

Heterogeneous Palladium–Cobalt Bimetal Catalyst for the Oxidative Carbonylation of Bisphenol A to Polycarbonate

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ABSTRACT: Polycarbonates (PCs) were prepared by the oxidative carbonylation of bisphenol A and carbon monoxide with a hydrotalcite-supported Pd–Co complex, a Pd–Co–poly(4-vinylpyridine) complex [Pd–Co–(p-4vpy)], a Pd–Co–polystyrene-supported triphenylphosphine complex (Pd–Co–PS–TPP), or a Pd–Co–polyvinylpyrrolidone complex (Pd–Co–pvp) as a heterogeneous Pd–Co bimetal catalyst to separate the PC solution and the Pd–Co bimetal

catalyst after the reaction. Propylene carbonate was used as a halogen-free solvent. Pd–Co–(p-4vpy) and Pd–Co–PS–TPP showed recycling potential, whereas Pd–Co–pvp, though not having recycling potential, yielded a high turnover number with a maximum of 1462. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2226–2234, 2009

Key words: catalysts; polycarbonates; polycondensation

INTRODUCTION

Polycarbonates (PCs) are excellent engineering thermoplastics because of their good impact strength, thermal resistance, and transparency.¹ They can be prepared mainly in two ways. One is the solvent method involving bisphenol A (BPA) and phosgene, and the other is the melt method involving BPA and diphenyl carbonate.² However, there is a problem with the solution method, namely, the use of halogenated solvents, which negatively affect the environment. The melt method includes a melt process that can be considered environmentally favorable because a solvent is not used, but a large amount of heat is needed. Moreover, it includes additional phenol recycling and diphenyl carbonate reproduction processes. Therefore, a more environmentally favorable technology for PC synthesis other than the melt process must be developed. Recently, a new PC production technology, a modified solution method, has been attracting interest for the direct preparation of PC from carbon monoxide and BPA with Pd compound/redox catalyst/onium halide systems.^{3,4} A study reported that the molecular weight of PC obtained with these catalyst systems via oxidative carbonylation was high, and the highest number-

average molecular weight of PC was 9400. However, dichloromethane, a halogenated solvent that negatively affects the environment, was used.

In previous articles, we reported that propylene carbonate as a halogen-free solvent is a peculiar solvent for the oxidative carbonylation reaction,⁵ and we introduced several homogeneous Pd catalysts⁶ and heterogeneous Pd catalysts for the oxidative carbonylation reaction. We found that heterogeneous Pd catalysts have recycling potential.⁷ This article describes the oxidative carbonylation of BPA to PC using propylene carbonate and catalyzed by heterogeneous Pd–Co bimetal compounds. As heterogeneous bimetal catalysts, Pd–Co catalysts supported by inorganic layered compounds (smectite and hydrotalcite) and Pd–Co catalysts supported by polymers [poly(4-vinylpyridine) (p-4vpy), polystyrene-supported triphenylphosphine (PS–TPP), and polyvinylpyrrolidone (pvp)] were used so that we could examine their PC yields, catalyst recycling potential, and turnover number (TON).

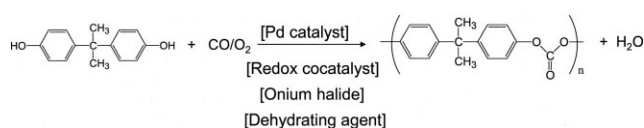
EXPERIMENTAL

Materials

The synthetic smectite Lucentite SWN, manufactured by Co-op Chemical Co., Ltd. (Tokyo, Japan), was used. The synthetic hydrotalcites used were KW-500 [Mg₆Al₂(OH)₁₆CO₃·4H₂O] and KW-1000 [Mg_{4.5}Al₂(OH)₁₃CO₃·3.5H₂O], which were manufactured by Kyowa Chemical Industry Co., Ltd. (Kagawa, Japan). p-4vpy was supplied by Koei Chemical Co., Ltd. (Chiba, Japan). The PS–TPP used was manufactured

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Scheme 1 Oxidative carbonylation of BPA.

by Biotage Japan, Ltd. (Tokyo Japan). Synthetic zeolite (A-3 powder through 75 μm) was dried *in vacuo* at 160°C for 12 h. Carbon monoxide and oxygen gases (99.99%) were used without further purification. All other reagents were used as received.

Preparation of the smectite-supported PdCl₂ and CoCl₂ complex (Pd-Co-SWN)

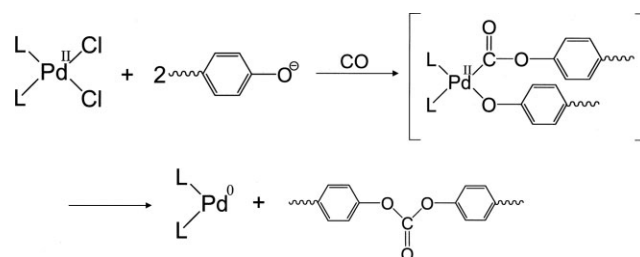
Lucentite SWN (8.00 g) was stirred at room temperature for 24 h in a 60-mL acetone solution of PdCl₂(PhCN)₂ (192 mg, 0.50 mmol), and then a 30-mL acetone solution of CoCl₂ (324 mg, 2.5 mmol) was added; the mixture was stirred at room temperature for 24 h. The obtained slurry was filtered, washed three times with acetone, and dried *in vacuo* at 100°C for 12 h.

Preparation of the hydrotalcite-supported PdCl₂ and CoCl₂ complex (Pd-Co-KW-500)

KW-500 (1.50 g) was stirred at room temperature for 1 h in a 70-mL acetone solution of PdCl₂(PhCN)₂ (384 mg, 1.00 mmol), and then a 70-mL acetone solution of CoCl₂ (649 mg, 5.00 mmol) was added; the mixture was stirred at room temperature for 48 h. The obtained slurry was filtered, washed three times with acetone, and dried *in vacuo* at 100°C for 12 h.

Preparation of the p-4vpy-supported PdCl₂ and CoCl₂ complex [Pd-Co-(p-4vpy)]

Poly(2-vinylpyridine) (1.273 g) and PdCl₂(PhCN)₂ (387 mg, 1.01 mmol) were mixed in dichloromethane



Scheme 2 Formation of the carbonate bond by the Pd catalyst.

(70 mL) at room temperature, and a 70-mL acetone solution of CoCl₂ (655 mg, 5.05 mmol) was added instantly; the mixture was stirred at room temperature for 2 h. The obtained slurry was filtered, washed three times with acetone, and dried *in vacuo* at 60°C for 12 h.

Preparation of the PS-TPP-supported PdCl₂ and CoCl₂ complex (Pd-Co-PS-TPP)

PS-TPP (lot 01740; loading: 1.51 mmol/g, 3.97 g) was stirred at room temperature for 4 h in a 40-mL acetone solution of PdCl₂(PhCN)₂ (192 mg, 0.50 mmol), and then a 35-mL acetone solution of CoCl₂ (325 mg, 2.50 mmol) was added; the mixture was stirred at room temperature for 48 h. The obtained slurry was filtered, washed three times with acetone, and dried *in vacuo* at 60°C for 12 h.

Preparation of the pvp (linear)-supported PdCl₂ and CoCl₂ complex [Pd-Co-pvp(linear)]

pvp (*K* value = 30, 1.334 g) and PdCl₂(PhCN)₂ (384 mg, 1.00 mmol) were mixed in dichloromethane (120 mL) at room temperature, and a 70-mL acetone solution of CoCl₂ (649 mg, 5.00 mmol) was added instantly; the mixture was stirred at room temperature for 2 h. The obtained slurry was filtered, washed three times with acetone, and dried *in vacuo* at 60°C for 12 h.

TABLE I
Oxidative Carbonylation of BPA Catalyzed by Smectite-Supported PdCl₂ and CoCl₂

Run	Bimetal catalyst	Inorganic redox catalyst	PC yield (%)	GPC ^c		
				<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
1-1	Pd-Co-SWN	—	4	1980	2490	1.26
1-2	Pd-Co-SWN	Co(OAc) ₂ ·4H ₂ O ^b	20	2110	2790	1.32
1-3	Pd-Co-SWN + Pd(OAc) ₂ ^a	—	11	2050	2730	1.33

The reaction conditions were as follows: 4.16 mmol of BPA, 0.025 mmol of Pd, 0.125 mmol of Co, 0.625 mmol of (*n*-Bu)₄NBr, 0.625 mmol of 1,4-benzoquinone, 1 g of synthetic zeolite, 10 mL of propylene carbonate, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol. The concentration of Pd was 0.0625 mmol/g of SWN, and the concentration of Co was 0.3125 mmol/g of SWN. *M_n* = number-average molecular weight; *M_w* = weight-average molecular weight.

^a 0.025 mmol.

^b 0.125 mmol.

^c Calculated with a calibration curve for polystyrene.

TABLE II
Oxidative Carbonylation of BPA Catalyzed by Hydrotalcite-Supported PdCl₂ and CoCl₂

Run	Bimetal complex	Metal content (mmol/g of hydrotalcite)	PC yield (%)	GPC ^b		
				<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
2-1	Pd-Co-KW-500	Pd: 0.33 Co: 1.67	55	2550	4200	1.65
2-2	Pd-Co-KW-500 (recycling)	Pd: 0.33 Co: 1.67	0	—	—	—
2-3	Pd-Co-KW-1000	Pd: 0.33 Co: 1.67	56	2600	4410	1.70
2-4	Pd-Co-KW-1000 (recycling)	Pd: 0.33 Co: 1.67	0	—	—	—
2-5	Pd-Co-KW-500	Pd: 0.05 Co: 0.25	0	—	—	—
2-6	Pd-Co-KW-1000	Pd: 0.67 Co: 3.33	54	2510	3930	1.57
2-7	Pd-Co-KW-1000 (recycling)	Pd: 0.67 Co: 3.33	0	—	—	—
2-8	Pd-Co-KW-1000	Pd: 1.33 Co: 2.67	55	2680	4250	1.59
2-9	Pd-Co-KW-1000 (recycling)	Pd: 1.33 Co: 2.67	0	—	—	—
2-10	Pd(OAc) ₂ + Co(OAc) ₂ ·4H ₂ O ^a	—	58	2540	4230	1.67

The reaction conditions were as follows: 4.16 mmol of BPA, 0.025 mmol of Pd, 0.625 mmol of 1,4-benzoquinone, 0.625 mmol of (*n*-Bu)₄NBr, 1 g of synthetic zeolite, 10 mL of propylene carbonate, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol. *M_n* = number-average molecular weight; *M_w* = weight-average molecular weight.

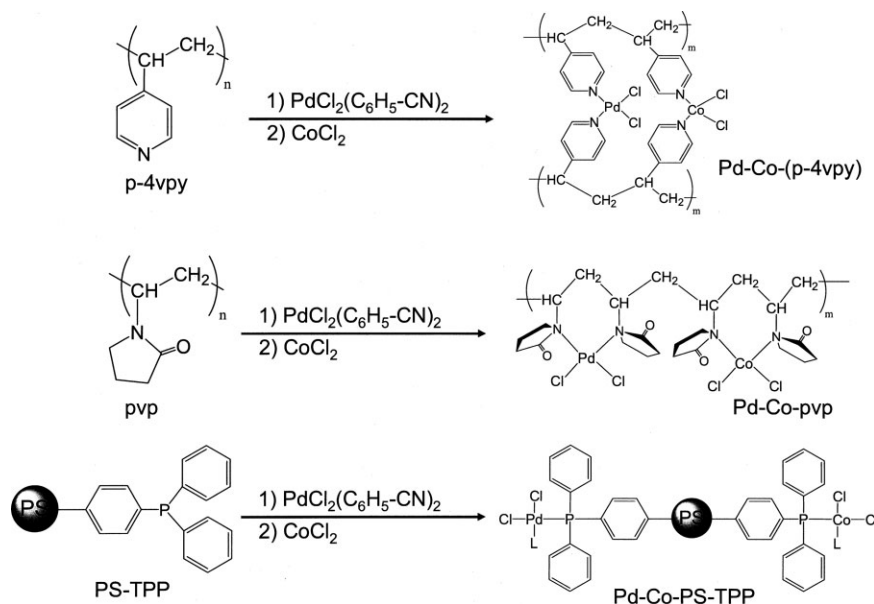
^a 0.025 mmol.

^b Calculated with a calibration curve for polystyrene.

Preparation of the pvp (crosslinked)-supported PdCl₂ and CoCl₂ complex [Pd-Co-pvp(crosslinked)]

Crosslinked pvp (6.669 g) was stirred at room temperature for 2 h in an 80-mL acetone solution of

PdCl₂(PhCN)₂ (384 mg, 1.00 mmol), and then a 35-mL acetone solution of CoCl₂ (649 mg, 5.00 mmol) was added; the mixture was stirred at room temperature for 17 h. The obtained slurry was filtered, washed three times with acetone, and dried *in vacuo* at 60°C for 12 h.



Scheme 3 Preparation of Pd-Co bimetal complexes.

TABLE III
Oxidative Carbonylation of BPA Catalyzed by p-4vpy-Supported PdCl₂ and CoCl₂

Run	Bimetal catalyst	PC yield (%)	GPC ^a		
			<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
3-1	Pd-Co-(p-4vpy)	63	3120	4820	1.54
3-2	Pd-Co-(p-4vpy) (first recycling)	45	2730	3810	1.40
3-3	Pd-Co-(p-4vpy) (second recycling)	12	2110	2620	1.24

The reaction conditions were as follows: 4.16 mmol of BPA, 0.025 mmol of Pd, 0.125 mmol of Co, 0.625 mmol of (*n*-Bu)₄NBr, 0.125 mmol of 1,4-benzoquinone, 1 g of synthetic zeolite, 10 mL of propylene carbonate, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol. The concentration of Pd was 0.793 mmol/g of p-4vpy, and the concentration of Co was 3.96 mmol/g of p-4vpy. *M_n* = number-average molecular weight; *M_w* = weight-average molecular weight.

^a Calculated with a calibration curve for polystyrene.

Polymerization

A typical run was as follows [Run 7-4 (shown later in Table VII)]. Pd-Co-PS-TPP (43.9 mg; 0.005 mmol of Pd and 0.025 mmol of Co), 1,4-benzoquinone (13.5 mg, 0.125 mmol), (*n*-Bu)₄NBr (101.6 mg, 0.3125 mmol), synthetic zeolite (1 g), BPA (950 mg, 4.16 mmol), and propylene carbonate (10 mL) were charged into an SUS-316 30-mL autoclave, and this was followed by the charging of CO (6.0 MPa) and O₂ (0.3 MPa). The autoclave was placed in an oil bath and kept at 100°C.

After 24 h, the reaction was quenched via the cooling of the autoclave in a water bath and gas purging. After filtration of the reaction mixture, the product was isolated by reprecipitation from the reaction mixture by the addition of excess methanol (200 mL) to produce a PC yield of 78% (823 mg).

Confirmation of the recycling potential

After polymerization, the bimetal catalyst was collected with synthetic zeolite, which acted as a

TABLE IV
TON of the p-4vpy-Supported PdCl₂ and CoCl₂ Bimetal Catalyst

Run	BPA/Pd	(<i>n</i> -Bu) ₄ NBr/BPA	(<i>n</i> -Bu) ₄ NBr/Pd	PC yield (%)	TON (mol of CB/mol of Pd)	GPC ^a		
						<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
4-1	333	0.150	50	64	213	3940	6310	1.60
4-2	416	0.150	63	64	266	3950	6800	1.72
4-3	555	0.150	83	63	350	3900	6110	1.57
4-4	832	0.150	125	64	532	3820	5980	1.57
4-5	924	0.150	139	55	508	2700	4010	1.49
4-6	1040	0.150	156	38	395	2450	3380	1.38
4-7	1189	0.150	179	22	262	2390	3280	1.37
4-8	1387	0.150	208	4.4	61	2720	3540	1.30
4-9	1664	0.150	250	0.3	5	4140	5560	1.34
4-10	333	0.075	25	70	233	3220	5370	1.67
4-11	416	0.075	31	71	295	2720	4910	1.81
4-12	555	0.075	42	76	422	3170	6620	2.09
4-13	832	0.075	63	68	566	3210	5590	1.74
4-14	924	0.075	69	57	527	2570	3910	1.52
4-15	1040	0.075	78	39	406	2230	3090	1.39
4-16	1189	0.075	89	20	238	2230	2930	1.31
4-17	1387	0.075	104	6.1	85	2430	3210	1.32
4-18	333	0.075	25	70	233	3220	5370	1.67
4-19	416	0.060	25	48	200	3110	4190	1.35
4-20	555	0.045	25	18	100	2580	3160	1.22
4-21	832	0.030	25	0	0	—	—	—

The reaction conditions were as follows: 4.16 mmol of BPA, a 1,4-benzoquinone/Pd ratio of 25, 1 g of synthetic zeolite, 10 mL of propylene carbonate, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol. The concentration of Pd was 0.793 mmol/g of p-4vpy, and the concentration of Co was 3.96 mmol/g of p-4vpy. CB = produced carbonate bond; *M_n* = number-average molecular weight; *M_w* = weight-average molecular weight.

^a Calculated with a calibration curve for polystyrene.

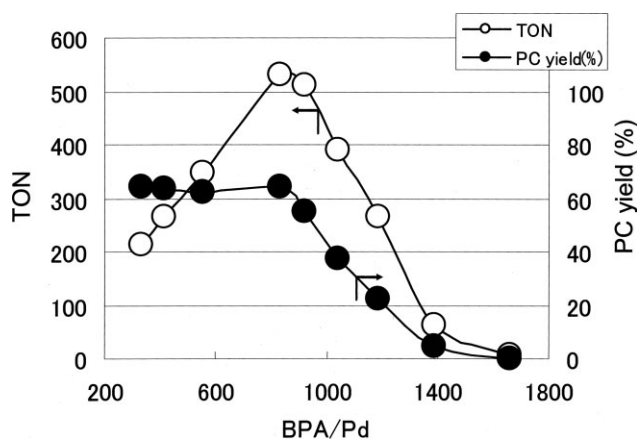


Figure 1 TON and PC yield with Pd–Co–(p-4vpy) [(*n*-Bu)₄NBr/BPA: 0.15; Co/Pd: 5; 1,4-benzoquinone/Pd: 25].

dehydration agent. After the catalyst and synthetic zeolite were dried *in vacuo* at 110°C for 12 h, polymerization was executed again with them.

Measurements

The molecular weights and molecular weight distributions of PCs were determined by gel permeation chromatography (GPC) on a Jasco Gulliver system (Hachioji, Tokyo, Japan) equipped with a Shodex K-804L column (Minatoku, Tokyo, Japan) with polystyrene standards and with chloroform as the eluent.

RESULTS AND DISCUSSION

The catalyst system consists of a Pd catalyst, inorganic and organic redox cocatalysts, an onium salt, and a dehydrating agent (Scheme 1). The formation of a carbonate bond by the Pd catalyst is shown in

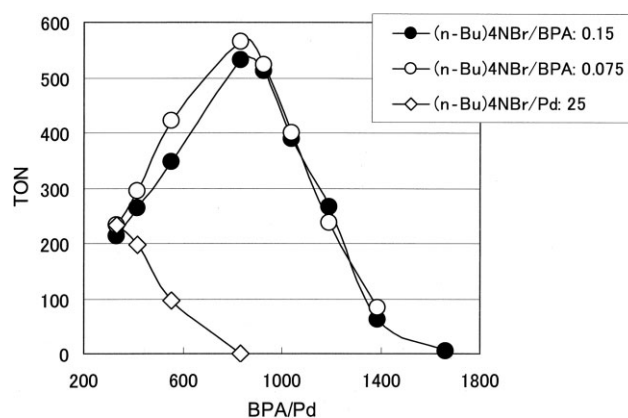


Figure 2 Relationship between BPA/Pd and TON with Pd–Co–(p-4vpy) (Co/Pd: 5; 1,4-benzoquinone/Pd: 25).

Scheme 2. The redox cocatalysts are necessary to form Pd(II) again by oxidation of Pd(0) through reductive elimination of the carbonate structure. As the inorganic redox cocatalyst, Co, which produces a good PC yield,^{5–7} was selected. Through the use of the heterogeneous Pd–Co bimetal catalyst, it is possible to separate the PC solution and the Pd–Co bimetal catalyst after the reaction. The role of the onium salt could be considered the activation of phenols to form palladium phenolates.

Preparation of the bimetal catalyst

When we used smectite, hydrotalcite, PS-TPP, or crosslinked pvp, each of which is an insoluble catalyst support, stirring was conducted at room temperature in an acetone solution of PdCl₂(PhCN)₂ until the brown color of the solution disappeared. Then, an acetone solution of CoCl₂ was added, and the

TABLE V
TON of the Hydrotalcite-Supported PdCl₂ and CoCl₂ Bimetal Catalyst

Run	BPA/Pd	<i>(n</i> -Bu) ₄ NBr/BPA	<i>(n</i> -Bu) ₄ NBr/Pd	PC yield (%)	TON (mol of CB/mol of Pd)	GPC ^a		
						<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
5-1	333	0.150	25	72	240	2870	5390	1.88
5-2	416	0.150	31	64	266	2590	5030	1.94
5-3	555	0.150	42	52	289	2510	4500	1.79
5-4	832	0.150	63	0	0	—	—	—
5-5	185	0.135	25	74	137	2970	6600	2.22
5-6	208	0.120	25	77	160	2760	6240	2.26
5-7	238	0.105	25	77	183	2920	6360	2.18
5-8	277	0.090	25	80	222	2900	6990	2.41
5-9	333	0.075	25	53	176	2580	4710	1.83
5-10	416	0.060	25	7.5	31	2200	3350	1.52
5-11	555	0.045	25	0	0	—	—	—

The reaction conditions were as follows: 4.16 mmol of BPA, 1 g of synthetic zeolite, 10 mL of propylene carbonate, a 1,4-benzoquinone/Pd ratio of 25, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol. The concentration of Pd was 0.67 mmol/g of KW-500, and the concentration of Co was 3.33 mmol/g of KW-500. CB = produced carbonate bond; *M_n* = number-average molecular weight; *M_w* = weight-average molecular weight.

^a Calculated with a calibration curve for polystyrene.

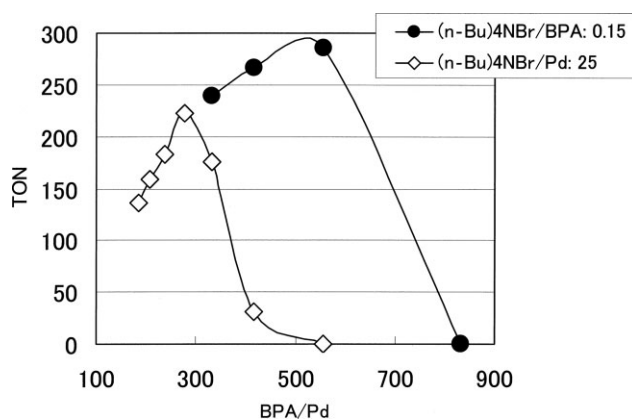


Figure 3 Relationship between BPA/Pd and TON with Pd-Co-KW-500 (Co/Pd: 5; 1,4-benzoquinone/Pd: 25).

mixture was stirred until the cobalt blue color of the solution disappeared. The disappearance of the color implied that the Pd-Co bimetal complex was formed. On the other hand, when we used poly(2-vinylpyridine) or linear pvp, each of which is a soluble catalyst support, a dichloromethane solution of PdCl₂(PhCN)₂ was added to the dichloromethane solution of the catalyst support. As precipitation began to appear immediately, an acetone solution of CoCl₂ was added instantly. In a short time (2 h), the Pd-Co bimetal complex was formed.

Inorganic-layered-compound-supported catalyst

Smectite and hydrotalcite were examined as inorganic layered compounds supporting Pd and Co. With Pd-Co-SWN, the oxidative carbonylation of BPA to PC

TABLE VI
Oxidative Carbonylation of BPA Catalyzed by PS-TPP-Supported PdCl₂ and CoCl₂

Run	Bimetal catalyst	BQ/Pd	PC yield (%)	GPC ^a		
				M_n	M_w	M_w/M_n
6-1	Pd-Co-PS-TPP	25	61	3160	5120	1.62
6-2	Pd-Co-PS-TPP (first recycling)	25	59	3130	4880	1.56
6-3	Pd-Co-PS-TPP (second recycling)	25	0	—	—	—
6-4	Pd-Co-PS-TPP	5	50	2560	3740	1.46
6-5	Pd-Co-PS-TPP (first recycling)	5	45	2780	4200	1.51
6-6	Pd-Co-PS-TPP (second recycling)	5	0	—	—	—

The reaction conditions were as follows: 4.16 mmol of BPA, 0.025 mmol of Pd, 0.125 mmol of Co, 0.625 mmol of (*n*-Bu)₄NBr, 1 g of synthetic zeolite, 10 mL of propylene carbonate, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol. The concentration of Pd was 0.125 mmol/g of PS-TPP, and the concentration of Co was 0.525 mmol/g of PS-TPP. BQ = 1,4-benzoquinone; M_n = number-average molecular weight; M_w = weight-average molecular weight.

^a Calculated with a calibration curve for polystyrene.

TABLE VII
TON of the PS-TPP-Supported PdCl₂ and CoCl₂ Bimetal Catalyst

Run	BPA/Pd	PC yield (%)	TON (mol of CB/mol of Pd)	GPC ^a		
				M_n	M_w	M_w/M_n
7-1	333	72	239	3460	5820	1.68
7-2	416	55	227	2440	3650	1.50
7-3	555	74	412	4300	17,900	4.16
7-4	832	78	647	4030	8950	2.22
7-5	924	59	548	2830	4340	1.53
7-6	1040	46	473	2570	3690	1.44
7-7	1189	24	282	2550	3330	1.31
7-8	1387	19	268	2590	3390	1.31

The reaction conditions were as follows: 4.16 mmol of BPA, a Co/Pd ratio of 5, a 1,4-benzoquinone/Pd ratio of 25, an (*n*-Bu)₄NBr/BPA ratio of 0.075, 1 g of synthetic zeolite, 10 mL of propylene carbonate, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol. The concentration of Pd was 0.125 mmol/g of PS-TPP, and the concentration of Co was 0.525 mmol/g of PS-TPP. CB = produced carbonate bond; M_n = number-average molecular weight; M_w = weight-average molecular weight.

^a Calculated with a calibration curve for polystyrene.

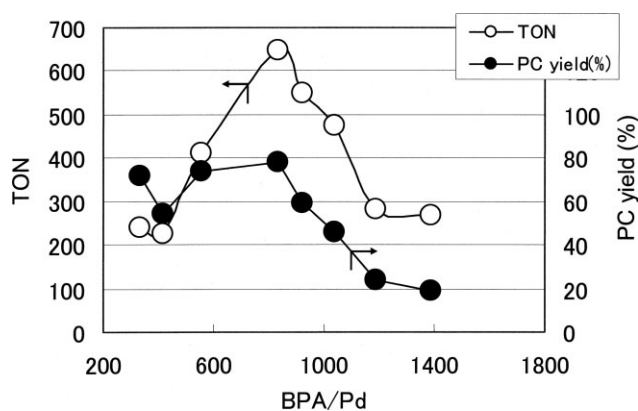


Figure 4 TON and PC yield with Pd–Co–PS–TPP [(*n*-Bu)₄NBr/BPA: 0.075; Co/Pd: 5; 1,4-benzoquinone/Pd: 25].

was conducted. The metal contents of Pd and Co were made to be 0.0625 and 0.3125 mmol/g of SWN, respectively, by consideration of the fact that the cation-exchange capacity of SWN is about 0.8 mequiv/g.⁸ The results are summarized in Table I. Pd–Co–SWN was found to hardly produce catalytic activity, although it produced PC when Co(OAc)₂·H₂O or Pd(OAc)₂ was added. It is thought that both Pd and Co have catalytic ability, but the interaction between Pd and Co is weak when they exist only in Pd–Co–SWN.

Pd and Co can be supported on hydrotalcite as they are on smectite. With Pd–Co–KW-500 and Pd–Co–KW-1000, the oxidative carbonylation of BPA to PC and its recycling potential were examined. The cation-exchange capacity of hydrotalcite is about 10 times greater than that of smectite. The results are summarized in Table II. Unlike the case in which a smectite-supported catalyst was used, the hydrotalcite-supported catalyst showed catalytic activity without the addition of an inorganic re-

dox cocatalyst. However, when the metal content of the catalyst was reduced, catalytic activity was not observed (Run 2-5). It is thought that when the distance of Pd and Co on the same carrier shortens, an interaction between Pd and Co occurs, providing catalytic activity to the Pd–Co bimetal compound. The reason that the smectite-supported catalyst Pd–Co–SWN was found to hardly produce catalytic activity seems to be that its metal content was low and the distance between Pd and Co was long. On the other hand, in the hydrotalcite case, the PC yield did not change when the metal content (both Pd and Co) of the catalyst was increased by twice the amount (Run 2-6). When the metal content (only Pd) was increased even more, catalytic activity was observed, and the necessary amount of Co was almost 2 times that of Pd (Run 2-8). Its PC yield was the same as that when the homogeneous catalyst system of Pd(OAc)₂ and Co(OAc)₂·4H₂O was used. However, Pd–Co–KW did not have recycling potential at all (Runs 2-2, 2-4, 2-7, and 2-9).

Polymer-supported catalyst

p-4vpy, PS-TPP, and pvp were examined as polymers supporting Pd and Co. The heterogeneous Pd–Co bimetal catalysts were prepared according to Scheme 3. The structures of the complexes (Scheme 3) were not identified.

With Pd–Co–(p-4vpy), the oxidative carbonylation of BPA to PC and its recycling potential were examined. The results are summarized in Table III. The bimetal catalyst was found to have catalytic activity. It yielded PC as far as the second recycling process, although the yield decreased gradually. To examine the PC yield and TON, BPA/Pd was increased by a reduction of the feed of the bimetal catalyst to the autoclave. TON was based

TABLE VIII
Oxidative Carbonylation of BPA Catalyzed by pvp-Supported PdCl₂ and CoCl₂

Run	Bimetal catalyst	BQ/Pd	PC yield (%)	GPC ^c		
				<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
8-1	Pd–Co–pvp(linear) ^a	25	58	2680	3850	1.44
8-2	Pd–Co–pvp(linear) (recycling)	25	0	—	—	—
8-3	Pd–Co–pvp(linear)	5	63	2870	4230	1.47
8-4	Pd–Co–pvp(linear) (recycling)	5	0	—	—	—
8-5	Pd–Co–pvp(crosslinked) ^b	25	55	2880	4140	1.44
8-6	Pd–Co–pvp(crosslinked) (recycling)	25	0	—	—	—
8-7	Pd–Co–pvp(crosslinked)	5	56	2670	3840	1.44
8-8	Pd–Co–pvp(crosslinked) (recycling)	5	0	—	—	—

The reaction conditions were as follows: 4.16 mmol of BPA, 0.025 mmol of Pd, 0.125 mmol of Co, 0.625 mmol of (*n*-Bu)₄NBr, 1 g of synthetic zeolite, 10 mL of propylene carbonate, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. BQ = 1,4-benzoquinone; *M_n* = number-average molecular weight; *M_w* = weight-average molecular weight.

^a The concentration of Pd was 0.750 mmol/g of pvp, and the concentration of Co was 3.75 mmol/g of pvp.

^b The concentration of Pd was 0.150 mmol/g of pvp, and the concentration of Co was 0.75 mmol/g of pvp.

^c Calculated with a calibration curve for polystyrene.

TABLE IX
TON of the pvp (Linear)-Supported PdCl₂ and CoCl₂ Bimetal Catalyst

Run	BPA/Pd	PC yield (%)	TON (mol of CB/mol of Pd)	GPC ^a		
				<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
9-1	333	72	239	3420	5590	1.63
9-2	416	70	290	4000	6960	1.74
9-3	555	81	450	4430	19,100	4.31
9-4	832	78	645	4080	11,900	2.92
9-5	924	79	731	3430	5870	1.71
9-6	1040	73	758	3290	5480	1.67
9-7	1189	70	835	3080	5030	1.63
9-8	1388	65	906	2870	4480	1.56
9-9	1664	78	1290	3680	6580	1.79
9-10	2080	59	1225	2770	4220	1.52
9-11	2773	29	790	2430	3250	1.34
9-12	4160	8	320	2690	3500	1.30

The reaction conditions were as follows: 4.16 mmol of BPA, a Co/Pd ratio of 5, a 1,4-benzoquinone/Pd ratio of 25, an (*n*-Bu)₄NBr/BPA ratio of 0.075, 1 g of synthetic zeolite, 10 mL of propylene carbonate, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. The concentration of Pd was 0.750 mmol/g of pvp, and the concentration of Co was 3.75 mmol/g of pvp. CB = produced carbonate bond; *M_n* = number-average molecular weight; *M_w* = weight-average molecular weight.

^a Calculated with a calibration curve for polystyrene.

on the moles of added Pd and the moles of the produced carbonate bond in isolated PC. It was calculated with the following equations:

$$\text{TON} = \frac{\text{(Moles of the produced carbonate bond)}}{\text{(Moles of the added Pd)}}$$

$$\begin{aligned} &\text{Moles of the produced carbonate bond} \\ &= \frac{\text{(Weight of the isolated PC)}}{\text{[Molecular weight of the PC unit(254.3)]}} \end{aligned}$$

The results are summarized in Table IV. The PC yield and TON are plotted versus BPA/Pd in Figure 1. Until BPA/Pd rose to about 900, the PC yield remained almost constant, whereas TON increased. When BPA/Pd exceeded 900, the PC yield decreased, and TON decreased as well. The cases in which the feed of the onium salt (*n*-Bu)₄NBr was decreased or not decreased along with a decreasing amount of the bimetal catalyst (onium salt/Pd: constant) were compared. Figure 2 shows the relationship between BPA/Pd and TON. When the feed of

TABLE X
TON of the pvp (Crosslinked)-Supported PdCl₂ and CoCl₂ Bimetal Catalyst

Run	BPA/Pd	PC yield (%)	TON (mol of CB/mol of Pd)	GPC ^a		
				<i>M_n</i>	<i>M_w</i>	<i>M_w/M_n</i>
10-1	333	79	263	3920	6500	1.66
10-2	416	80	334	4450	7710	1.73
10-3	555	78	430	4310	15,700	3.64
10-4	832	77	636	3920	11,700	2.98
10-5	924	67	618	2910	4560	1.57
10-6	1040	71	736	2940	4600	1.56
10-7	1189	62	737	3820	7060	1.85
10-8	1388	72	992	3540	6180	1.75
10-9	1664	75	1246	3900	7300	1.87
10-10	2080	70	1462	3320	5510	1.66
10-11	2773	15	402	2340	3040	1.30
10-12	4160	1	58	3000	4010	1.34

The reaction conditions were as follows: 4.16 mmol of BPA, a Co/Pd ratio of 5, a 1,4-benzoquinone/Pd ratio of 25, an (*n*-Bu)₄NBr/BPA ratio of 0.075, 1 g of synthetic zeolite, 10 mL of propylene carbonate, 6.0 MPa of CO, 0.3 MPa of O₂, 100°C, and 24 h. The concentration of Pd was 0.150 mmol/g of pvp, and the concentration of Co was 0.75 mmol/g of pvp. CB = produced carbonate bond; *M_n* = number-average molecular weight; *M_w* = weight-average molecular weight.

^a Calculated with a calibration curve for polystyrene.

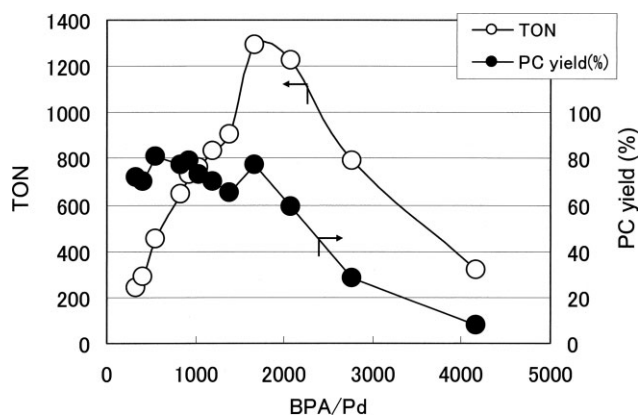


Figure 5 TON and PC yield with Pd-Co-pvp(linear) [$(n\text{-Bu})_4\text{NBr}$ /BPA: 0.075; Co/Pd: 5; 1,4-benzoquinone/Pd: 25].

the onium salt was decreased along with a reduction of the bimetal catalyst, the PC yield and TON decreased rapidly. It is thought that a certain constant amount of the onium salt is necessary for BPA to yield a high TON. The maximum TON of Pd-Co-(p-4vpy) was 566 (Run 4-13).

This examination was similarly executed for Pd-Co-KW-500, whose catalyst support was hydrotalcite, to compare the maximum TONs. The results are summarized in Table V and Figure 3. The maximum TON of Pd-Co-KW-500 was 289 (Run 5-3).

With Pd-Co-PS-TPP, the oxidative carbonylation of BPA to PC and its recycling potential were examined. The results are summarized in Table VI. The bimetal catalyst was found to have catalytic activity and maintained the PC yield in the first recycling process (Runs 6-2 and 6-5). However, in the second recycling process, catalytic activity was not seen at all (Runs 6-3 and 6-6). To examine the PC yield and TON, BPA/Pd was increased while the feed of the bimetal catalyst to the autoclave was reduced. The results are summarized in Table VII and Figure 4. The maximum TON of Pd-Co-PS-TPP was 647 (Run 7-4).

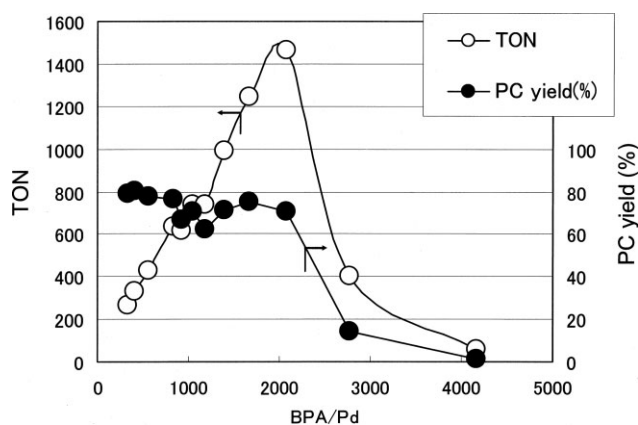


Figure 6 TON and PC yield with Pd-Co-pvp(cross-linked) [$(n\text{-Bu})_4\text{NBr}$ /BPA: 0.075; Co/Pd: 5; 1,4-benzoquinone/Pd: 25].

TABLE XI
Relationship Between the Catalyst Support of the Heterogeneous Pd-Co Bimetal Catalyst, the Recycling Potential, and the Maximum TON

Catalyst support	Recycling potential	Maximum TON
Hydrotalcite	No	286
p-4vpy	Yes	566
PS-TPP	Yes	647
Linear pvp	No	1290
Crosslinked pvp	No	1462

With Pd-Co-pvp, the oxidative carbonylation of BPA to PC and its recycling potential were examined. The results are summarized in Table VIII. Both the linear type and crosslinked type were found to have catalytic activity. However, they did not have recycling potential at all. Similarly, BPA/Pd was increased while the feed of the bimetal catalysts to the autoclave was reduced to examine the PC yield and TON. The results are summarized in Tables IX and X and Figures 5 and 6. The bimetal catalysts showed high TONs. The maximum TONs of the linear type and the crosslinked type were 1290 and 1462, respectively (Runs 9-9 and 10-10).

The relationships between the catalyst support of the heterogeneous Pd-Co bimetal catalyst, the recycling potential, and the maximum TON are shown in Table XI.

CONCLUSIONS

With propylene carbonate, a halogen-free solvent, PCs were prepared by the oxidative carbonylation of BPA and CO, which was catalyzed by a heterogeneous bimetal complex consisting of Pd (the main catalyst) and Co (an inorganic redox cocatalyst). Smectite, hydrotalcite, p-4vpy, PS-TPP, and pvp were used as catalyst supports of the bimetal catalyst. Pd-Co-(p-4vpy) and Pd-Co-PS-TPP showed recycling potential, whereas Pd-Co-pvp, though not having recycling potential, yielded a high TON with a maximum of 1462.

References

- Freitag, D.; Fengler, G.; Morbitzer, L. *Angew Chem Int Ed Engl* 1991, 30, 1598.
- Schnell, H. *Chemistry and Physics of Polycarbonate*; Interscience: New York, 1964.
- Okuyama, K.; Sugiyama, J.; Nagahata, R.; Asai, M.; Ueda, M.; Takeuchi, K. *Macromolecules* 2003, 36, 6953.
- Ishii, H.; Goyal, M.; Ueda, M.; Asai, M.; Takeuchi, K.; Asai, M. *Macromol Rapid Commun* 2001, 22, 376.
- Okamoto, M.; Sugiyama, J.; Takeuchi, K. *J Appl Polym Sci* 2007, 106, 2840.
- Okamoto, M.; Ishii, H.; Sugiyama, J. *J Appl Polym Sci* 2008, 109, 758.
- Okamoto, M.; Sugiyama, J.; Yamamoto, T. *J Appl Polym Sci* 2008, 110, 3902.
- Ishido, T. *J Geogr* 2005, 114, 885.