

Oxidative carbonylation of phenol to diphenyl carbonate over supported palladium catalysts

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Abstract

Oxidative carbonylation of phenol to form diphenyl carbonate (DPC) was investigated in the multi-step electron transfer system containing homogeneous or heterogeneous palladium as the main component. Carbon-supported Pd catalyst showed a better DPC yield than the best homogeneous system with $\text{Pd}(\text{OAc})_2$ for the same amount of palladium. For the supported palladium catalyst, the hydrophobicity of the supports appeared to be critical for high yields of DPC. The palladium remained in the metallic state and dissolution into the reaction solution was, if there was any, negligible. Effects of promoters in carbon-supported Pd catalyst system were also examined. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polycarbonate, classified as one of the major engineering thermoplastics, is commercially produced by the reaction of bisphenol A (BPA) with phosgene [1]. This conventional route has the possibility of causing environmental problems by the highly toxic phosgene and excessive amounts of CH_2Cl_2 used as solvent. Non-phosgene processes have been proposed to replace the traditional phosgene process. One such process is composed of the synthesis of diphenyl carbonate (DPC) followed by the transesterification between DPC and BPA [1].

The oxidative carbonylation of phenol has been considered as one of possible routes for DPC synthesis [2].

Palladium compounds have been reported to promote the non-catalytic carbonylation [3–6] and the catalytic (in the presence of cocatalyst) oxidative carbonylation of methanol to produce dimethyl carbonate [7]. However, the analogous reactions with phenol to DPC are not so efficient because of the lower basicity of phenols and the ease of phenol oxidation, which leads to several side reactions. Hallgren et al. reported that oxidative carbonylation of phenol into DPC could be accomplished in the catalyst system composed of a palladium compound, oxidation cocatalysts, a base, and a dehydrating material [8,9]. To speed up the oxidation, various components that assist the multi-step electron trans-

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fer have been developed [10–40]. Hallgren and Matthews [32] reported that diaryl carbonates could be produced only when PdClCO was substituted for PdCl₂ in the absence of cocatalysts and concluded that Pd(I) might be the active state. However, Goyal et al. [13] reported that all of the Pd(I) and Pd(II) complexes were equally effective Pd sources in the presence of Cu(OAc)₂ as an oxidation cocatalyst. Recently, Pd–Sn heterobinuclear complexes, which do not require ammonium halides, have been reported [33]. Heterogeneous Pd/C [34–39] and giant palladium-561 clusters [40] have also been examined. In spite of the potential advantage in practical applications, heterogeneous Pd catalysts have not been studied intensively compared with homogeneous Pd catalysts. Takagi et al. [39] studied Pd/C–PbO–NMe₄Br system and reported that Pd species seemed to work as a homogeneous catalyst although heterogeneous Pd/C was used as a palladium source.

In this study, various heterogeneous Pd catalysts are compared for DPC synthesis and the causes of their differences in activities are discussed.

2. Experimental

2.1. Catalysts and materials

Five percent Pd/C was purchased from Alfa and was utilized without any further treatment. Other supported catalysts were prepared by an incipient wetness method to impregnate supports with a solution of Pd(OAc)₂ dissolved in acetone. Support materials were γ -Al₂O₃ (Alfa, BET surface area: 170 m²/g), activated carbon (AC, Aldrich, BET surface area: 1075 m²/g), SiO₂ (Aldrich, BET surface area: 300 m²/g), and MgO (Aldrich, BET surface area: 169 m²/g). Impregnated catalysts were dried at 393 K overnight and then reduced in a dihydrogen stream at different temperatures. For brevity, a catalyst code system was used to represent different catalysts: 5% Pd/C-300 K is a commer-

cial Pd/C catalyst containing 5 wt.% palladium, reduced at 300 K with H₂; and AC(673 K) is the carbon support prepared by reducing AC at 673 K with H₂ to remove the acidic surface functional groups. All reagents were used as received.

2.2. Oxidative carbonylation of phenol

Given the amounts of Pd catalyst, an inorganic cocatalyst, tetrabutylammonium bromide (Bu₄NBr), benzoquinone, and dried phenol were charged into a 200-ml autoclave reactor (Parr). After purging the reactor with CO, 77 kg/cm² CO and 5.8 kg/cm² O₂ were successively charged and the reaction temperature was adjusted to 381 K. Products were analyzed by Chrompack 9000 GC (DB1 capillary column) with an FID detector.

2.3. Characterization of catalysts

2.3.1. CO pulse injection for the determination of palladium metal surface area

CO chemisorption on palladium was carried out at 300 K with a pulse injection method following the same experimental and data handling procedures as reported by Heal and Mkayula [41]. The amount of sample normally used was between 0.10 and 0.20 g. The flow rate of hydrogen carrier gas was 50 ml/min and the volume of CO per injection was 0.05 ml. For highly dispersed palladium samples, several injections were necessary to obtain final peaks that were reproducible and had equal areas corresponding to zero CO uptake. A mass selective detector (HP5971 MSD) was utilized for the analysis of CO. In calculating Pd dispersions from CO chemisorption data, it was assumed that CO was chemisorbed in a bridged form (a chemisorbed CO molecule per two exposed Pd atoms) [41] and that the number of palladium atoms per unit area was 1.2×10^{19} , assuming the catalyst surface is comprised of an equal population of three crystallographic planes of (100), (110), and (111) [42].

2.3.2. Temperature programmed desorption (TPD)

Samples were pretreated with He at 323 K for 1 h before weighing. TPD was conducted in a He stream heated from 373 to 1173 K at a rate of 10 K/min monitoring gas products with an HPR20 Quadruple Mass Spectroscopy (Hiden Analytical).

2.3.3. X-ray diffraction (XRD)

X-ray powder diffraction patterns were obtained at room temperature using a M18X-HF(MAC Science) with Ni-filtered Cu K α radiation. The X-ray tube was operated at 40 kV and 200 mA. In order to observe the change in the bulk state of palladium catalyst before and after the reaction, 0.51 g of 5% Pd/AC-573 K catalyst, Ce(OAc)₃ 0.24 mmol, Bu₄NBr 1.3 mmol, benzoquinone 2.4 mmol, and phenol 0.20 mol were charged into the reactor vessel. This mixture of catalysts and phenol were washed with 200 ml toluene several times at ambient temperature followed by drying at 393 K before and after 2 h of the oxidative carbonylation at 381 K, respectively. Samples were packed into a glass holder having an 18 × 18 × 2 mm opening. No adhesive or binder was necessary. The 2 θ angle was scanned at a rate of 4° min⁻¹.

2.3.4. Inductively coupled plasma atomic emission spectrometry (ICP-AES)

ICP analysis was conducted to quantify the amount of soluble palladium in the reaction medium. After dilution of reaction medium with toluene and filtering with 0.2- μ m ceramic filter, the filtrate was analyzed with an ICP-Flame-EOP (Spectro Analytical Instruments).

3. Results and discussion

3.1. Pd dispersion for supported Pd catalysts

CO chemisorption data for supported Pd catalysts are listed in Table 1. The Pd dispersion appeared to depend on the support, the amount of palladium, and the reduction temperature. Pd dispersions for 5% Pd/C and 5% Pd/Al₂O₃ are almost the same even though surface properties of them are quite different. Pd dispersions for various supports decrease in the order of Al₂O₃ > SiO₂ > activated carbon (AC) > MgO when prepared under the same conditions. For carbon-supported Pd catalysts with different Pd loadings, Pd dispersions are almost the same except for 10% Pd/AC, which has a lower Pd

Table 1
CO adsorption data for heterogeneous Pd catalysts

No.	Sample	Pd surface area, A_{Pd} (m ² Pd/g cat.)	Pd surface area, A'_{Pd} (m ² Pd/g Pd)	% dispersion, D_{Pd}
1	5%Pd/C-300 K	11.69	233.7	49.5
2	5%Pd/Al ₂ O ₃ -573 K	11.92	238.3	50.5
3	5%Pd/SiO ₂ -573 K	9.22	184.0	39.0
4	5%Pd/MgO-573 K	1.97	39.31	8.30
5	1%Pd/AC-573 K	0.86	85.88	18.2
6	1%Pd/AC-673 K	0.42	42.00	8.80
7	3%Pd/AC-573 K	2.49	83.00	17.6
8	5%Pd/AC-573 K	4.59	92.00	19.4
9	10%Pd/AC-573 K	6.26	62.59	13.3
10	5%Pd/AC-473 K	8.59	172.0	36.4
11	5%Pd/AC-673 K	1.92	38.40	8.10
12	5%Pd/AC-773 K	0.36	7.17	1.50
13	5%Pd/AC-873 K	0.26	5.18	1.10
14	5%Pd/AC(673)-473 K ^a	8.33	167.0	35.3

^aCarbon supports were pre-reduced with H₂ at 673 K.

Table 2

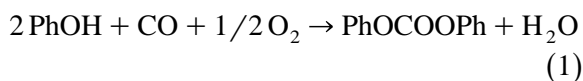
Activity comparison between Pd(OAc)₂ and Pd/CReaction condition: Co(OAc)₂ 0.36 mmol, Bu₄NBr 10.0 mmol, benzoquinone 1.85 mmol; phenol 0.39 mol, time 12 h.

No.	Pd catalyst (0.36 mmol)	Additives	PhOH conversion (%)	DPC selectivity (%)	DPC yield (%)
1	Pd(OAc) ₂		25.7	49.9	12.8
2	5% Pd/C		35.8	60.25	21.5
3	Pd(OAc) ₂	AC (0.72 g)	26.0	65.0	16.0
4			16.0	15.0	2.4
5		AC (1.0 g)	24.0	29.0	7.0

dispersion than those of other lower Pd-loading catalysts. Pd dispersion also decreases as the reduction temperature increases. Pd catalyst supported on a pre-reduced AC (No. 14 in Table 1) has almost same Pd dispersion of catalyst supported on a fresh AC (No. 10 in Table 1).

3.2. Oxidative carbonylation of phenol with homogeneous and heterogeneous Pd catalysts

The oxidative carbonylation of phenol to DPC proceeds by reaction (1):



This reaction has been reported to occur with the formation of by-products that include the oxidative dimerization and trimerization products such as *p*-phenoxyphenol, phenylsalicylate, and oligomeric compounds [11]. In addition, carbon monoxide is also consumed by the reaction of oxygen to carbon dioxide [11]. The formation of oligomeric compounds has been reported to accelerate by increasing the reaction temperatures [11] and this was confirmed in our experiments. Thus, the optimum reaction temperature of 381 K was selected in an initial screening experiment. Takagi et al. [39] have reported that the product distribution was dependent on the employed cocatalyst as was also observed in our experiments. Throughout our experiments, the main by-product was found to be the phenylsalicylate.

In the homogeneous Pd catalyst system, Pd(OAc)₂ was reported to be at least equal or superior to other homogeneous Pd catalysts [11–26]. This was confirmed in our screening test for Pd precursors which showed that Pd(OAc)₂ exhibited a much better DPC yield than Pd(NO₃)₂, PdCl₂, PdBr₂, and palladium acetylacetonate. Thus, activities for DPC synthesis between Pd(OAc)₂ and Pd/C was compared for the same amount of palladium. As shown in Table 2, Pd/C gave a substantially higher DPC yield than homogeneous Pd(OAc)₂. Both the phenol conversion and the selectivity to DPC were higher for the heterogeneous catalyst. Addition of activated carbon into the reaction mixture containing Pd(OAc)₂ improved the DPC yield by increasing DPC selectivity, but not up to the level of Pd/C (Run 3). Activated

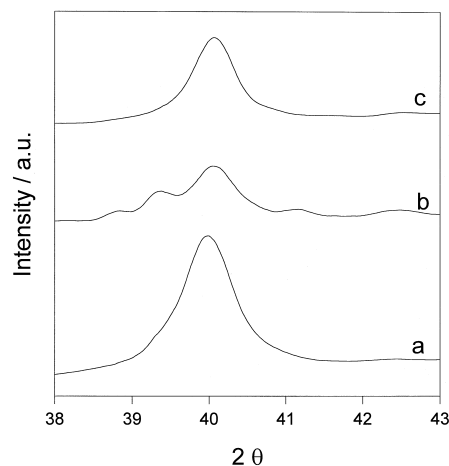


Fig. 1. X-ray diffraction patterns of fresh 5% Pd/AC-573 K. (a) Catalysts before a reaction (b) and after a reaction (c).

Table 3

Activity comparison among cocatalysts in the Pd/C system

Reaction conditions: 5% Pd/C 1.02 g (0.48 mmol), Bu₄NBr 1.3 mmol, benzoquinone 2.4 mmol; phenol 0.53 mol, time 4 h.

Cocatalyst (0.48 mmol)	PhOH conversion (%)	DPC selectivity (%)	DPC yield (%)
Mn(OAc) ₂	18	57	10.3
Ce(OAc) ₃	37.6	72	26.8
Ce(NO ₃) ₂	23.7	53.1	12.6
Cu(NO ₃) ₂	18.8	39.5	7.4
CuO	17.2	51.8	8.9
AgNO ₃	10	47.6	4.8
Co(OAc) ₂	27.2	77	16.7

carbon without Pd compounds was found to have a certain catalytic activity for DPC synthesis when the cocatalyst and other promoters were present (Runs 4 and 5).

We tried to determine whether the higher activity of Pd/C is due to a homogeneous palladium species dissolved into the reaction mixture. However, any soluble Pd could not be detected in the ICP analysis of the filtrate of the reaction mixture after reaction. The detection limit of this analysis is ca. 1 ppm and thus, at most 1.0 ppm of soluble palladium could be present during the reaction. To observe the change in the bulk palladium during reaction, XRD patterns were obtained for 5% Pd/AC-573 K catalyst mixed with the cocatalyst and other additives before and after the reaction, and compared with the fresh catalyst alone in Fig. 1 for the peak at 40° representing Pd metal. The fresh catalyst showed a particle size of 7.5 nm from the application of Scherrer equation to the broadening of the peak [43]. This is comparable

with the particle size obtained from CO chemisorption (5.2 nm). When the catalyst was mixed with other cocatalysts and phenol at ambient temperatures, the peaks in Fig. 1b was obtained. Palladium retained almost the same particle size (7.5 nm). The extra peak appears to originate from Ce(OAc)₃, which is only partially soluble in phenol at room temperature. This peak became strengthened after the reaction at 381 K for 2 h. Thus, it is obvious that the dominant state of palladium during the reaction should be metallic. The apparent sintering of palladium giving Pd particles with a size of 9.6 nm during the reaction is probably due to the reducing reaction atmosphere, which contains excess CO. Thus, it appears that zerovalent palladium particles are active catalyst for the oxidative carbonylation of phenol. The heterogeneous Pd/C catalyst is much more active than the most active homogeneous system with Pd(OAc)₂. The difference should be much greater than shown in Table 2 when the activity per palladium atom is compared because only the palladium atoms present on the surface have actually contributed to the reaction in the heterogeneous catalyst.

For 5% Pd/C catalyst, a screening test was conducted for cocatalysts that has been known for promoting the homogeneous palladium catalysts. As shown in Table 3, cerium salts are better than Mn, Co, and Cu salts. Recently, PbO was reported to give a better DPC yield than above cocatalysts, but produced a significant amount of unwanted bromophenol [39]. Thus, Ce(OAc)₃ was adopted for the cocatalyst for

Table 4

Activity comparison among heterogeneous Pd catalysts on different supports

Reaction conditions: catalyst 1.02 g (0.48 mmol), Ce(OAc)₃ 0.48 mmol, Bu₄NBr 1.3 mmol, benzoquinone 2.4 mmol; phenol 0.53 mol, time 7 h.

No.	Pd catalysts	PhOH conversion (%)	DPC selectivity (%)	DPC yield (%)
1	5%Pd/C-300 K	30.3	69.5	21.1
2	5%Pd/Al ₂ O ₃ -573 K	12.5	60	7.5
3	5%Pd/SiO ₂ -573 K	19	50	9.5
4	5%Pd/MgO-573 K	9	53.5	4.8

Table 5

Activity comparison among carbon-supported Pd catalysts with different loadings

Reaction conditions: $\text{Ce}(\text{OAc})_3$ 0.24 mmol, Bu_4NBr 1.3 mmol, benzoquinone 2.4 mmol; phenol 0.53 mol, time 4 h.

No.	Pd catalysts (0.24 mmol Pd)	PhOH conversion (%)	DPC selectivity (%)	DPC yield (%)
1	5%Pd/C-300 K	24	59	14
2	1%Pd/AC-573 K	35	60	21
3	3%Pd/AC-573 K	27	58	16
4	5%Pd/AC-573 K	20	50	10
5	10%Pd/AC-573 K	15	44	7

this heterogeneous Pd catalyst system. Heterogeneous Pd catalysts on different supports were compared in Table 4. Carbon support was proved to be superior to any other support materials. In case of the highly dispersed alumina-supported Pd catalyst, DPC yield was much lower than that of the carbon-supported Pd catalyst due mainly to the lower phenol conversion.

Then, why does Pd/C perform better in oxidative carbonylation of phenol than heterogeneous catalysts and other heterogeneous catalysts? In the heterogeneous Pd catalyst system, the surface property of support material seems to be critical. As discussed elsewhere [44–46], alumina has various surface hydroxyl groups and is considered to have hydrophilic surface property. However, carbon support is considered to be hydrophobic. In DPC synthesis, one equivalent mole of H_2O per DPC is produced and it has been considered to be an inhibitor for DPC synthesis [8,9]. Therefore, the reduced population of water around palladium metal over hydrophobic carbon appears responsible for the higher DPC yield compared with hydrophilic supports such as Al_2O_3 and SiO_2 . Addition of activated carbon into the $\text{Pd}(\text{OAc})_2$ -catalyzed homogeneous catalyst system improved the DPC yield by increasing the selectivity, but not up to the level of the heterogeneous Pd/C catalyst system as shown in Table 2. Thus, it seems important to carry out the reaction in the hydrophobic carbon pores.

3.3. Carbon-supported Pd catalyst system

Carbon-supported Pd catalysts appeared to give higher DPC yields than catalysts prepared

with any other supports. Thus, different carbon-supported Pd catalysts were prepared and their activities for the DPC synthesis were compared to understand this catalyst system. Catalysts containing different loadings of Pd were prepared and tested. In all cases, the amount of palladium in the reaction system was kept the same by employing a larger amount of catalyst for a lower loading catalyst. As shown in Table 5, as the palladium loading increases, lower DPC yields were obtained. When 5% Pd/C-300 K and 1% Pd/AC-573 K are compared, the better-dispersed catalyst (5% Pd/C-300 K) does not always give higher DPC yield. To find out the difference in surface properties of these two catalysts, TPD was conducted. As shown in Fig. 2, CO_2 evolved at moderate temperatures (323–673 K) due to the decomposition of surface oxide groups, which are believed to contribute to the hydrophilic property of carbon support [47–49]. The amount of evolved CO_2 was much greater for 5% Pd/C-300 K. Thus, the lower

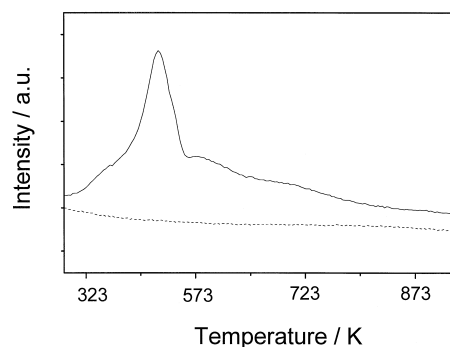


Fig. 2. The amount of CO_2 evolution with temperatures during the TPD experiment of 5% Pd/C-300 K (solid line) and 1% Pd/AC-573 K (dotted line).

Table 6

Activity comparison among carbon-supported Pd catalysts with different reduction temperatures

No.	Pd catalyst	PhOH conversion (%)	DPC selectivity (%)	DPC yield (%)
1	5%Pd/AC-473 K ^a	18	60	11
2	5%Pd/AC-673 K ^a	22	58	13
3	5%Pd/AC-773 K ^a	22	57	12
4	5%Pd/AC-873 K ^a	18	50	9
5	5%Pd/AC(673 K)-473 K ^b	21.5	66.5	14.3
6	5%Pd/AC-673 K ^b	22	58	13

^aCatalyst 0.51 g (0.24 mmol), Ce(OAc)₃ 0.24 mmol, Bu₄NBr 1.3 mmol, benzoquinone 2.4 mmol; phenol 0.53 mol, time 4 h.

^bCatalyst 0.40 g (0.19 mmol), Ce(OAc)₃ 0.38 mmol, Bu₄NBr 1.9 mmol, benzoquinone 0.93 mmol; phenol 0.53 mol, time 2h.

DPC yield of 5% Pd/C-300 K than 1% Pd/AC-573 K could be understood in terms of greater hydrophilicity of the former that attracts more water into the reaction sites and reduces the reaction rate as discussed in the previous section. Five percent Pd/AC catalysts prepared with different reducing temperatures were compared in Table 6. DPC yield increased from 11% to 13% and then decreased to 9% as the reduction temperature increased from 473 to 873 K. As shown in Table 1, the Pd dispersion decreased with increasing reduction temperatures. Thus, this relation between DPC yield and the reduction temperature cannot be explained only by Pd dispersion. It has been shown that acidic surface functional groups of carbon can be removed into CO₂ with the high-temperature treatment. To remove the possibility of changes in carbon surface during reduction, Pd catalysts

supported on pre-reduced activated carbon (No. 5 in Table 6) were prepared and compared with those supported on fresh activated carbon (No. 6 in Table 6). Now for the same surface condition, the catalysts with the higher Pd dispersion gave higher DPC yield. This relation between the reactivity and catalyst dispersion also supports our suggestion that the working state in the Pd/C system is a heterogeneous catalysis.

3.4. Effects of promoters in the carbon-supported Pd catalyst system

To find out the optimized catalyst compositions in the heterogeneous Pd catalyst system, DPC yields were compared with different ratio of [Ce(OAc)₃]/[Pd] and [Bu₄NBr]/[Pd]. As shown in Figs. 3 and 4, the DPC yield increased as the amount of promoters was increased at

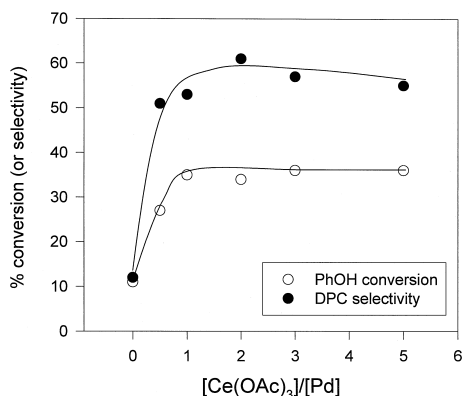


Fig. 3. Effect of [Ce(OAc)₃]/[Pd] ratio on the DPC yield. Catalysts were 1% Pd/AC-673 K 2 g (0.19 mmol Pd), Bu₄NBr 1.9 mmol and benzoquinone 0.93 mmol; phenol 0.53 mol, time 4 h.

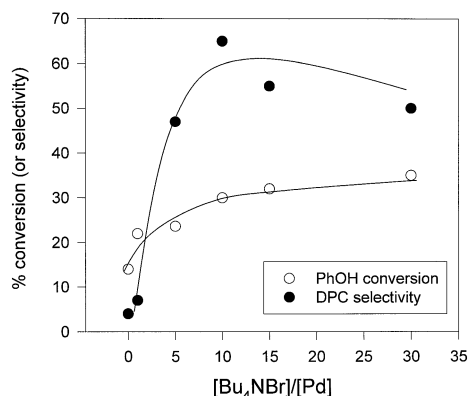


Fig. 4. Effect of [Bu₄NBr]/[Pd] ratio on the DPC yield. Catalysts were 1% Pd/AC-673 K 2 g (0.19 mmol Pd), Ce(OAc)₃ 0.19 mmol and benzoquinone 5.6 mmol; phenol 0.53 mol, time 4 h.

low ratios of $[\text{Ce}(\text{OAc})_3]/[\text{Pd}]$ and $[\text{Bu}_4\text{NBr}]/[\text{Pd}]$, and became flat at high ratios. From these experiments, the recommended ratios of $[\text{Ce}(\text{OAc})_3]/[\text{Pd}]$ and $[\text{Bu}_4\text{NBr}]/[\text{Pd}]$ were found to be 2 and 10, respectively.

4. Conclusions

Carbon-supported Pd catalyst showed a better DPC yield than the best homogeneous system with $\text{Pd}(\text{OAc})_2$ for the same amount of palladium. In the supported palladium catalyst, the surface characteristics of the supports and the Pd dispersion appeared to be critical to the yield of DPC. The well-dispersed metallic palladium supported over hydrophobic carbon gave the higher DPC yield. In this heterogeneous Pd catalyst system, the optimum ratios of $[\text{Ce}(\text{OAc})_3]/[\text{Pd}]$ and $[\text{Bu}_4\text{NBr}]/[\text{Pd}]$ are found to be 2 and 10, respectively.

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