



Research Article

# Stabilization of Nano-sized Pd Particles under Hydrogen Atmosphere

T. Hioki\*, A. Ichiki and T. Motohiro

*Materials Science and Energy Engineering Division, Green Mobility Research Institute, Institutes of Innovation for Future Society,  
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

---

## Abstract

To enhance the reproducibility of anomalous heat effects reported in gas loaded experiments using nano-sized metal particle systems, stabilization of the nano-sized metal particles under hydrogen atmosphere and at elevated temperatures seems to be important. In this paper, the synthesis of nano-Pd particles embedded in the meso-pores of a mesoporous-silica is reported. We have succeeded in synthesizing nano-Pd particle systems with an average Pd particle size of 3.60 nm and a standard deviation of 0.64 nm. It was found that the synthesized nano-Pd particle system is very stable, i.e., the average size of the Pd particle is unchanged when exposed to a hydrogen atmosphere at temperatures ranging from room temperature up to 773 K. The hydrogen absorption capacity of the nano-Pd particles in the mesoporous silica host at room temperature was smaller than that of the Pd bulk.

© 2017 ISCMNS. All rights reserved. ISSN 2227-3123

*Keywords:* Elevated temperature, Hydrogen atmosphere, Hydrogen absorption capacity, Mesoporous silica, Nano-size, Pd nanoparticles, Stabilization, Synthesis

---

## 1. Introduction

Nano-sized particles of Pd, Ni, and their alloys have attracted attention because these particle systems have been reported to produce anomalous heat when they interact with hydrogen isotope gases at room temperature [1–6] and elevated temperatures [4,7–9]. However, the anomalous heat production phenomenon has not been widely recognized in the scientific communities. One of the reasons seems to be the lack of reproducibility of the phenomenon.

It is well known that nano-sized metallic particles are easy to coalesce and grow under reductive environments at elevated temperatures. Nano-sized Pd or PdO particles have been observed to grow once they are exposed to hydrogen even at room temperature [10]. The heat of hydrogen absorption for Pd and/or the heat of reduction of PdO are enough to cause the growth. Therefore, if the anomalous heat production phenomenon is closely related to the existence of nano-sized metallic particles, the growth of the particles under hydrogen atmosphere has to be suppressed to improve the reproducibility of the anomalous heat production and to clarify the mechanism of the phenomenon.

In this paper, a trial to stabilize nano-sized Pd particles under hydrogen atmosphere is reported: we have tried to precipitate Pd particles only inside the pores of mesoporous silica's (MPS) using the conventional incipient wetness

---

\*Corresponding author. E-mail: hioki@gvm.nagoya-u.ac.jp.

impregnation method followed by a process of washing out the mixture of MPS powder and Pd precursor with n-octane [11]. With the washing out process, the Pd precursor adhered to the outer wall of the mesoporous silica could be removed completely. The Pd/MPS system thus prepared contained only Pd particles with sizes ranging from 2 to 5 nm and showed excellent stability under hydrogen atmosphere, i.e., X-ray diffraction patterns and transmission electron microscopy confirmed that the sizes of the Pd particles in these systems were unchanged when the systems were exposed to hydrogen even at an elevated temperature of 773 K.

## 2. Experiment

### 2.1. Synthesis method

The MPS used in the present study was TMPS-4R obtained from Taiyo Kagaku Co. Ltd. The average pore size of the MPS was 4.2 nm. To precipitate Pd particles inside the pores of the MPS, Pd(NO<sub>3</sub>)<sub>2</sub> aqueous solution was used as a Pd precursor. TMPS-4R powder was added to a mixed solution of the Pd precursor and citric acid. Then, the mixture was stirred with a magnetic stirrer for about 24 h at room temperature. After the impregnation process, the Pd precursor was separated from TMPS-4R powder with a centrifuge. Then, the TMPS-4R powder was replenished with n-octane and subjected to ultrasonic treatment to remove the Pd precursor adhered to the outer surface of the TMPS-4R particle. Subsequently, the resultant mixture was dried at 423 K for about 10 h and calcined at 673 K for 2 h in air.

### 2.2. Characterization method

X-ray diffraction (XRD) analyses using CuK $\alpha$  radiation were performed to characterize the crystallographic changes of Pd particles and host MPS. The XRD measurements were performed before and after being exposed to deuterium of 0.2 MPa at elevated temperatures.

The concentration of the Pd in the TMPS-4R was determined to be 6.7 wt% with ICP-analysis operated at Aichi Center for Industry and Science Technology.

The morphology and sizes of Pd particles were observed with transmission electron microscopy (TEM) operated at 200 kV.

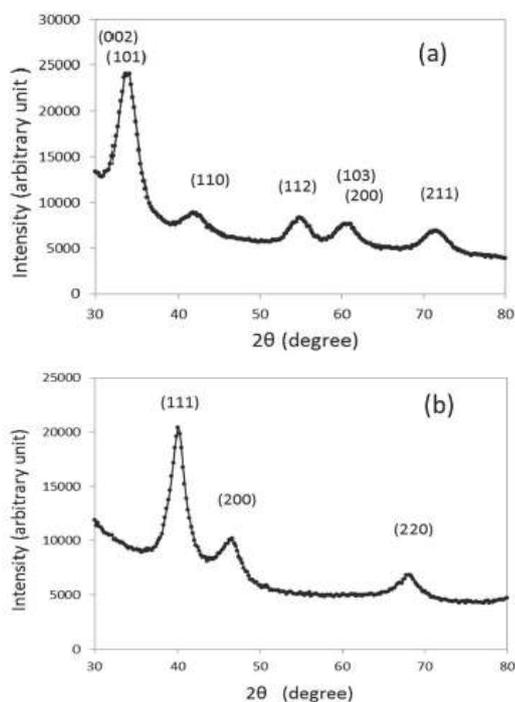
A standard volumetric method (Sievert's method) was used to evaluate the hydrogen absorption properties of Pd nanoparticles in the samples. The measurements were carried out at room temperature up to hydrogen equilibrium pressure of 0.02 MPa. The measurements were performed three times for each sample. The first run was employed as a preliminary treatment to reduce PdO in the as-prepared sample to metallic Pd. Thereby, in the first run more hydrogen was consumed than in the following second run and third runs. The data obtained in the second run was almost the same as that of the third run. Therefore, the data of the second run was used to evaluate the hydrogen absorption capacity of the Pd nanoparticles embedded in the MPS.

## 3. Results and Discussion

### 3.1. Characterization of Pd particles embedded in TMPS-4R

In Fig. 1, XRD profiles for the Pd/TMPS-4R are shown for the samples as-synthesized and after exposure to deuterium of 0.2 MPa for ~1 h at room temperature. It is seen that in the as-synthesized sample there exists PdO with tetragonal crystal structure, and the PdO crystals are reduced to metallic Pd with a face centered cubic crystal structure, once the sample is exposed to hydrogen. From the width of the XRD profiles, the average grain sizes of the PdO and Pd are estimated using the Scherrer equation [12],

$$D = 0.9\lambda/\beta \cos \theta, \quad (1)$$



**Figure 1.** XRD profiles for (a) as-synthesized sample, indices are for PdO and (b) the sample after exposure to deuterium at room temperature, indices are for Pd.

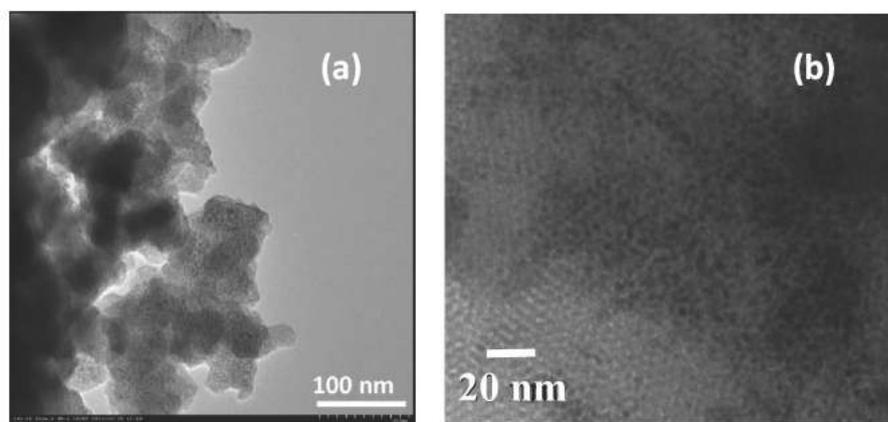
where  $D$  is the grain size (nm),  $\lambda$  the wavelength of the incident X-ray (nm),  $\beta$  the full width at half maximum (FWHM) of the peak (radian) and  $\theta$  the center angle of the peak.

For the as-synthesized sample, the average grain size of PdO calculated with a (101) peak was 3.1 nm. After exposure to deuterium, the PdO crystals were reduced to metallic Pd and the average grain size of the metallic Pd particles calculated with a (111) peak was 3.9 nm. The grain size of PdO crystals are considerably smaller than the size of the pores of the MPS host, which strongly suggests that almost all the PdO particles are inside the pores of the MPS. Upon exposure to deuterium, the PdO crystals were reduced to metallic Pd and the size of the resultant Pd particle was still smaller than 4.2 nm, the pore size of TMPS-4R. This fact suggests that almost all the Pd crystals remain inside the pores of the MPS host. The metallic Pd crystals were a little larger than the initial PdO crystals. Because the heat of the reduction reaction is rather large, the sample is heated when it is exposed to deuterium. This heat is assumed to result in the growth of Pd crystals. However, it is noted that the size of the Pd crystals is still a little smaller than the size of the pores of the MPS host. The growth of the Pd crystals is considered to be limited by the size of the pores. This fact also strongly suggests that the Pd crystals are inside the channels of the MPS host.

Figure 2 shows the TEM images for the sample after exposure to deuterium. As seen in Fig. 2 (a) at low magnification, no coarse Pd particles exist on the outside surface of the MPS host. As suggested in Fig. 2 (b), the Pd particles seem to be embedded inside the pores of the TMPS-4R. This is consistent with the XRD results.

To determine the size of the Pd particles with TEM observation, 150 Pd particles in the high-magnification images were randomly chosen and the size of the particle image was measured. The result is shown in Fig. 3.

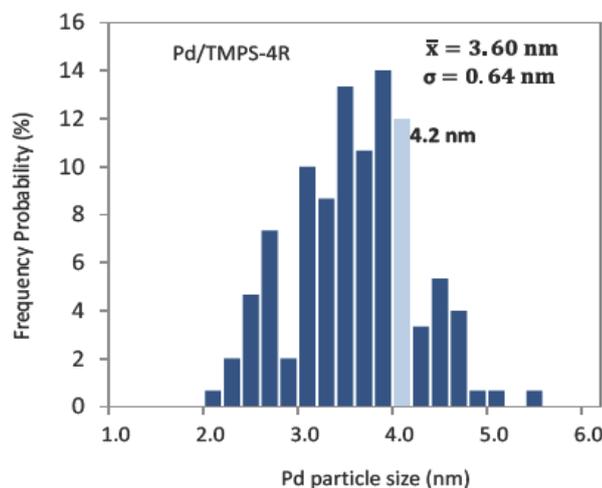
The average size of the Pd particles was 3.60 nm, which was close to the value estimated with the XRD profile.



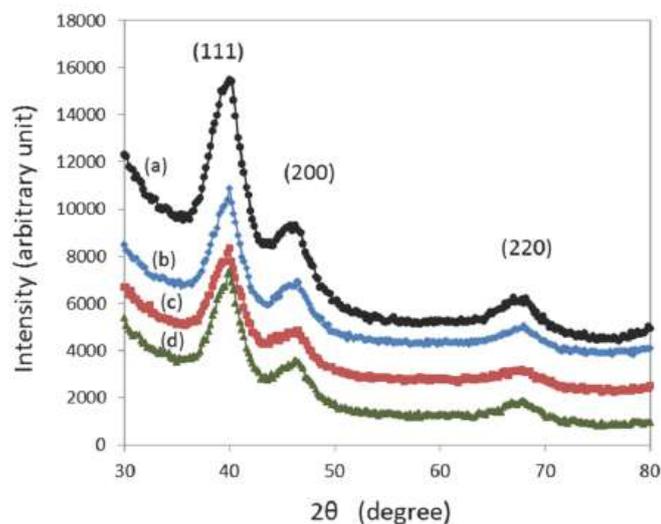
**Figure 2.** TEM observation of Pd/TMPS-4R after deuterium exposure at room temperature. (a) Low-magnification image and (b) high-magnification image.

The standard deviation was 0.64 nm, which indicated that the distribution for the size of the Pd particles is very narrow. Figure 3 indicates that 99% of the Pd crystals are smaller than 5.0 nm. Furthermore, 89% are smaller than 4.2 nm, the pore size of the TMPS-4R, indicating that the Pd crystals are largely inside the pores of the host MPS.

From the XRD and TEM analyses, it has been clearly demonstrated that almost all the Pd particles are inside the pores of the TMPS-4R and no coarse Pd particles larger than 5 nm exist in the sample. Furthermore, upon exposure to deuterium, the size of the PdO particles was largely unchanged. This is contrary to what happened with the samples previously used in flow calorimetry experiments showing heat evolution upon pressurization with hydrogen isotope gases [6,10], e.g., for Pd nanopowder AY-4030<sup>TM</sup> used in the previous experiments, the average size of the Pd particles



**Figure 3.** Size distribution for Pd particles in Pd/TMPS-4R.

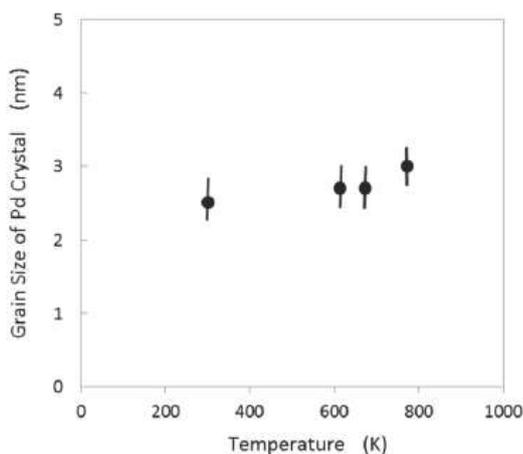


**Figure 4.** XRD profiles after heat treatment under  $D_2$  atmosphere at (a) 300 K, (b) 613 K, (c) 673 and (d) 773 K.

was initially 10–20 nm, whereas that of the Pd particles after hydrogen absorption measurements at room temperature was increased to about 50 nm [10].

### 3.2. Thermal stability of Pd particles embedded in TMPS-4R

To investigate the stability of the Pd particles embedded in the pores of TMPS-4R, a sample of Pd/TMPS-4R was heat treated under deuterium atmosphere of 0.2 MPa for 2 h at 300, 613, 673 and 773 K. The XRD profiles after each



**Figure 5.** The size of Pd crystals VS. temperature at which the sample was heat-treated under 0.2 MPa deuterium.

treatment are shown in Fig. 4.

It is seen that the peaks are broad even at the elevated temperature of 773 K. The size of the Pd particles was calculated using Eq. (1) for the (111) peak, and the result is shown in Fig. 5.

The grain size is almost unchanged up to 773 K within the error bars. This fact indicates that the Pd crystals inside the pores of the MPS host are stable under hydrogen atmosphere even at 773 K.

### 3.3. Hydrogen absorption property

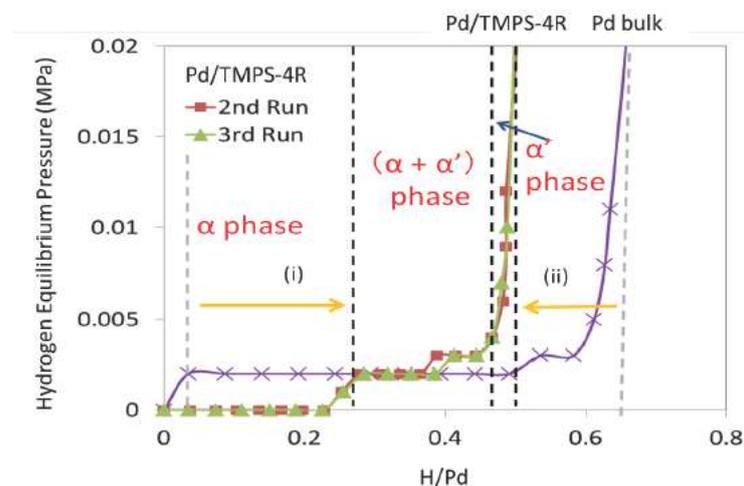
To investigate the effect of grain size on the hydrogen absorption property of Pd, the hydrogen absorption capacity was measured at room temperature using the standard volumetric method for a powder sample of Pd/TMPS-4R. In Fig. 6, the results are compared with those for a reference sample of bulk Pd.

The reference sample was prepared by mixing Pd powder (AY4030<sup>TM</sup>: Tanaka Kikinzoku Kogyo Co. Ltd.) and pure TMPS-4R powder.

As seen in Fig. 6, the ratio of absorbed hydrogen atoms to Pd atoms, H/Pd, at 0.02 MPa is 0.65 for the reference sample, which is in good agreement with literature values for Pd bulk. For Pd/TMPS-4R, the value is 0.50, which is smaller than the bulk value. It is also noted that the concentration limit of the solid solution phase ( $\alpha$  phase) is increased and the plateau region ( $(\alpha + \alpha')$  phase) is narrowed in the Pd/TMPS-4R sample. These results are consistent with those for polymer-coated Pd nanoparticles with sizes  $2.6 \pm 0.4$  and  $7.0 \pm 0.9$  nm as reported by Yamauchi et al. [13].

## 4. Conclusion

We have succeeded in preparing a Pd-nanoparticle/mesoporous silica system, where a large percent of the Pd particles are confined in the pores of the MPS host, using TMPS-4R with a pore size of 4.2 nm: the average size of the Pd crystals was less than the pore size of the host MPS. The Pd nanocrystals confined in the pores of TMPS-4R were thermally



**Figure 6.** Hydrogen absorption capacity VS. equilibrium pressure at room temperature for Pd/TMPS-4R and Pd bulk.

very stable: their sizes were nearly unchanged when they were heated up to 773 K under hydrogen atmosphere. The hydrogen absorption capacity per Pd atom, H/Pd, for a Pd/TMPS-4R sample was smaller than the value for Pd bulk.

### Acknowledgements

We would like to thank Y. Ichikawa and K. Kawai for experimental support. A part of this work was supported by Grant-in-Aid for challenging Exploratory Research 16K13718 from Japan Society for the Promotion of Science.

### References

- [1] Y. Arata and Y. Zhang, *Proc. ICCF10*, Cambridge, August 24–29, 2003, p.139.
- [2] Y. Arata and Y. Zhang, *J. High Temp. Soc.* **34** (2008) 85.
- [3] A. Kitamura, T. Nohmi, Y. Sasaki, A. Taniike, A. Takahashi, R. Seto and Y. Fujita, *Phys. Lett. A* **373** (2009) 3109.
- [4] F. Celani, A. Spallone, E. Righi, G. Trenta, V. Andreassi, A. Marmigi, P. Quercia, G. Cappuccio, D. Hampai, P. Marini, V. DiStrfano, M. Nakamura, F. Todarello, E. Purchi, A. Mancini, U. Mastromatteo, F. Falcioni, M. Marchesini, P. DiBiagio, P.G. Sona, F. Fontana, L.Gamberale and D. Garbelli, *Proc. ICCF13*, Dagomys, Russia, June25–July1, 2007, p. 181.
- [5] J. Biberian and N. Armanet, *Proc. ICCF13*, Dagomys, Russia, June25–July1, 2007, p. 170.
- [6] T. Hioki, N. Sugimoto, T. Nishi, A. Itoh and T. Motohiro, *J. Condensed Matter Nucl. Sci.* **13** (2014) 223.
- [7] F. Celani, E. F. Marano, B. Ortenzi, S. Pella, S. Bartalucci, F. Micciulla, S. Bellucci, A. Spallone, A. Nuvoli, E. Purchi, M. Nakamura, E. Righi, G. Trenta, G. L. Zangari and A. Ovidi, *J. Condensed Matter Nucl. Sci.* **13** (2014) 56.
- [8] A. Kitamura, A. Takahashi, R. Seto, Y. Fujita, A. Taniike and Y. Furuyama, *Current Sci.* **108** (4) (2015) 589.
- [9] A. Kitamura, E. F. Marano, A. Takahashi, R. Seto, T. Yokose, A. Taniike and Y. Furuyama, Heat evolution from zirconia-supported Ni-based nano-composite samples under exposure to hydrogen isotope gas, *Proc. JCF16*, 2016, p. 1.
- [10] T. Hioki, H. Azuma, T. Nishi, A. Itoh, S. Hibi, J. Gao and T. Motohiro, *J. Condensed Matter Nucl. Sci.* **4** (2011) 69.
- [11] Y. Ichikawa, T. Hioki, N. Sugimoto, A. Ichiki and T. Motohiro, *J. Nanosci. Nanotechnol.* **16** (2016) 12947.
- [12] A. L. Patterson, *Phys. Rev.* **56** (1939) 978.
- [13] M. Yamauchi, R. Ikeda, H. Kitagawa and M. Tasaka, *J. Phys. Chem. C* **112** (2008) 3294.