to possess larger amounts of catalytically active palladium species, presumably palladium nanoparticles, as a result of etching with HCl. This fact implies that the oxide layer on the GaAs surface prevented either adsorption of Pd(OAc)₂ or reduction of Pd(II) species to Pd(0).

Table 2 reveals changes in catalytic activity depending on the time allowed for adsorption of palladium species. As expected, longer heating times correlated with higher catalytic activity.

These results indicate that active species are gradually generated during heating. In the cases of B-24 and B-48, absorptions of AcO⁻ were observed in the DRIR spectra indicating the presence of unchanged Pd(OAc)₂ on the surface.

Table 1. Comparison of catalytic activity between A-24, B-24 and C-24.

catalyst	yield / % ^a				average of yields / %
	1st	2nd	3rd	4th	
A-24	85 (0)	31	23	24	41
B-24	93 (25)	63 (0)	41	29	57
C-24	95 (1)	4 (0)	8	6	28

^aDetermined by ¹H NMR.

^bResults of deposit tests were shown in parentheses.

Table 2. Catalytic activity depending on heating time with Pd(OAc)₂.

catalyst	yield / % ^a				average of yields / %
	1st	2nd	3rd	4th	
B-0.5	58 (0)	27	13	0	25
B-1	65 (0)	27	9	5	27
B-6	78 (3)	48 (0)	28	20	44
B-12	78 (32)	63 (0)	43	12	49
B-24	93 (25)	63 (0)	41	29	57
B-48	93 (41)	88 (1)	54 (0)	42	70

^aDetermined by ¹H NMR.

^bResults of deposit tests were shown in parentheses.

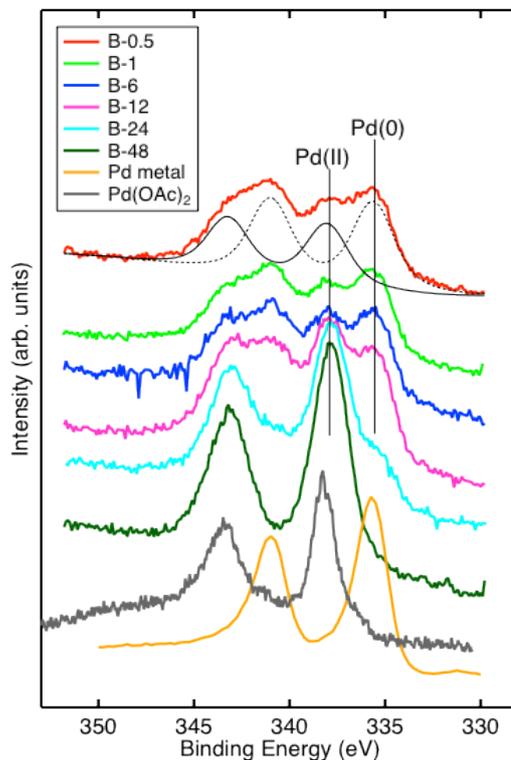


Fig. 3 Pd 3d XPS spectra from GaAs-Pd for various heating time of Pd(OAc)₂ absorption (series B). Spectra from Pd metal and Pd(OAc)₂ powder are shown as references.

The existence of Pd(0) on the surface of the series B samples was confirmed by XPS measurements. As shown in Fig. 3, Pd 3d core-level photoemission spectra are reasonably decomposed into two components with Pd 3d_{5/2}-Pd 3d_{3/2} spin-orbit splitting. In the component with lower binding energies, the Pd 3d_{5/2} peak appears at ~335.6 eV, which is very close to the corresponding peak of palladium metal. This suggests that Pd(OAc)₂ is reduced at the GaAs surface and that Pd(0) species are generated. The Pd 3d_{5/2} peak of the other component is located very close to that of Pd(OAc)₂ (~338.0 eV), indicating the existence of Pd(II) species on the surface.

The latter component (Pd(II) component) is relatively intensified with increasing heating time and finally overwhelms the former component (Pd(0) component). Taking into account that the IR absorption due to AcO⁻ also increases with heating time, this behavior is explained by the accumulation of unreacted Pd(OAc)₂, which becomes thick enough to mask the Pd(0) species on the surface after heating for 48 h.

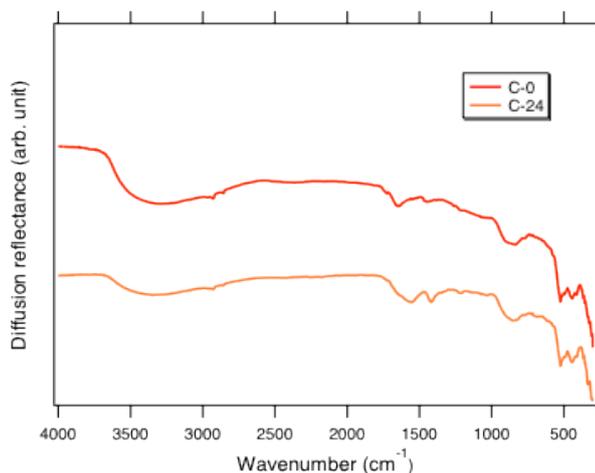


Fig. 4 DRIR spectra for GaAs-Pd powder (series C) and GaAs powder treated with Piranha solution.

It is well-known that the Pd(0) species catalyzes the cross-coupling reaction.¹⁻⁵ Hence, a reducing agent is necessary to convert Pd(II) to Pd(0). We hypothesized that hydroxy groups both attract Pd(II) to the surface as well as reduce it. In order to confirm the hypothesis, GaAs powder was treated with H₂O₂ to oxidize surface hydroxy groups beforehand (C-24). In the DRIR spectrum, C-24 exhibited a large absorption for AcO⁻, indicating the adsorption of Pd(OAc)₂, which might be due to the diminished reducing ability of C-24 (Fig. 4). In addition, the Heck reaction and deposit test also showed different reactivity in comparison with B-24. Although B-24 and C-24 showed similar catalytic activity in the first run, a considerable decrease in the yield in the second run was observed in the case of C-24 (Table 1). This means that the surface of C-24 is mainly covered with Pd(OAc)₂, which is not reduced. The physically adsorbed Pd(OAc)₂ dissolved into the solution and catalyzed the Heck reaction homogeneously after the reduction by NEt₃ in the first run. Since most of the palladium species on the surface had been washed away, the catalytic activity of C-24 was lost in a single run. In addition, the total amount of palladium species on the

surface of C-24 was considered to be low on the basis of the results of the deposit test.

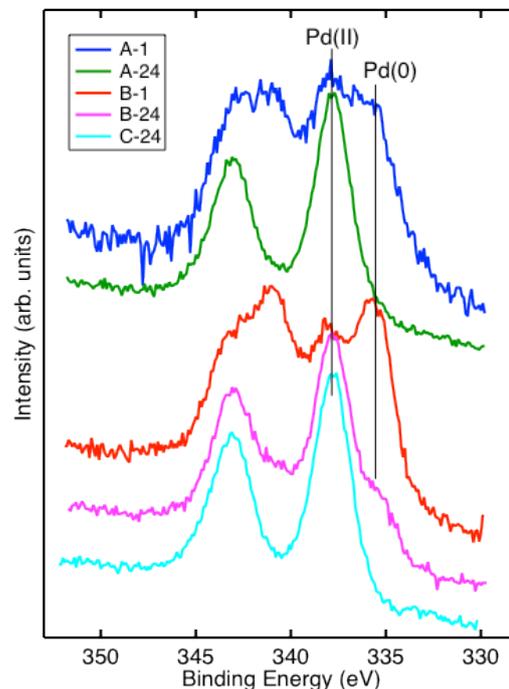


Fig. 5 Pd 3d XPS spectra from GaAs-Pd for different surface pre-treatment; as received (series A), treated with HCl (series B) and treated with HCl and H₂O₂ (series C).

Supporting evidence for the above-mentioned hypothesis about the hydroxy group was obtained via XPS measurements (Fig.5). The intensity ratio of the Pd(0) component to the Pd(II) component is smaller in A-1 than in B-1 and the same is true between A-24 and B-24. Since the GaAs surface without any pre-treatment is highly oxidized, the surface of series A is expected to be less hydroxylated than that of series B. In addition, the Pd(II) component in C-24, the GaAs powder pre-treated with H₂O₂, is almost comparable with A-1. Thus, the observed feature indicates that a less-hydroxylated surface produces less Pd(0).

Reduction of Pd(II) by the hydroxy groups provokes the oxidation of GaAs. In order to confirm this, we performed HX-PES measurements, which are suitable for detecting photoelectrons from the GaAs surface covered with a thick layer of Pd(OAc)₂. As shown in Fig. 6, the As 2p_{3/2} photoemission spectrum from D-0 exhibits two peaks, a distinct peak at 1323.1 eV and a smaller one at 1326.1 eV. The former peak is assigned to the photoemission from the bulk GaAs and the latter to oxidized arsenic, such as As₂O₃.³¹ After heating with Pd(OAc)₂ in MeCN (D-12), the intensity of the oxide peak increases, indicating that surface oxidation is promoted as a result of reduction. In accordance with this, the increase of oxidized gallium after the heating treatment is also observed in the Ga 2p_{3/2} spectra, although the amount of peak shift due to oxidation is smaller in the Ga 2p_{3/2} peak than in the As 2p_{3/2} peak (Fig. 7).

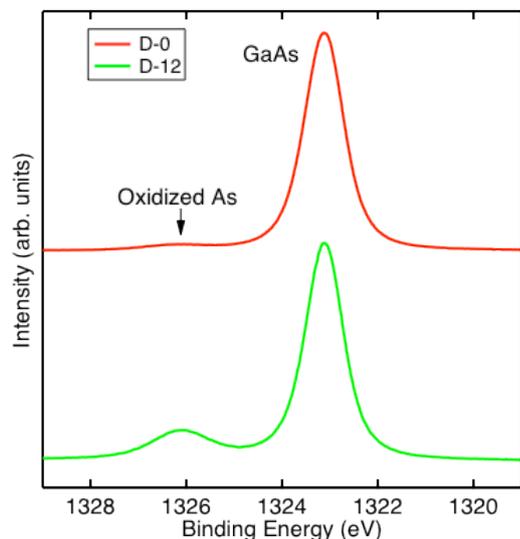


Fig. 6 As $2p_{3/2}$ HX-PES spectra from GaAs(100) as received (D-0) and GaAs(100)-Pd catalyst (D-12).

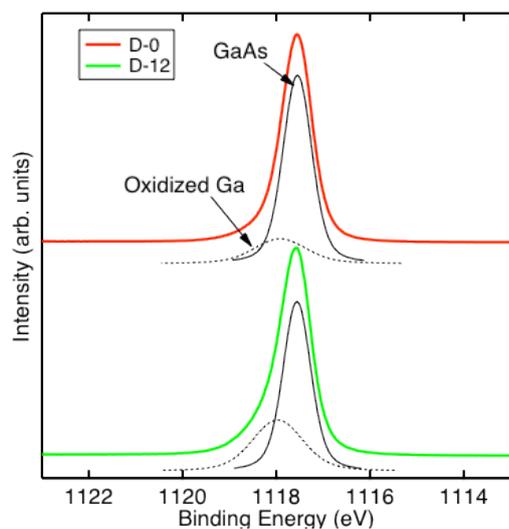


Fig. 7 Ga $2p_{3/2}$ HX-PES spectra from GaAs(100) as received (D-0) and GaAs(100)-Pd catalyst (D-12).

Bulk-sensitive HX-PES is also used to identify Pd(0) species, which are expected to exist under the thick Pd(OAc)₂ layer. As shown in Fig. 8, the Pd 3d_{5/2} peak from D-12 is decomposed into three components: a major one at ~335.7 eV, a small shoulder one at ~335.0 eV, and a broad, faint one at ~337.3 eV. Compared with the spectra in Fig. 3 or Fig. 5, it is clear that the relative intensity of the Pd(II) component is significantly reduced. The binding energy of the major component is slightly higher than that of palladium metal and much lower than that of Pd(OAc)₂. This component is reasonably assigned to Pd(0) nanoparticles, because the positive shift in core-level peaks is one of the signatures of nanoparticles.^{25,32-35} In fact, the observed shift,

0.7 eV, is comparable with the one reported,^{25,32,33,35} and almost identical to the one observed for the Pd(0) nanoparticles prepared by a similar method on an S-terminated GaAs surface.³⁵ The shoulder peak appears at the binding energy almost identical to that of palladium metal, indicating that inactive metallic palladium such as Pd-black, is formed by the aggregation of Pd(0) nanoparticles. The small broad peak is assigned to Pd(II) species, such as PdO, generated from Pd(OAc)₂ by the reaction at the surface. In fact, the Pd 3d peak from PdO appears at slightly higher than that of Pd metal and significantly lower than that of Pd(OAc)₂.^{36,37}

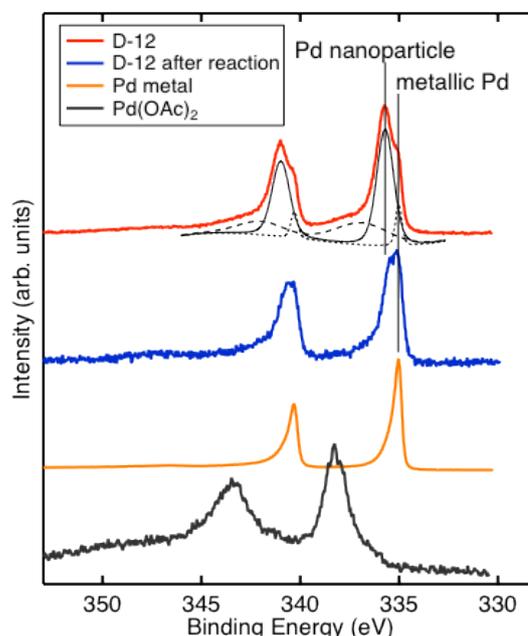
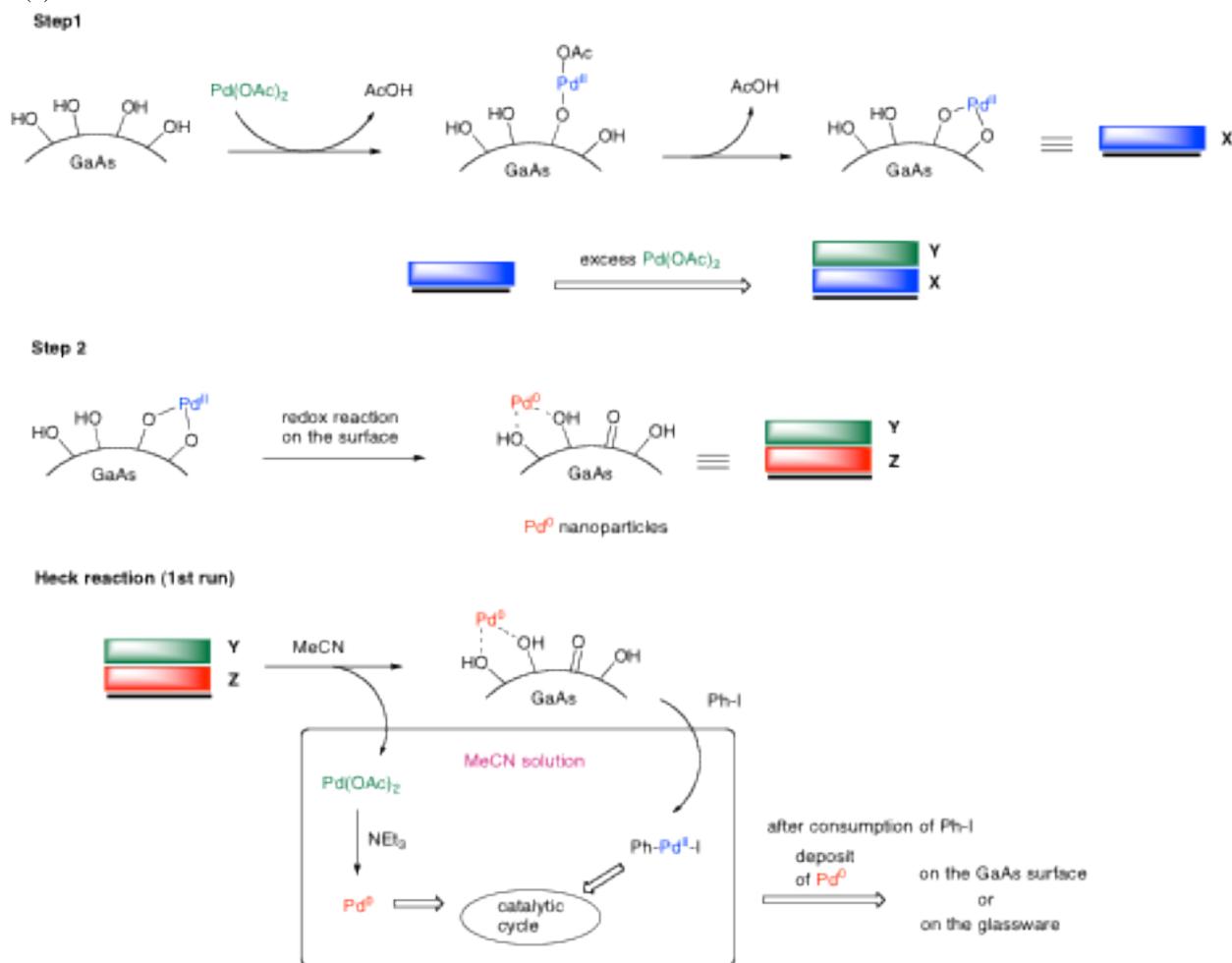


Fig. 8 Pd 3d HX-PES spectra from GaAs-Pd (100) before and after subjecting to the Heck reaction.

After the first run of the Heck reaction, the relative amount of Pd(0) nanoparticles decreases. This is highly likely due to the failure of nanoparticle re-deposition after the reaction in solution. It is also likely that the aggregation of nanoparticles progresses during the reaction.

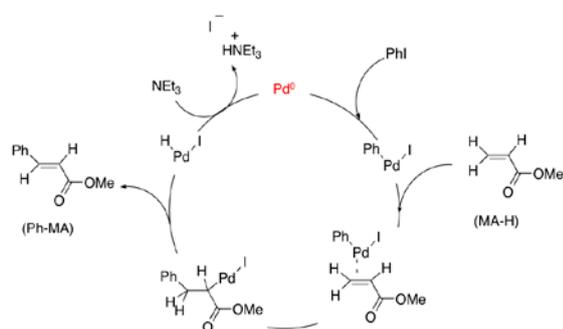
On the basis of the abovementioned results, a plausible mechanism is provided in Scheme 2. Initially, Pd(OAc)₂ is adsorbed on the GaAs surface (**Step 1**), in which hydroxy groups on the surface attract Pd(II) by anion exchange to form layer **X**. This is supported by the result of a DRIR measurement, in which an absorption band due to hydroxy groups disappeared when the GaAs powder was treated with Pd(OAc)₂. However, excess amounts of Pd(OAc)₂ are adsorbed over layer **X** (layer **Y**) during treatments of longer duration. In layer **Y**, Pd(II) species are physically bound on the GaAs surface, hence, it is easily washed away when the GaAs-Pd powder is subjected to the Heck reaction. The adsorbed Pd(II) species are subsequently reduced to Pd(0) by hydroxy group to form the layer **Z** (**Step 2**), which is confirmed by the observation of the Pd(0) component in the XPS measurement. At the same time, Pd(0) nanoparticles are formed, which is confirmed by the HX-PES measurement. The pre-

oxidized GaAs powder did not exhibit catalytic activity in the second Heck reaction because the Pd(II) species were not reduced to Pd(0) on the GaAs surface.



Scheme 2 A plausible mechanism: **Step 1**; the adsorption of Pd species on the GaAs surface, **Step 2**; the redox reaction on the GaAs-Pd, Heck reaction (1st run); dissolution and deposition of Pd(0) nanoparticles.

10



Scheme 3 A catalytic cycle of the Heck reaction.

In the Heck reaction, Pd(0) nanoparticles are dissolved as a result of oxidative addition with Ph-I, and they catalyze the cross-coupling reaction. After consumption of the Ph-I that stabilizes the Pd(0) nanoparticle in the solution, Pd(0) is redeposited on the

GaAs surface or on the glassware.

Conclusions

A novel use of GaAs, namely, as a scaffold for a heterogeneous palladium catalyst, is proposed. Hydroxy groups are considered to play two roles in this system: they 1) attract Pd(II) species on the surface by anion exchange, and 2) reduce the Pd(II) to Pd(0). These changes were analyzed by surface-sensitive measurement methods, DRIR and XPS. In addition, a more bulk-sensitive measurement, HX-PES, also supported our suppositions. The amounts of Pd(0) nanoparticles on the surface were evaluated by catalytic activity, yield, and recyclability for the Heck reaction in addition to the deposit test. All measurements and experimental results of the catalytic reaction well supported our hypothesis.

The GaAs surface is found to serve as the binding and reductive staff for palladium species. The present results might be applicable to other metal species or other oxides, which should be helpful for developing other functional surface than the support

of heterogeneous catalyst.

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Notes and references

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