

Article

Effect of Oxide Supports on the Activity of Pd Based Catalysts for Furfural Hydrogenation

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Abstract: We investigated the effect of oxide supports on the hydrogenation of furfural over Pd catalysts on various supports (Al_2O_3 , SiO_2 , TiO_2 , CeO_2 , and ZrO_2). Pd catalysts (5 wt%) prepared by chemical reduction on various supports. The dispersion and uniformity of Pd were affected by the properties of the support and by the nucleation and growth of Pd. The conversion of furfural was enhanced by greater Pd dispersion. The selectivity for cyclopentanone and tetrahydrofurfuryl alcohol was affected by physicochemical properties of Pd catalyst and reaction parameters. High Pd dispersion and high acidity of the catalyst led to greater C=C hydrogenation, thereby, generating more tetrahydrofurfuryl alcohol. The Pd/ TiO_2 catalyst showed the highest cyclopentanone yield than other catalysts. The Pd/ TiO_2 catalyst exhibited the >99% furfural conversion, 55.6% cyclopentanone selectivity, and 55.5% cyclopentanone yield under the optimal conditions; 20 bar of H_2 , at 170 °C for 4 h with 0.1 g of catalyst.

Keywords: furfural; cyclopentanone; hydrogenation; Pd nanoparticles; metal dispersion

1. Introduction

Lignocellulosic biomass is considered a potential source of renewable energy for mitigating the energy crisis created by the depletion of crude oil. In recent decades, furfural formed from biomass-derived resources has been used as a raw material to produce highly valuable materials, such as tetrahydrofurfuryl alcohol (THFAL), furfuryl alcohol (FAL), and cyclopentanone (CPO) [1–4].

CPO is regarded as an important fine chemical intermediate material for the synthesis of medicine, perfume, and rubber chemicals. CPO is produced by the rearrangement of FAL. Many researchers have investigated the hydrogenation of furfural to CPO, which is generally performed over Co/ ZrO_2 - La_2O_3 , CuZnAl, Cu/CNT, Pd/C, and Ru/C catalysts; the reaction pathways are shown in Figure 1 [5–8]. Attempts have been made to use non-noble-metal-supported catalysts for furfural hydrogenation. However, non-noble metals carry disadvantages, such as leaching and deactivation, and noble metal catalysts remain as mainstay catalysts. Certain factors affect the activity and selectivity of a catalyst, such as the metal dispersion, acid/base properties, surface chemical state, and metal-support interaction. These factors are mainly influenced by the support properties, which affect the catalyst activity and selectivity.

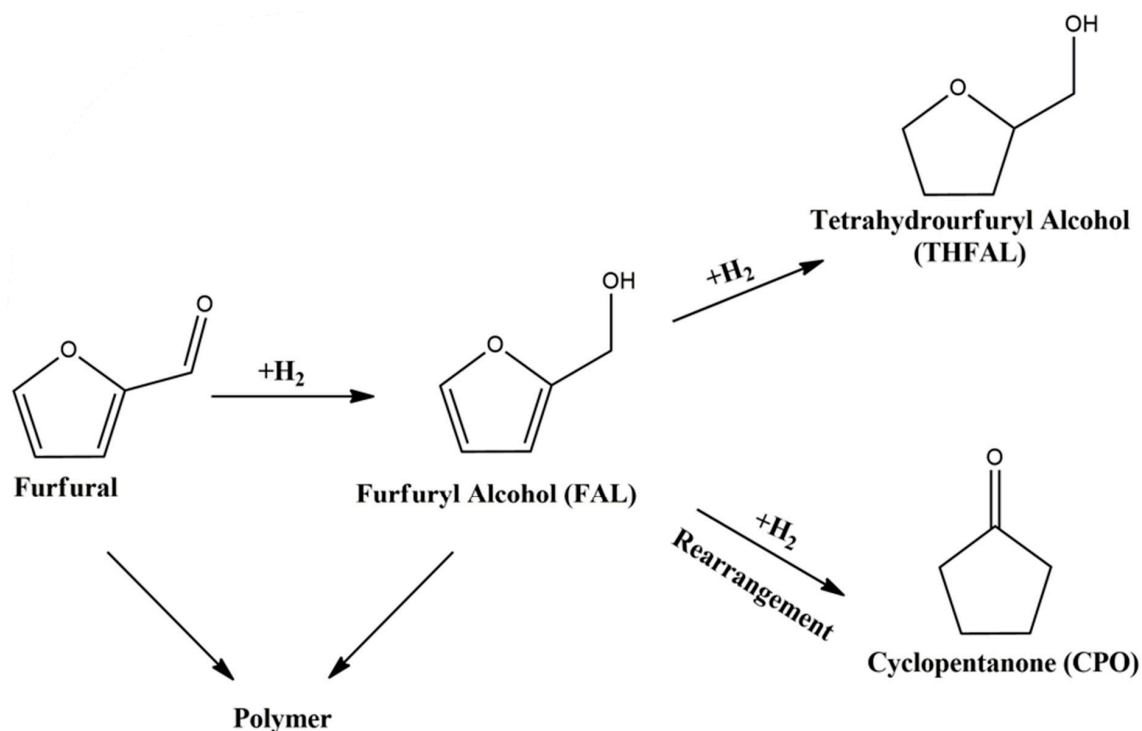


Figure 1. Reaction pathways in liquid phase hydrogenation of furfural.

Recently, metals supported catalysts have been investigated in furfural hydrogenation. Albiilali et al. prepared Pd supported various supports (TiO_2 , Al_2O_3 , MgO , Carbon, and Fe_2O_3) for selective hydrogenation of furfural to THFAL [9]. The Pd/ TiO_2 catalyst provided the highest yield of THFAL. Li et al. reported that hydroxyapatite-bound Pd (HAP) catalysts exhibited 100% furfural conversion and 100% THFAL yield [10]. The physicochemical properties of support affected to metal dispersion and electron density which improved the catalytic activity. Bhogeswararao et al. investigated Pd and Pt supported catalyst for selective hydrogenation of furfural to FAL or THFAL [11]. The products selectivity changed with hydrogenolysis and ring opening depending on the support acidity.

Only a few studies, however, have reported the effects of oxide supports on the catalytic performance of Pd catalysts for furfural hydrogenation. Most of the previous researches, furfural hydrogenation was performed on a relatively small scale. Herein, we prepare Pd supported on different oxide supports (Al_2O_3 , SiO_2 , TiO_2 , CeO_2 , and ZrO_2) by a chemical reduction method for the catalytic hydrogenation of furfural to produce CPO. We performed relatively large scale of furfural hydrogenation. The results confirm that the Pd dispersion affects the conversion of furfural. Furthermore, the physicochemical properties of the Pd catalysts affect the selectivity of the resulting product distribution.

2. Results and Discussion

2.1. Characterization of Supports and Pd Catalysts

Table 1 summarizes the physical properties of the supports and Pd catalysts. The Al_2O_3 and SiO_2 supports showed relatively high specific surface areas of 135 and 170 m^2/g and pore volumes of 0.73 and 0.33 cm^3/g , respectively. The specific surface areas changed after deposition of Pd onto the supports. Especially, the specific surface areas of the Pd/ Al_2O_3 and Pd/ CeO_2 catalysts increased from 135 to 150 m^2/g and 69 to 73 m^2/g , respectively. In contrast, that of the Pd/ SiO_2 and Pd/ TiO_2 catalyst decreased from 179 to 161 m^2/g , and 51 to 43 m^2/g . However, the Pd/ ZrO_2 catalysts did not change significantly. These results suggested that the Pd particle size affected the specific surface area. Smaller

Pd particles were well-dispersed on the catalysts supports, thereby, increasing the specific surface area. A decreased specific surface area was caused by large Pd particles blocking the support pores. After the Pd loading, the Pd/SiO₂ and Pd/TiO₂ catalysts showed relatively large pore volume and pore diameter than other catalysts. During the preparation of catalysts, precipitating agent of NaOH may be fills small pore of support. We suggested that support pores filled with NaOH was collapsed into small pore structure, resulting in the produce of large pores.

Table 1. Physicochemical properties of supports and Pd catalysts.

Samples	S_{BET} (m ² /g)	V_{Total} (cm ³ /g)	Pore Diameter (nm)	Acid Site Density (mmol/g) ^a		
				Weak	Medium and Strong	Total
Al ₂ O ₃	135	0.73	20.3	-	-	-
SiO ₂	170	0.33	11.2	-	-	-
TiO ₂	51	0.15	12.5	-	-	-
CeO ₂	69	0.16	8.4	-	-	-
ZrO ₂	35	0.19	21.8	-	-	-
Pd/Al ₂ O ₃	150	0.75	19.2	0.278	0.435	0.713
Pd/SiO ₂	161	0.84	25.7	0.134	0.149	0.283
Pd/TiO ₂	43	0.34	29.2	0.150	0.131	0.281
Pd/CeO ₂	73	0.20	10.1	0.337	0.252	0.589
Pd/ZrO ₂	34	0.22	24.4	0.163	0.164	0.327

^a measured by NH₃-TPD.

Figure 2 shows the nitrogen adsorption-desorption isotherms and pore size distributions of the supports and Pd catalysts. The Al₂O₃, SiO₂, TiO₂, and ZrO₂ supports showed type IV isotherms with H1 hysteresis loops, which indicate mesoporous materials and cylindrical pores. The CeO₂ support showed a type IV isotherm with an H3 hysteresis loop, which represents a mesoporous materials and slit-shaped pores [12]. All the supported Pd catalyst nitrogen adsorption-desorption isotherms exhibited results similar to the catalyst supports. The Pd/Al₂O₃ and Pd/SiO₂ catalysts had relatively larger pore volumes than the other catalysts.

The XRD patterns of the prepared supports and Pd catalysts are shown in Figure 3. As shown in Figure 3a, TiO₂ exhibited a mix of anatase (JCPDS 71-1166) and rutile phases (JCPDS 73-1763). The Al₂O₃, SiO₂, CeO₂, and ZrO₂ supports exhibited γ -Al₂O₃ (JCPDS 29-0063), amorphous silica, cubic fluorite CeO₂ (JCPDS 34-0394), and monoclinic ZrO₂ (JCPDS 37-1484) phases, respectively. As shown in Figure 3b, all the prepared Pd catalysts showed characteristic Pd peaks at $2\theta = 40.2^\circ$, 46.6° , and 67.6° , which correspond to the (111), (200), and (220) planes of the face-centered cubic crystal structure, respectively. The main Pd peak of the Pd/Al₂O₃ catalyst overlapped with the Al₂O₃ phase at $2\theta = 40.2^\circ$. The Pd/SiO₂ catalyst exhibited the largest Pd peaks, whereas the Pd/CeO₂ catalyst exhibited the smallest. The intensities of the Pd peaks differed depending on the support, which is related to two causes: Crystalline sizes of Pd and Pd nanoparticles or Pd ions incorporated into the crystal lattices of the supports. Small Pd peak intensities in Pd catalysts indicated that small Pd particles were homogeneously dispersed on the support.

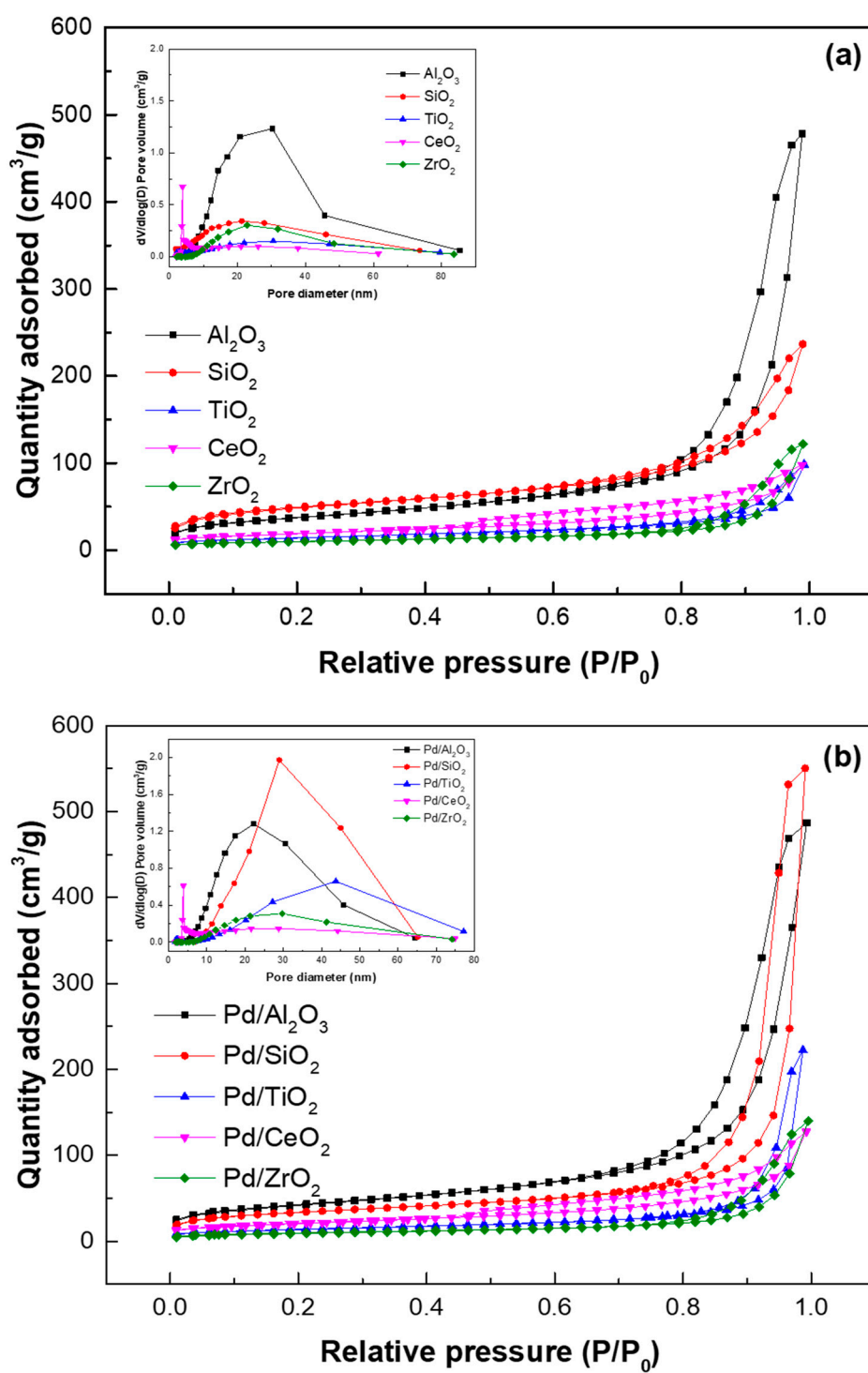


Figure 2. N_2 adsorption-desorption isotherms and pore size distributions (insets) of (a) supports and (b) supported Pd catalysts.

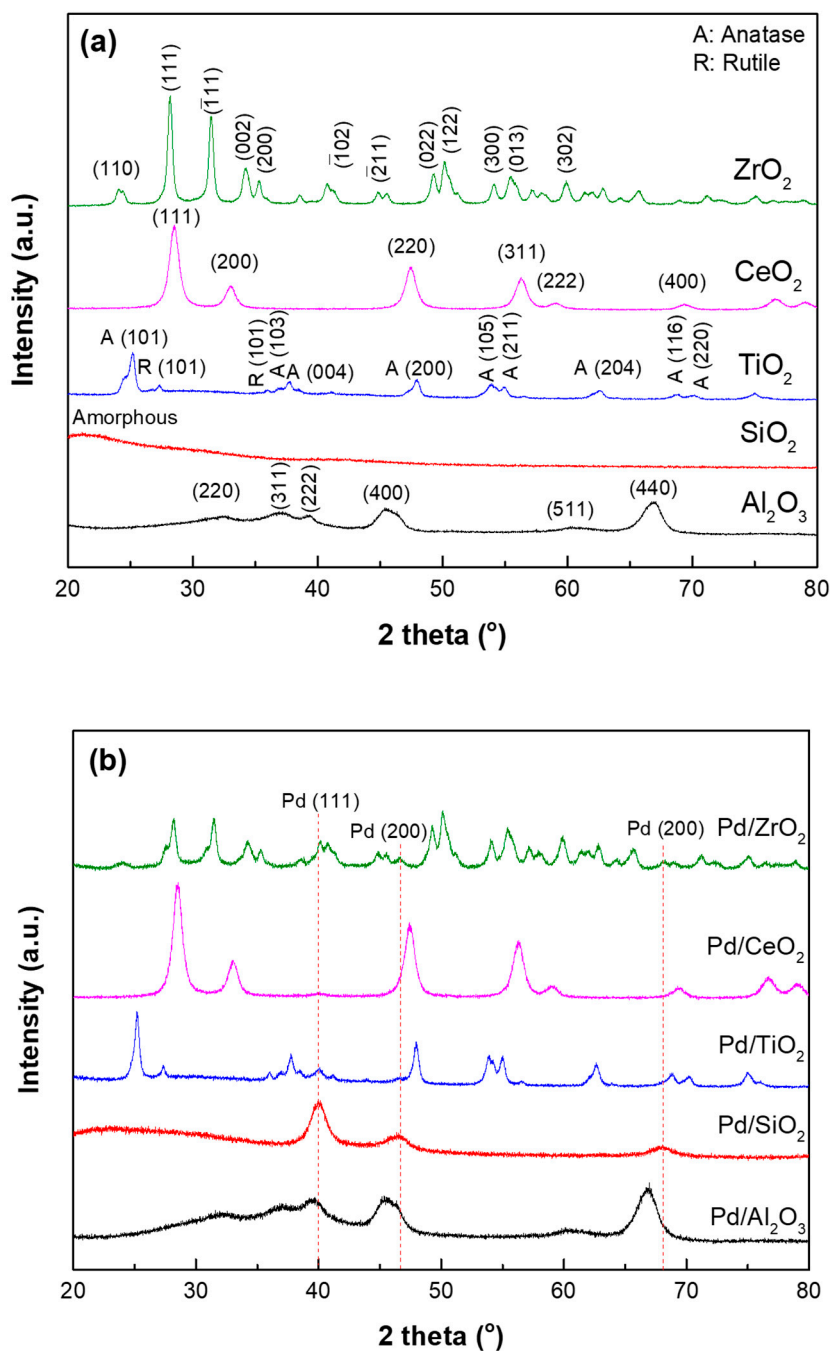


Figure 3. XRD patterns of (a) supports and (b) supported Pd catalysts.

To verify the reduction properties of the Pd catalysts, H₂-TPR analysis was performed, and the results are shown in Figure 4. All the prepared Pd catalysts showed negative peaks in the range of 60 to 90 °C, which is related to formation of PdH_x before the analysis began [13–15]. Each Pd catalyst showed a different intensity of this negative PdH_x peak in the 60 to 90 °C range, where the intensity was the smallest for Pd/CeO₂ and the largest for Pd/SiO₂. The results indicated that larger Pd particles lead to a greater formation of PdH_x. The Pd/CeO₂ and Pd/SiO₂ samples exhibited positive peak regions at approximately 300 and 700 °C, and 750 °C, respectively. These positive peaks indicated that bulk PdO_x species were reduced to Pd⁰ or hydrogen spillover [15,16].

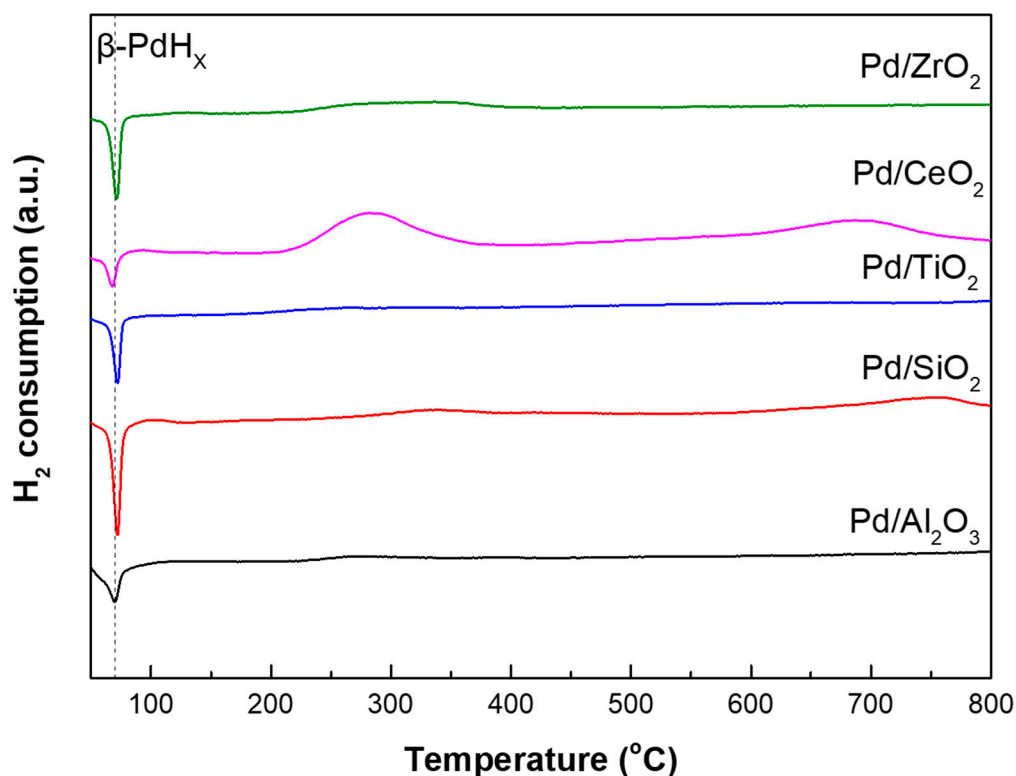


Figure 4. H₂-TPR profiles of Pd catalysts.

The acid properties of the Pd catalysts were analyzed by NH₃-TPD, as shown in Table 1, Figure 5. The Pd catalysts showed two desorption peak around 100–250 °C and 250–600 °C, corresponding to weakly acid sites and medium and strong acid sites, respectively. The order of decreasing total acidity of Pd catalyst was Pd/Al₂O₃ > Pd/CeO₂ > Pd/ZrO₂ > Pd/SiO₂ > Pd/TiO₂. The Pd/Al₂O₃ catalyst showed the higher acidity than other catalysts.

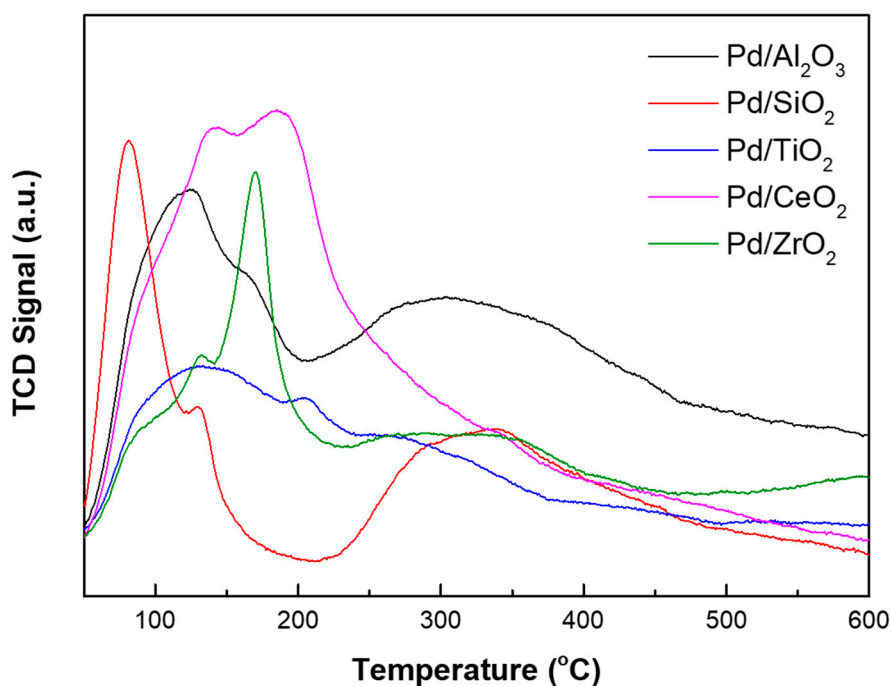


Figure 5. NH₃-TPD profiles of Pd catalysts.

The XPS (X-ray photoelectron spectroscopy) spectra of the Pd catalysts in the Pd 3d region are shown in Figure 6. All the Pd catalysts showed both metallic Pd and Pd²⁺ species. The Pd 3d_{5/2} binding energy at 335.2 eV and 336.0 eV, which is corresponding to metallic Pd and Pd²⁺ [17,18]. In the case of Pd/CeO₂ catalysts, the Pd 3d_{5/2} peak positions observed positive shifts in binding energy, which is could be ascribed to the strong metal-support interaction. In the case of Pd/TiO₂ and Pd/ZrO₂ catalysts, the Pd 3d_{5/2} peak positions observed negative shifts in binding energy, which is could be ascribed to high ratio of metallic Pd [19]. The surface atomic ratio of Pd catalysts are summerized in Table 2. The atomic ratio of Pd/support decreased as following orders; Pd/CeO₂ > Pd/Al₂O₃ > Pd/TiO₂ > Pd/ZrO₂ > Pd/SiO₂. The surface atomic ratio of Pd on Pd/CeO₂ catalyst is at least 2 times higher than Pd/Al₂O₃, suggesting that the Pd nanoparticles are well dispersed on CeO₂ surface.

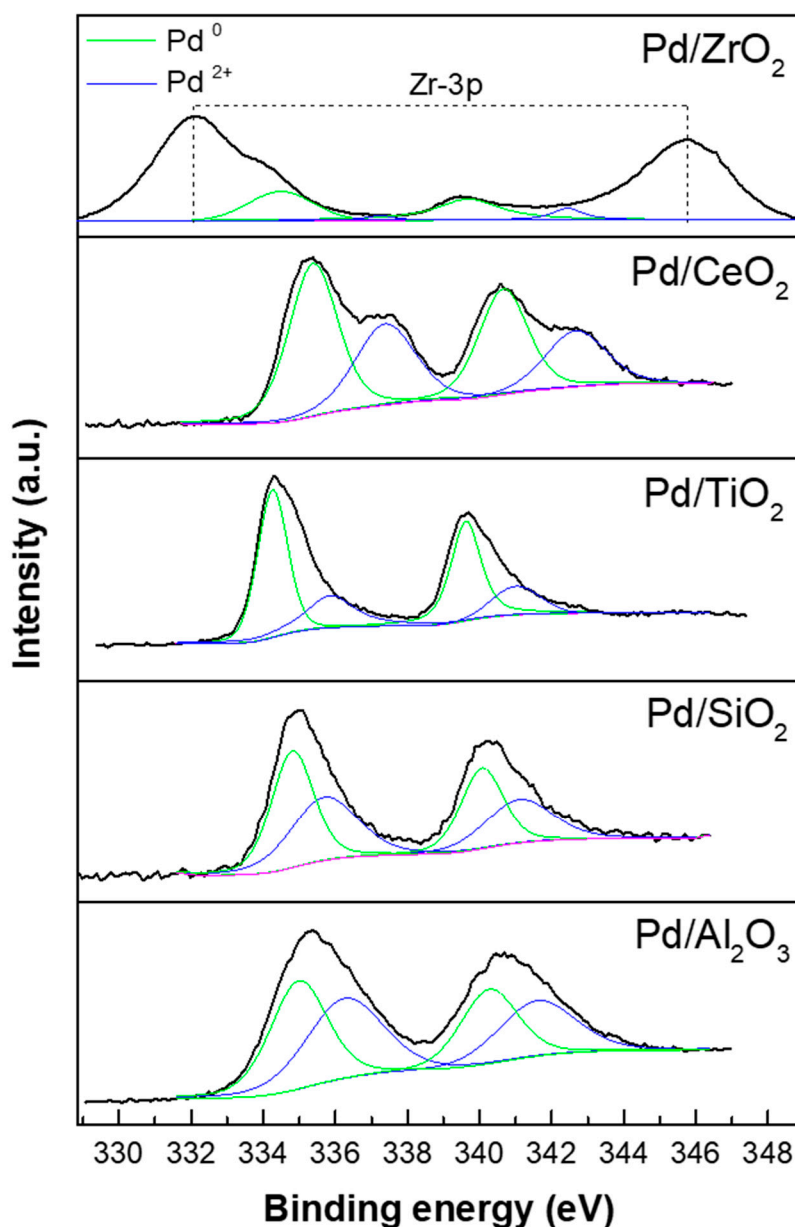


Figure 6. XPS spectra of Pd catalysts.

Table 2. Characterization of Pd catalysts.

Catalysts	Pt Contents ^a	Metal Dispersion (%)		Metallic Surface Area (m ² /g) ^c	Binding Energy of Pd 3d _{5/2} (eV) ^d		Atomic Ratios ^d
		CO Chemisorption	FE-TEM ^b		Pd ²⁺	Pd ⁰	
Pd/Al ₂ O ₃	4.9	26	38	115.2	336.2	334.9	0.09
Pd/SiO ₂	4.8	5	12	38.8	335.7	334.8	0.01
Pd/TiO ₂	4.9	10	25	45.5	335.9	334.2	0.05
Pd/CeO ₂	4.9	32	42	142.1	337.3	335.3	0.26
Pd/ZrO ₂	5.0	8	21	35.8	337.2	334.4	0.03

Note: ^a Measured by ICP-OES. ^b Estimated assuming clean spherical average particle size. ^c Measured by CO chemisorption. ^d Measured by XPS.

Figure 7 shows the FE-SEM (Field mission scanning Electron Microscope) images and EDX (energy dispersive X-Ray spectroscopy) spectra of the Pd catalysts; the EDX spectra confirmed their Pd distributions. It appeared that the distribution of Pd particles differed depending on the support. The Pd/Al₂O₃, Pd/TiO₂, and Pd/CeO₂ catalysts showed uniform distributions, whereas the Pd/SiO₂ and Pd/ZrO₂ catalysts showed non-uniform distributions. Figure 8 shows the FE-TEM images and particle size distributions of the Pd catalysts. The Pd/CeO₂ and Pd/Al₂O₃ catalysts exhibited well-dispersed Pd on the support and narrower particle size distributions than the other catalysts. The Pd/SiO₂ and Pd/ZrO₂ catalysts exhibited poorly dispersed Pd on the support and aggregation of Pd particles. Average particle sizes were estimated over 200 spherical Pd particles. The order of increasing Pd particle size was Pd/CeO₂ (2.7 nm) < Pd/Al₂O₃ (2.9 nm) < Pd/TiO₂ (4.3 nm) < Pd/ZrO₂ (5.2 nm) < Pd/SiO₂ (9.2 nm).

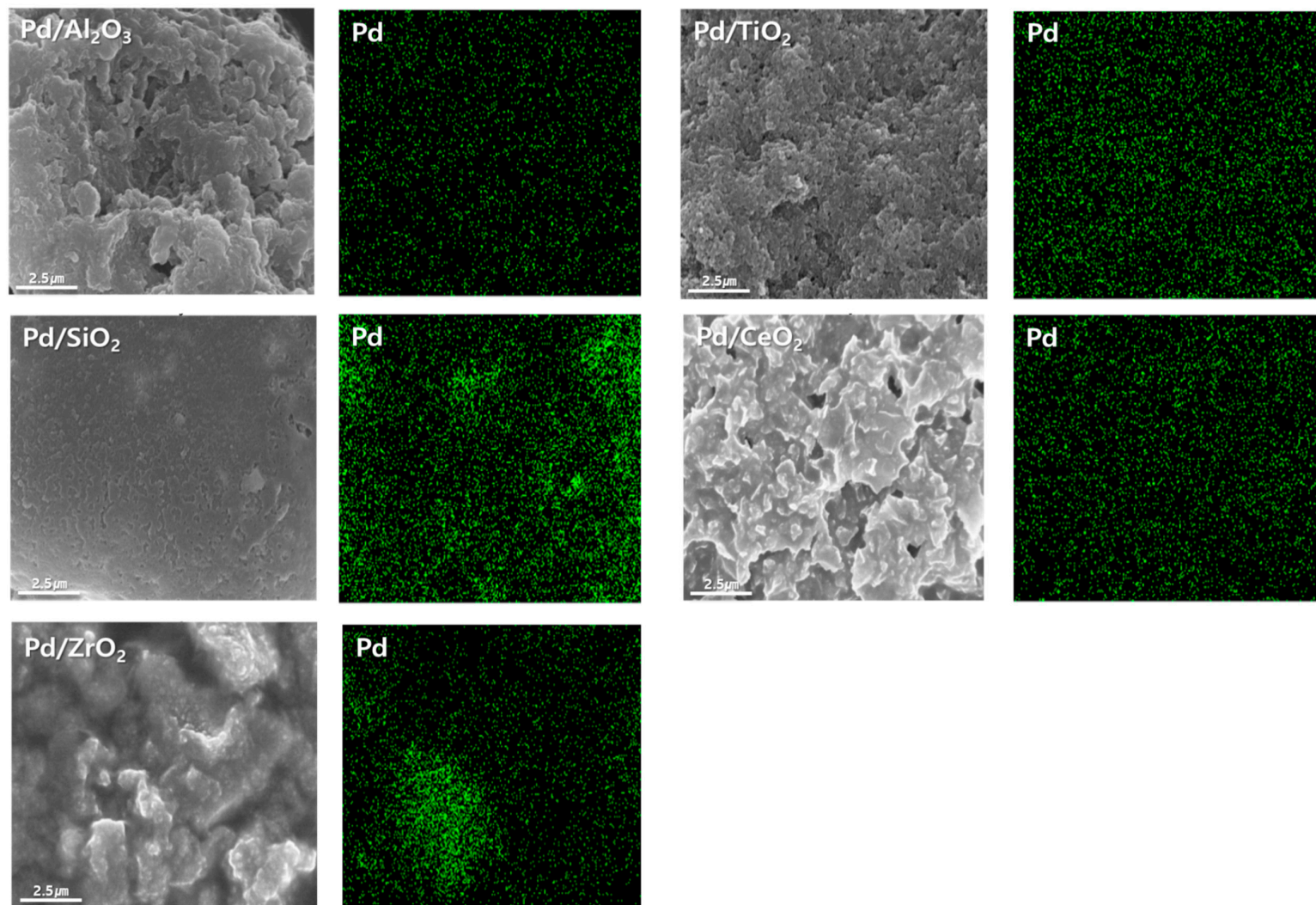


Figure 7. FE-SEM images and EDX spectra of Pd catalysts.

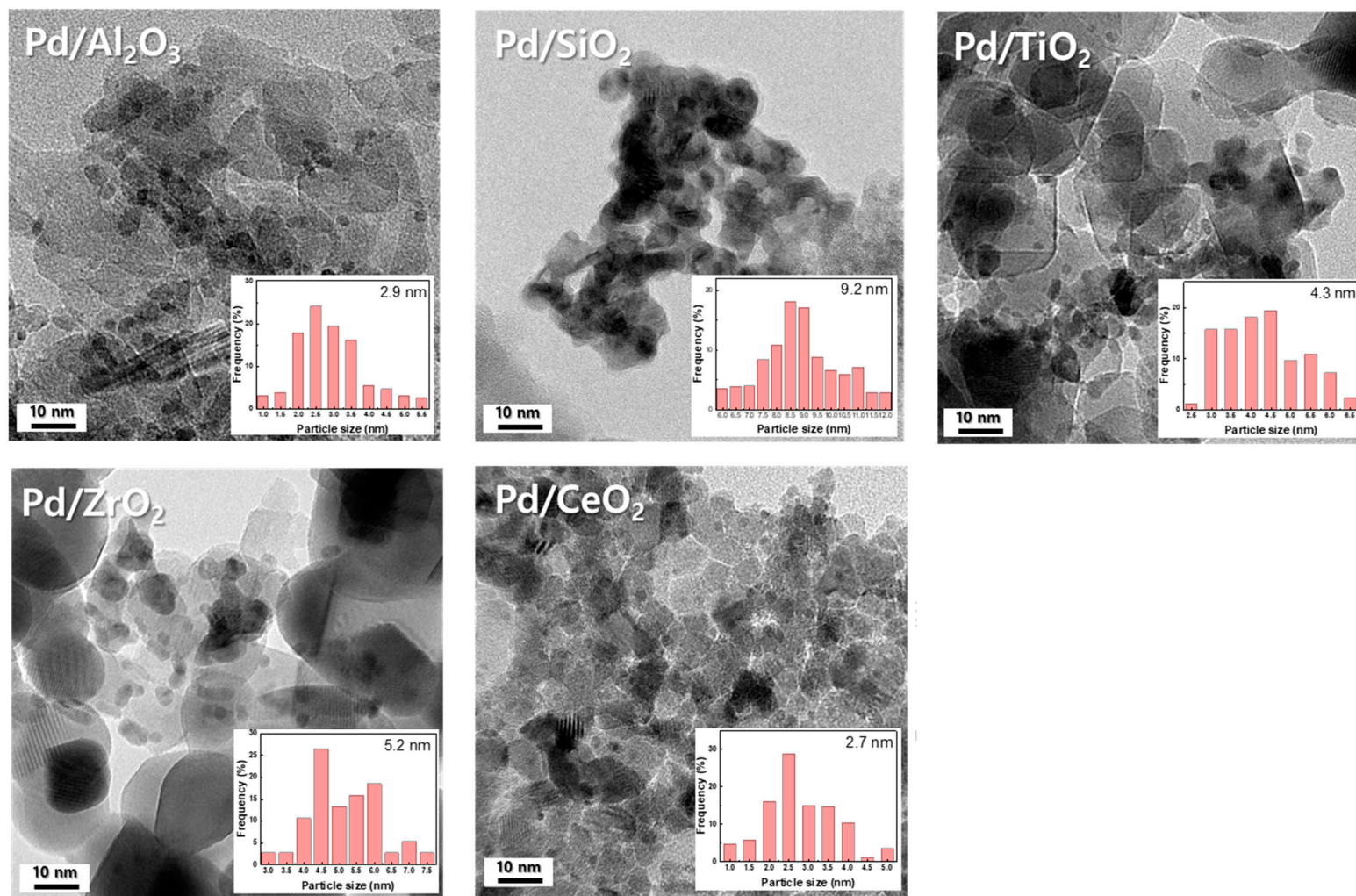


Figure 8. FE-TEM images and particle size distributions of Pd catalysts.

To estimate the catalyst Pd dispersions, CO chemisorption analysis was performed, and the results are summarized in Table 2. The Pd/CeO₂ catalyst had the highest Pd dispersion of 32%, whereas the Pd/SiO₂ catalyst had the lowest Pd dispersion of 5%. We also estimated Pd dispersion based on the FE-TEM images, which indicated much higher Pd dispersion values than the CO chemisorption analysis. These results suggested that some Pd particles were covered by the support. However, both CO chemisorption and FE-TEM analyses yielded the same order of Pd dispersion: Pd/CeO₂ > Pd/Al₂O₃ > Pd/TiO₂ > Pd/ZrO₂ > Pd/SiO₂. These results are in agreement with other analyses. We considered that Pd dispersion was affected by several factors, such as isoelectric point, nucleation and growth of Pd, ionic strength between Pd and support, etc. [20–24]. In particular, we focused on pH and support isoelectric point. Many researchers have reported that metal dispersion is affected by support properties and synthetic parameters such as pH values and solution temperature. Generally, Al₂O₃, CeO₂, TiO₂, and ZrO₂ show higher isoelectric points of 5 to 7 than that of SiO₂ (−2) [21,25–27]. During Pd catalyst synthesis, the H₂PdCl₄ precursor existed predominantly as PdCl₄^{2−} (at pH 2), and thus, the interactions between Pd ions and the SiO₂ support did not easily occur. The Pd dispersions differed because the nucleation and growth of Pd nanoparticles differed depending on the synthesis pH and support type. The Pd/CeO₂ catalyst had the highest dispersion and most uniform Pd distribution with a solution temperature of 0 °C and pH of 7.0.

2.2. Hydrogenation of Furfural

The effect of Pd dispersion and support properties on catalytic activity and selectivity of Pd catalysts were investigated with respect to the liquid-phase hydrogenation of furfural the results are summarized in Table 3. The reactions were performed 20 bar of H₂ at 150 °C for 1 h with 0.03 g of catalyst. The conversion of furfural decreased with decreasing Pd dispersion in the order: Pd/CeO₂ > Pd/Al₂O₃ > Pd/TiO₂ > Pd/ZrO₂ > Pd/SiO₂. FAL and CPO were the main products, generated via the hydrogenation of furfural or the rearrangement of furfural. The Pd/SiO₂, Pd/TiO₂, and Pd/ZrO₂ catalysts showed higher selectivity for CPO than the Pd/Al₂O₃ and Pd/CeO₂ catalysts. The Pd/TiO₂ catalyst exhibited highest CPO yield as 12.7%.

Table 3. Hydrogenation of furfural over Pd catalysts ^a.

Catalysts	Catalyst Amount (g)	Temp. (°C)	Hydrogen Pressure (bar)	Time (h)	Conversion (%)	Selectivity (%)					Yield of CPO (%)
						FAL	2-MF	THFAL	CPO	NI ^b	
Pd/Al ₂ O ₃	0.03	150	20	1	56.1	15.6	-	3.1	13.9	67.4	7.8
	0.1	100	20	4	98.4	15.9	-	17.1	-	67	-
	0.1	130	20	4	98.9	-	-	13.7	16.9	69.4	16.7
	0.1	150	20	4	99.2	-	-	10.3	23.7	66	23.5
	0.1	170	20	4	>99	-	2.8	6.0	38.4	52.8	38.4
	0.1	190	20	4	>99	-	2.9	5.6	42.8	48.7	42.8
	0.1	170	10	4	98.7	-	2.7	1.7	34.1	61.5	33.7
	0.1	170	30	4	>99	-	3.0	0.9	42.5	53.6	42.5
Pd/SiO ₂	0.03	150	20	1	19.7	27.4	-	5.1	32.3	35.2	6.4
	0.1	150	20	4	77	-	-	1.7	43.4	54.9	33.4
Pd/TiO ₂	0.03	150	20	1	44.6	14.2	-	4.9	28.5	52.4	12.7
	0.1	100	20	4	97.7	18.2	-	8.9	0.001	72.9	0.0009
	0.1	130	20	4	98	-	-	7.8	41.0	51.2	40.2
	0.1	150	20	4	98.5	-	-	3.7	45.9	50.4	45.2
	0.1	170	20	4	>99	-	3.6	3.9	55.6	36.9	55.5
	0.1	190	20	4	>99	-	4.3	3.7	59.1	32.9	59.0
	0.1	170	10	4	91.2	-	3.1	0.2	36.4	60.3	33.2
	0.1	170	30	4	100	-	3.7	15.3	45.3	35.7	45.3
Pd/CeO ₂	0.03	150	20	1	70.9	34.3	-	4.0	6.1	55.6	4.3
	0.1	150	20	4	>99	9.4	-	23.3	25.9	41.4	25.9
Pd/ZrO ₂	0.03	150	20	1	27.6	31.1	-	6.5	28.2	34.2	7.8
	0.1	150	20	4	88	-	-	3.8	46.3	49.9	40.7

Note: ^a Reaction conditions: furfural (2.5 g), distilled water (100 mL), stirring rate (500 rpm). ^b Non-identified products.

Figure 9 shows conversion and product distribution in furfural hydrogenation over Pd based catalysts under the following conditions: 20 bar of H_2 at 150 °C for 4 h with 0.1 g of catalyst. Under these conditions, CPO and THFAL were the main products, generated via the rearrangement of furfural or the hydrogenation of FAL. The conversion of furfural decreased with decreasing Pd dispersion in the order: $Pd/CeO_2 > Pd/Al_2O_3 > Pd/TiO_2 > Pd/ZrO_2 > Pd/SiO_2$. The Pd/SiO_2 , Pd/TiO_2 , and Pd/ZrO_2 catalysts showed greater selectivity for CPO than the Pd/Al_2O_3 and Pd/CeO_2 catalysts. The Pd/Al_2O_3 and Pd/CeO_2 catalysts exhibited greater selectivity for THFAL than the other catalysts. Furfural is converted to FAL, which can be further polymerized to oligomers by heat or strong acid sites [28,29]. Based on NH_3 -TPD analysis, the Pd/Al_2O_3 catalyst was more acidic than the other catalysts. The acidity was comparable for the other catalysts. Therefore, the Pd/TiO_2 , Pd/SiO_2 , and Pd/ZrO_2 catalysts exhibited higher selectivity for CPO. However, the Pd/CeO_2 catalyst exhibit low selectivity for CPO and high selectivity for THFAL, despite the low acidity. THFAL can be produced by over-hydrogenation of FAL. The higher Pd dispersion in the Pd/Al_2O_3 and Pd/CeO_2 catalysts led to high selectivity for THFAL. Non-identified materials may be produced by polymerization reaction [6,7]. The Pd/TiO_2 catalyst exhibited highest CPO yield as 45.2%. The Pd/TiO_2 catalyst was the most effective for furfural hydrogenation to CPO at 150 °C. Among the Pd-supported catalysts, the Pd/Al_2O_3 and Pd/TiO_2 catalysts were selected for further evaluation of the effect of the reaction temperature and hydrogen pressure.

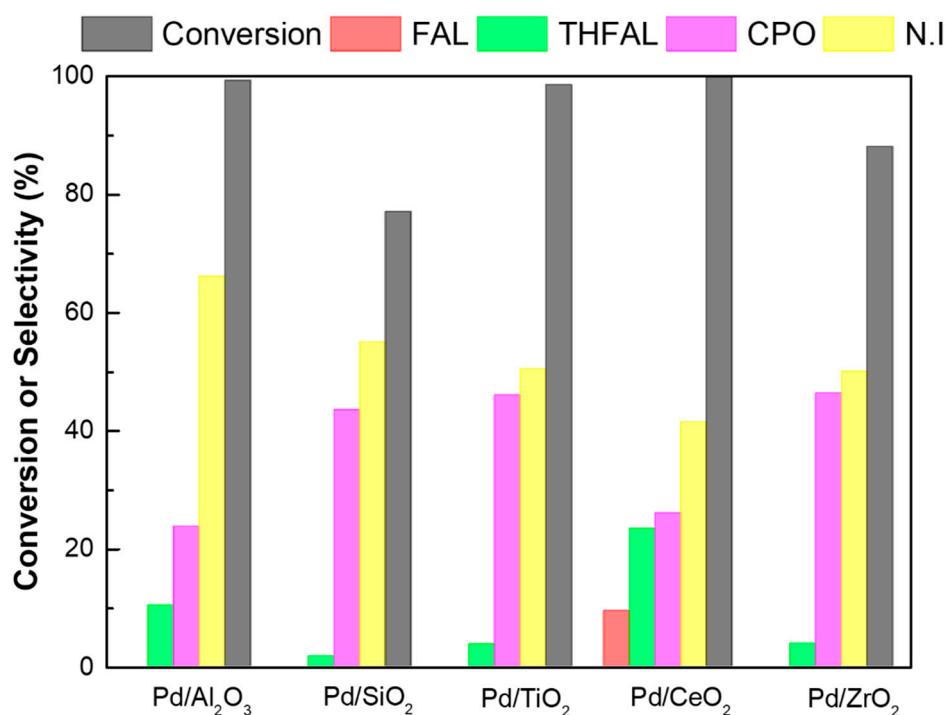


Figure 9. Conversion and product distribution in furfural hydrogenation over Pd based catalysts. Reaction conditions: furfural (2.5 g), distilled water (100 mL), catalyst (0.1 g), H_2 pressure (20 bar), reaction temperature (150 °C), reaction time (4 h), and stirring rate (500 rpm).

The effect of the reaction temperature (100–190 °C) on furfural hydrogenation over the Pd/Al_2O_3 and Pd/TiO_2 catalysts was investigated under 20 bar of H_2 over the course of 4 h. FAL was generated with the use of the Pd/Al_2O_3 and Pd/TiO_2 catalysts at 100 °C. However, the selectivity for THFAL was higher with the Pd/Al_2O_3 catalyst having a high Pd dispersion, due to over-hydrogenation of FAL. The furfural conversion and CPO selectivity of the Pd/Al_2O_3 and Pd/TiO_2 catalysts gradually increased as the reaction temperature was increased from 100 to 190 °C, whereas the selectivity for THFAL gradually decreased from 13.7% to 5% with the Pd/Al_2O_3 catalyst. In contrast, the THFAL

selectivity remained unchanged for the Pd/TiO₂ catalyst. Via hydrogenolysis over the metal sites, 2-MF was produced at a high temperature [30]. Therefore, an optimum reaction temperature of 170 °C was selected for further study.

The effect of the H₂ pressure (10–30 bar) on furfural hydrogenation over the Pd/Al₂O₃ and Pd/TiO₂ catalysts at 170 °C for a reaction time of 4 h was investigated. When the H₂ pressure was increased from 10 to 20 bar, the furfural conversion, CPO selectivity and CPO yield increased with the Pd/Al₂O₃ and Pd/TiO₂ catalysts. In the H₂ pressure range of 20–30 bar, the CPO selectivity increased slightly with the use of the Pd/Al₂O₃ catalyst. However, the CPO selectivity decreased, whereas the THFAL selectivity increased, with the Pd/TiO₂ catalyst, due to differences in the adsorption strength. The Pd/Al₂O₃ catalyst was more prone to rearrangement under high H₂ pressure than the Pd/TiO₂ catalyst. Hronec et al. reported that the selectivity for THFAL and CPO was affected by the hydrogen pressure and metal catalyst in the hydrogenation of FAL [1]. When Pd exposed to H₂ gas, α-PdH_x (x < 0.03) is formed. Increasing the H₂ pressure, Pd absorbed a large amount of H₂ with formation of β-PdH_x (x > 0.03) [31]. Increasing the H₂ pressure and metal concentration led to increased H₂ dissolution. The more H₂ dissolution in mixture can be more active and stabilized on the Pd catalyst surface, which is attributed to more formation of THFAL or CPO products.

The Pd/Al₂O₃ and Pd/TiO₂ catalysts showed similar results in that the CPO selectivity decreased or changed slightly. Nandan et al. reported that the Lewis acid sites of PdO affect the rearrangement of FAL to CPO [32]. Based on the XPS results, the Pd²⁺/Pd ratio of the Pd/TiO₂ catalyst was lower than that of the Pd/Al₂O₃ catalyst. We suggest that a larger amount of metallic Pd species on the catalyst surface leads to greater hydrogenation of the C=C bonds. Therefore, the Pd/TiO₂ catalyst showed higher selectivity for THFAL than the Pd/Al₂O₃ catalyst under high H₂ pressure. The Pd/TiO₂ catalyst produced the highest furfural conversion and CPO selectivity at 170 °C under 20 bar of H₂.

The effect of the reaction time (1–5 h) on furfural hydrogenation over the Pd/TiO₂ catalyst was investigated under 20 bar of H₂ at 170 °C, as shown in Figure 10. As the reaction time increased from 1 to 5 h, the furfural conversion increased from 85.7 to 100%. The CPO selectivity gradually increased from 40 to 55.6% when the reaction time was increased from 1 to 4 h. The CPO selectivity remained unchanged when the reaction was extended to 5 h. The selectivity for THFAL and 2-MF increased slightly with increasing reaction time. Under the optimal conditions of 20 bar of H₂ at 170 °C for 4 h, 100% furfural conversion, 55.9% CPO selectivity, and 56.6% CPO Yield were achieved with the Pd/TiO₂ catalyst.

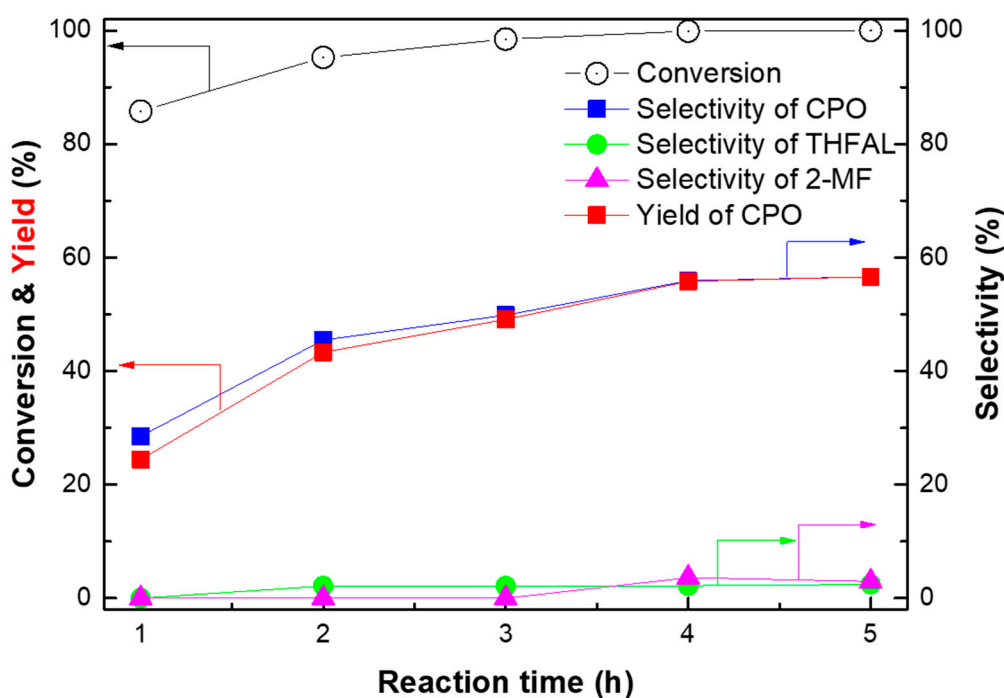


Figure 10. Effect of reaction time on furfural conversion, products selectivity and CPO yield in Pd/TiO₂ catalyst.

3. Experimental

3.1. Preparation of Pd Catalysts

Al₂O₃ (Aladin, γ phase), SiO₂ (Degussa, Aerosil 200), TiO₂ (Degussa, P25), CeO₂ (Alfa-Aesar, nanopowder), and ZrO₂ (Sigma-Aldrich, nanopowder) were used as catalyst supports. The supported Pd catalysts, containing 5 wt% Pd, were prepared by chemical reduction method. An H₂PdCl₄ precursor was prepared by dissolving PdCl₂ (Sigma-Aldrich, 90%) in a 38% HCl solution. An aqueous solution containing 0.225 mmol of sodium tartrate dibasic dehydrate (Sigma-Aldrich, 99.0%) as a stabilizer was brought to 0 °C, and then the H₂PdCl₄ precursor was added to the solution. The support was added to the mixture and stirred with a high shear mixer. The Pd precursor solution containing the support was adjusted to a pH of 7.0 by adding 0.02 M NaOH (Sigma-Aldrich, 97.0%). The mixture was then stirred for 2 h at 0 °C. Reduction of the catalyst was carried out in the liquid phase using a 100 mL of 0.3 M sodium borohydride (Sigma-Aldrich, 99.0%) solution for 2 h at 0 °C. The suspension was then filtered and washed with distilled water. All catalysts were dried at 85 °C for 24 h.

3.2. Characterization of Supports and Pd Catalysts

The crystal structures of the supports and supported Pd catalysts were analyzed by x-ray diffraction (XRD) (D8 Focus, Bruker, Germany) at 50 kV and 50 mA using a Cu K α radiation source ($\lambda = 1.5406$ Å). Specific surface areas and pore sizes/volumes were determined by BET and BJH analyses of N₂ adsorption-desorption isotherms (ASAP 2020, Micromeritics, Norcross, GA, USA). The Pd contents were verified by inductively coupled plasma–optical emission spectroscopy (NexION 300D, PerkinElmer, Shelton, CT, USA) analysis. The reduction and acid properties of catalysts were tested using H₂-temperature-programmed reduction (H₂-TPR, AutoChem 2920, Micromeritics, Norcross, GA, USA) and NH₃-temperature-programmed reduction (NH₃-TPD, AutoChem 2920, Micromeritics, GA, USA) [33]. The H₂-TPR measurements, 0.1 g of each catalyst was placed in a U-shaped quartz tube under He flow at 150 °C for 120 min, and then cooled to 50 °C. The catalyst was heated to 800 °C at a heating rate of 10 °C/min under 5% H₂/He flow. The NH₃-TPD measurements, 0.1 g of each catalyst

was placed in a U-shaped quartz tube under He flow at 150 °C for 120 min. Then, NH₃ (10% NH₃ in He) adsorption was allowed to proceed at 50 °C for 30 min. The catalyst was flushed under the He flow. Finally, the catalysts were heated to 500 °C at a heating rate of 10 °C/min under He flow. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Waltham, MA, USA) measurements were performed using Al K α radiation. Before the XPS measurement, all Pd catalysts were pre-reduced with hydrogen (4% H₂ in N₂) at 250 °C for 2 h.

The surface morphologies and Pd distributions of the Pd catalysts were analyzed by SEM (SU8020, Hitachi, Tokyo, Japan) with EDX at an accelerating voltage of 15 kV. Pd dispersions were measured by CO chemisorption (ASAP 2020C, Micromeritics, Norcross, GA, USA). Each catalyst (0.4 g) was reduced under H₂ flow at 250 °C for 2 h. The amount of adsorbed CO was evaluated by assuming a stoichiometry of one CO molecule to one surface Pd site [34,35]. The dispersion of Pd was calculated using Equations (1) and (2):

$$\text{Metal dispersion} = \frac{\text{Chemisorption Site}}{\text{Metal Atomicity}} \times 100 \quad (1)$$

$$= \frac{V_{\text{chem}} \cdot \text{SF} \cdot M_w}{C/100} \times 100 \quad (2)$$

V_{chem} : CO chemisorption volume, M_w : Pd atomic weight, SF: stoichiometry factor, and $C/100$: supported metal weight.

Particle sizes and Pd distributions were analyzed by FE-TEM (JEM-2100F, JEOL, Tokyo, Japan) at an accelerating voltage of 200 kV. Moreover, Pd dispersions were also evaluated with FE-TEM images using the following Equation (3) [36],

$$D(\text{dispersion}) = \frac{6 \left(\frac{v_m}{a_m} \right)}{d_{VA}} \quad (3)$$

where $a_m (\text{\AA}^2)$: area occupied by a surface atom, $v_m (\text{\AA}^3)$: volume occupied by an atom in the bulk metal, and d_{VA} : the average particle size.

3.3. Hydrogenation of Furfural

Furfural hydrogenation was performed in a 250 mL stainless-steel autoclave using 2.5 g of furfural and 100 mL of distilled water as solvent. Prior to the start of the reaction, 0.1 g of each Pd catalyst was reduced with hydrogen (4% H₂ in N₂) at 250 °C for 2 h. The reaction mixture containing the reduced catalyst was rapidly transferred into the autoclave, and then the reactor was purged with nitrogen three times to remove air. The sealed reactor was stirred at 500 rpm. After the reaction temperature reached at desire temperature, hydrogen was pressured to 20 bar, and the reaction was carried out for 4 h. After completion of the reaction, the reactor was cooled down to room temperature. The products were centrifuged and added to 2-propanol (volume 1:10). The reaction products were analyzed by gas chromatography (GC, 7890A, Agilent, Santa Clara, CA, USA) using a flame ionization detector (FID) and a DB-Wax (30 m $\times$ 0.32 mm $\times$ 0.25 μ m) [37]. The quantitative of reaction products was done by external standard method. The furfural (Sigma-Aldrich), FAL (Sigma-Aldrich), CPO (Sigma-Aldrich), THFAL (Sigma-Aldrich), and 2-MF (Sigma-Aldrich) standard were analytical grade and used without purification. The conversion and selectivity were calculated as follows:

The conversion and product selectivity were calculated per the following equations:

$$\text{Conversion (\%)} = \frac{(\text{Initial mole of reactant}) - (\text{final mole of reactant})}{(\text{Initial mole of reactant})} \times 100 \quad (4)$$

$$\text{Selectivity (\%)} = \frac{\text{mole of desired product}}{(\text{Initial mole of reactant}) - (\text{final mole of reactant})} \times 100 \quad (5)$$

4. Conclusions

Pd catalysts were prepared on various supports (Al_2O_3 , SiO_2 , TiO_2 , CeO_2 , and ZrO_2) by a chemical reduction method. The dispersion and uniformity of Pd were affected by the properties of the support and by the nucleation and growth of Pd. The effects of the Pd dispersion and support properties on the catalytic activity and selectivity for furfural hydrogenation were investigated. The conversion of furfural was enhanced by greater Pd dispersion. The selectivity for CPO and THFAL was affected by the Pd dispersion, surface chemical state, acidity of the Pd catalyst, and reaction parameters (catalyst amount, temperature, H_2 pressure, and time). The Pd/ TiO_2 catalyst showed the highest CPO yield than other catalysts. High Pd dispersion and high acidity of the catalyst led to greater C=C hydrogenation, thereby generating more THFAL. The Pd/ TiO_2 catalyst exhibited the >99% furfural conversion, 55.6% CPO selectivity, and 55.5% CPO Yield under the optimal conditions; 20 bar of H_2 , at 170 °C for 4 h with 0.1 g of catalyst.

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Abbreviations

BET: Brunauer–Emmett–Teller; BJH: Barrett–Joyner–Halenda; CPO: cyclopentanone; ICP-OES: by inductively coupled plasma–optical emission spectroscopy, 2-MF: 2-methylfuran; FE-TEM: field emission–transmission electron microscopy, FAL: furfuryl alcohol, FE-SEM: field-emission scanning electron microscope, EDX: energy dispersive X-ray spectroscopy, THFAL: tetrahydrofurfuryl alcohol TPD: temperature-programmed desorption, TPR: temperature-programmed reduction; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffraction.

References

1. Hronec, M.; Fulajtárova, K.; Soták, T. Highly Selective Rearrangement of Furfuryl Alcohol to Cyclopentanone. *Appl. Catal. B Environ.* **2014**, *154–155*, 294–300. [\[CrossRef\]](#)
2. Jiménez-Gómez, C.P.; Cecilia, J.A.; Márquez-Rodríguez, I.; Moreno-Tost, R.; Santamaría-González, J.; Mérida-Robles, J.; Maireles-Torres, P. Gas-Phase Hydrogenation of Furfural over Cu/ CeO_2 Catalysts. *Catal. Today* **2017**, *279*, 327–338. [\[CrossRef\]](#)
3. Alonso, D.M.; Bond, J.Q.; Dumesic, J.A. Catalytic Conversion of Biomass to Biofuels. *Green Chem.* **2010**, *12*, 1493–1513. [\[CrossRef\]](#)
4. Wang, Y.; Zhao, D.; Rodríguez-Padrón, D.; Len, C. Recent Advances in Catalytic Hydrogenation of Furfural. *Catalysts* **2019**, *9*, 796. [\[CrossRef\]](#)
5. Zhou, M.; Li, J.; Wang, K.; Xia, H.; Xu, J.; Jiang, J. Selective Conversion of Furfural to Cyclopentanone over CNT-Supported Cu Based Catalysts: Model Reaction for Upgrading of Bio-Oil. *Fuel* **2017**, *202*, 1–11. [\[CrossRef\]](#)
6. Ma, Y.-F.; Wang, H.; Xu, G.-Y.; Liu, X.-H.; Zhang, Y.; Fu, Y. Selective Conversion of Furfural to Cyclopentanol over Cobalt Catalysts in One Step. *Chin. Chem. Lett.* **2017**, *28*, 1153–1158. [\[CrossRef\]](#)
7. Guo, J.; Xu, G.; Han, Z.; Zhang, Y.; Fu, Y.; Guo, Q. Selective Conversion of Furfural to Cyclopentanone with CuZnAl Catalysts. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2259–2266. [\[CrossRef\]](#)
8. Shen, T.; Hu, R.; Zhu, C.; Li, M.; Zhuang, W. Production of Cyclopentanone from Furfural over Ru/C with $\text{Al}_{11.3}\text{PO}_{23.7}$ and Application in the Synthesis of Diesel Range Alkanes. *RSC Adv.* **2018**, *8*, 37993–38001. [\[CrossRef\]](#)
9. Albilali, R.; Douthwaite, M.; He, Q.; Taylor, S.H. The Selective Hydrogenation of Furfural over Supported Palladium Nanoparticle Catalysts Prepared by Sol-Immobilisation: Effect of Catalyst Support and Reaction Conditions. *Catal. Sci. Technol.* **2018**, *8*, 252–267. [\[CrossRef\]](#)

10. Li, C.; Xu, G.; Liu, X.; Zhang, Y.; Fu, Y. Hydrogenation of Biomass-Derived Furfural to Tetrahydrofurfuryl Alcohol over Hydroxyapatite-Supported Pd Catalyst under Mild Conditions. *Ind. Eng. Chem. Res.* **2017**, *56*, 8843–8849. [\[CrossRef\]](#)
11. Bhogeswararao, S.; Srinivas, D. Catalytic Conversion of Furfural to Industrial Chemicals over Supported Pt and Pd Catalysts. *J. Catal.* **2015**, *327*, 65–77. [\[CrossRef\]](#)
12. Clair, B.; Yamamoto, H.; Chang, S.-S.; Di Renzo, F.; Zhao, G.-J.; Ruelle, J.; Beauchene, J.; Quignard, F.; Gril, J. Mesoporosity as a New Parameter for Understanding Tension Stress Generation in Trees. *J. Exp. Bot.* **2009**, *60*, 3023–3030.
13. Qi, B.; Di, L.; Xu, W.; Zhang, X. Dry Plasma Reduction to Prepare a High Performance Pd/C Catalyst at Atmospheric Pressure for CO Oxidation. *J. Mater. Chem. A* **2014**, *2*, 11885–11890. [\[CrossRef\]](#)
14. Jiang, H.; Yu, X.; Nie, R.; Lu, X.; Zhou, D.; Xia, Q. Selective Hydrogenation of Aromatic Carboxylic Acids over Basic N-Doped Mesoporous Carbon Supported Palladium Catalysts. *Appl. Catal. A Gen.* **2016**, *520*, 73–81. [\[CrossRef\]](#)
15. Zheng, Q.; Farrauto, R.; Deeba, M. Part II: Oxidative Thermal Aging of Pd/Al₂O₃ and Pd/Ce_xO_y-ZrO₂ in Automotive Three Way Catalysts: The Effects of Fuel Shutoff and Attempted Fuel Rich Regeneration. *Catalysts* **2015**, *5*, 1797–1814. [\[CrossRef\]](#)
16. Palma, V.; Ruocco, C.; Meloni, E.; Ricca, A. Renewable Hydrogen from Ethanol Reforming over CeO₂-SiO₂ Based Catalysts. *Catalysts* **2017**, *7*, 226. [\[CrossRef\]](#)
17. Gopinath, R.; Babu, N.S.; Kumar, J.V.; Lingaiah, N.; Prasad, P.S. Influence of Pd Precursor and Method of Preparation on Hydrodechlorination Activity of Alumina Supported Palladium Catalysts. *Catal. Lett.* **2008**, *120*, 312–319. [\[CrossRef\]](#)
18. Garcia, S.; Smith, R.; Deacon, L.; Euaruksakul, C.; Held, G. The Partial Oxidation of Methane Over Pd/Al₂O₃ Catalyst Nanoparticles Studied In-Situ by Near Ambient-Pressure X-ray Photoelectron Spectroscopy. *Top. Catal.* **2016**, *59*, 516–525.
19. Liu, J.; Chen, Y.; Wang, H.; Yang, M.; Wu, Y.; Chen, Z. Effects of Atmosphere Pretreatment on the Catalytic Performance of Pd/T-Al₂O₃ Catalyst in Benzene Degradation II: Crystal Structure Transformation of Pd Active Species. *Catal. Today* **2017**, *297*, 211–218. [\[CrossRef\]](#)
20. Song, S.; Sheng, Z.; Liu, Y.; Wang, H.; Wu, Z. Influences of PH Value in Deposition-Precipitation Synthesis Process on Pt-Doped TiO₂ Catalysts for Photocatalytic Oxidation of NO. *J. Environ. Sci.* **2012**, *24*, 1519–1524. [\[CrossRef\]](#)
21. Estruga, M.; Domingo, C. Dispersion and Surface Functionalization of Oxide Nanoparticles for Transparent Photocatalytic and UV-Protecting Coatings and Sunscreens. *Sci. Technol. Adv. Mater.* **2013**, *14*, 023001.
22. Centeno, M.Á.; Carrizosa, I.; Odrizola, J.A. Deposition—Precipitation Method to Obtain Supported Gold Catalysts: Dependence of the Acid-Base Properties of the Support Exemplified in the System TiO₂-TiO_x N_y-TiN. *Appl. Catal. A Gen.* **2003**, *246*, 365–372. [\[CrossRef\]](#)
23. Qian, K.; Fang, J.; Huang, W.; He, B.; Jiang, Z.; Ma, Y.; Wei, S. Chemical Understanding the Deposition–Precipitation Process for the Preparation of Supported Au Catalysts. *J. Mol. Catal. A* **2010**, *320*, 97–105. [\[CrossRef\]](#)
24. Byun, M.Y.; Kim, J.S.; Park, D.-W.; Lee, M.S. Influence of Synthetic Parameters on the Particle Size and Distribution of Pd in Pd/Al₂O₃ Catalysts. *J. Nanosci. Nanotechnol.* **2018**, *18*, 6283–6287. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Kiwi, J. The Effect of Promoters on the Photochemical Water Cleavage in Suspensions of Pt-Loaded TiO₂ with Increased Light to Chemical Conversion Efficiency. In *Homogeneous and Heterogeneous Photocatalysis*; D. Reider Publishing: Boston, MA, USA, 1986; pp. 275–302.
26. Wu, Z.; Overbury, S.H. Infrared Spectroscopic Insights into the Role of the Support in Heterogeneous Gold Catalysis. In *Heterogeneous Gold Catalysts and Catalysis*; Royal Society of Chemistry: London, UK, 2014; pp. 512–532.
27. Spivey, J.J.; Roberts, G.W.; Dooley, K.M. Catalysis of Acid/Aldehyde/Alcohol Condensations to Ketones. In *Catalysis*; Royal Society of Chemistry: London, UK, 2004; pp. 293–319.
28. Kim, T.; Assary, R.S.; Pauls, R.E.; Marshall, C.L.; Curtiss, L.A.; Stair, P.C. Thermodynamics and Reaction Pathways of Furfuryl Alcohol Oligomer Formation. *Catal. Commun.* **2014**, *46*, 66–70. [\[CrossRef\]](#)
29. Guigo, N.; Mija, A.; Vincent, L.; Sbirrazzuoli, N. Chemorheological Analysis and Model-Free Kinetics of Acid Catalysed Furfuryl Alcohol Polymerization. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5359–5366. [\[CrossRef\]](#)

30. Lee, J.; Burt, S.P.; Carrero, C.A.; Alba-Rubio, A.C.; Ro, I.; O'Neill, B.J.; Kim, H.J.; Jackson, D.H.K.; Kuech, T.F.; Hermans, I.; et al. Stabilizing Cobalt Catalysts for Aqueous-Phase Reactions by Strong Metal-Support Interaction. *J. Catal.* **2015**, *330*, 19–27. [[CrossRef](#)]
31. Dekura, S.; Kobayashi, H.; Kusada, K.; Kitagawa, H. Hydrogen in Palladium and Storage Properties of Related Nanomaterials: Size, Shape, Alloying, and Metal-Organic Framework Coating Effects. *ChemPhysChem* **2019**, *20*, 1158–1176. [[CrossRef](#)]
32. Date, N.S.; Kondawar, S.E.; Chikate, R.C.; Rode, C.V. Single-Pot Reductive Rearrangement of Furfural to Cyclopentanone over Silica-Supported Pd Catalysts. *ACS Omega* **2018**, *3*, 9860–9871. [[CrossRef](#)]
33. Byun, M.Y.; Kim, J.S.; Park, D.; Lee, M.S. Influence of Calcination Temperature on the Structure and Properties of Al₂O₃ as Support for Pd Catalyst. *Korean J. Chem. Eng.* **2018**, *35*, 1083–1088. [[CrossRef](#)]
34. Zou, W.; Gonzalez, R.D. The Preparation of Silica Supported Pd Catalysts: The Effect of Pretreatment Variables on Particle Size. *Catal. Lett.* **1992**, *12*, 73–86. [[CrossRef](#)]
35. Sangeetha, P.; Shanthi, K.; Rao, K.S.R.; Viswanathan, B.; Selvam, P. Hydrogenation of Nitrobenzene over Palladium-Supported Catalysts-Effect of Support. *Appl. Catal. A Gen.* **2009**, *353*, 160–165. [[CrossRef](#)]
36. Ertl, G.; Knozinger, H.; Weitkamp, J. (Eds.) Characterization of Solid Catalysts. In *Handbook of Heterogeneous Catalysis*; Wiley: Hoboken, NJ, USA, 1997; Volume 438, pp. 427–582.
37. Nguyen-Huy, C.; Kim, J.S.; Yoon, S.; Yang, E.; Kwak, J.H.; Lee, M.S.; An, K. Supported Pd Nanoparticle Catalysts with High Activities and Selectivities in Liquid-Phase Furfural Hydrogenation. *Fuel* **2018**, *226*, 607–617. [[CrossRef](#)]



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