

Hard x-ray photoemission spectroscopic investigation of palladium catalysts immobilized on a GaAs(001) surface

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We present studies on the structure and chemical states of a catalyst developed by immobilizing palladium on S-terminated GaAs(001). Hard x-ray photoelectron spectroscopy (HX-PES) of core-level and valence band photoemission consistently indicates that the organopalladium molecules are reduced on the surface yielding Pd nanoparticles with a metallic nature. This finding is supported by high-resolution observations using scanning electron microscopy and backscattered electron image. HX-PES results also reveal that a portion of S atoms forming the S-termination is oxidized during the formation of Pd nanoparticles. © 2010 American Institute of Physics.

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I. INTRODUCTION

Immobilization of catalysts is an important technology from the viewpoint of green chemistry. This is because immobilization simplifies the separation of catalysts from products and makes the recycling of catalysts easier. Therefore, for a particular catalyst, finding an appropriate method of immobilization and a suitable material where the catalyst is immobilized is desired. However, it is generally not very easy to immobilize a catalyst rigidly without seeing it lose its catalytic activity over multiple cycles of use.

We have recently found a promising way of immobilizing palladium on S-terminated GaAs(001) (SGA hereinafter) using organopalladium, such as palladium acetate [Pd(OCOCH₃)₂], as a palladium source.¹⁻⁵ The immobilized catalyst is confirmed to be active enough in the Heck reaction, a well-known palladium-catalyzed reaction for promoting carbon-carbon bond formation between an alkene and an aryl halide (see recent review books^{6,7}), for over ten 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}

Although it has been found that the developed catalyst has major potentiality for practical use, many unanswered questions remain. The most essential one is the chemical form of palladium species because it is key to understanding the high catalytic activity. Another question is the role of

sulfur. It is well known that S poisons 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 contributes positively to this catalyst's activity. However, even the presence of S after immobilization has not been confirmed yet, and therefore, the structure of this catalyst and the chemical states of Pd and S on the surface need to be elucidated.

In this paper, we report the results of hard x-ray photoemission spectroscopy (HX-PES) studies together with scanning electron microscopy (SEM) and backscattered electron image (BEI) observations on the palladium-immobilized surface of SGA both before and after the Heck reaction. It was demonstrated that organopalladium molecules are reduced at the surface yielding Pd nanoparticles. It was also revealed that the S-termination is almost intact even after multiple cycles of catalytic reactions, except that a portion of S is oxidized during immobilization.

II. EXPERIMENTAL

Pieces of GaAs substrates were cut from a GaAs disk with a mirror-finished (001) surface. N-type (Si-doped) GaAs was used to reduce charging during HX-PES and SEM measurements. Immobilization was carried out as follows: (1) S-termination of GaAs(001) by immersing GaAs plates in aqueous ammonium polysulfide [(NH₄)₂S_x] (Refs. 8 and 9); (2) adsorption of Pd(OCOCH₃)₂ in acetonitrile; and (3) heated-washing in xylene. This process is almost identical to

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that described in previous reports.^{3,5} The catalyst thus obtained is hereinafter referred to as PSGA (Pd-immobilized S-terminated GaAs). Among several pieces of PSGA, one of them was kept fresh (fresh-PSGA), and the rest were subjected to the Heck reaction of iodobenzene and methyl acrylate for up to ten times. The activity of these used catalysts was evaluated by the yield of the product (methyl trans-cinnamate) after 12 h reaction at 100 °C (bath temperature). It was confirmed that all the catalysts exhibited nearly 100% yield. These used but still fully active catalysts are hereinafter referred to as used-PSGA. Details of the Heck reaction and yield measurements are described in Ref. 4. It should be noted that “catalyst N” in Ref. 4 was prepared by almost the same process as PSGA and exhibited the catalytic performance comparable to PSGA.

HX-PES was performed at the synchrotron radiation facility BL15XU in SPring-8. Spectra of core-levels and valence band photoemission 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 make electrical short-circuits between the sample surface and the sample holder to avoid charging at the surface. As a result, peak shift caused by charging was very small and corrected by using the binding energy of the C $1s$ peak. As references, GaAs (as cut from the disk), SGA and bulk Pd were measured in the same way. Insulating $\text{Pd}(\text{OCOCH}_3)_2$ powder, which was used in the preparation of catalysts, was mixed with carbon powder to reduce charging and measured on the conductive tape. PdSO_4 powder, another insulating reference, was also measured by using carbon powder.

A particular necessity of HX-PES is that the high-energy x-ray radiation makes it possible to detect the isolated peak of S $1s$ photoemission that appears at ~ 2470 eV. In conventional x-ray photoelectron spectroscopy (XPS) with Al/Mg $K\alpha$ radiation ($h\nu=1487/1254$ eV), which we used in previous studies,¹⁻⁴ signals of S $2s$ and S $2p$ photoemission are extremely weak and practically undetectable due to overlapping strong photoemission and Auger peaks from the GaAs substrate. In addition, these signals are much more reduced when molecules, like $\text{Pd}(\text{OCOCH}_3)_2$, are adsorbed on the surface.

A drawback of using the high-flux beam is the decomposition of molecules during measurements, which causes deformation of spectra. This phenomenon is distinctively observed for $\text{Pd}(\text{OCOCH}_3)_2$. Therefore, the spectrum from $\text{Pd}(\text{OCOCH}_3)_2$ shown here is obtained as an accumulation of several spectra observed in a very short time from separate parts of the sample in order both to minimize the effect of the decomposition and to improve the signal-to-noise ratio.

High-resolution SEM and BEI images were observed using a HITACHI S-5500 at an acceleration voltage of 20 kV. In contrast to SEM, which gives the outer shape of samples and no inside information, BEI gives images reflecting the composition of the material because the amount of backscattered electrons is proportional to the mean atomic number of the material. For selected samples, electron-excited Auger

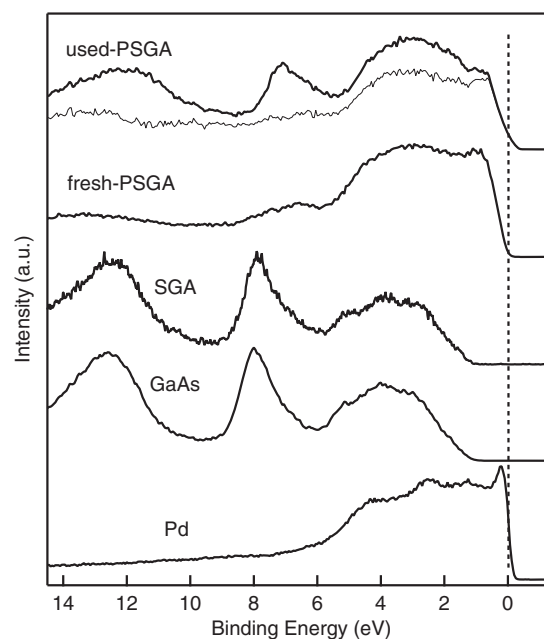


FIG. 1. Valence band spectra from used-PSGA (after the tenth run of the Heck reaction), fresh-PSGA, SGA, GaAs, and the bulk Pd reference. Thin curve is calculated from the spectrum of used-PSGA by subtracting that of SGA so as to the Ga $4s$ band at 7 eV vanishes.

analysis was performed using a JEOL JAMP-9500F. These measurements were carried out after HX-PES experiments.

III. RESULTS AND DISCUSSION

A. Valence band photoemission

Valence band spectra from the catalysts (fresh-PSGA and used-PSGA) and the reference samples are shown in Fig. 1. The features of the valence band spectrum are not significantly changed by S-termination. In fact, the spectrum of SGA is almost identical to that of GaAs as follows: the valence band edge is located at ~ 1 eV below the Fermi energy (E_F) and broad peaks corresponding to Ga $4s$ and As $4s$ bands appear at ~ 8 eV and ~ 12 eV, respectively.¹⁰

In contrast, immobilization of Pd causes drastic changes, as seen in the spectrum of fresh-PSGA. The valence band edge of fresh-PSGA shifts to lower binding energies and a small but finite density of state (DOS) emerges at E_F . The finite DOS at E_F is characteristic of metallic materials, and therefore consistent with the asymmetric line shape of the Pd $3d$ peak (see below). In addition, features originated from GaAs have almost vanished, and the overall line shape is very similar to that of the Pd reference. These results indicate that the surface of the catalysts is covered by a metallic overlayer of Pd species, which is significantly thick, making the substrate almost invisible, even for the bulk-sensitive HX-PES.

This argument is also true for used-PSGA, except that the features at deeper levels (such as Ga $4s$ and As $4s$ bands) have appreciably recovered to those of SGA and GaAs. This suggests that the overlayer of the Pd species becomes thinner during the catalytic reaction. However, the shape of Pd component is not significantly changed after the

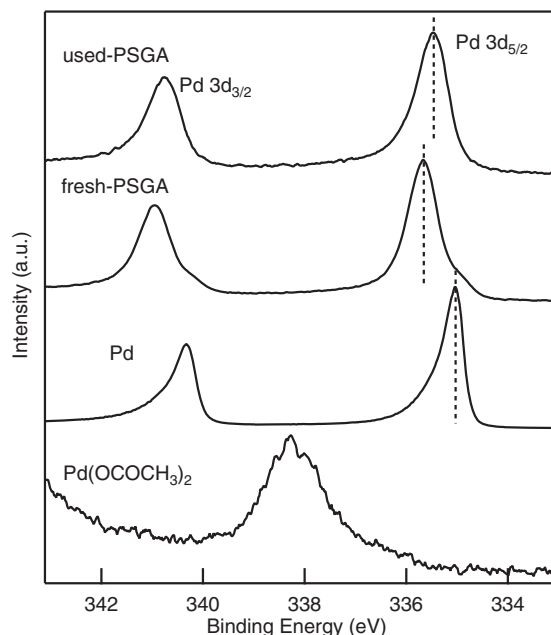


FIG. 2. Pd 3d spectra from used-PSGA (after the tenth run of the Heck reaction), fresh-PSGA, the bulk Pd reference, and the Pd(OCOCH₃)₂ powder. Vertical lines are given at the position of Pd 3d_{5/2} peaks to make the shift and the asymmetry more visible.

reactions as shown in thin curve, which is calculated from the spectrum of used-PSGA by subtracting that of SGA so as to the Ga 4s band at ~ 7 eV is eliminated.

The Pd species created as a result of immobilization are highly likely to be Pd nanoparticles. Previous photoemission studies on Pd nanoparticles have revealed that the following features are enhanced for smaller particles: (a) valence band narrowing accompanied by a less steep band edge, and (b) a shift in valence band centroid, valence band edge, and core-level peaks toward higher binding energies.^{11–15} Among these features, the less steep band edge is prominent in the current catalysts, although the narrowing of valence bands is not visible here. In addition, the observed small DOS at E_F is explained by the positive shift in the valence band edge. These shifts are interpreted as the final state effects caused by a positive charge induced by photoemission into electrically isolated particles.^{16–19} Thus, the observed features strongly suggest the presence of sufficiently electrically isolated Pd nanoparticles.

B. Pd 3d photoemission

Figure 2 shows the Pd 3d spectra of the catalysts and the reference samples. A sharp Pd 3d_{5/2} peak is observed from fresh-PSGA. The binding energy (335.7 eV) of this peak is slightly higher than that of the Pd reference (335.0 eV) and much lower than that of Pd(II)(OCOCH₃)₂ (338.3 eV). This indicates that the Pd(II)(OCOCH₃)₂ molecules react at the surface of SGA and that consequently different Pd(0) species emerge. It should be noted that the existence of Pd(0) is essential for the Heck reaction. This Pd(0) species is reasonably assigned to Pd nanoparticles as follows.

First, as mentioned in Sec. III A, the positive shift in core-level peaks is one of the signatures of Pd nanoparticles.

The observed shift, 0.7 eV, is comparable with the reported.^{11,12,14} Alternatively, the positive peak shift might be assigned to PdO, because the Pd 3d_{5/2} peak of PdO is observed at slightly higher binding energies of that of Pd metal.^{20–24} However, the O 1s peak originated from PdO, which should appear at lower binding energy by 2 eV from the Pd 3p_{3/2} peak,²⁰ is not detected in the spectrum of fresh-PSGA. In addition, the observed valence band spectrum of fresh-PSGA is totally different from that of PdO.²⁰ Thus, the possibility of the PdO formation is excluded.

Another feature suggesting Pd nanoparticles is rather symmetric peak of fresh-PSGA. Generally, metallic materials show asymmetric core-level peaks with a longer tail toward the higher binding energies.²⁵ In fact, this asymmetry is quite prominent for bulk Pd as shown in Fig. 2. Since the degree of asymmetry depends on the DOS at the Fermi level, the indistinctive asymmetry for fresh-PSGA indicates lower DOS at the Fermi level in comparison with bulklike Pd, which is consistent with the formation of Pd nanoparticles. A small shoulder found at the tail of the lower binding energies can be assigned to bulklike Pd, which is likely to be produced during heated-washing.

These following features are mostly true for the Pd 3d spectrum of used-PSGA after the tenth run of the Heck reaction: a modestly asymmetric Pd 3d_{5/2} peak is observed at 335.5 eV. This means that the Pd nanoparticles are stable enough until the tenth run, which is consistent with the sustainment of the high catalytic activity for repeated use. However, the peak shift (0.5 eV) is slightly small and asymmetry is rather distinguishable in comparison with fresh-PSGA. These facts suggest that the Pd nanoparticles become larger as a result of the reaction.

Note that the rather broad peak of Pd(OCOCH₃)₂ is due to gradual decomposition of the molecule during the measurement, caused by the intense x-ray beam. The decomposition produces reduced Pd species which have peaks at lower binding energies than Pd(OCOCH₃)₂, making a tail toward the lower binding energy side.

Nishiwaki *et al.*²⁶ have recently proposed a mechanism for the reaction of Pd(OCOCH₃)₂ at the S-terminated surface, on the basis of studies on S-terminated GaN. According to their model, an –SH group is formed on the S–Ga bond of the S-termination in the solvent during immobilization. This –SH group attracts Pd(OCOCH₃)₂ molecules and subsequently reduces them, yielding Pd(0) species. If this is the case, it is likely that the Pd(0) species self-assemble and condense into Pd nanoparticles.

C. S 1s photoemission

Figure 3 shows S 1s spectra of the catalysts (fresh-PSGA and used-PSGA) and SGA. A distinct peak of S 1s photoemission is observed at 2470.1 eV for SGA. This peak is reasonably attributed to photoemission from the S-termination.

In contrast, the spectrum of fresh-PSGA shows a following multicomponent feature: A main peak at ~ 2470 eV, a broader peak at ~ 2472 eV and a separated peak at ~ 2477 eV. Judging from the binding energy, the main peak

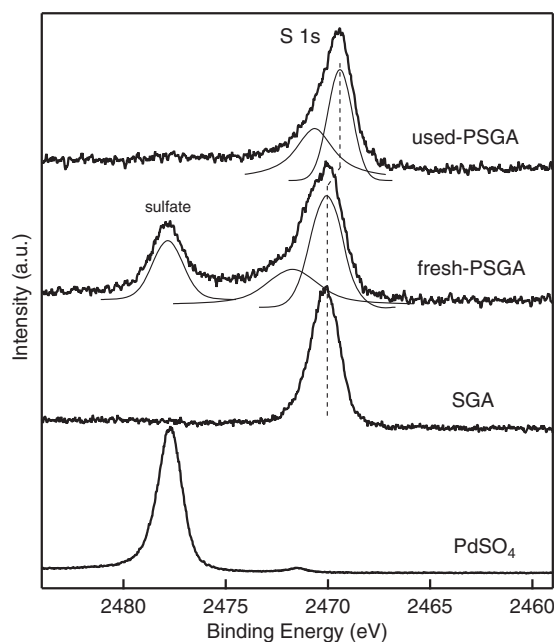


FIG. 3. S $1s$ spectra from used-PSGA (after a tenth run of the Heck reaction), fresh-PSGA, SGA, and PdSO_4 .

of fresh-PSGA is reasonably assigned to S forming the S-termination. The broader peak emerges after Pd immobilization, suggesting that this component is assigned to S atoms which are in charge of the coupling between the substrate and Pd nanoparticles. Since it is suggested that the Pd nanoparticles are coated by organic molecules (see below), it is highly likely that a chemical bond between S and the molecule is formed. The separated peak can be assigned to sulfate generated during immobilization, since the binding energy is very close to the main S $1s$ peak of PdSO_4 . The emergence of sulfate suggests that S is oxidized in exchange for the reduction in Pd.

This multicomponent feature is also true for used-PSGA. However, the spectrum is shifted to lower binding energies by 1.1 eV and the sulfate component is negligibly-small. The shift is due to band offset at the interface between the S-termination and the overlayer formed by immobilization, since consistently almost the same amount of shift is observed for the As $2p_{3/2}$ and the Ga $2p_{3/2}$ peaks. It is also found that the intensity ratio of the S $1s$ peak from S-termination to the As $2p_{3/2}$ is not significantly decreased from SGA to used-PSGA. Since the ratio is regarded as an indicator of S coverage, it follows that a large portion of S-termination is maintained after the catalytic reaction. Thus, S is kept away from the Pd nanoparticles, and therefore, is not poisonous to the catalyst. The disappearance of sulfate is likely due to elution during the reaction.

D. SEM and BEI

Figures 4(a) and 4(b), respectively, show SEM and BEI images of the surface of fresh-PSGA. The SEM image reveals that this surface is covered by small particles 3–5 nm in diameter. The BEI image, which is taken from the same area as the SEM image, seems rather uniform. However, a closer inspection of this image shows that the surface is densely

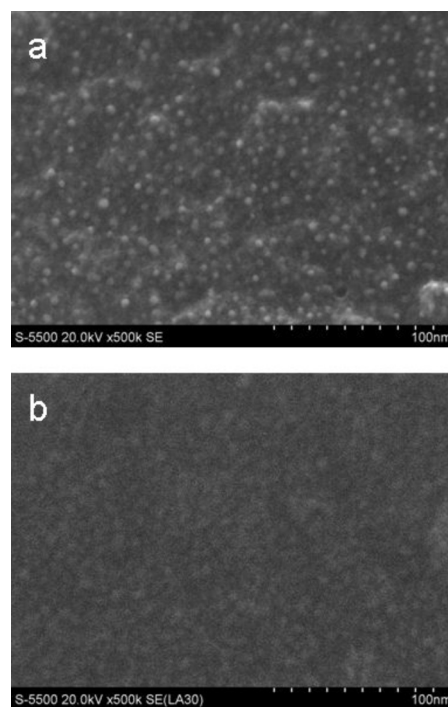


FIG. 4. (a) SEM image of the surface of fresh-PSGA. (b) BEI image of the same area of (a).

covered with small particles, although it is hard to be recognized in the presented contrast. The uniform BEI image suggests that the surface composition is homogeneous, since BEI is sensitive to atomic weight (the heavier, the brighter).

These features appear consistent with the interpretation of HX-PES observations: a thick layer of Pd nanoparticles covers the substrate. However, the nature of the HX-PES spectra, such as the positive shift in the core-level peak and the valence band edge, is interpreted as the photoemission final state effect due to electrically isolated nanoparticles, while the particles in the SEM image are aggregated and seemingly in electrical contact with each other. This contradiction is resolved by assuming that the surface of the particles is covered by less conductive material, e.g., organic molecules. Such a layer might be created during immobilization and make the particles effectively separated from each other. The basis for this assumption was obtained by a preliminary Auger analysis on the surface of used-PSGA, where the electron-excited Auger signal from Pd (Pd MVV ~ 325 eV) is much smaller than expected, whereas the signal from C (C KVV ~ 255 eV) is much larger. [MVV represents the process that, as a result of the relaxation that a core hole in M-shell (M) is filled by a valence band electron (V), another electron in valence band (V) is excited. KVV represents the similar process where a core hole in K-shell (K) is involved.] Since Auger measurement is more sensitive to surfaces than HX-PES, this implies that the Pd nanoparticles are covered by organic materials.

A SEM image from the surface of used-PSGA is shown in Fig. 5(a). The small particles 3–5 nm in diameter remain on the surface, while much larger particles 10–20 nm in size also appear. The corresponding BEI image [Fig. 5(b)] shows a following clear contrast between the particles and their

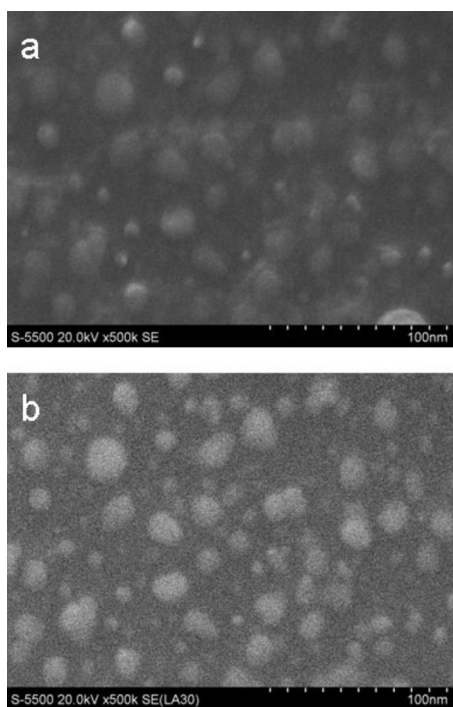


FIG. 5. (a) SEM image of the surface of used-PSGA. (b) BEI image of the same area of (a).

surrounding area: regardless of size, particles show a similar level of contrast and are much brighter than their surroundings. These findings can be interpreted as coalescence of Pd nanoparticles and consequent exposure of the substrate. This interpretation is consistent with the changes of Pd $3d$ and valence band spectra.

IV. CONCLUSION

We have performed HX-PES and SEM/BEI studies on the Pd catalysts immobilized on S-terminated GaAs(001). Pd $3d$ core-level spectra reveal that the organopalladium molecules, Pd(OCOCH₃)₂, are reduced at the substrate surface, producing Pd(0) species. In addition, the asymmetric Pd $3d$ peak, the positive energy shift in both the Pd $3d$ peak and the valence band edge and the small but finite DOS at E_F indicate the formation of metallic Pd nanoparticles, which are the most likely origin of the catalytic activity. The comparison between fresh-PSGAs and used-PSGAs reveals that the Pd nanoparticles are stable enough for repeated use in the Heck reaction, although the particle size is changed. These findings are confirmed by SEM and BEI observations. The role of Pd nanoparticles in the catalytic cycle, however, is not understood yet. To reveal their true role will require further careful investigation of their dynamic behavior in the catalytic cycle. The presence of S is also confirmed. In fact, it is revealed that a large portion of S-termination is intact even after multiple reaction cycles. This explains why S is not poisonous to the catalyst.

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