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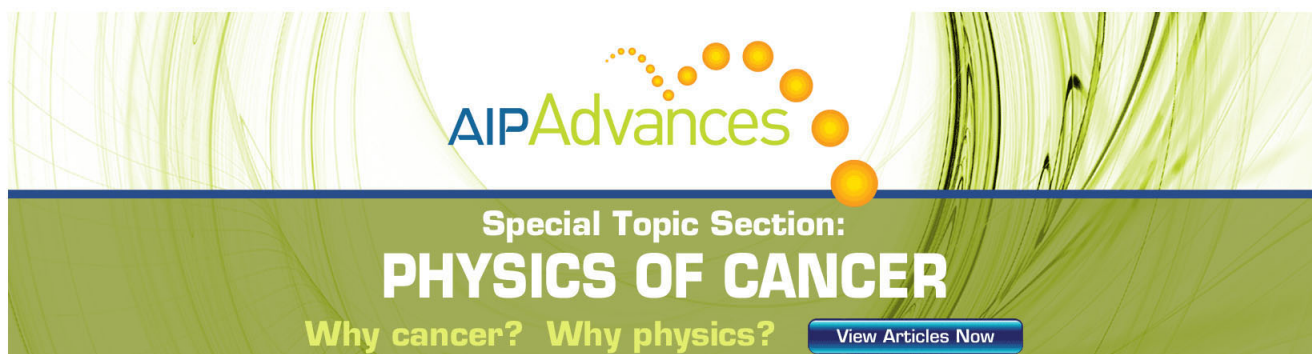
Sulfur-mediated palladium catalyst immobilized on a GaAs surface

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We present a hard x-ray photoelectron spectroscopy study on the preparation process of palladium catalyst immobilized on an S-terminated GaAs(100) surface. It is revealed that Pd(II) species are reduced on the GaAs surface and yield Pd nanoparticles during the process of Pd immobilization and the subsequent heat treatment. A comparison with the results on GaAs without S-termination suggests that the reduction of Pd is promoted by hydroxy groups during the Pd immobilization and by S during the heat treatment. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4730377]

I. INTRODUCTION

Immobilization of catalysts is an important technology from the viewpoint of green chemistry, since it simplifies the separation process of the product and reduces the consumption of precious materials, including rare metals. Hence, for a particular catalyst, finding a suitable supporting material as well as an appropriate method of immobilization is of key importance. However, it is generally not very easy to immobilize a catalyst rigidly without losing its catalytic activity over multiple cycles of use.

We have recently found a promising way of immobilizing catalytically active palladium on S-terminated GaAs surface using organopalladium, such as palladium acetate (Pd(O-COCH$_3$)$_2$), as a palladium source.[1–5] The heterogeneous catalyst thus obtained is confirmed to be sufficiently active in the Heck reaction, a palladium-catalyzed reaction that promotes carbon-carbon bond formation between alkenes and aryl halides (see recent review books[6,7]), over 10 times while maintaining high chemical yields. The leaching of Pd after the catalytic reaction can be suppressed to below 1 ppm if the catalyst is prepared with suitable treatments.[4,5]

One of the astonishing features of this catalyst is the presence of S, generally regarded as a poison of various catalytic reactions, including Pd-catalyzed ones. In our catalyst, however, immobilization without S-termination results in a catalyst with lower activity and less efficient recyclability.[1] This suggests that S adds to this catalyst's activity.

In a previous study, we performed hard x-ray photoemission spectroscopy (HX-PES) measurements and scanning electron microscopy (SEM) observations to gain insight into the structure of this heterogeneous catalyst and to identify the species responsible for the catalytic activity.[8] It was revealed that organopalladium molecules are reduced at the surface and that Pd nanoparticles are created. Since the presence of zero-valent Pd (Pd(0)) is essential in the Heck reaction, we concluded the Pd nanoparticles to be the origin of the catalytic activity. It was also demonstrated that S-termination remains almost intact even after multiple catalytic cycles, except that a portion of S is oxidized during the immobilization. Although this result confirms that S does not poison the catalyst, its role in catalytic activity is still unexplained.

In this paper, we report the results of an HX-PES study of the Pd-immobilized surfaces of both the S-terminated and bare GaAs substrates. The experiments were designed to elucidate the role of S by measuring the chemical states of S and Pd at the various stages of sample preparation. It was demonstrated that the reduction of Pd is promoted by hydroxy groups on the GaAs surface during the Pd immobilization and by S during the subsequent heat treatment. We propose a mechanism for the redox process in which catalytically active Pd nanoparticles are produced.

II. EXPERIMENTAL

Pieces of GaAs plates were cut from a GaAs disk with a mirror-finished (001) surface. N-type (Si-doped) GaAs was used to reduce charge buildup during HX-PES measurements. The catalyst samples were prepared as follows:

(1) S-termination: the GaAs plates were immersed in a 5% ammonium polysulfide ((NH$_4$)$_2$S$_X$) aqueous solution at 60 °C for 0.5 h and then washed with water (3 ml × 3) and acetonitrile (3 ml × 3).[9,10]

(2) Pd-immobilization: once dry, the plates were immersed in a solution of Pd(OCOCH$_3$)$_2$ (5 mg) in acetonitrile (3 ml) at 80 °C for 12 h and washed with acetonitrile (3 ml × 3).

(3) Heat-treatment: after drying, the plates were heated in xylene (3 ml) to fix the immobilized Pd at 130 °C for 0, 0.5, and 6 h.

The procedure is similar to the previous one[5,8] and optimized for better reproducibility. The catalysts thus obtained are hereinafter referred to as Series S or S0, S05, and S6,

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according to the heating time. To examine the effect of the catalytic reaction, S6 was subjected twice to the Heck reaction between iodobenzene and methyl acrylate in acetonitrile(CH$_3$CN) at 130 °C for 6 h. This catalyst is named S6H when referring to the data after the first reaction and S6HH after the second reaction. Details of the Heck reaction and yield measurements are described elsewhere.[4,11]

Another set of catalysts was prepared in the same way as described above except for S-termination. These S-free catalysts are referred to as Series F or F0, F05, and F6, according to the heating time. Catalyst F6 was also subjected to the Heck reaction twice and referred to F6H and F6HH after the first and the second reaction, respectively.

HX-PES was performed on the BL15XU synchrotron radiation facility at SPring-8. Core-level photoemission spectra were observed by using high-energy x-ray radiation of $h\nu = 5945$ eV. The energy resolution, estimated at the Fermi edge of Au, was 0.26 eV. The binding energy was calibrated using Au 4f$_{7/2}$ photoemission (84.0 eV). Each sample was mounted on a Cu holder with conductive adhesive tape. The tape was also used to create an electrical short-circuit between the sample's surface and the sample holder to avoid charge buildup on the surface during the measurements. As a result, peak shifts caused by charging were very small and corrected reasonably using the binding energy of the C 1s peak.

III. RESULTS

A. S 1s photoemission

Figure 1 shows the S 1s photoemission spectra of the Series S catalysts. A distinct peak is observed at 2470 eV in all
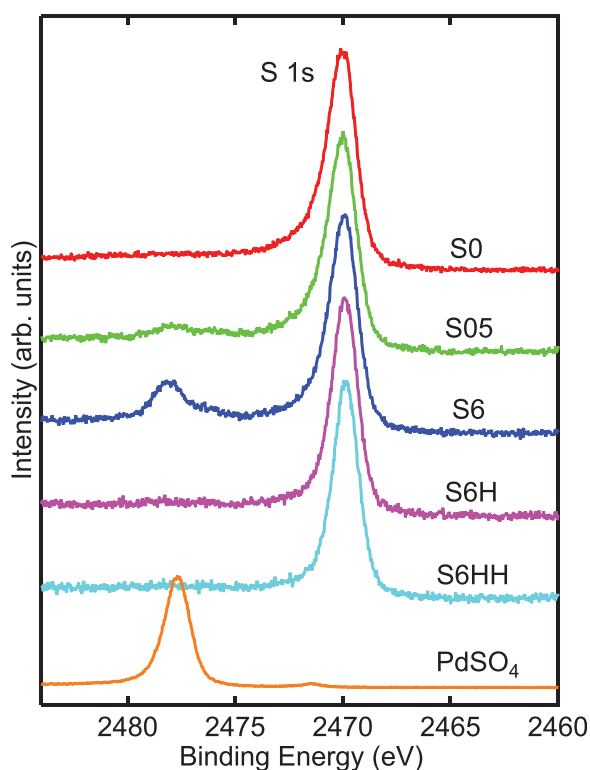
spectra. Since it was confirmed in previous studies[8] that the S 1s peak from the S-termination of GaAs surface is observed at 2470.1 eV, this peak is assigned to the S-termination.

A small peak appears at 2478 eV for S6. The origin of this peak is oxidized S, which terminates the GaAs surface as sulfinic acid or sulfonic acid, as described below. The S 1s spectrum of PdSO$_4$ is shown in Fig. 1 as an example of oxidized S. Since the only source of S is the S-termination of GaAs, this oxidized S is generated from the S in the S-termination during the preparation. A faint peak is also recognized for S05 at almost the same binding energy as for S6. However, no trace of oxidized S is observed for S0, S6H, or S6HH. This finding indicates that the oxidation of S progresses only during the heat treatment. It is highly likely that the disappearance of this peak after the Heck reaction is due to the elution of oxidized S as gaseous SO or SO$_2$. Acetonitrile used in the Heck reaction is a polar solvent that induces elution more efficiently than non-polar xylene in the heat treatment.

B. Pd 3 d photoemission

Figure 2 shows the Pd 3d$_{5/2}$ spectra of Series S. Spectra from the bulk Pd reference and the Pd(OCOCH$_3$)$_2$ powder are shown for comparison. The spectra of Series S show similar multi-peak structures, indicating that Pd atoms in different chemical states are present on the surface throughout the
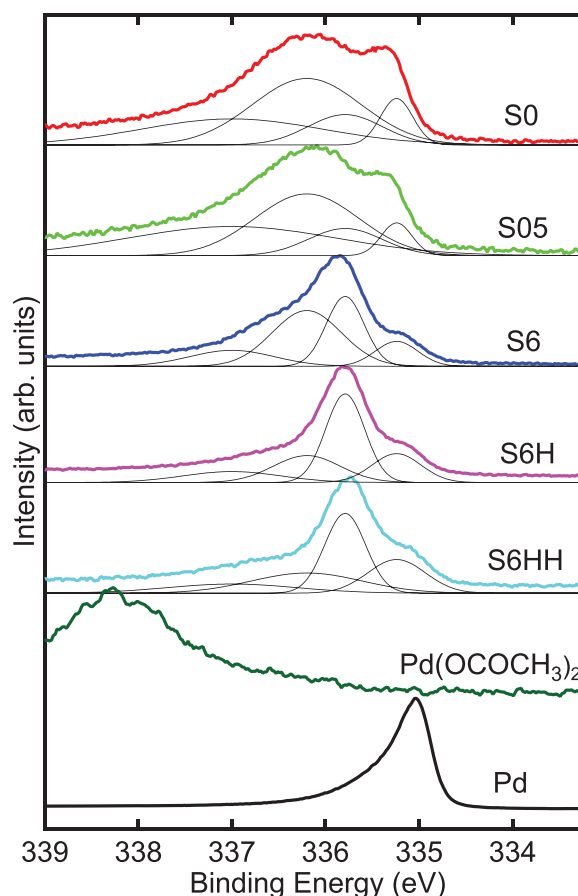

FIG. 1. S 1s spectra for Series S.

FIG. 2. Pd 3d$_{5/2}$ spectra for Series S. Each spectrum is broken down into four components whose peak binding energies are fixed at 335.2, 335.8, 336.2, and 337.0 eV.

experiment. To evaluate these chemical states, we applied multi-peak curve-fitting with a Gaussian function to these spectra.

In the case of S6, the spectrum is decomposed into four components with different binding energies of 335.2, 335.8, 336.2, and 337.0 eV. The peak at 335.2 eV is very close to that of the Pd reference (335.0 eV) and therefore is assigned to metallic Pd. The small difference in the binding energy is mainly due to the neglect of asymmetry in the curve-fitting. As is well known, metallic Pd has a rather asymmetric peak shape.[12]

Of these four components, the peak at 335.8 eV is the largest and located at a binding energy that is slightly higher than that of the Pd reference (335.0 eV) and much lower than that of Pd(II)(OCOCH$_3$)$_2$ (338.3 eV). This peak is therefore attributed to Pd nanoparticles on the basis of our previous SEM and HX-PES studies; it was revealed that Pd nanoparticles are generated on the surface of the catalyst prepared using the same procedure as S6 and that the Pd 3d peak of nanoparticles is located at 335.7 eV.[8] The observed shift, 0.8 eV, is comparable with that reported.[13–15] The formation of Pd-nanoparticles suggests that Pd(II) in Pd(OCOCH$_3$)$_2$ is reduced during the immobilization and heat treatment processes. As mentioned above, the presence of Pd(0), including as nanoparticles, is essential for the Heck reaction.

The other two peaks are somewhat broader and are located at around 336.2 and 337.0 eV. These two peaks are probably not intrinsic ones. Instead, it is highly likely that they represent over-adsorbed Pd(II) species: an assembly of
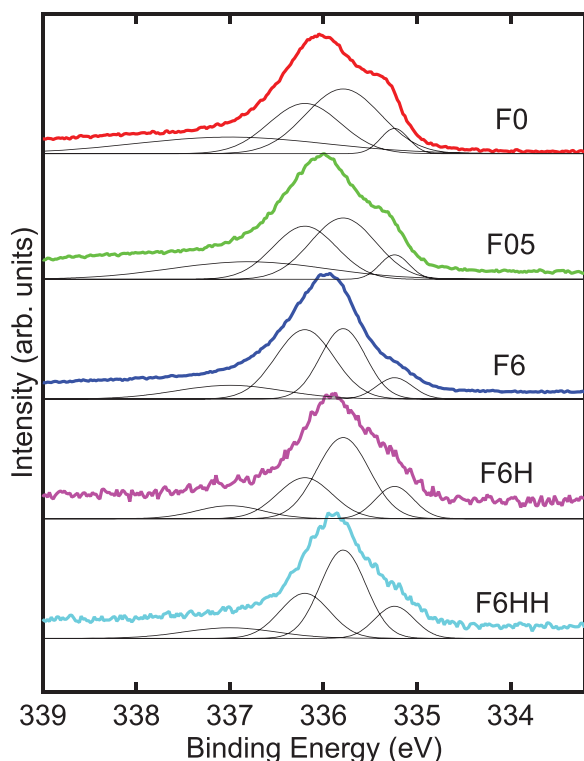
unreacted Pd(II)(OCOCH$_3$)$_2$ and other Pd(II) species derived from Pd(II)(OCOCH$_3$)$_2$. As reported previously, Pd(II)(OCOCH$_3$)$_2$ is gradually broken down by the intense x-ray beam, and consequently a rather broad peak is yielded.[8]

All the other spectra were analyzed using the same curve-fitting procedure with four Gaussian functions. The binding energies of the four peaks are, however, fixed at the same values of 335.2, 335.8, 336.2, and 337.0 eV, as determined for S6. The results are summarized in Fig. 2 for Series S and Fig. 3 for Series F. It should be noted that these spectra are displayed at equal peak height and that the relative intensity among them is not significant. This is because the intensity of the observed spectra varies significantly from sample to sample, as shown in Fig. 4, mainly due to differences in experimental geometry, such as the angle of incidence of the x-ray beam. Palladium species on the surface are also partially redissolved in the solvent during the Heck reaction. Thus, there is no practical way to normalize these spectra. Even so, qualitative analyses of these figures provide the following meaningful information:

(1) Photoemission signals from Pd nanoparticles and metallic Pd are already present at S0 and F0. This means that the reduction of Pd(II) starts during Pd immobilization, regardless of the existence of S.

(2) For Series S, the relative photoemission intensity of Pd nanoparticles to metallic Pd increases during the heat treatment (S05 → S6) and remains almost unchanged after the Heck reaction (S6 → S6H → S6HH). This suggests that the reduction of Pd(II) continues during the heat treatment and that Pd nanoparticles and metallic Pd are fairly stable throughout the preparation and the Heck reaction.

(3) For Series F, the ratio of the photoemission intensity between Pd nanoparticles and metallic Pd is not significantly changed during the heat treatment (F0 → F05 → F6),
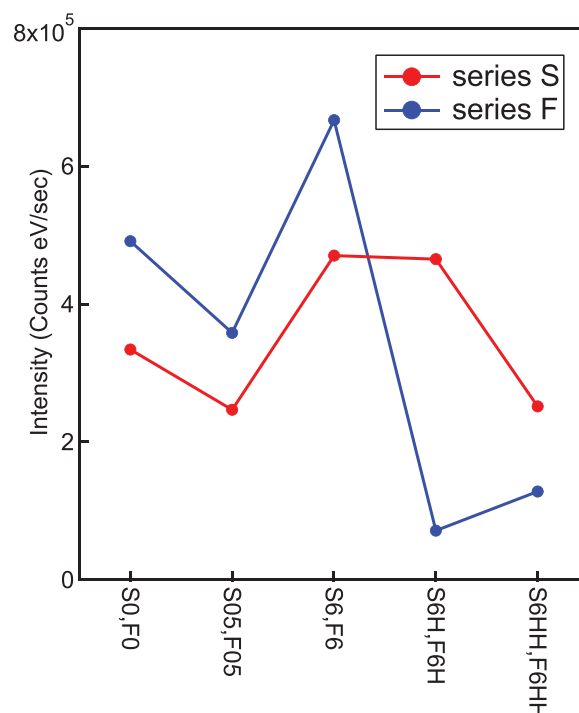

FIG. 3. Pd 3d$_{5/2}$ spectra for Series F. Each spectrum is broken down into four components whose peak binding energies are fixed at 335.2, 335.8, 336.2, and 337.0 eV.

FIG. 4. Integrated intensity of Pd 3d$_{5/2}$.

suggesting that no reduction occurs during the heat treatment. This ratio appears to be almost unchanged by the Heck reaction (F6 → F6H → F6HH). However, the total spectrum intensity shows a strong decrease after the first Heck reaction (see Fig. 4). This decrease in the spectrum intensity exceeds that likely due to geometrical effects alone, indicating that a considerable amount of Pd species is lost during the first run of the Heck reaction. This suggests that, in Series F, Pd nanoparticles and metallic Pd are only weakly bonded to the surface.

A similar loss of Pd species was also observed in previous experiments, in which these lost Pd species were dissolved in the solvent and re-deposited on the surface of the test tube.[16] It is confirmed that such re-deposited Pd species act as a source of active Pd for the Heck reaction. A similar change in the intensity ratio is observed for Series S, but is very minor, suggesting little loss of Pd species.

(4) For Series S, the contribution from the Pd(II) species including unreacted $Pd(II)(OCOCH_3)_2$ decreases gradually with the progress of the sample preparation and the catalytic reaction (S0 → S6HH). This is partially due to the generation of Pd(0). Another reason for this decrease is the loss of Pd species.

(5) For Series F, the contribution of the Pd(II) species shows no significant change during the heat treatment (F0 → F05 → F6) and a strong decrease as a result of the Heck reaction (F6 → F6H).

C. As 2p and Ga 2p photoemission

Figure 5 shows the As $2p_{3/2}$ and Ga $2p_{3/2}$ photoemission spectra of the Series S catalysts and the reference GaAs. The As $2p_{3/2}$ spectra exhibit two peaks in common, a large peak at 1323.3 eV and a smaller one at 1326.2 eV. The former is assigned to photoemission from the bulk GaAs and the latter to oxidized arsenic, such as As_2O_3, in the surface. The oxide
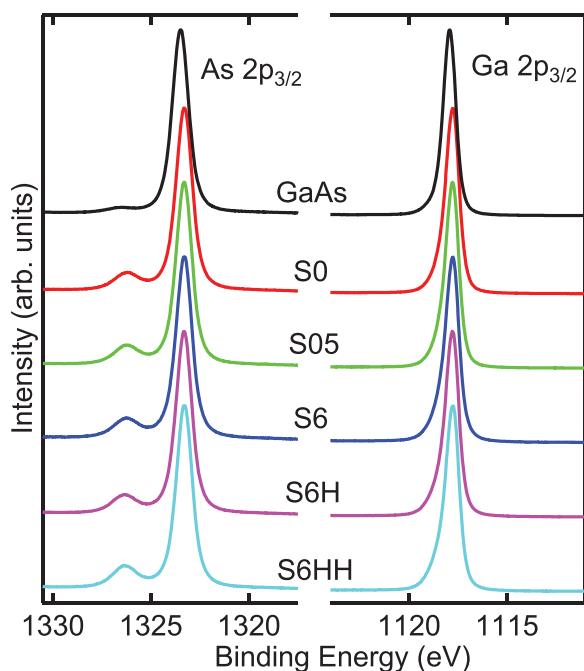
peak increases during Pd immobilization and keeps a steady relative intensity to the main peak.

Similar features are also observed for the Ga 2p spectra, where photoemission from the bulk GaAs is observed at 1117.8 eV. The peak from the oxidized gallium is located at 1118 eV and appears as a tail of the main peak. Clearly, there is no significant difference in spectrum shape among the Series S catalysts. The same is true for the As $2p_{3/2}$ and Ga $2p_{3/2}$ photoemission spectra of the Series F catalysts, as shown in Fig. 6. We therefore conclude that, regardless of the existence of the S-termination, the GaAs substrate undergoes no more oxidation during the heat treatment and the catalytic reaction.

IV. DISCUSSION

The results described above are discussed here, along with the process of catalyst preparation. The mechanism of the redox process and the role of S are also discussed.

A. Pd-immobilization

Regardless of the presence or absence of S-termination, the GaAs substrate is oxidized, and in return, Pd(II) is reduced during the Pd immobilization. Pd nanoparticles are also generated in this step, suggesting that S-termination has no significant effect on the generation of Pd nanoparticles at this point. The redox process during Pd immobilization is, in fact, promoted by the hydroxy groups.

In our previous studies, where Pd was immobilized on the GaAs substrate without S-termination, we elucidated the details of the process of the redox reaction on the surface: the hydroxy groups on the GaAs surface attract Pd(II) species and subsequently reduce them to Pd(0) in exchange for oxidation of the GaAs surface.[16] The role of the hydroxy

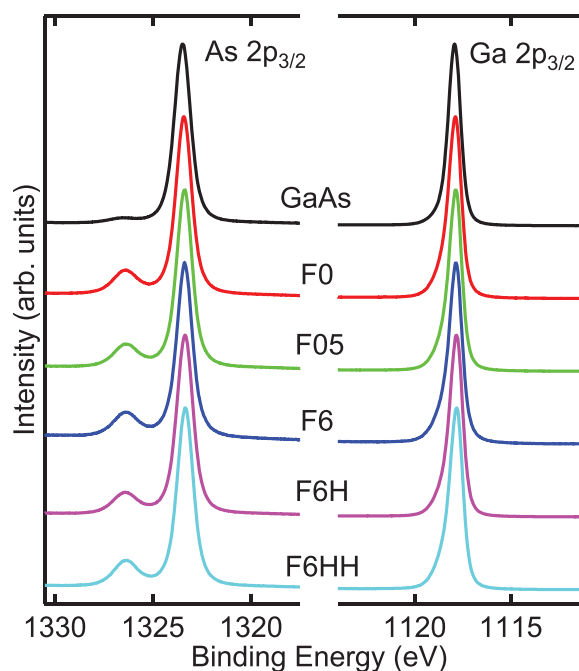FIG. 5. As $2p_{3/2}$ and Ga $2p_{3/2}$ spectra for Series S.

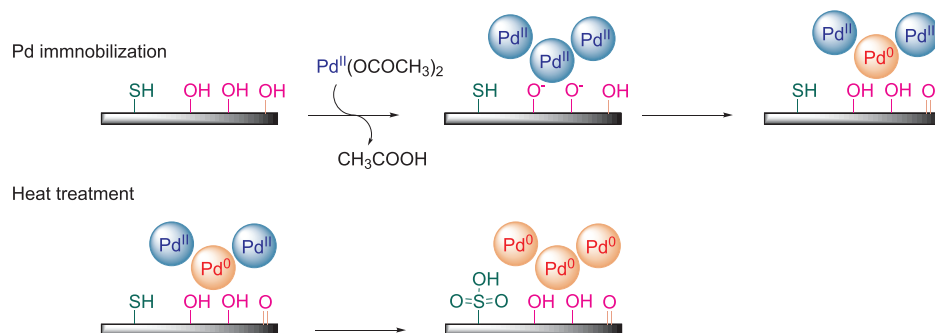FIG. 6. As $2p_{3/2}$ and Ga $2p_{3/2}$ spectra for Series F.

FIG. 7. Plausible process for Pd immobilization and the heat treatment.

groups on the GaAs surface is also confirmed for the S-terminated GaAs by FT-IR measurements.[17]

B. Heat treatment

In Series S, oxidation of the GaAs substrate progresses no further: instead, oxidized S is generated during the heat treatment. Since the relative photoemission intensity from Pd nanoparticles increases, it is likely that the reduction of Pd(II) and the generation of Pd nanoparticles progress in exchange for the oxidation of S. For Series F, the oxidation of the GaAs substrate and the relative signal intensity of Pd nanoparticles remain almost unchanged. This suggests no further reduction of Pd(II) in this step.

C. The Heck reaction

For Series S, no significant change in the contribution from Pd nanoparticles is observed, suggesting that Pd nanoparticles and metallic Pd are fairly stable during the Heck reaction. On the other hand, a significant loss of Pd species, including Pd nanoparticles and metallic Pd, is observed for Series F.

D. Plausible mechanism

On the basis of these findings, together with our previous results,[16] we propose a plausible mechanism for the redox process which produces catalytically active Pd nanoparticles, as shown in Fig. 7.

During Pd immobilization, $Pd(OCOCH_3)_2$ is adsorbed on the GaAs surface, a process in which hydroxy groups on the surface attract Pd(II) by anion exchange. The adsorbed Pd(II) species are subsequently reduced to Pd(0) by the hydroxy groups. At the same time, Pd nanoparticles are generated, as observed in S0 and F0. Since this redox process progresses regardless of the presence or absence of S, S is not involved in this step.

In the heat treatment, the over-adsorbed Pd(II) species are reduced by S, which exist as mercapto (-SH) groups in aqueous solution, as a result of which Pd nanoparticles are generated. In exchange, thiols (GaAs-SH) are oxidized to sulfinic acids (GaAs-SO_2H) or sulfonic acids (GaAs-SO_3H). Hydroxy groups are not involved in this step because of their low reducing ability and, therefore, the Pd(II) species remain intact in Series F. Thus, the quantity of Pd(II) species (unreacted $Pd(II)(OCOCH_3)_2$ and other Pd(II) species derived from $Pd(II)(OCOCH_3)_2$) decreases in Series S but remains unchanged for Series F.

E. The role of sulfur

As described above, S promotes the reduction of Pd during the heat treatment. Another role is suggested by the finding that Pd nanoparticles are more stable in the presence of S (Secs. III B (2) and III B (3)). This implies that mercapto groups induce an enhancement of the bonding between the GaAs substrate and Pd nanoparticles. Although the details of the mechanism of this enhancement are not yet known, it is certain that S contributes to the high recyclability of the catalyst.

V. CONCLUSION

We performed HX-PES studies on Pd catalysts immobilized on S-terminated GaAs(001). Pd 3 d core-level photoemission spectra reveal that Pd(II) species are reduced on the surface and yield Pd nanoparticles during the process of Pd immobilization and the subsequent heat treatment. We conclude, from a comparison with the results for the catalyst prepared on the GaAs surface without S-termination, that reduction of Pd(II) species is promoted by hydroxy groups during Pd immobilization and by S during the heat treatment.

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