

Catalysis of nanosized Pd metal catalyst deposited on Ti-containing zeolite by a photo-assisted deposition (PAD) method*

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Abstract: Using a photo-assisted deposition (PAD) method, nanosized Pd metal can be highly dispersed on Ti-containing silicalite zeolite (TS-1) under UV-light irradiation (PAD-Pd/TS-1). The nanosized Pd metal was deposited directly on the photo-excited tetrahedrally coordinated titanium oxide species (tetra-Ti-oxide) of TS-1 zeolite. Under the flow of H₂ and O₂ in water solvent, the efficient formation of H₂O₂ could be observed by the PAD-Pd/TS-1 catalyst under mild reaction conditions (ambient temperature and atmospheric pressure). Furthermore, the presence of phenol in this reaction system led to the formation of the products from the partial oxidation of phenol with the formed H₂O₂.

Keywords: nano Pd metal; photo-assisted deposition; single-site photocatalysts; zeolites.

INTRODUCTION

The unique and fascinating properties of zeolites involving transition metals within the zeolite cavities and framework have opened new possibilities for many application areas not only in catalysis but also for various photochemical processes [1–3]. The transition-metal oxide moieties in metallosilicate catalysts are considered to be highly dispersed at the atomic level and also to be well-defined catalysts which exist in the specific structure of the zeolite framework. These transition-metal oxide moieties such as tetrahedrally coordinated titanium oxide moieties incorporated and isolated within silica matrix of zeolite and mesoporous silica have been named “single-site photocatalysts” [4–6]. As single-site photocatalysts, isolated Ti, Cr, V, and Mo oxide moieties can be incorporated in the silica matrix of zeolite or mesoporous silica and can perform the unique photocatalytic reactions [7–11]. Under UV-light irradiation, these single-site photocatalysts form charge-transfer excited state which can show the highly active and selective photocatalytic performance. A Ti-containing zeolite such as TS-1 is especially prominent as a unique photocatalyst and catalyst [1–8,12,13].

The TS-1 has the isolated tetrahedrally coordinated titanium oxide moieties included within the frameworks of silicalite zeolite. These tetrahedrally coordinated titanium oxide moieties perform not only as the catalyst for the partial oxidation of alkanes and alkenes using H₂O₂ as an oxidant in the liq-

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uid-phase reactions, but also as the single-site photocatalyst. Although the previous studies for the utilization as photocatalyst have mainly been focused on its photocatalytic activity [4–11], the applications of single-site photocatalyst for the synthesis of conventional catalysts such as nanosized metal catalysts have not been investigated so far.

Nanosized metal catalysts such as Pd, Pt, and Au have been used widely for various reactions [14–16]. Achieving the precise control of particle size and overall particle size distribution is one of the most important challenges to providing unique chemical properties. The development of a convenient approach to control the size of metal particles loaded on support is essential to the design of the highly active metal catalyst. It can be expected that the metal precursor species can be easily deposited on the excited state of single-site photocatalyst to form well-controlled sized metal particles by simple photo-irradiation. In our previous study [17], we have successfully utilized the single-site photocatalyst (Ti-containing mesoporous silica) as the platform for the synthesis of nanosized Pt metal by the advanced photo-assisted deposition (PAD) method.

In the present study, nanosized Pd metal catalyst has been deposited on the Ti-containing silicalite zeolite (TS-1) using the PAD method. This synthesized catalyst (Pd loaded on TS-1) possesses two types of active sites, the nanosized Pd metal for the synthesis of H_2O_2 from H_2 and O_2 gas and the tetrahedral coordinated titanium oxide moieties for the partial oxidation of organic compounds using H_2O_2 as oxidizing reagent. Using this combination of effective catalytically active sites, in this study, the partial oxidation of phenol has been carried out in a flow of mixture with H_2 and O_2 gas.

RESULTS AND DISCUSSION

Under UV-light irradiation of the slurry of TS-1 in an aqueous PdCl_2 solution, the Pd metal can be deposited on the TS-1. On the other hand, the UV-light irradiation of silicalite zeolite without titanium oxide and the utilization of TS-1 without UV-light irradiation cannot realize the deposition of Pd metal on the supports. The photo-excited state of tetrahedrally coordinated titanium oxide is generated by the combination of UV-light and tetrahedrally coordinated titanium oxide moieties and indispensable for the deposition of Pd.

The Fourier transforms of Pd K-edge extended X-ray absorption fine structure (EXAFS) spectra of the Pd metal powder, imp-Pd/TS-1 and PAD-Pd/TS-1 catalysts are shown in Fig. 1. The presence of the peak assigned to the contiguous Pd–Pd bond at around 2.5 \AA indicates the formation of Pd metal on TS-1 zeolites. The intensity of the Pd–Pd peak of the PAD-Pd/TS-1 catalyst is smaller than those of the Pd metal powder and the imp-Pd/TS-1 catalyst, indicating that the size of Pd metal particles depends on the preparation method and that the Pd metal particles on the photo-deposited catalyst (PAD-Pd/TS-1) are smaller than the metal particles on the impregnated catalyst (imp-Pd/TS-1). The

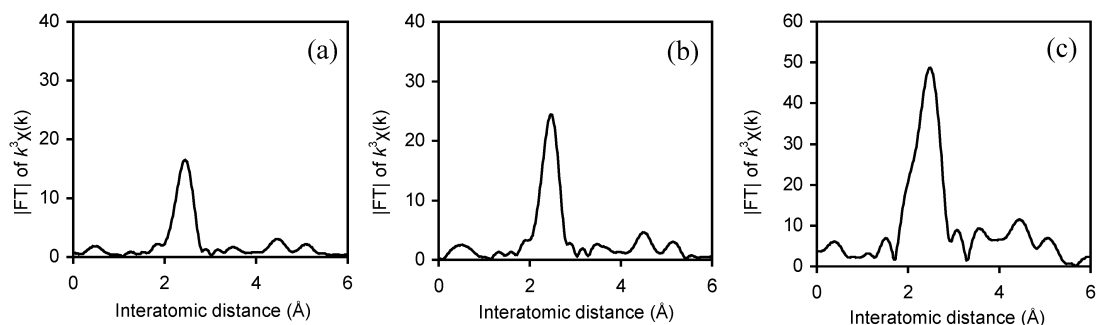


Fig. 1 Fourier transforms of Pd K-edge EXAFS spectra with the (a) PAD-Pd/TS-1, and (b) imp-Pd/TS-1 catalysts after H_2 treatment at 473 K and (c) Pd metal powder.

transmission electron microscopy (TEM) images of the Pd/TS-1 catalysts are shown in Fig. 2. On the PAD-Pd/TS-1 catalyst, the formation of small Pd metal particles with controlled size is observed (Fig. 2a), although the aggregated large Pd metal and the metal in various size are observed on the imp-Pd/TS-1 catalyst (Fig. 2b). These observations also support the results of XAFS measurement. The highly dispersed deposition of metal precursor on the photo-excited titanium oxide moiety may play an important role for the efficient suppression of the growth of metal particles.

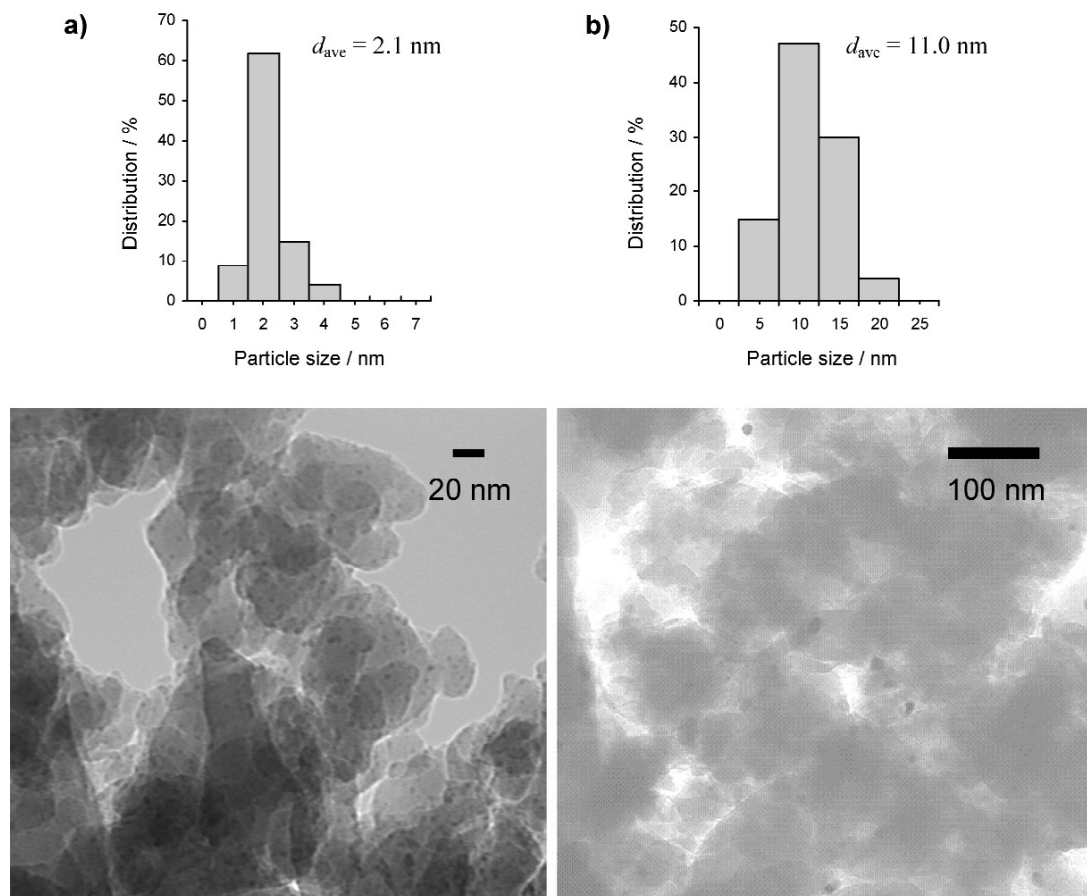


Fig. 2 Size distribution diagram and TEM images of the (a) PAD-Pd/TS-1 and (b) imp-Pd/TS-1 catalysts (Pd: 1.4 wt %) after H_2 treatment at 473 K.

With the flow of H_2 and O_2 into the aqueous slurry of Pd/TS-1 catalysts, the H_2O_2 can be produced at room temperature. In the absence of the Pd, no H_2O_2 was detected. As shown in Fig. 3, the PAD-Pd/TS-1 catalyst can exhibit the higher reactivity than the imp-Pd/TS-1 catalyst in the region of the low Pd loading. Probably the high dispersion of Pd metal particle in the PAD-Pd/TS-1 with low Pd loading is preferable for the formation of H_2O_2 [18]. The amount of Pd loadings have also affected the productivity of H_2O_2 synthesis. It is considered that the decomposition of H_2O_2 into H_2O and O_2 and/or hydrogenation to H_2O might be enhanced with the increasing of Pd loadings.

Using in situ produced H_2O_2 from H_2 and O_2 as an oxidant, the oxidation of phenol can be catalyzed by the tetrahedrally coordinated titanium oxide moieties of the PAD-Pd/TS-1. The PAD-Pd/TS-1 catalyst exhibited the higher catalytic activity for the oxidation of phenol than the imp-Pd/TS-1 catalyst

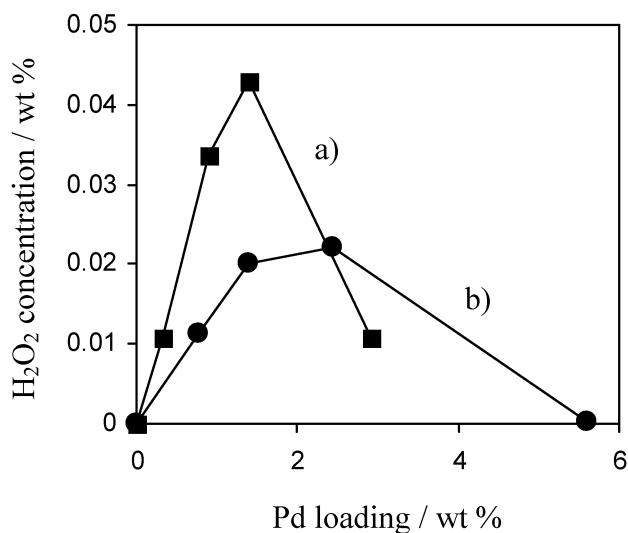
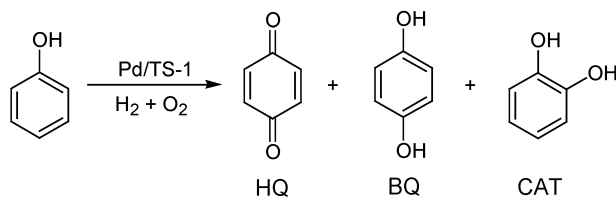


Fig. 3 H₂O₂ formation on the (a) PAD-Pd/TS-1 (Pd: 0.33, 0.89, 1.40, 2.91 wt %) and (b) imp-Pd/TS-1 (0.77, 1.40, 2.43, 5.6 wt %) catalysts with a flow of H₂ and O₂. Reaction conditions: Pd/TS-1 (0.1 g), 0.01 M HCl (50 ml), flow of H₂ and O₂ (80 ml min⁻¹, H₂:O₂ = 1:1) 6 h, at room temperature.

(entry 1 vs. 5 in Table 1). It is apparent that the TS-1 without Pd has no oxidation ability toward phenol in the presence of H₂ and O₂. The efficiency for the oxidation of phenol in the flow of H₂ and O₂ gas depends on the ratio of H₂ and O₂ gas. Among those examined, the 1:1 ratio of H₂ and O₂ led the highest reactivity in this reaction system. Moreover, the catalytic activity of the PAD-Pd/TS-1 using H₂ and O₂ exceeded that of the TS-1 in the presence of the 30 % aq. H₂O₂ solution. The micropores and the tetrahedrally coordinated titanium oxide moieties of TS-1 zeolite are suitable for the partial oxidation of phenol with H₂O₂, which are formed from H₂ and O₂ on the nanosized Pd metal deposited on TS-1.

Table 1 Oxidation of phenol on the Pd/TS-1 (1.4 wt %) catalysts at 343 K in acetonitrile.



Entry	Catalyst	Flow ratio H ₂ :O ₂	Total yield / %	Select./ %		
				HQ ^a	BQ ^a	CAT ^a
1	PAD-Pd/TS-1	1:1	7	29	0	71
2	PAD-Pd/TS-1	2:1	1	0	0	>99
3	PAD-Pd/TS-1	1:2	2	0	0	>99
4	PAD-Pd/TS-1	0:1	0	0	0	0
5	imp-Pd/TS-1	1:1	2	20	5	75
6 ^b	TS-1	H ₂ O ₂	1	10	50	40

^aBQ: benzoquinone, HQ: hydroquinone, CAT: catechol

^bMethanol was used as solvent.

CONCLUSION

Under UV-light irradiation of the aqueous slurry of TS-1 and PdCl₂ (PAD method), Pd metal particles with high dispersion state can be deposited on the photo-excited tetrahedrally coordinated titanium oxide moieties of TS-1. This nanosized Pd metal performs as the effective catalyst for the H₂O₂ synthesis from H₂ and O₂ gas. The combination of catalysis of nanosized Pd metal for the H₂O₂ synthesis and the catalysis of tetrahedrally coordinated titanium oxide moieties for oxidation using H₂O₂ reagent can be realized on the PAD-Pd metal catalyst loaded on TS-1 (PAD-Pd/TS-1), and promote the partial oxidation of phenol efficiently in the flow of mixture of H₂ and O₂ gas. The direct interaction between the nanosized Pd metal and the photo-excited tetrahedrally coordinated titanium oxide moieties realized by the PAD method has possibility to design the unique and active catalytic system with nanosized metal (Fig. 4).

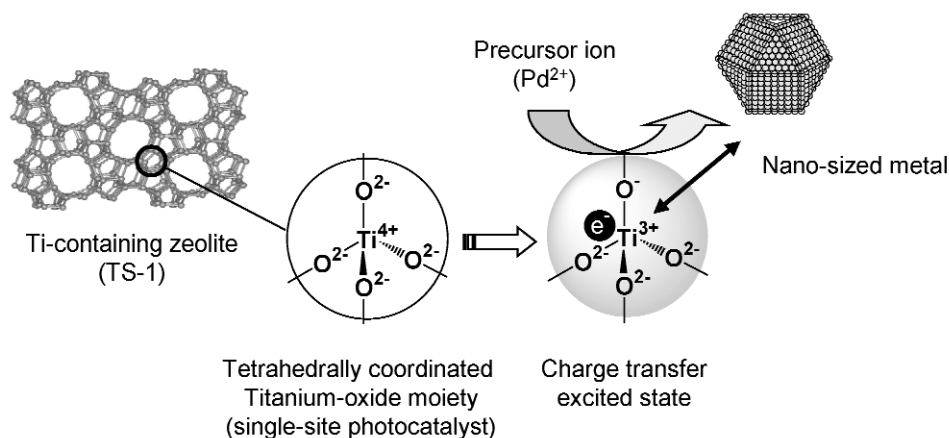


Fig. 4 Scheme for the synthesis of nanosized metal catalyst by the PAD method using single-site photocatalyst (tetrahedrally coordinated titanium oxide moieties) included within zeolites.

EXPERIMENTAL

The synthesis of the TS-1 zeolite (MFI structure, Si/Ti ratio: 60) was carried out by using tetraethylorthosilicate and titanium isopropoxide as the starting materials and TPAOH as template [7,8]. The coordination geometry of titanium oxide moieties in the present TS-1 zeolite has been confirmed by XAFS and UV-vis absorption measurements. The Ti K-edge XAFS spectra were recorded at room temperature in the fluorescence mode at BL-7C of Photon Factory of KEK. The presence of an intense pre-edge peak of X-ray absorption near-edge spectroscopy (XANES) spectra and the result from curve-fitting analysis of EXAFS spectra indicated that the tetrahedrally coordinated titanium oxide moieties existed within the framework of TS-1 zeolite [12,13]. The observation of the band at around 250 nm in UV-vis absorption spectra also supports the presence of tetrahedrally coordinated titanium oxide moieties.

The Pd loaded on TS-1 (PAD-Pd/TS-1, 1.4 wt % as Pd metal) was prepared using the PAD method: Pd metal precursor was deposited on TS-1 from 4.3×10^{-3} M aq. solution of PdCl₂ (Wako Pure Chemical Ind., Ltd., 99.9 %) under UV-light irradiation using a high-pressure Hg lamp at 295 K. The samples were dried at 378 K and reduced by H₂ (20 ml min⁻¹) at 473 K for 1 h (PAD-Pd/TS-1). The impregnated catalyst (1.4 wt % as Pd metal) was also prepared as a reference (imp-Pd/TS-1) by the conventional impregnation method using an aqueous solution of PdCl₂. The Pd K-edge XAFS spectra of these catalysts were recorded in transmittance mode at BL01B1 of Spring-8 [19].

The direct synthesis of H_2O_2 from H_2 and O_2 was carried out in the slurry of Pd/TS-1 catalysts and water with 0.01 M HCl in a flow of H_2 and O_2 (80 ml min^{-1} , $\text{H}_2:\text{O}_2 = 1:1$) for 6 h at room temperature, and the amount of formed H_2O_2 was monitored by a chemical redox titration method. The oxidation of phenol was carried out in the slurry of Pd/TS-1 catalysts and acetonitrile with 0.01 M HCl in a flow of H_2 and O_2 (80 ml min^{-1}) for 6 h at 343 K, and the products in the phenol oxidation were monitored by gas chromatography.

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REFERENCES

1. J. M. Thomas. *Angew. Chem., Int. Ed.* **38**, 3588 (1999).
2. A. Corma. *Chem. Rev.* **97**, 2373 (1997).
3. B. Notari. *Adv. Catal.* **41**, 253 (1996).
4. M. Anpo, M. Che. *Adv. Catal.* **44**, 119 (1999).
5. M. Anpo, J. M. Thomas. *Chem. Commun.* 3273 (2006).
6. H. Yamashita, M. Anpo. *Curr. Opin. Solid State Mater. Sci.* **7**, 471 (2004).
7. H. Yamashita, K. Ikeue, T. Takewaki, M. Anpo. *Top. Catal.* **18**, 95 (2002).
8. H. Yamashita, Y. Ichihashi, M. Anpo, M. Hashimoto, C. Louis, M. Che. *J. Phys. Chem.* **100**, 16041 (1996).
9. H. Yamashita, K. Yoshizawa, M. Ariyuki, S. Higashimoto, M. Che, M. Anpo. *Chem. Commun.* 435 (2001).
10. M. Anpo, S. G. Zhang, S. Higashimoto, M. Matsuoka, H. Yamashita, Y. Ichihashi, Y. Matsumura, Y. Souma. *J. Phys. Chem. B* **103**, 9295 (1999).
11. N. Ichikuni, H. Murayama, K. K. Bando, S. Shimazu, T. Uematsu. *Anal. Sci.* **17s**, i1193 (2001).
12. G. Sankar, J. M. Thomas. *Top. Catal.* **8**, 1 (1999).
13. J. M. Thomas, G. Sankar. *Acc. Chem. Res.* **34**, 571 (2001).
14. K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda. *J. Am. Chem. Soc.* **126**, 10657 (2004).
15. D. Astruc, F. Lu, J. R. Aranzaes. *Angew. Chem., Int. Ed.* **44**, 7852 (2005).
16. M. A. El-Sayed. *Acc. Chem. Res.* **34**, 257 (2001).
17. S. E. Park, L. Huang, C. W. Lee, J. S. Chang. *Catal. Today* **61**, 117 (2000).
18. H. Yamashita, T. Shimizu, M. Shimada, N. Mimura, K. Mori, M. Sakata, H. Mori, T. Ohmichi, I. Katayama. *Stud. Surf. Sci. Catal.* **172**, 461 (2007).
19. F. Montilla, E. Morallon, A. De Battisti, A. Benedetti, H. Yamashita, J. L. Vazquez. *J. Phys. Chem. B* **108**, 5044 (2004).