

Facilitation of the Reduction of Pd(II) by the Glass Surface -Development of a Glass-Supported Palladium Catalyst-

Nagatoshi Nishiwaki,^{a,b,*} Yasuyuki Mori,^a Erina Fukuoka,^a Haruyasu Asahara,^{a,b}
Shotaro Hirao,^a Jun Sawayama,^a Kazuhiko Saigo,^{a,b} Tomoya Konishi^c and Masahiko
Shimoda^d

^a School of Environmental Science and Engineering, Kochi University of Technology,
Tosayamada, Kami, Kochi 782-8502, Japan. Fax: +81 887 57 2520; Tel: +81 887 57
2517; E-mail:nishiwaki.nagatoshi@kochi-tech.ac.jp

^b Research Center for Material Science and Engineering, Kochi University of
Technology, Tosayamada, Kami, Kochi 782-8502, Japan.

^c Center for Collaborative Research, Anan National College of Technology, Aoki,
Minobayashi, Anan, Tokushima 774-0017, Japan

^d Surface Physics and Structure Unit, Surface Physics Group, National Institute for
Material Science, Sengen, Tsukuba, Ibaraki 305-0047, Japan

Abstract: A glass-supported palladium catalyst was developed. The catalyst could be used repeatedly (12 times) with a low catalytic loading (0.05 mol%) for the Heck reaction with a turnover number of 45000, and no special treatment was necessary before catalyst reuse. The catalytic activity was maintained even after the catalyst was left to stand in air for one month. Furthermore, it was found that the glass surface assisted the adsorption and reduction of the Pd(II) species, through which catalytically active Pd(0) nanoparticles were formed and stabilized.

Highlight:

A glass-supported palladium catalyst was prepared with simple manipulations.

The catalyst was recovered from the reaction mixture without any special treatment.

The catalyst was repeatedly (12 times) used with low catalytic loading (0.05 mol%).

The glass surface reduce Pd(II) species and stabilize the Pd(0) nanoparticles.

An amine added as the reductant prevents the nanodispersion of palladium species.

Keywords: Supported Catalyst; Glass; Nanoparticles; Palladium; Hydroxy Group

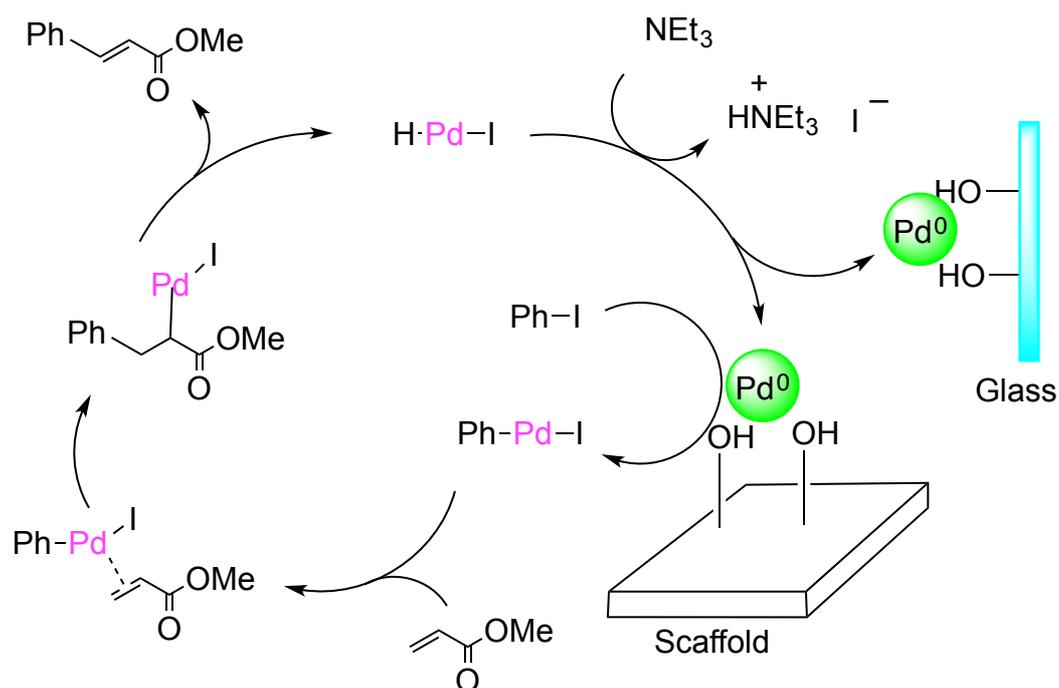
1 Introduction

Transition metal catalysts have been applied in many useful reactions and are indispensable in our present way of life. Despite great progress in catalyst chemistry, the development of new catalysts and new catalytic reactions is still in high demand from both academic and industrial standpoints.

Decreasing the required catalyst loads is also important in terms of reducing the amounts of noble metals used. As catalytic efficiency increases, trace amounts of catalyst can be used to cause a reaction to proceed. Although this is a welcome result, it brings about a new problem: it is difficult to be sure of the effect of the catalyst. For example, a catalytic reaction sometimes proceeds easily even in the absence of a catalyst when old glassware is used, which indicates that a trace amount of catalytically active species still remains on the inside surface of the glassware. Hence, glassware should be washed very carefully after catalytic reactions. To avoid this problem, wealthy researchers use new glassware each time they conduct a catalytic reaction.

This problem is also encountered when a solid-supported catalyst is employed, especially in reactions using aryl iodide as a substrate. A mechanism for the palladium catalyzed Heck reaction is illustrated in Scheme 1. The reaction is initiated by the oxidative addition of iodobenzene to Pd(0) in Pd(0) nanoparticles on a scaffold [1–10]. The stabilized adduct dissolves in a solution, and serves as an actual active species to catalyze the reaction homogeneously. After C–C bond formation accompanied by reductive elimination, the Pd(0) is redeposited on the scaffold as nanoparticles [1–10]. This catalytic cycle is repeated until the iodobenzene is consumed completely. In

returning to the scaffold, some of the Pd(0) is adsorbed on the glassware, which causes the abovementioned problem. In this case, the solid-supported catalyst does not serve as a heterogeneous catalyst, but as a gradual releaser of a homogeneous catalyst.



Scheme 1. A catalytic cycle of a solid-supported catalyst

From a different point of view, the glass surface can catch floating Pd(0), which indicates that glass can be used as a scaffold for the immobilization of transition metal catalysts. This consideration prompted us to develop a glass-supported palladium catalyst.

2 Experimental

2.1 Reagents and Glassware. A screw capped test tube is commercially available (Maruemu corporation), and is made from borosilicate glass, which consists of SiO₂ 73.0%, B₂O₃ 11.0%, Al₂O₃ 6.5%, Na₂O 6.0%, K₂O 2.0%, BaO 1.0%, CaO 0.5%. A cover glass and a glass wool were also commercially available, however, the composition is not unknown. All reagents and solvents were purchased from commercial source, and were used as received.

2.2 Preparation of Glass-Supported Catalysts. In a screw capped test tube, a 3.3×10^{-2} mM solution of palladium acetate (3 mL, 0.1 μ mol) in acetonitrile was heated at 120 °C for 12 h. After decanting the solution, the test tube was washed with acetonitrile (5 mL \times 2). The test tube was air-dried, and used as catalyst **B** for the C-C bond coupling reactions.

The catalyst **A** and the glass wool supported catalyst were prepared in a same way.

2.3 Heck Reaction. In the test-tube catalyst B, a mixture of acetonitrile (5 mL), iodobenzene (23 μ L, 0.2 mmol), methyl acrylate (23 μ L, 0.25 mmol), and triethylamine (35 μ L, 0.25 mmol) was heated at 120 °C for 12 h. After removal of the solvent, the residue was dissolved in deuterated chloroform, and the yield of methyl cinnamate was determined by ¹H NMR (Bruker Ascend-400 at 400 MHz), in which 1,1,2,2-tetrachloroethane was used as an internal standard. After decanting the solution, the test tube was washed with acetonitrile (5 mL \times 2). The test tube was air-dried, and used for another Heck reaction in the same way repeatedly.

2.4 X-ray photoelectron spectroscopy (XPS). XPS was performed with a VG ESCALAB MkII spectrometer. The analysis chamber base pressure was better than 1×10^{-8} Pa. Photoemissions from Pd 3d core-level were observed by using MgK α radiation (1254 eV). The binding energy was calibrated with respect to C 1s photoemission at 285.0 eV. Multi-peak curve-fitting with a Voigt function was employed to estimate the chemical states of the immobilized Pd.

3. Results and Discussion

3.1 Preparation of Glass-Supported Catalyst in the Presence of Triethylamine

Triethylamine (50 equiv.) was added as a reductant to a solution of palladium acetate in acetonitrile. The resultant solution was heated in a screw-capped test tube at 120 °C for 12 h. The test tube became slightly black, and the color remained even after washing with acetonitrile (catalyst A). Seventy-five percent of the initial palladium acetate was immobilized inside the test tube, as estimated by inductively coupled plasma mass spectroscopy (ICP-MS) after dissolution of all the palladium species in nitric acid.

The catalytic activity of the glass-supported palladium was evaluated by conducting the Heck reaction with iodobenzene and methyl acrylate to afford methyl cinnamate. From the environmental viewpoint, the reuse of the catalyst with high efficiency is very desirable; hence, the number of repeated reactions affording the product in over 80% yield was used as an index of catalytic ability. When 5 mol% of

palladium acetate (based on iodobenzene) was used, no decrease in yield was observed after over 40 repetitions of the reactions. Even when the catalyst load was decreased to 0.05 mol%, the catalyst could be reused nine times with an average yield of 92% (Table 1). On the basis of the results of the Heck reaction and ICP-MS, the turnover number (TON) was calculated to be 36000. Aggregated palladium, so called palladium cluster or palladium black, is not catalytically active; therefore, not all the immobilized palladium species on the glass could always serve as the catalyst, which implies that the actual TON should be higher than 36000.

Table 1. The Heck reaction using test-tube catalysts **A** and **B**

run	1	2	3	4	5	6	7	8	9	10	11	12	13
cat. A	98	80	93	95	98	91	95	93	75	61			
cat. B	99	89	88	100	87	80	80	80	82	87	80	80	58

3.2 Preparation of Glass-Supported Catalyst in the Absence of Triethylamine

The test-tube catalyst **B** was also prepared in the absence of the reductant triethylamine. To our surprise, it revealed a higher catalytic ability than catalyst **A**; catalyst **B** could be used for the Heck reaction 12 times with 86% average yield under 0.05 mol% loading (Table 1), with a TON of 45000. Scanning electron microscope

(SEM) observation of the two test-tube catalysts **A** and **B** revealed different morphologies of the palladium species on the surface (Figure 1). In the case of catalyst **A**, the palladium species aggregated, and hardly any nanoparticles were found. On the contrary, many nanoparticles were observed in the case of catalyst **B**. These results indicate that the use of triethylamine as the reductant prevents the formation of a catalytically active surface. Moreover, notably, palladium nanoparticles were immobilized on the glass surface even in the absence of the reductant triethylamine; in this case, the glass surface is considered to play an important role.

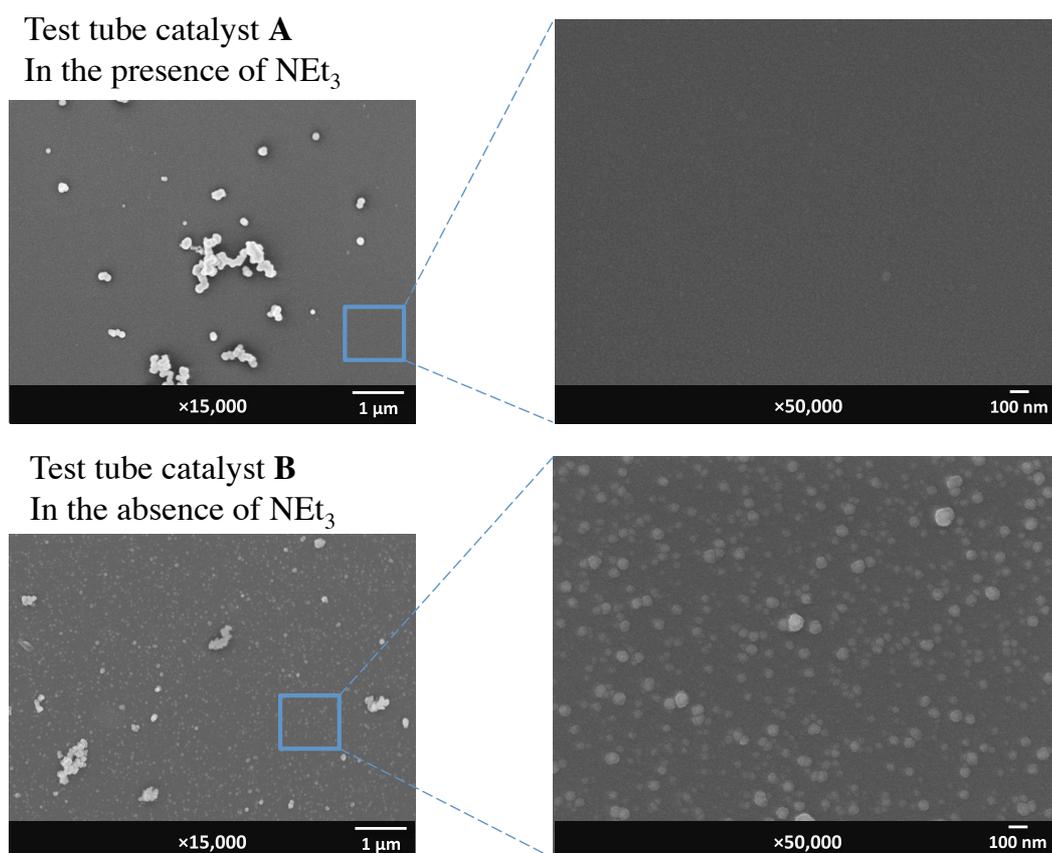


Figure 1. The different glass surface of two catalysts **A** and **B** observed by SEM

3.3 Study on the Role of the Glass Surface

X-ray photoelectron spectroscopy (XPS) was employed (Figure 2) to determine the change in the oxidation state of the palladium species during its adsorption on glass [11]. Upon soaking a cover glass in an acetonitrile solution of palladium acetate at room temperature for 24 h, the palladium species remained as Pd(II) (**RT**). On the other hand, the reduction of the palladium species was observed when the cover glass was heated in a solution of palladium acetate at 120 °C without any added reductant (**1h**, **3h**, and **12h**). A large amount of Pd(II) was converted to Pd(0) after heating for 1 h, and the reduction was almost completed within 3 h. Note that the heating temperature (120 °C) was considerably lower than the decomposition temperature of palladium acetate (205 °C), which indicates that the surface of the glass assisted the reduction of the palladium species. Indeed, when a polypropylene test tube was used instead of a glass test tube, a considerable amount of Pd(II) still remained (**PP**) even after heating for 3 h.

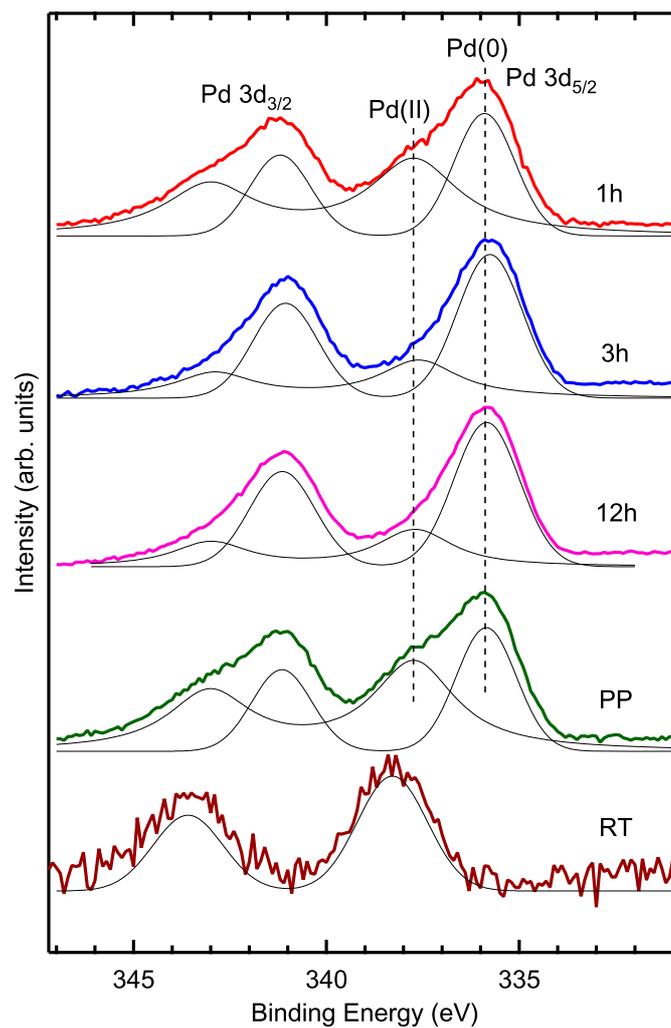
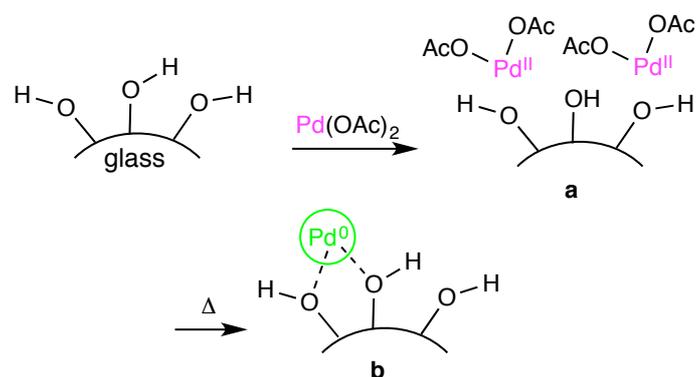


Figure 2. Pd 3d core-levels photoemission spectra from Pd-immobilized glass

Different chemical shifts of the Pd(II) species were observed in the XPS spectra for **RT** and the other samples (Figure 2). In the case of **RT**, palladium acetate was adsorbed only physically on the glass surface [12]. On the other hand, the peak of the Pd(II) species shifted to a lower binding energy when the cover glass was heated at 120 °C. This change indicates another Pd(II) species was present in a different chemical state.



Scheme 2. A plausible role of hydroxy groups on a glass surface

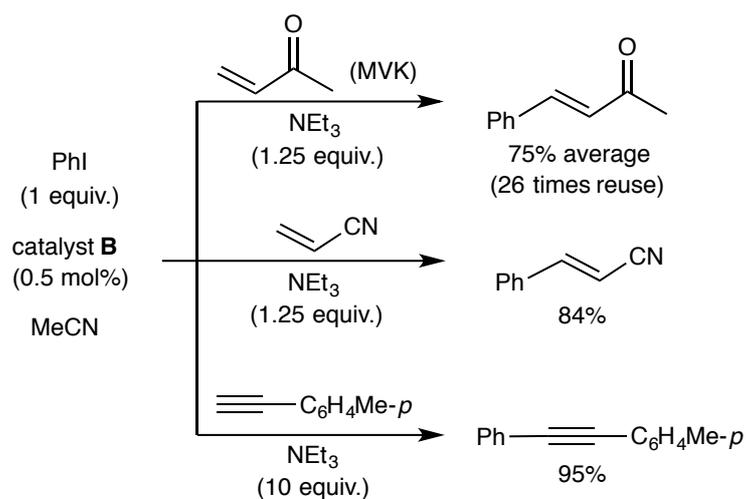
On the basis of the results mentioned so far, we propose the role of the glass surface in the immobilization of a palladium species (Scheme 2). When a cover glass is soaked in a solution of palladium acetate in acetonitrile at room temperature, the palladium acetate is adsorbed physically on the glass surface (state **a**). When it is heated, the physically adsorbed palladium acetate is converted to a chemically adsorbed Pd(II) species between states **a** and **b**. As a result, the palladium species decomposes at a considerably low temperature, causing the reduction that leads to Pd(0) species (state **b**), although the actual reductant is still unknown. In this process, the hydroxy groups on the glass surface surely assist the reduction and stabilize the nanoparticles formed [9]. Indeed, even when the catalyst was allowed to stand in air for one month, the Heck reaction proceeded efficiently with no decrease in catalytic activity.

3.4 Preparation of Glass Wool Supported Catalyst

For the practical application of the glass-supported catalyst, the palladium nanoparticles were immobilized on glass wool, which has a large surface area. The amount of immobilized palladium species should be smaller than that in the test-tube catalyst, because the palladium species was immobilized not only on the glass wool, but also on the vessel. When the catalyst was applied to the Heck reaction (0.05 mol%), it could be reused six times with a TON of 25000.

3.5 Application of the Catalyst to Other C-C Bond Formation Reactions

The test-tube catalyst **B** was applied to the Heck reaction with other substrates, methyl vinyl ketone (MVK) and acrylonitrile; in both cases, the Heck reaction proceeded efficiently to afford the corresponding unsaturated ketone and nitrile, respectively. In the case of MVK, although the efficiency of the Heck reaction was somewhat lower under the same conditions as those employed for methyl acrylate, the catalyst could be reused 26 times with an average yield of 75%. Catalyst **B** also catalyzed the Sonogashira reaction, leading to a diarylacetylene in 95% yield (Scheme 3).



Scheme 3. The Heck and Sonogashira reactions using other substrates, which were conducted with heating at 120 °C for 12 h in a sealed tube

Furthermore, catalyst **B** could be used for the Suzuki reaction. The coupling reaction proceeded efficiently under milder conditions to give biphenyl derivatives, in which electron-rich boronic acids ($G = \text{MeO}$ and Me) showed higher reactivities than electron-poor boronic acids ($G = \text{Cl}$ and NO_2) (Table 2). In the reaction using methylbenzeneboronic acid, catalyst **B** was reused seven times with an average yield of 78%.

Table 2. Suzuki reactions using test-tube catalyst **B**

The reaction scheme shows the Suzuki-Miyaura cross-coupling of an iodobenzene derivative (1 equiv.) with a boronic acid derivative (1.1 equiv.) to form a biaryl product. The reaction conditions are: catalyst **B** (0.5 mol%), K_2CO_3 (1.25 equiv.), MeCN/H₂O (1/1), 80 °C, 2 h in a sealed tube.

G	Reused number of the catalyst	Average yield / %
MeO	4	84
Me	7	78
Cl	2	74
NO ₂	1	93

3.6 Features of the Glass-Supported Catalyst

As mentioned above, the glass-supported palladium serves as a catalyst that can be applied for organic syntheses. The catalyst possesses the following features: 1) it is stable in air, which means it can be treated safely without special care needed with regard to moisture and oxygen; 2) it is easily recovered from the reaction mixture without any special treatment; and 3) it can be reused several times, maintaining a high catalytic activity. In addition to these features, glass is a cheap scaffold, and it is easily deformed on demand. Consequently, this catalyst may serve as a new practically applicable solid-supported catalyst.

4 Conclusion

A glass-supported palladium catalyst was developed. The catalyst could be used repeatedly (12 times) with low catalytic loading (0.05 mol%) for the Heck reaction with a TON of 45000. The catalyst was highly stable, so it could be reused without any special treatment or care. The catalyst also catalyzed the Sonogashira and Suzuki reactions efficiently.

It was found that the glass surface assisted the reduction of the Pd(II) species with the formation and stabilization of catalytically active Pd(0) nanoparticles on the glass surface. Hence, glassware should be washed well after catalytic reactions; otherwise, unexpected reactions might proceed even in the absence of a catalyst.

5 References

- [1] M. Genelot, V. Dufaud, L. Djakovitch, *Adv. Synth. Catal.* 355 (2013) 2604–2616.
- [2] M. Pagliaro, V. Pandarus, R. Ciriminna, F. Béland, P.D. Carà, *ChemCatChem* 4 (2012) 432–445.
- [3] V.P. Ananikov, I.P. Beletskaya, *Organometallics* 31 (2012) 1595–1604.
- [4] L. Huang, T.P. Ang, Z. Wang, J. Tan, J. Chen, P.K. Wong, *Inorg. Chem.* 50 (2011) 2094–2111.
- [5] L. Huang, P.K. Wong, J. Tan, T.P. Ang, Z. Wang, *J. Chem. Phys. C* 113 (2009) 10120–10130.

- [6] Y.-F. Yang, M.-L. Lu, B. Xu, Z.-X. Zeng, *Chin. J. Chem.* 26 (2008) 30–34.
- [7] S.S. Soomro, F.L. Ansari, K. Chatziapostolou, K. Köhler, *J. Catal.* 273 (2010) 138–146.
- [8] S.S. Pröckl, W. Kleist, M.A. Gruber, K. Köhler, *Angew. Chem. Int. Ed.* 43 (2004) 1881–1882.
- [9] M.T. Reetz, J.G. de Vries, *Chem. Commun.* 2004, 1559–1563.
- [10] F. Zhao, B. M. Bhanage, M. Shirai, M. Arai, *Chem. Eur. J.* 2000, **6**, 843–848.
- [11] M. Shimoda, T. Konishi, N. Nishiwaki, Y. Yamashita, H. Yoshikawa, *J. Appl. Phys.* 111 (2012) 124908.
- [12] N. Nishiwaki, T. Konishi, S. Hirao, Y. Yamashita, H. Yoshikawa, M. Shimoda, *Phys. Chem. Chem. Phys.* 14 (2012) 1424–1430.