XAFS Study on Nano-Sized Metal Catalyst Prepared by a Photo-Assisted Deposition Using Ti-Containing Mesoporous Silica Thin Film Photocatalyst

Makoto Shimada, Shinichiro Nishio, Toshiaki Shimizu, Kohsuke Mori, Tetsutaro Ohmichi, Iwao Katayama, and Hiromi Yamashita

Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University
2-1 Yamada-oka, Suita, Osaka 565-0871, JAPAN

Abstract. Transparent Ti-containing mesoporous silica (TMS) thin films can be prepared on quartz plates using the spin-coating sol-gel method. These thin films have performed super-hydrophilic surface property. Using a photo-assisted deposition (PAD) method, nano-sized Pt metal can be highly deposited on TMS thin films under UV-light irradiation. XAFS measurement indicates that TMS thin films contain isolated and tetrahedrally coordinated Ti-oxide moieties in the frameworks and nano-sized Pt particles can be highly deposited on the photo-excited Ti species in TMS thin films. Measurement of contact angle of droplet water showed that the surface property of Pt/TMS thin film is also hydrophilic as comparable to that of original TMS thin film.

Keywords: mesoporous silica thin films, single-site photocatalyst, titanium oxide, Pt nano-particles, photo-induced super-hydrophilic property.
PACS: 82.50.Nd

INTRODUCTION

Platinum is one of the most efficient catalyst metals in the industrial area [1]. Particularly, nano-sized Pt particles have attracted a wide range of scientific and practical interest because of their unique properties [2,3]. The development of convenient and useful methods to prepare nano-sized Pt metals loaded on supports is essential to the design of active metal catalysts [4,5]. On the other hand, Ti-containing mesoporous silica (TMS) thin films show super-hydrophilic surface property as well as unique photocatalytic activity [6,7]. In this study, the photoexcitation ability of TMS thin films under UV-light irradiation was used to disperse Pt highly. Using a photo-assisted deposition (PAD) method [8], nano-sized Pt metals can be highly deposited on the photo-excited TMS thin films. The structure of the Ti species in TMS thin films and nano-sized Pt metals were observed by XAFS analysis. The benefits of the combination of the PAD method and the TMS thin films as support to prepare the active nano-sized Pt metal catalysts were demonstrated. Furthermore, Pt/TMS thin films exhibit a strong hydrophilic surface property. XAFS measurement is one of the powerful methods to clarify the local structure at atomic level which is responsible to this unique property.

EXPERIMENTAL

The Ti-containing mesoporous silica (TMS) thin film was prepared by the spin-coating sol-gel method using tetraethyl orthosilicate (TEOS) and tetraethyl orthotitanate (TEOT) as the starting materials, $C_{12}H_{25}(OCH_2CH_2)_4OH$ (Brij^{R}30) as template, hydrochloric acid, and ethanol. The above mixture was stirred for 15 min at 298 K, dripped onto a quartz substrate (10 mm × 10 mm × 1 mm), spread homogeneously, and spin coated with at a spinning rate of 4000 rpm for 1 min. The thin film thus obtained was calcined in air at 523 K for 5 h to remove the template from the film materials. The Ti/Si ratio was changed from 0 to 0.1. The Pt loaded on TMS thin films (Pt/TMS thin films) was prepared using the PAD method: Pt metal was deposited on TMS thin films from an aqueous solution of H_2PtCl_6 under UV-light irradiation using a high-pressure Hg lamp at 298 K. The sample was dried at 473 K and reduced by H_2 (20 ml/min) at 473 K for 1 h.

UV-vis absorption spectra were recorded with a Shimadzu UV-2550 spectrometer at 295 K. XRD

patterns were recorded with a Rigaku Mini-flex using Cu Kα radiation of λ=1.5418 Å. The XAFS spectra (XANES and EXAFS) were measured in fluorescence mode at the BL-9A line of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba and at the BL01B1 line of SPring-8. The hydrophilic property of the film surface was checked by the contact angle of pure water using DropMaster 300.

RESULTS AND DISCUSSION

The prepared Ti-containing mesoporous silica (TMS) thin films and Pt loaded on TMS thin films (Pt/TMS thin films) were transparent and well-fixed on the quartz plate substrate. As shown in Fig. 1, they are colorless and totally transparent like the original quartz plate. Furthermore, this result indicates that the nano-sized Pt particles are highly dispersed.

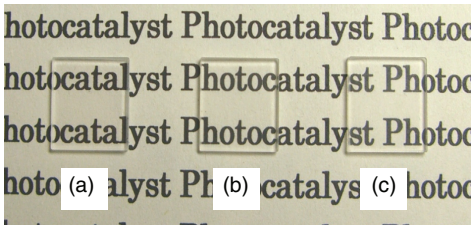

FIGURE 1. Sample photograph of (a) quartz plate, and plates coated with (b) Ti-containing mesoporous silica (TMS) thin film (Ti / Si = 0.02), and (c) Pt / TMS thin film (Ti / Si = 0.02).

Figure 2 shows XRD patterns of TMS thin films. The TMS thin films exhibit a diffraction peak at around 2-4 degrees indicating the presence of hexagonal mesoporous structure. Although the thickness of a wall of TMS changed depending on the Ti/Si ratios, the wall width of TMS was larger than that of mesoporous silica films.

Ti K-edge XANES spectra of TMS thin films (a-c) exhibit an intense single preedge peak (Fig. 3), which is different from that of bulk TiO_2 showing several preedge peaks (d) (Fig. 3.1). In the FT-EXAFS spectra, only a strong peak at around 1.6 Å due to the Ti-O bond could be detected for all TMS samples. This observation suggests that the titanium oxide moieties in TMS thin films exist in highly dispersed tetrahedral coordination geometry.

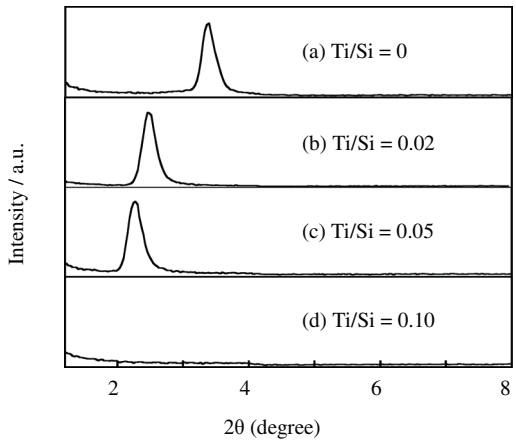

FIGURE 2. XRD patterns of Ti-containing mesoporous silica thin films. The Ti / Si ratio was (a) 0, (b) 0.02, (c) 0.05 and, (d) 0.10.

From the results of UV-vis absorption spectra of TMS thin films, absorption bands of TMS thin films are observed in the UV wavelength region. When the Ti/Si ratio of TMS thin films becomes lower, the absorption edge shifts towards the wavelength region shorter than 250 nm. These results also indicate the formation of the isolated and tetrahedrally-coordinated titanium oxide moieties in the TMS thin films.

Under UV-light irradiation of the slurry of TMS thin films in an aqueous H_2PtCl_6 solution, the Pt metal can be deposited on the TMS thin films. The Pt L_{III}-edge XANES spectra of the catalysts are shown in Fig. 4. The results show that the Pt nano particles exist as Pt metal, not platinum oxide.

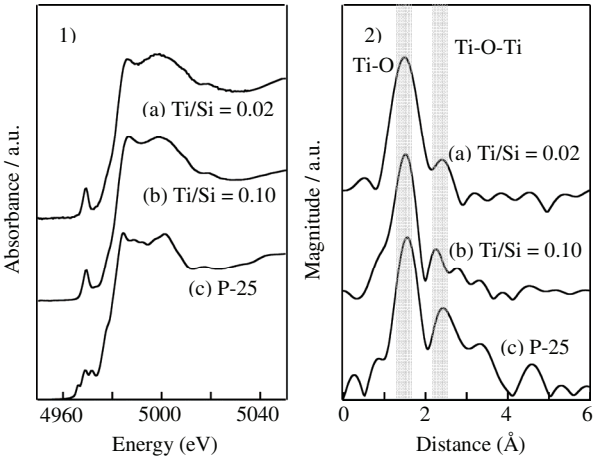

FIGURE 3. Ti K-edge XANES and FT-EXAFS of Ti-containing mesoporous silica thin films and (c) P-25 as a reference. The Ti/Si ratio was (a) 0.02 and, (b) 0.10.

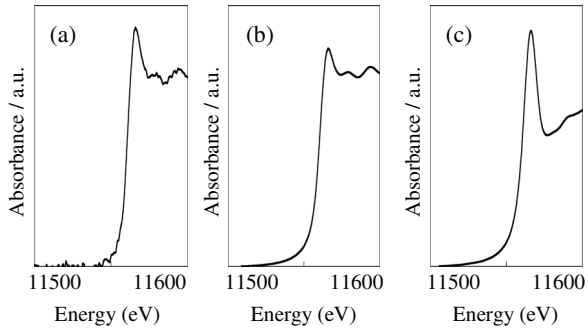

FIGURE 4. Pt L_{III}-edge XANES spectra of (a) Pt/Ti-containing mesoporous silica thin films, (b) Pt metal, and (c) PtO_2.

On the other hand, Pt metal particles could not be loaded on mesoporous silica thin films without Ti-oxide moieties by PAD method. It was found that Pt metals were deposited directly on the photo-excited tetra-Ti-oxide moieties of TMS.

Figure 5 shows the contact angles of water droplets on the mesoporous silica and TMS thin films deposited on quartz plate. The water contact angles on TMS thin films were much smaller than on mesoporous silica thin films even before UV-light irradiation. After UV-light irradiation, the water contact angle on TMS thin films became very small, while the water contact angle on mesoporous silica thin films did not make any changes. In the case of Pt/TMS thin films, hydrophilic surface property could be observed as that of TMS thin films not only under UV-light irradiation but also before UV-light irradiation. The charge transfer excited state of tetra-Ti-oxide moieties plays an important role in the photo-induced super-hydrophilic property.

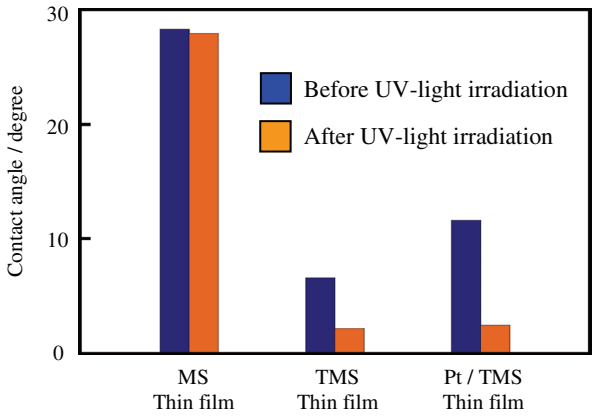

FIGURE 5. The changes in the contact angles of water droplets observed before and after UV-light irradiation on the mesoporous silica, Ti-containing mesoporous silica (TMS) thin films and Pt / TMS thin films (Ti / Si = 0.02).

CONCLUSION

The synthesis of the Ti-containing mesoporous silica(TMS) thin films was carried out by using the spin-coating sol-gel method. Using a photo-assisted deposition (PAD) method, nano-size Pt metal can be highly dispersed on TMS thin films under UV-light irradiation. These thin films are colorless transparent and well-fixed on the quartz plate substrate. With a Ti/Si ratio of 0.01-0.05, the Ti-oxide species were present as tetrahedrally-coordinated titanium oxide moieties in the TMS thin films. Nano-sized Pt metals were highly deposited on the photo-excited tetra-Ti-oxide moieties of TMS.

TMS thin films exhibited a strong hydrophilic surface property even before UV-light irradiation. After UV-light irradiation on the TMS thin films, the appearance of the super-hydrophilic surface property was observed. Pt/TMS thin films also exhibited a strong hydrophilic surface property like TMS thin films.

ACKNOWLEDGEMENT

The present work is supported by the Grant-in-Aid for Scientific Research (KAKENHI) in Priority Area “Molecular Nan Dynamics” from the Ministry of Education, Culture, Sports, Science and Technology (No. 17360388), (No.1734036) & (No. 18656238). The X-ray absorption experiments were performed at the Photon Factory of KEK (2005G039) and the SPring-8 (2006A1278-NXa-np). This work is partly performed under the project of collaborative research at the Joining and Welding Research Institute (JWRI) of Osaka University.

REFERENCES

1. M. Watanabe, H. Uchida, H. Okubo and H. Igarashi, *Appl. Catal. B* **46,** 595 (2003).
2. J. U. Kohler and J. S. Bradley, *Catal. Lett.* **45,** 203(1997).
3. T. Teranishi, M. Hosoe, T. Tanaka and M. Miyake, *J. Phys. Chem. B* **103**, 3818 (1999).
4. A. Fukuoka, H. Araki, J. Kimura, Y. Sakamoto, T. Higuchi, N. Sugimoto, S. Inagaki and M. Ichikawa, *J. Mater. Chem.* **14,** 752 (2004).
5. A. Fukuoka, H. Araki, Y. Sakamoto, N. Sugimoto, H. Tsukada, Y. Kumai, Y. Akimoto and M. Ichikawa, *Nano Lett.* **2,** 793 (2002).
6. H. Yamashita, S. Nishio, I. Katayama, N. Nishiyama and H. Fujii, *Catal. Today* **111,** 254 (2006).
7. S. Nishio, T. Tanaka, H. Tada, N. Nishiyama, H. Fujii, T. Ohmichi, I. Katayama and H. Yamashita, *Stud. Surf. Sci. Catal.* **158**, 1605 (2005).
8. H. Yamashita, T. Shimizu and K. Mori, *Stud. Surf. Sci. Catal.*, in press.