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Surface study of organopalladium molecules on S-terminated GaAs

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Organopalladium species ($\{Pd\}$) immobilized on an S-terminated GaAs substrate (S/GaAs) effectively catalyzes C-C bond formation in the Mizoroki-Heck reaction with cycle durability. However, the immobilizing mechanism of $\{Pd\}$ is unknown. In this study, we deposited $Pd(OCOCH_3)_2$ on S/GaAs in two different methods, namely dry-physical vapor-deposition and wet-chemical deposition, and compared the catalytic activities in the Mizoroki-Heck reaction.

Also, S-termination and $\{Pd\}$ -immobilization on GaAs grains were performed by the wet-chemical method to monitor the change in the surface chemical structure during the preparation process with diffuse reflectance Fourier transform infrared spectroscopy (FT-IR). FT-IR measurements implied that the immobilization of catalytic active $\{Pd\}$ was related to the OH groups on the S-terminated surface. $\{Pd\}$ -S/GaAs prepared dry-physically showed poor catalytic activity, because $\{Pd\}$ was not immobilized under absence of OH groups.

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1 Introduction Pd catalysts are widely used for organic syntheses in chemical industries since they effectively catalyze C-C bond formation such as the Mizoroki-Heck reaction [1, 2]. We have recently discovered a promising way of immobilizing catalytically active Pd species (indicated as $\{Pd\}$ hereafter) derived from $Pd(OCOCH_3)_2$ on an S-terminated GaAs(001)-(2 \times 6) (S/GaAs hereafter) surface by using a wet-chemical process [3–6]. The new immobilized catalyst is best described as the three-component system $\{Pd\}$ -S/GaAs. It efficiently catalyzes the Mizoroki-Heck reaction for more than 10 runs with nearly 100 % yield [4, 5].

Generally, S is known as a catalyst poison that considerably degrades transition metal catalysts because of the formation of a strong metal-S bond [7]. It is interesting that the high catalytic activity and stability of $\{Pd\}$ -S/GaAs are

maintained even with the presence of S. It is reported that S terminates a GaAs(001) surface with (2 \times 6) surface reconstruction, a unit of which consists of five S-S adatom dimers and one missing dimer [8,9]. We also performed the preparation of $\{Pd\}$ -S/GaAs by using a dry-physical process, which is vapor-deposition of S and following $Pd(OCOCH_3)_2$ on a buffer-grown GaAs(001) surface in an ultra high vacuum (UHV) [11]. Surface analysis by using reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM) showed that the (2 \times 6) surface reconstruction of the S layer was intact after the deposition owing to the high Ga-S bonding strength.

Despite the fascinating catalytic property of $\{Pd\}$ -S/GaAs, however, a mystery is how $\{Pd\}$ is immobilized on the S-terminated surface. In this paper, we report the preparation of $\{Pd\}$ -S/GaAs catalysts in dry-physical and

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wet-chemical methods, and compare the catalytic activities in the Mizoroki-Heck reaction. We have also monitored the change of the surface chemical states during the wet-chemical preparation of {Pd}-S/GaAs.

2 Experimental

2.1 {Pd}-S/GaAs plate catalysts A GaAs buffer layer was grown on a GaAs(001) substrate ($11 \times 13 \text{ mm}^2$) under $1 \times 10^{-4} \text{ Pa}$ of an arsenic atmosphere. The substrate was exposed to $1 \times 10^{-3} \text{ Pa}$ of S vapor for 5 min, followed by annealing at 400°C for 12 h in UHV [8,9]. The S-termination of the surface was confirmed with X-ray crystal truncation rod (CTR) measurement [10]. The (0,0, L) CTR ($0 < L < 4$) was measured by using synchrotron radiation BL11XU, SPring-8. The data was fitted by the model assuming a GaAs(001) surface terminated by a monolayer of (2×6) S-termination. Next, one S-terminated substrate was dry-physically deposited with $\text{Pd}(\text{OCOCH}_3)_2$ vapor with the pressure of $6 \times 10^{-5} \text{ Pa}$ for 0.5 h [11]. Another S-terminated substrate was deposited with $\text{Pd}(\text{OCOCH}_3)_2$ in a wet-chemical method [3–6]. The substrate was immersed in a Pd-source solution, which was prepared by dissolving 5 mg of $\text{Pd}(\text{OCOCH}_3)_2$ in 3 ml of acetonitrile, and heated at 80°C for 12 h. The catalytic activities of the two {Pd}-S/GaAs catalysts were compared in terms of the yield in the repeated Mizoroki-Heck coupling reaction of iodobenzene and methyl acrylate [6].

2.2 {Pd}-S/GaAs grain catalysts {Pd}-S/GaAs in a grain form was also prepared to monitor the surface structure change with diffuse reflectance Fourier transform infrared spectroscopy (FT-IR) during the wet-chemical process as follows: (1) Pieces of GaAs (50 mg) were ground (100 mesh) with an agate mortar and pestle in air. (2) The GaAs grains were cleaned in a 10 % HCl aqueous solution for 60 s and immersed in a 5 % $(\text{NH}_4)_2\text{S}_x$ aqueous solution at 60°C for 1 h, filtrated, and dried [13,14]. (3) The grains were heated in a vacuum at 250°C for 1 h. (4) The grains were immersed in the Pd-source solution, described above, at 80°C for 12 h, filtrated, and dried. (4') As for the step (4), an FT-IR spectrum was recorded after 1 h of immersing also. (5) The grains were heated in xylene at 120°C for 12 h, filtrated, and dried. A portion of the sample was taken out after each step of the process to record diffuse reflectance FT-IR spectra.

3 Results and discussion From CTR measurements, the distance between the S layer and the Ga layer was evaluated as 1.6 \AA . This is greater than 1.3 \AA in the literature [12]. For more precise discussion, the data should be fitted by a more suitable model considering the surface roughness than the simple model using only a monolayer of S with (2×6) surface reconstruction. The rod profile significantly changed by the deposition of $\text{Pd}(\text{OCOCH}_3)_2$, although we were unable to fit the data because of the resulting high complexity of the surface morphology.

Table 1 shows the yield of the Mizoroki-Heck reaction catalyzed by {Pd}-S/GaAs. While the catalyst prepared wet-chemically maintained the yield $\sim 90\%$ up to at least the third run, the catalyst prepared in the dry-physical method resulted in the low yield and no cycle durability.

Figure 1 shows the diffuse reflectance FT-IR spectra recorded after each step of the {Pd}-S/GaAs grains preparation. The spectra are normalized to the intensities of the phonon absorption bands of GaAs at 440 and 523 cm^{-1} . The spectra of $(\text{NH}_4)_2\text{S}_x$ and $\text{Pd}(\text{OCOCH}_3)_2$ are also shown in Fig. 1 as references.

The as-ground GaAs sample has a broad absorption band near 3400 cm^{-1} assigned to stretching vibration of O-H bonds in OH groups. This indicates that the surface of GaAs is covered with OH groups.

The sample after immersing in the $(\text{NH}_4)_2\text{S}_x$ aqueous solution showed several peaks which are comparable to those of the spectrum of the $(\text{NH}_4)_2\text{S}_x$ reference sample. It is represented that considerable amount of $(\text{NH}_4)_2\text{S}_x$ is deposited on the surface. The peaks completely disappeared after vacuum drying because the excess amount of $(\text{NH}_4)_2\text{S}_x$ evaporated to form a monolayer of S-termination on the GaAs surface [13,14]. The formation of the S-termination by heating at 250°C has been confirmed with RHEED, STM, CTR measurements [8,9,11,12]. As a result, a similar spectrum to that of GaAs with OH groups was obtained whereas the vibration bands related to S were too faint to be detected. The absorption band of O-H stretching vibration is still seen. Since the spectrum did not change after heating in only acetonitrile (hydrophilic) at 80°C for 12 h, the absorption band is not due to simple water-adsorption but chemical hydroxylation. It is likely either that parts of GaAs surface have not been terminated by S, due to the non-planar surfaces resulting from grinding, or that a mostly complete S-termination layer is itself hydroxylated by ambient moisture.

After the immersion of the sample in the Pd-source solution for 1h, new absorption bands appeared near 1408, 1430 and 1494 cm^{-1} , and the absorption band of OH groups significantly disappeared. As shown in the figure, $\text{Pd}(\text{OCOCH}_3)_2$ has similar peaks at 1330, 1406 and 1570 cm^{-1} which are associated with the $\text{CH}_3\text{-O}$ bending vibration, the C=O symmetric stretching vibration and the C=O asymmetric vibration in the OCOCH_3 groups, respectively [15,16]. However, the peak positions of the Pd-source-immersed sample considerably differ from those of $\text{Pd}(\text{OCOCH}_3)_2$, and the peaks finally disappeared after 12 h. These facts imply that $\text{Pd}(\text{OCOCH}_3)_2$ is deposited but has changed its molecular structure on the surface.

Table 1 Yield (%) of the Mizoroki-Heck reaction catalyzed by {Pd}-S/GaAs.

Runs	1st	2nd	3rd
Catalyst prepared dry-physically	50	0	0
Catalyst prepared wet-chemically	91	90	88

The change in the molecular form should be brought by some chemical reaction with the OH groups because the absorption band of the OH groups significantly disappeared. As shown in the diagram of Fig. 1, one possible reaction is the anion exchange by the OH group accompanying elimination of acetic acid. In this case, {Pd} is chemically immobilized on the surface, substituting the proton [6, 17]. Following reduction of Pd(II) to Pd(0) is assumed [6, 17] but cannot be discussed with FT-IR. For the dry-physical deposition in UHV, however, Pd(OCOCH₃)₂ was simply settled as it was on the S-termination without OH groups. Because Pd(OCOCH₃)₂ is highly soluble in an organic solution, probably considerable amount of Pd(OCOCH₃)₂ was rinsed off from the substrate in the first run of the Mizoroki-Heck reaction to lose the catalytic activity. It was shown that the formation of catalytic active {Pd} is related to the OH groups on the S-terminated surface.

4 Conclusion We prepared {Pd}-S/GaAs catalysts dry-physically and wet-chemically, and compared their catalytic activities. Dry-physical deposition of Pd(OCOCH₃)₂ on S/GaAs was confirmed with CTR. However, it exhibited poor catalytic activity. Diffuse reflectance FT-IR measurement during the Pd-S/GaAs grains preparation implied that not only S-termination but also OH groups are crucial to immobilize catalytically active {Pd}. The S-terminated GaAs surface thus provided such reaction field. On the other hand, catalytic active {Pd} was not immobilized by the dry-physical deposition under absence of OH groups in UHV and resulted in poor catalytic activity.

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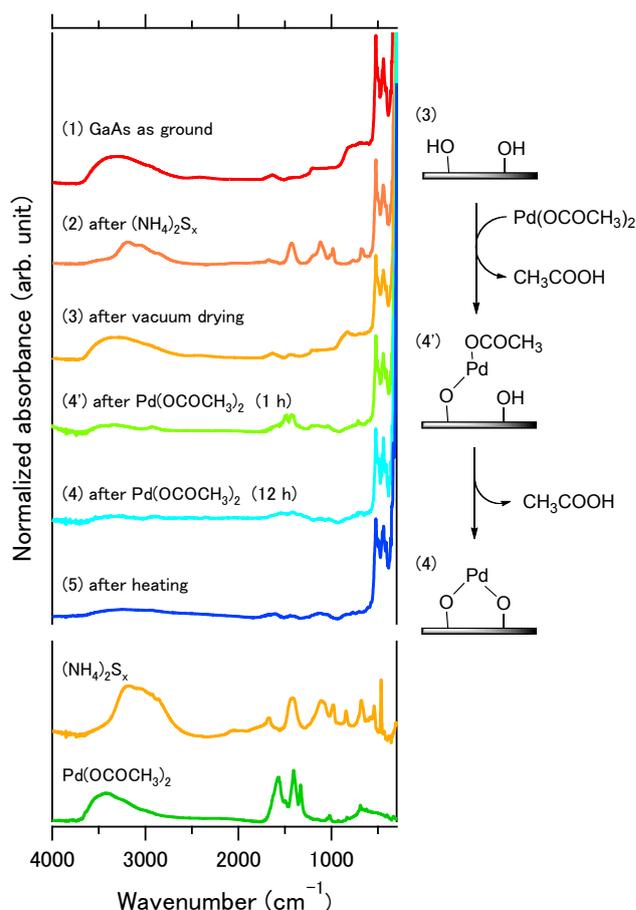


Figure 1 Diffuse reflectance FT-IR spectra recorded at each step of {Pd}-S/GaAs grain preparation along with those of (NH₄)₂S_x and Pd(OCOCH₃)₂. Schematic diagrams of possible surface structure are also illustrated aside.

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