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Synthesize of nano-sized Pd metal catalyst on Ti-containing zeolite using a photo-assisted deposition (PAD) method

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Using a photo-assisted deposition (PAD) method, the nano-sized Pd metal can be highly deposited on Ti-containing silicalite zeolite (TS-1). This nano-sized Pd metal can exhibit the high efficiency for H_2O_2 production under a flow of H_2 and O_2 and further applied to the subsequent partial oxidation of phenol on TS-1.

KEY WORDS: photo-assisted deposition (PAD); single-site photocatalyst; nano-sized Pd metal; Ti-containing zeolite.

1. Introduction

Nano-sized metal catalysts such as Pd, Pt, and Au have attracted a great deal of attention as potentially advanced materials possessing unique electronic, optic, and magnetic properties as well as catalytic functions [1–3]. One of the most important factors for controlling catalytic activity of these metal catalysts is the particle size. The development of convenient and useful method to prepare the nano-sized metal loaded on support with controlled particle size and size distribution is essential to design of the highly active metal catalyst.

On the other hand, Ti-containing zeolites such as TS-1 and Ti-Beta were used as unique photocatalysts and catalysts [4–10]. In the TS-1, the tetrahedrally coordinated titanium oxide moieties can be included and isolated within the frameworks of silicalite zeolite. These transition metal oxide moieties such as tetrahedrally coordinated titanium oxide species incorporated and isolated within silica matrix of zeolite and mesoporous silica have been named as ''single-site photocatalysts'' [4,5]. As the ''single-site photocatalysts'', Ti, Cr, V and Mo oxide moieties can be incorporated and isolated in the silica matrix of zeolite and can demonstrate the unique photocatalytic properties [4–14]. Under UV-light irradiation, these single-site photocatalysts generate charge transfer excited state which can show the highly active and selective photocatalytic performances. In the previous studies [4–14], the main focus has been made only on the photocatalytic reactivity but the applications of single-site photocatalyst for the synthesis of conventional catalysts such as nano-sized metal catalyst has yet been reported. 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 from the mixture of single-site photocatalyst in the aqueous solution with metal precursor.

In this study, the photoexcitation of titanium oxide moieties included within TS-1 silicalite zeolite under UV-light irradiation was applied to disperse Pd metal highly. Using a photo-assisted deposition (PAD) method, uniform nano-sized Pd metal can be highly deposited on the photo-excited TS-1. The size and distribution of nano-sized Pd metal were characterized by XAFS and TEM analysis. The benefits of combination of the PAD method and the Ti-containing zeolite (single-site photocatalyst) as support to prepare the active nano-sized Pd metal catalyst for the production of H_2O_2 from H_2 and O_2 and the subsequent partial oxidation of phenol using produced H_2O_2 were clarified.

2. Experimental

The synthesis of the Ti containing silicalite zeolite (TS-1, MFI structure, Si/Ti = 60) was carried out by using tetraethylorthosilicate and titanium isopropoxide as the starting materials and TPAOH as template [7–10]. The Pd loaded on TS-1 (PAD-Pd/TS-1, 1.4 wt% as Pd metal) was prepared using the photo-assisted deposition (PAD) method: Pd metal precursor was deposited on TS-1 from an aqueous solution of $PdCl_2$ under UV-light

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irradiation using a high-pressure Hg lamp at 295 K. The samples were dried at 378 K and reduced by H_2 (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 from an aqueous solution of $PdCl_2$. The Ti K-edge XAFS spectra were recorded at room temperature in the fluorescence mode at BL-7C of Photon Factory of KEK, and the Pd K-edge XAFS spectra of these catalysts were recorded in transmittance mode at BL01B1 of SPring-8 [7,15]. The direct synthesis of H_2O_2 from H_2 and O_2 and the oxidation of phenol was carried out in the slurry of Pd/TS-1 catalysts and water (0.01 M HC1) and/or acetnitril in a flow of H_2 and O_2 (80 mL min^{-1}, H_2:O_2 = 1:1). The amount of formed H_2O_2 was monitored by a chemical redox titration method and the products in the phenol oxidation was monitored by gas chromatography.

3. Results and discussion

The XRD pattern of crystalline TS-1 was characteristic of MFI topology. The specific surface area measured by N_2 adsorption was approximately 263 m^2/g. The coordination geometry of titanium oxide moieties in the present TS-1 zeolite has been confirmed by XAFS analysis. The presence of an intense preedge peak of XANES spectra and the result from curve fitting analysis of EXAFS spectra indicated that the tetrahedrally coordinated titanium oxide moieties (tetra-Ti-oxide) existed within the framework of TS-1 zeolite [16,17]. The observation of band at around 250 nm in UV-vis absorption spectra also supports the presence of tetra-Ti-oxide moieties.

Under UV-light irradiation of the slurry of TS-1 in aqueous $PdC1_2$ solution, the Pd metal can be successfully deposited on the TS-1. The almost no Pd deposition was observed both on the silicalite zolite without titanium oxide under UV-light irradiation and the TS-1 zeolite without UV-light irradiation. These results indicate that the presence of photo-exited state of tetra-Ti-oxide is indispensable for the deposition of Pd species. The Pd K-edge XANES spectrum of the Pd/TS-1 was similar to that of the Pd foil but differed from that of PdO, suggesting that the coordination symmetry of the Pd/TS-1 is similar to the Pd metal of face-centered cubic (fcc) structure. The Fourier transforms of Pd K-edge EXAFS spectra of the Pd/TS-1 catalysts are shown in figure 1. The presence of the peak assigned to the Pd-Pd bond of Pd metal at around 2.5 Å indicates the formation of nano-sized Pd metal. The intensity of the Pd-Pd peak of the PAD-Pd/TS-1 catalyst is smaller than the Pd metal powder and the imp-Pd/TS-1 catalyst. Curve-fitting analysis revealed that the coordination number (CN) and interatomic distance (R) in the PAD-Pd/TS-1 are 6.4 and 2.75 Å. The R value is consistent with that of the Pd foil (2.75 Å), whereas the CN value was smaller than that of the Pd foil (12). These results clearly suggest that the size of Pd metal particles depends on the preparation method and that the smaller Pd metal particles are formed on the photo-deposited catalyst (PAD-Pd/TS-1) than the impregnated catalyst (imp-Pd/TS-1).

The TEM image of the PAD-Pd/TS-1 catalyst shown in figure 2 and the particle distribution obtained from the analysis of TEM images and shown in figure 3 also support the results of XAFS measurement. The nano-sized Pd metals with a mean diameter (d) of ca. 21 Å having a narrow size distribution (standard deviation: σ = 6.5 Å) was formed on the PAD-Pd/TS-1, whereas the aggregated Pd metal with various size are observed on the img-Pd/TS-1 catalyst (d = 11 nm and σ = 38 Å).

Under the flow of H_2 and O_2 in the slurry of Pd/TS-1 catalysts and water, the formation of H_2O_2 was observed on the Pd/TS-1 catalysts (figure 4). The PAD-Pd/TS-1 catalyst can exhibit the higher reactivity than the imp-Pd/TS-1 catalyst. Because the higher dispersion of Pd metal particle is preferable for the formation of H_2O_2 [18], the results on the reaction of H_2O_2 synthesize also supports that the PAD method is useful to

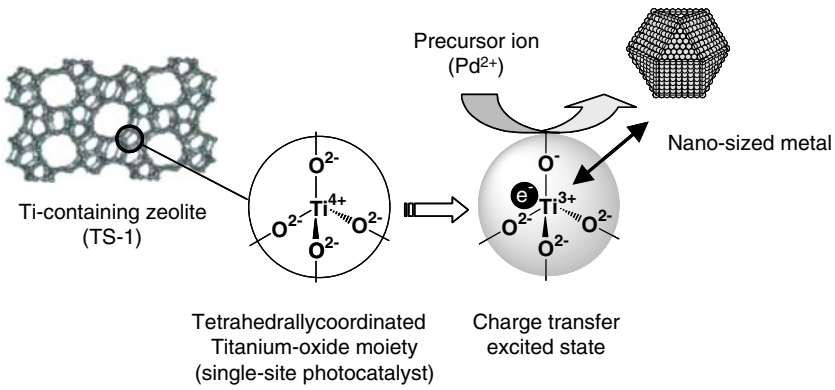

Figure 1. Synthesis of nano-sized metal catalyst by the photo-assisted deposition method using single-site photocatalyst.

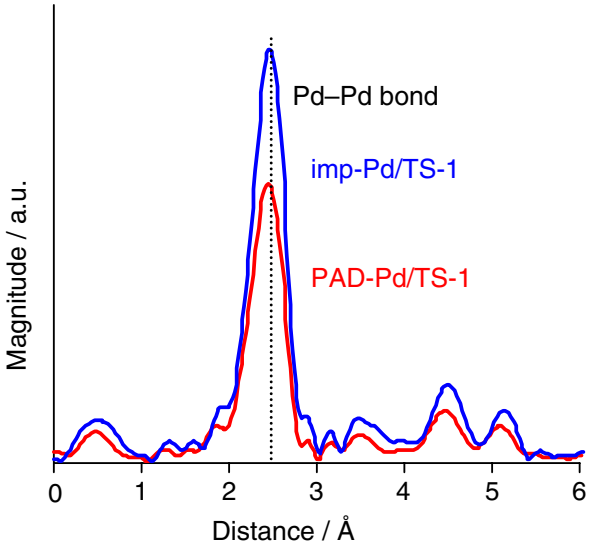

Figure 2. The Fourier transforms of Pd K-edge EXAFS spectra with the Pd/TS-1 catalysts after H_2 treatment at 473 K.

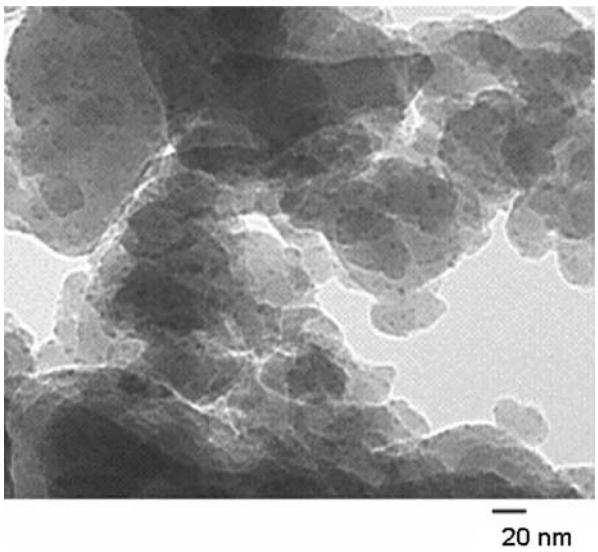

Figure 3. The TEM image of the PAD-Pd/TS-1 catalyst after H_2 treatment at 473 K.

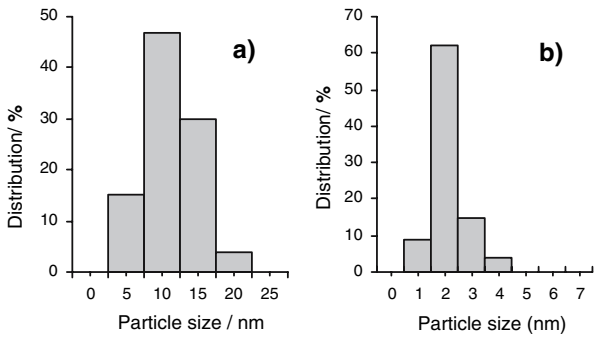

Figure 4. Size distribution diagrams of Pd metal obtained from the TEM images of the imp-Pd/TS-1 (a) and (b) PAD-Pd-TS-1 catalysts after H_2 treatment at 473 K.

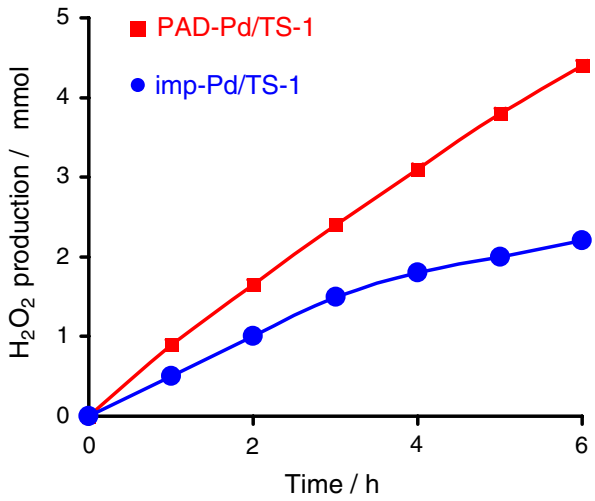

Figure 5. The reaction time profiles of H_2O_2 formation on the Pd/TS-1 catalysts in water with a flow of H_2 and O_2. Reaction conditions: Pd/TS-1 (0.1 g), 0.01 M HC1 (50 mL), flow of H_2 and O_2 (80 mL min^{-1}, H_2:O_2 = 1:1) at room temperature.

Table 1
The oxidation of phenol on the Pd/TS-1 catalysts at 343 K

Entry	Catalyst	Solvent	Yield/%	Select/%			
				HQ[a]	BQ[a]	CAT[a]	CH[a]
1	PAD-Pd/TS-1	MeOH	6.4	1	0	2	97
2	imp-Pd/TS-l	MeOH	1.7	13	3	35	48
3	PAD-Pd/TS-l	CH_3CN	7.0	17	0	83	0
4	imp-Pd/TS-1	CH_3CN	2.0	20	5	75	0

[a] HQ: Hydroquinone, BQ: Benzoquinone, CAT: Cathecol, CH: cyclohexanone

synthesize the nano-size Pd metal with the simple process using photo-irradiation (figure 5).

Furthermore, the presence of phenol in this reaction system led the formation of the products from the oxidation of phenol with the *in situ* produced H_2O_2 (table 1). The PAD-Pd/TS-1 catalyst exhibited the higher conversion of phenol than the imp-Pd/TS-1 catalyst. The micro-pores and the tetra-Ti-oxide moieties of TS-1 zeolite are suitable for the partial oxidation of phenol with H_2O_2 which are formed from H_2 and O_2 on the nano-size Pd metal deposited on TS-1. In the case of methanol solvent, the hydrogenation product of cyclohexanone was mainly formed. However, the selectivity toward oxidation products significantly improved with keeping the high total yield while using acetonitrile as a solvent.

4. Conclusions

Using the photo-assisted deposition (PAD) method with a single-site catalyst (tetra-Ti-oxide) included within the zeolite frameworks (TS-1), Pd metal particles

with high dispersion state can be deposited on the photo-excited tetra-Ti-oxide moieties. The direct interaction between the precusor of nano-sized Pd metal and the photo-excited tetra-Ti-oxide moieties realized by the PAD method has possibility to design the unique and active nano-sized metal catalyst.

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