1. Introduction

With an increasing concern about the depletion of petroleum resources, catalytic conversion of lignocellulosic biomass to fuels and feedstock chemicals has attracted considerable research interest because of the renewability of lignocellulose. Furfural is one of the attractive feedstock chemicals obtained from lignocellulosic biomass, because it can be selectively produced via the dehydration of pentose sugars (e.g., xylose) derived from the hemicellulose, while the hydration of hexose sugars (e.g., glucose) affords 5-hydroxymethylfurfural (HMF). Furfural can be transformed into furan via decarbonylation, and thus the obtained furan can be converted into basic chemicals including tetrahydrofuran (THF) as an organic solvent and 1,4-butanediol as a polymer precursor, via hydrogenation and hydrogenolysis, respectively. These pathways are more promising and greener alternative routes for the industrial production of THF and 1,4-butanediol. Therefore, the decarbonylation of biomass-derived furfural to produce furan is a key reaction for realizing efficient and economical production of basic chemicals from biomass sources.
Previous studies have manifested that liquid-phase decarbonylation of furfural takes place under milder reaction conditions with the temperature close to the boiling point of furfural (435 K), in which supported Pd catalysts act as effective catalysts. However, a highly pressurized condition in supercritical CO₂ and a high metal loading are needed to accelerate the reaction rate. Besides, the addition of inorganic bases (K₂CO₃) is required for neutralizing the trace amounts of acid in furfural. Therefore, the development of heterogeneous catalysts that show high catalytic activity under milder conditions without any additives has been desired to overcome the technical problems.

Recently, Ishida and Tokunaga et al. demonstrated decarbonylation of furfural over Pd/ZrO₂ catalyst in the absence of bases, and concluded that zero-valent small Pd clusters consisting of more than two Pd atoms are the real active species for this reaction. Titania (eg. TiO₂) provides another possible option to immobilize Pd nanoparticles (NPs), because of its chemical stability and amphoteric surface property similar to ZrO₂. Another intriguing property of titania is the photo-responsive property that causes charge carrier separation under the irradiation of ultraviolet (UV) light with wavelength sufficient to evoke band gap excitation (ca. below 400 nm). The photo-excited electrons generated on the conduction band of titania are capable of reducing metal cations to create metal NPs uniformly immobilized on titania surface (so-called "photo-assisted deposition (PAD) method").

In this study, we prepared a titania-supported Pd NPs catalyst by the PAD method utilizing the photo-reduction ability of various titania supports, and examined their catalytic performances in the liquid-phase decarbonylation of furfural to produce furan. Highly-dispersed small Pd NPs could be immobilized on titinate nanotubes (TNT) with tubular nanostructure and the associated high-surface-area via the PAD method, which exhibited a higher catalytic activity than the conventional supported Pd catalysts and those immobilized on other titania supports. The effects of Pd deposition method, type of support and size specificity of Pd NPs in the liquid-phase decarbonylation of furfural are discussed.

2. Experimental

Anatase TiO₂ (ST-01) and anatase/rutile TiO₂ (P25) were obtained from Ishihara Sangyo Kaisha, Ltd. and Evonik Industries, Ltd., respectively. Fumed silica was purchased from Sigma-Aldrich. γ-Al₂O₃ was purchased from Strem Chemicals Inc. Disodium tetrachloropalladate(II) (Na₂PdCl₄) and dihydrogen tetrachloropalladate(II) (H₂PdCl₄) as Pd precursors and other reagents for catalyst preparation and catalytic tests were purchased from Nacalai Tesque Inc. and used without further purification.

Titanate nanotube (TNT) materials were prepared according to a previously-reported method. H⁺-exchanged TNT (H⁺-TNT) was prepared from as-synthesized sodium titanate nanotubes (Na⁺-TNT) by HNO₃ treatment with a copious amount of HNO₃ aqueous solution (0.1 mol/L) until pH of the supernatant solution becomes below 7.0, followed by washing with deionized water and drying at 373 K.

Deposition of Pd NPs on titania support via PAD method was performed according to a previously-reported method. H⁺-exchanged TNT (H⁺-TNT) was prepared from as-synthesized sodium titanate nanotubes (Na⁺-TNT) by HNO₃ treatment with a copious amount of HNO₃ aqueous solution (0.1 mol/L) until pH of the supernatant solution becomes below 7.0, followed by washing with deionized water and drying at 373 K.

Deposition of Pd NPs on titania support via PAD method was performed as follows; 0.5 g of titania support was dispersed in a 200 mL of 2-propanol solution containing 20 mL of deionized water and 47.5 μmol of Na₂PdCl₄, so as to achieve 1 wt% of Pd loading. After sealing and purging with Ar gas, UV light irradiation from a high-pressure Hg lamp (HL100CH-4, SEN LIGHTS Co., Ltd.) was carried out with the suspension being stirred over the period of 4 h. The resulting solid was filtered, washed with deionized water and dried under vacuum to obtain titania-supported Pd NP catalyst. The comparative studies were concurrently conducted, whereby supported Pd catalysts were prepared by the wet impregnation method (Pd loading was fixed to 1 wt% for all samples). Typically, 0.5 g of support material was added to 20 mL of aqueous solution containing Na₂PdCl₄ (47.5 μmol), and the mixture was stirred at room temperature for 3 h, followed by evaporation of water under vacuum. The solid was treated under a flow of 10 % H₂/N₂ (100 mL/min) at 523 K for
3 h to reduce the Pd species.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.54056 Å) operated at 40 kV and 40 mA. Nitrogen physisorption measurement was performed at 77 K using a BELSORP-max system (MicrotracBEL Corp.). Samples were degassed at 473 K for 3 h under vacuum to remove any physisorbed water prior to each measurement. The diameters of the Pd NPs were estimated by CO pulse measurement using a BEL-METAL-1 (MicrotracBEL Corp.). The catalyst (ca. 30 mg) was pretreated under a flow of pure H₂ (50 mL/min) at 473 K for 1 h. After cooling to 323 K, CO pulse was introduced into the cell, and the amount of CO adsorbed was quantified. The Pd/CO ratio was set as 1 for the calculation of Pd dispersion and diameter. TEM observation was performed using a Hitachi H-800 FE-TEM at 200 kV accelerating voltage. XPS measurement was performed on a Shimadzu ESCA-3400 photoelectron spectrometer using Mg Kα radiation (1253.6 eV) X-ray source. Binding energies were calibrated using the adventitious carbon (C 1s) peak at 284.5 eV. Pd K-edge X-ray absorption fine structure (XAFS) measurement was carried out at the BL01B1 beamline station of SPring-8 (JASRI, Japan) with a Si(111) monochromator. The extended X-ray absorption fine structure (EXAFS) data were normalized by fitting the background absorption coefficient. Fourier transformation of the $k^3$-weighted normalized EXAFS data was carried out over the range of $3.0 < k/\text{Å}^{-1} < 12$.

Fourier transform infrared (FTIR) spectra were recorded on a JASCO FTIR-6300 instrument with a resolution of 4 cm⁻¹. Sample was pressed into a self-supported wafer, loaded into a quartz-made transmission FTIR cell and was pre-treated at 353 K in a flow of N₂ (30 mL/min) for 0.5 h to vaporize physisorbed water. After the pre-treatment, a vapor of furfural was introduced for 0.5 h to reach adsorption equilibrium, and then purged with N₂ for 0.5 h. FTIR difference spectra of furfural desorbed from furfural-saturated samples were collected upon increasing the temperature from 373 to 423 K with a ramping rate of 1 K/min under the flow of N₂ (30 mL/min).

Decarbonylation of furfural was performed using a stainless steel autoclave reactor (60 mL). Typically, catalyst (100 mg), furfural (1 mmol) and THF (3 mL) were charged into the reactor, purged three times with pure N₂ gas. The reactor was then heated to 413 K and magnetically stirred for 12 h. After the reactor was cooled down and depressurized, a portion of reaction solution was withdrawn using a syringe, filtered to remove any solids and analyzed by gas chromatograph (GC-14B, Shimadzu Corp.) equipped with a flame ionization detector and a ZB-FFAP capillary column (50 m × 0.32 mm) using biphenyl as an external standard. Turnover frequency (TOF) was calculated by dividing the mole of furfural converted per hour by the quantity of surface-exposed Pd atoms determined by CO pulse measurement.

3. Results and Discussion

3.1. Characterization of Catalyst

Characterization of the series of titania-supported Pd catalysts prepared by PAD method was performed by XRD, TEM and N₂ physisorption measurements. In XRD measurement (Fig. 2), Pd NPs supported on Na⁺-type and H⁺-type TNT showed diffraction peaks at around 9.1, 24.3, 28.3 and 48.4°, which correspond to those of the previously-reported titanate nanotubes, confirming that the nanotube structure is retained upon the deposition of Pd NPs. Pd/TiO₂(ST-01) showed main peaks at 25.3, 38.1 and 47.9° all attributable to anatase crystalline structure of TiO₂, while Pd/TiO₂(P25) showed the additional diffraction peaks ascribed to rutile phase at 27.4, 36.1 and 41.3°, verifying that the original crystalline structures remain unchanged even after the deposition of Pd NPs. Pd/TiO₂(P25) showed the additional diffraction peaks ascribed to rutile phase at 27.4, 36.1 and 41.3°, verifying that the original crystalline structures remain unchanged even after the deposition of Pd NPs. In all cases, the diffractions derived from metallic Pd were not observed, which could be due to the formation of highly-dispersed, small Pd NPs (vide infra).

N₂ physisorption isotherms of Pd/TiO₂(P25) showed a type-II isotherm, which is characteristic of a nonporous solid. Pd/TiO₂(ST-01) and Pd/TNT showed a combination of type II and IV isotherms with a notable increase in the quantity of adsorbed N₂ at the low pressure region ($p/p₀ < 0.05$), which is typical of porous materials with a certain degree of mesoporosity. The textural properties obtained from the N₂ physisorp-
tion isotherms revealed that Pd/TiO$_2$(ST-01) and Pd/TNT samples retain their inherent high specific surface area ($S_{BET}$) of 260-290 m$^2$/g and total pore volume ($V_{total}$) upon the deposition of Pd (Table 1), while Pd/TiO$_2$(ST-01) showed a lower specific surface area ($S_{BET}$) of 51 m$^2$/g and total pore volume due to its non-porous structure.

Figure 3 shows TEM images of titania-supported Pd catalysts prepared by PAD method. As shown in Figs. 3(a) and 3(b), TNT-supported Pd catalysts both showed a tubular structure with a diameter of about 10 nm, and Pd NPs uniformly deposited on TNT supports were observed, whereas slightly larger Pd NPs were deposited onto commercial TiO$_2$ particles (Figs. 3(c) and 3(d)) probably due to low specific surface area or absence of tubular structure. The mean diameters of the Pd NPs determined based on CO pulse measurement ($d_{CO}$) in Pd/Na$^+$-TNT, Pd/H$^+$-TNT, Pd/TiO$_2$(ST-01), and Pd/TiO$_2$(P25) were 3.7, 4.6, 4.2, and 4.4 nm, respectively. Considering that the diameter of Pd NPs immobilized on Na$^+$-TNT support by the conventional wet impregnation method ($d_{CO}$) of 6.6 nm are apparently larger than that immobilized by PAD method ($d_{CO}$ = 3.7 nm, cf. Figs. 7(a) and 7(c)), Na$^+$-TNT is considered as the most effective support for immobilizing uniformly-dispersed fine Pd NPs by the assist of UV light irradiation. TNTs exhibit light absorption bands in UV region (at $\lambda$~350 nm) owing to their semiconducting property, although they are slightly blue-shifted compared with those of anatase/rutile TiO$_2$ crystals (at $\lambda$~400 nm). It is likely that Pd precursor ions ([PdCl$_4$]$^{2-}$) are adsorbed on ion-exchange sites (either H$^+$ or Na$^+$) of TNT surface and are reduced by the photo-generated electrons under UV light irradiation to form Pd NP, in which high specific surface area of TNT plays a key role for the creation of highly-dispersed, small Pd NPs.

### 3.2. Decarbonylation of Furfural to Furan

The series of oxide-supported Pd catalysts were examined in the liquid-phase decarbonylation of furfural at 413 K. As summarized in Table 1, Pd supported on titania supports exhibited higher conversions and selectivities compared to other supports.

| Entry | Catalyst          | $S_{BET}$ | $V_{total}$ | $d_{CO}$ | Conv. | Furan sel. | Furan yield |
|-------|------------------|-----------|-------------|----------|-------|------------|-------------|
| 1     | Pd/Na$^+$-TNT    | 260       | 80          | 12.4     | 3.7   | 92         | 81          | 75          |
| 2     | Pd/Na$^+$-TNT$^b$| 227       | 77          | 13.5     | 6.6   | 31         | 70          | 22          |
| 3     | Pd/H$^+$-TNT     | 290       | 11.1        | 15.3     | 4.6   | 57         | 61          | 35          |
| 4     | Pd/TiO$_2$(ST-01)| 288       | 0.74        | 10.2     | 4.2   | 52         | 56          | 29          |
| 5     | Pd/TiO$_2$(P25)  | 51        | 0.46        | 36.5     | 4.4   | 36         | 87          | 31          |
| 6     | Pd/SiO$_2$      | 319       | 1.72        | 21.6     | 8.5   | 29         | >99         | 29          |
| 7     | Pd/γ-Al$_2$O$_3$ | 151       | 0.55        | 14.6     | 6.7   | 9          | 45          | 4           |
| 8     | H$^+$-TNT       | 332       | 0.92        | 11.1     | -     | 22         | -           | 0           |
| 9     | Na$^+$-TNT      | 355       | 1.25        | 14.0     | -     | 8          | -           | 0           |

*Reaction conditions: catalyst (100 mg, 1 mol% Pd), furfural (1 mmol), THF (3 mL), N$_2$ (0.1 MPa), 413 K, 12 h.
*Prepared by wet impregnation method, followed by H$_2$ reduction at 523 K for 3 h before use.
*Specific surface area determined by Brunauer-Emmett-Teller (BET) method.
*Total pore volume reported at $p/p_0 = 0.99$.
*Average pore diameter determined by Barrett-Joyner-Halenda (BJH) method.
*Average diameter of Pd particles determined by CO pulse measurement.
sorption kinetics of furfural on the most active Pd/Na\textsuperscript{+} catalysts measured at 373-423 K under a flow of N\textsubscript{2}.

Fig. 4 In-situ Differential FTIR Spectra of Furfural Adsorbed on Pd/Na\textsuperscript{+}-TNT, Na\textsuperscript{+}-TNT and Pd/γ-Al\textsubscript{2}O\textsubscript{3} Catalysts Measured at 373-423 K under a Flow of N\textsubscript{2}.

Fig. 5 Pd 3d XPS Spectra for Titania-supported Pd Catalysts Prepared by the Photo-assisted Deposition Method (Na\textsubscript{2}PdCl\textsubscript{4} was used as a metal precursor.)

superior catalytic activities to those supported on SiO\textsubscript{2} and γ-Al\textsubscript{2}O\textsubscript{3}, affording furan as a main product in 29-75 % yield after 12 h of reaction (entries 1-5). Pd/γ-Al\textsubscript{2}O\textsubscript{3}, which has been frequently used in this reaction\textsuperscript{24}, showed a poor catalytic activity (4 % yield of furan) (entry 7). Pd/SiO\textsubscript{2} showed a moderate catalytic activity (29 % yield of furan) with a high selectivity toward furan (>99 %) (entry 6). This high furan selectivity is probably due to the absence of strong acid sites, which trigger the polymerization of furfural. Pd/TiO\textsubscript{2}(ST-01) and Pd/H\textsuperscript{+}-TNT afforded conversions (52-57 %) and furan yields (29-35 %), which were similar to those of the Pd catalyst supported on ST-111 TiO\textsubscript{2} (\(S_{\text{BET}} = 312 \text{ m}^2/\text{g}\)) previously reported by Ishida and Tokunaga et al. (59 % conversion of furfural and 43 % yield of furan under similar reaction conditions (temp. = 413 K, N\textsubscript{2} 0.1 MPa))\textsuperscript{21}). On the other hand, Pd/Na\textsuperscript{+}-TNT exhibited a significantly higher furfural conversion (92 %) and furan yield (75 %) under the identical conditions (entry 1). It should be mentioned that Pd/TiO\textsubscript{2}(ST-01) and Pd/H\textsuperscript{+}-TNT exhibited lower conversions and furan selectivities despite having large specific surface areas (\(S_{\text{BET}} = 288-290 \text{ m}^2/\text{g}\)) comparable to that of Pd/Na\textsuperscript{+}-TNT, indicating that specific surface area of titania support is not a dominant factor affecting the catalytic activity. Considering the fact that use of H\textsuperscript{+}-TNT alone as a catalyst resulted in a formation of humin species (entry 8), while use of Na\textsuperscript{+}-TNT afforded a less amount of humin species (entry 9), it is deducible that the acidic property of titania support accelerates the polymerization of furfural, which results in a decreased furan selectivity. Thus, the selection of a suitable support for the immobilization of Pd NPs is critically important.

The decarbonylation reaction as well as adsorption/desorption kinetics of furfural on the most active Pd/Na\textsuperscript{+}-TNT catalyst were tracked by using in-situ FTIR measurement and were compared with those of pristine Na\textsuperscript{+}-TNT and Pd/γ-Al\textsubscript{2}O\textsubscript{3} catalysts (Fig. 4). On Pd/γ-Al\textsubscript{2}O\textsubscript{3} catalyst, peaks derived from the stretching vibration of aldehyde group (\(\nu(C=O)\)) were observed at 1713 cm\textsuperscript{-1} and 1644 cm\textsuperscript{-1}. Pd/Na\textsuperscript{+}-TNT catalyst exhibited an obvious shift of the peak seen at 1713 cm\textsuperscript{-1} to the lower wavenumber (1693 cm\textsuperscript{-1}), while the peaks assigned to the stretching vibration of olefinic C=C bond (ca. 1532 cm\textsuperscript{-1}, 1473 cm\textsuperscript{-1}) appeared at the same position. This result suggests that aldehyde group of some furfural molecules is more strongly chemisorbed on Na\textsuperscript{+}-TNT surface, whereas furfural on γ-Al\textsubscript{2}O\textsubscript{3} is weakly physisorbed, which might be due to the presence of stronger Lewis acid sites on Na\textsuperscript{+}-TNT\textsuperscript{25,26}. Upon raising temperature from 373 to 423 K, the peaks assigned to \(\nu(C=O)\) and \(\nu(C=C)\) both disappeared completely over the Pd/Na\textsuperscript{+}-TNT catalyst, representing the decarbonylation of furfural and the subsequent elimination of the produced furan and CO over the examined temperature range. Furfural remained adsorbed even at 423 K and decarbonylation hardly took place over the pristine Na\textsuperscript{+}-TNT, corroborating the fact that Pd NPs are the active site for this reaction. On the contrary, the adsorbed species remained even at 423 K over Pd/γ-Al\textsubscript{2}O\textsubscript{3} catalyst, even though a gradual decrease of the peak intensity was observed. This represents a lower reaction rate of Pd/γ-Al\textsubscript{2}O\textsubscript{3} than that of Pd/Na\textsuperscript{+}-TNT, which is in line with the catalyst activity results shown in Table 1.

3.3. Structure-activity Relationship

In order to elucidate the cause for the activity difference of Pd catalysts immobilized on various titania supports, the electronic state and nanostructure of Pd NPs were investigated by XPS and XAFS measurements. In the Pd 3d XPS spectrum (Fig. 5), all samples showed a dominant peak derived from zero-valent Pd.
and no obvious difference was observed in the electronic state of Pd. The existence of Pd\(^{2+}\) species might be derived from partially-oxidized Pd species formed at the interface of Pd NPs and titania supports via a Pd-O-Ti bonding. As shown in Fig. 6(a), the XANES spectra of titania-supported Pd samples all resembled that of Pd foil, but with higher energy shift of the absorption edges (\(E_0 = 24345\) eV) compared with that for Pd foil (\(E_0 = 24342\) eV). This result verifies that Pd NPs on titania supports dominantly exist as zero-valent Pd\(^0\) species with slightly electropositive charges, being consistent with XPS results.

The Fourier-transformed magnitude of the peak at 2.55 Å decreased in the order of Pd/H\(^\circ\)-TNT > Pd/TiO\(_2\)(ST-01) > Pd/Na\(^+\)-TNT, suggesting that the size of Pd NPs decreases accordingly. Coordination number (CN) calculated from the curve-fitting analysis of the FT-EXAFS spectrum for Pd/Na\(^+\)-TNT (CN \(= 6.0\)) was apparently lower than those for Pd/TiO\(_2\)(ST-01) (CN \(= 8.0\)) and Pd/H\(^+\)-TNT (CN \(= 8.7\)), indicating the formation of smaller size of Pd NPs on Na\(^+\)-TNT supports. These results are fairly consistent with the tendency of the Pd NP size determined by CO pulse measurement. Considering the fact that there is a tendency that a higher catalyst activity is obtained as the size of Pd NPs decreases, it can be hypothesized that the formation of smaller Pd\(^0\) NPs is a key for achieving a high catalytic efficiency.

Table 2  Textural Properties and Results in the Decarbonylation of Furfural at 413 K for Pd/Na\(^+\)-TNT Catalysts Prepared by Using Different Deposition Methods and Different Pd Precursors\(^a\)

| Deposition method | Pd precursor | \(d_{\text{CO}}\) [\(\text{nm}\)] | \(d_{\text{TEM}}\) [\(\text{nm}\)] | Pd K-edge XAFS | Furfural decarbonylation |
|------------------|--------------|------------------------------|------------------|-----------------|-------------------------|
|                  |              |                              |                  | CN\(^a\) | \(R_e\) [Å] | Conv. [%] | Furan sel. [%] | Furan yield [%] |
| PAD              | Na\(_2\)PdCl\(_4\) | 3.7                          | 3.3              | 6.0          | 2.76         | 92      | 81            | 75 |
| PAD              | H\(_2\)PdCl\(_4\) | 4.4                          | 4.2              | 9.2          | 2.75         | 65      | 87            | 57 |
| Impregnation     | Na\(_2\)PdCl\(_4\) | 6.6                          | 8.2              | 11.2         | 2.75         | 31      | 70            | 22 |
| Impregnation     | H\(_2\)PdCl\(_4\) | 9.0                          | 10.2             | 11.4         | 2.75         | 17      | 75            | 13 |

\(a\) Reaction conditions: catalyst (100 mg, 1 mol\% Pd), furfural (1 mmol), THF (3 mL), 413 K, N\(_2\) (0.1 MPa), 12 h.

\(b\) Average diameter of Pd particles determined by CO pulse measurement.

\(c\) Average diameter of Pd particles calculated from 100 particles randomly selected from the TEM images.

\(d\) Coordination number for Pd determined by curve-fitting analysis.

\(e\) Interatomic distance for Pd-Pd bond determined by curve-fitting analysis.

Fig. 6 (a) Pd K-edge XANES Spectra and (b) the Corresponding Fourier Transforms of \(k^3\)-Weighted EXAFS Spectra for Titania-supported Pd Catalysts Prepared by the Photo-assisted Deposition Method (Na\(_2\)PdCl\(_4\) was used as a metal precursor.)
To provide a comparison, Pd NPs immobilized on Na\(^+\)-TNT were prepared by using different Pd precursors (Na\(_2\)PdCl\(_4\) and H\(_2\)PdCl\(_4\)) or by the wet impregnation method (see the Experimental section). As summarized in Table 2, when H\(_2\)PdCl\(_4\) was used as a Pd precursor in the PAD method, catalytic activity apparently decreased, giving 65% conversion of furfural and 57% yield of furan after 12 h of reaction at 413 K. Figures 7(a) and 7(b) compare TEM images of Pd/Na\(^+\)-TNT catalysts prepared by PAD method using different Pd precursors, showing that the formation of some agglomerated Pd NPs outside the TNT nanotubes. The average size of Pd NPs determined by CO pulse measurement (\(d_{\text{CO}}\)) for the catalyst prepared using H\(_2\)PdCl\(_4\) was 4.4 nm, which was consistent with that determined by TEM observation (\(d_{\text{TEM}}\) = 4.2 nm), and the CN value determined by curve-fitting analysis of Pd K-edge FT-EXAFS spectrum was 9.2. These values were apparently larger than those observed for Pd/Na\(^+\)-TNT prepared using Na\(_2\)PdCl\(_4\) as a Pd precursor (\(d_{\text{CO}}\) = 3.7 nm, \(d_{\text{TEM}}\) = 3.3 nm, CN = 6.0). In addition, Pd/Na\(^+\)-TNT catalysts prepared by wet impregnation method provided significantly decreased catalytic activities, giving 22% and 13% furan yield after 12 h of reaction at 413 K, when Na\(_2\)PdCl\(_4\) and H\(_2\)PdCl\(_4\) were used as Pd precursors, respectively (Table 2). As shown in Figs. 7(c) and 7(d), these catalysts were composed of aggregated Pd particles with a size larger than 10 nm immobilized outside the nanotubes. The average sizes of Pd particles determined by CO pulse measurement (\(d_{\text{CO}}\)) were 6.6 nm and 9.0 nm, which were close to those determined by TEM observation (\(d_{\text{TEM}}\) = 8.2 nm and 10.2 nm), and the CN values were determined to be 11.2 and 11.4, when Na\(_2\)PdCl\(_4\) and H\(_2\)PdCl\(_4\) were used as Pd precursors, respectively. These values were significantly larger compared with those of the Pd/Na\(^+\)-TNT analogues prepared by PAD method. These results clearly demonstrate that PAD method is an effective method to immobilize uniformly-dispersed smaller Pd NPs with high catalytic activity on a titania support, and that the choice of Pd precursor is also an important factor to be considered.

Herein, the correlation between the catalytic activity (TOF) and the average particle size of Pd NPs (\(d_{\text{CO}}\)) of four Pd/Na\(^+\)-TNT catalysts with different mean diameters is depicted in Fig. 8(a), in which TOF was calculated based on the number of surface-exposed Pd atoms determined by CO pulse measurement. As is apparent...
from Fig. 8(a), the catalytic activity tends to increase as the Pd particle size decreases, indicating that decarbonylation of furfural over Pd NP catalysts is a structure-sensitive reaction. To clarify the active site, TOF per a number of specific Pd atoms were calculated, and were plotted against the average Pd NP size (Fig. 8(b))\textsuperscript{20,21}. Given that the present Pd NPs are cuboctahedral in shape with a cubic close packed structure and the model of full-shell NPs is adopted, the total number of Pd atoms contained in the NP ($N_T$) can be calculated from Eq. (1).

$$d_{sph} = 1.105 \cdot d_a N_T^{1/3}$$  \hspace{1cm} (1)

where $d_{sph}$ is the mean diameter of the Pd NPs and $d_a$ is the diameter of Pd atom (0.274 nm). Note that the average NPs diameter determined by CO pulse measurement ($d_{CO}$) was employed as $d_{sph}$ in this study. Based on the value of $N_T$, the number of $m$ is calculated by Eq. (2), and the number of surface-exposed Pd atoms ($N_{Surf}$) is given by Eq. (3).

$$N_T = \frac{10m^3 - 15m^2 + 11m - 3}{3}$$  \hspace{1cm} (2)

$$N_{Surf} = 10m^2 - 20m + 12$$  \hspace{1cm} (3)

Furthermore, the surface sites can be divided into the high-coordinated Pd sites ($N_{HS}$) which are located at the flat surface and low-coordinated Pd sites ($N_{LS}$) which are located at the edges and corners, according to Eqs. (4) and (5), respectively.

$$N_{HS} = 6(m - 2)^2 + 4(m - 3)(m - 2)$$  \hspace{1cm} (4)

$$N_{LS} = 24(m - 2) + 12$$  \hspace{1cm} (5)

If all surface Pd atoms of the Pd NPs act as the same active sites, the TOF values per $N_{Surf}$ are expected to be independent of the Pd particle sizes. However, the TOF values per $N_{Surf}$ decreased as the size of Pd particles increased, suggesting that not all the surface-exposed Pd atoms have an equal catalytic activity towards the decarbonylation of furfural. The TOF values based on $N_{HS}$ also depended on the Pd particle size, while the TOF values calculated based on $N_{LS}$ was almost constant regardless of the particle size. This fact indicates that the low-coordinated Pd site functions as the main active site of this reaction, being in agreement with previous report on Pd clusters consisting of several Pd atoms on ZrO\textsubscript{2} support\textsuperscript{21}. As the Pd particle size becomes smaller, the ratio of edge and corner sites generally increases, thereby leading to an increased catalytic activity.

4. Conclusion

The decarbonylation of furfural to furan was examined using Pd NP catalysts immobilized on various titania supports. Highly-dispersed smaller Pd NPs were formed on titania supports by employing the photo-assisted deposition method compared with those prepared by the conventional impregnation method. In particular, Na\textsuperscript{+}-type titanate nanotube (TNT) with tubular nanostructure and the associated high-surface-area served as an effective support to create highly-active small Pd NPs, which exhibited superior catalytic performance in the liquid-phase decarbonylation of furfural without any additives, compared with the conventional supported Pd catalysts. A clear relationship was observed between reaction rates and the size of Pd NPs, and further detailed analysis suggested that zero-valent small Pd\textsuperscript{0} NPs possessing an increased fraction of coordinatively-unsaturated Pd atoms locating at the edge/corner sites are the highly-active species for this reaction. Although further detailed assessments on the stability of metal NPs and the reusability of catalyst are needed, this study provides an effective synthetic method to create highly-active small metal NPs stabilized on titania support, which may facilitate further progress and expand applications of metal NP catalysts in related research fields.

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要 旨

光触媒的なチタニア担持Pdナノ粒子を用いたフルフラール脱カルボニル化によるフラン合成

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バイオマスからフルフラールの脱カルボニル化反応が見られるが、高分子を担持する方法として利用できるため、本反応はバイオマス資源有限利用へ向けた重要な反応の一つである。これまで、Pdナノ粒子触媒が本反応に有効であることが示されているが、高圧高圧の厳しい反応条件が必要とされていた。本研究では、チタニアの光応答性を利用した光触媒法（PAD法）によりチタニア担持Pdナノ粒子触媒を調製した。透析型電子親和性レシオX線吸収微細構造測定により、PAD法を用いることで従来の合成法に比べより微細なPdナノ粒子をチタニア担体上に高分散担持できることが分かった。特に、チューーブ構造と高表面積を有するNa”型酸化チタンナノチーブ（TNT）を担体に用いた場合に高活性なPdナノ粒子が得られ、液相でのフルフラールの脱カルボニル化反応において、従来法で調製したPdナノ粒子触媒に比べて高い触媒性能を示した。触媒活性と担体上に固定化されたPdナノ粒子の粒径との関係を明らかにしたが、幾何学的考察から、Pdナノ粒子のエッジやコーナーサイトに位置する配位不飽和なPd種が本反応の活性点であると推察された。