

Heterogeneous Pd Catalyst for Oxidative Carbonylation of Bisphenol A to Polycarbonate

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ABSTRACT: Polycarbonates (PCs) were prepared by oxidative carbonylation of bisphenol A and carbon monoxide, using a Pd-polybipyridyl complex, Pd-polyvinylpyridine complex, smectite-supported Pd complex, or hydrotalcite-supported Pd complex as a heterogeneous Pd catalyst to separate the PC solution and the Pd catalyst after the reaction. Propylene carbonate was used as a

halogen-free solvent. When $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was used as the inorgano-redox catalyst, all of the Pd compounds gave a good PC yield with the recycling potential of the catalyst. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3902–3907, 2008

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 by the solvent method of bisphenol A (BPA) with phosgene, and the other is by the melt method of BPA with diphenyl carbonate.² However, there is a problem with the solution method that used halogenated solvents, which negatively affect the environment. The melt method includes a melt process that can be an environmentally favorable technology from the point of not using a solvent, but a large amount of heat is needed. Moreover, it includes additional phenol recycling and DPC reproducing processes. Therefore, a more environmentally favorable technology for PC synthesis must be developed other than the melt process. Recently, a new PC producing technology, a modified solution method, has been attracting interest to prepare PC directly from carbon monoxide and BPA using Pd compound/redox catalyst/onium halide systems.^{3,4} A study reported that, via oxidative carbonylation, the molecular weight of PC obtained with these catalyst systems was high, and the highest number-average molecular weight (M_n)

of PC was 9400. However, dichloromethane, a halogenated solvent that negatively affects the environment, was used in it.

In previous articles, we reported that halogen-free, propylene carbonate is a peculiar solvent for oxidative carbonylation⁵ and introduced several homogeneous Pd catalysts for the oxidative carbonylation reaction.⁶ This article describes oxidative carbonylation of BPA to PC using propylene carbonate, catalyzed by heterogeneous Pd compounds. It is expected that the heterogeneous catalyst can be recycled after polymerization. As the heterogeneous catalyst, Pd catalysts that are supported by polymers (polybipyridyl and polyvinylpyridine) and Pd catalysts that are supported by inorganic layered compounds (smectite and hydrotalcite) were used to examine their PC yields and catalyst recycling potential.

EXPERIMENTS

Materials

Poly(2,2'-bipyridine-5,5'-diyl) and poly(6,6'-dimethyl-2,2'-bipyridine-5,5'-diyl) prepared according to previous reports.⁷ Poly(2-vinylpyridine), poly(4-vinylpyridine), and poly(6-methyl-2-vinylpyridine) were supplied by Koei Chemical. (Narashino, Chiba, Japan). The synthetic smectite used was Lucentite SWN manufactured by Co-op Chemical. (Chiyodaku, Tokyo, Japan). The synthetic hydrotalcites used were KW-500 ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) and KW-1000 ($\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$) manufactured

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TABLE I
Oxidative Carbonylation of BPA Catalyzed by Supported Polymer-Supported Pd^a

Run	Pd complex	Redox catalyst	PC yield (%)	GPC ^b		
				M_n	M_w	M_w/M_n
1-1	1a	Ce(OAc) ₃ ·H ₂ O	0	–	–	–
1-2	1a	Mn(OAc) ₂ ·4H ₂ O	8	2,050	3,170	1.55
1-3	1a	Co(OAc) ₂ ·4H ₂ O	58	2,470	3,970	1.61
1-4	1a	Mn(TMHD) ₃ ^c	81	2,480	5,880	2.37
1-5	1b	Ce(OAc) ₃ ·H ₂ O	0	–	–	–
1-6	1b	Mn(OAc) ₂ ·4H ₂ O	33	1,770	2,860	1.62
1-7	1b	Co(OAc) ₂ ·4H ₂ O	67	2,240	3,880	1.73
1-8	1b	Mn(TMHD) ₃	49	2,140	4,260	1.99
1-9	2a	Ce(OAc) ₃ ·H ₂ O	65	2,790	4,900	1.76
1-10	2a	Mn(OAc) ₂ ·4H ₂ O	1	–	–	–
1-11	2a	Co(OAc) ₂ ·4H ₂ O	60	2,850	4,620	1.62
1-12	2a	Mn(TMHD) ₃	79	2,200	5,170	2.35
1-13	2b	Ce(OAc) ₃ ·H ₂ O	0	–	–	–
1-14	2b	Mn(OAc) ₂ ·4H ₂ O	0	–	–	–
1-15	2b	Co(OAc) ₂ ·4H ₂ O	67	2,480	4,400	1.77
1-16	2b	Mn(TMHD) ₃	54	3,230	6,130	1.90
1-17	3	Ce(OAc) ₃ ·H ₂ O	0	–	–	–
1-18	3	Mn(OAc) ₂ ·4H ₂ O	0	–	–	–
1-19	3	Co(OAc) ₂ ·4H ₂ O	60	2,480	4,400	1.77
1-20	3	Mn(TMHD) ₃	14	2,060	4,080	1.98
1-21	Pd(OAc) ₂	Co(OAc) ₂ ·4H ₂ O	58	2,540	4,230	1.67

^a Reaction conditions: BPA (4.16 mmol), Pd (0.025 mmol), redox catalyst (0.125 mmol), 1,4-benzoquinone (0.625 mmol), (*n*-Bu)₄NBr (0.625 mmol), synthetic zeolite (1 g), propylene carbonate (10 mL), CO (6.0 MPa), O₂ (0.3 MPa), 100°C, 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by adding excess methanol.

^b Calculated by using calibration curve for polystyrene.

^c TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionate.

by Kyowa Chemical Industry. (Sakaide, Kagawa, 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 {poly(2,2'-bipyridine-5,5'-diyl)}palladium(II) dichloride (**1a**)

Poly(2,2'-bipyridine-5,5'-diyl) (73 mg) was stirred at room temperature for 18 h in 25 mL of dichloromethane solution of PdCl₂(PhCN)₂ (187 mg, 0.488 mmol). The obtained slurry was filtered, washed three times with dichloromethane, and dried under vacuum at 60°C for 12 h. Yield: 128 mg.

Preparation of {poly(2-vinylpyridine)}palladium(II) dichloride (**2a**)

Poly(2-vinylpyridine) (537 mg) and PdCl₂(PhCN)₂ (978 mg, 2.55 mmol) were mixed in dichloromethane (80 mL) at room temperature for 15 min. The obtained slurry was filtered, washed three times with dichloromethane, and dried under vacuum at 60°C for 12 h. Yield: 962 mg.

Preparation of smectite-supported Pd complex (PdCl₂-SWN)

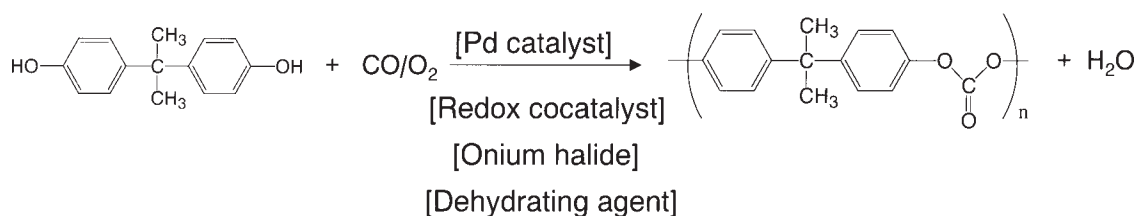
Lucentite SWN (4.00 g) was stirred at room temperature for 24 h in a 60 mL of dichloromethane solution of PdCl₂(PhCN)₂ (192 mg, 0.50 mmol). The obtained slurry was filtered, washed three times with dichloromethane, and dried under vacuum at 60°C for 12 h.

Preparation of hydrotalcite-supported Pd complex (PdCl₂-KW-500)

KW-500 (500 mg) was stirred at room temperature for 24 h in a 60 mL of dichloromethane solution of PdCl₂(PhCN)₂ (384 mg, 1.0 mmol). The obtained slurry was filtered, washed three times with dichloromethane, and dried under vacuum at 60°C for 12 h.

Polymerization

A typical run was as follows (Run 1-11 in Table I). **2a** (9.7 mg), Co(OAc)₂·4H₂O (31.1 mg, 0.125 mmol), 1,4-benzoquinone (67.6 mg, 0.625 mmol), (*n*-Bu)₄NBr (201.5 mg, 0.625 mmol), synthetic zeolite (1 g), BPA (950 mg, 4.16 mmol), and propylene carbonate (10 mL) were charged to a 30 mL SUS-316 in an



Scheme 1 Oxidative carbonylation of BPA.

autoclave followed by charging 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 by cooling the autoclave in a water bath and by gas purging. After filtering the reaction mixture, the product was isolated by reprecipitation from the reaction mixture by adding excess methanol (200 mL) to give a PC yield of 60% (638 mg).

Measurement

The molecular weight and molecular weight distribution of PCs were determined using a JASCO Gulliver GPC equipped with a SHODEX K-804L column, using polystyrene as standards and chloroform as eluent.

RESULTS AND DISCUSSION

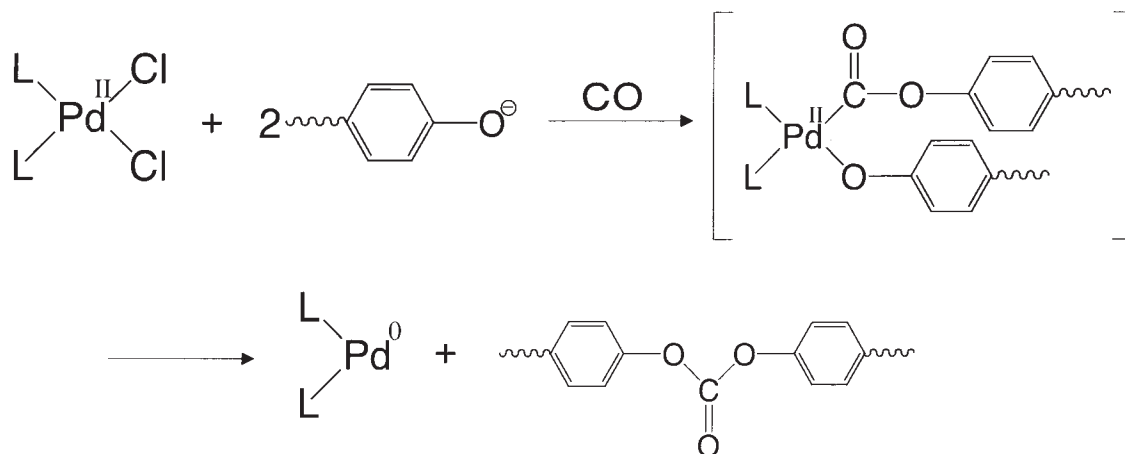
The catalyst system consists of a Pd catalyst, inorganic and organic redox cocatalysts, onium salt, and dehydrating agent (Scheme 1). The formation of carbonate bond by the Pd catalyst is shown in Scheme 2. The redox cocatalysts are necessary to form Pd(II) again by oxidation of Pd(0) which was formed by reductive elimination of the carbonate structure. By using the heterogeneous Pd catalyst, it is possible to separate the PC solution and the Pd catalyst after the reaction. The role of onium salt can be consid-

ered to activate phenols to form palladium phenolates.

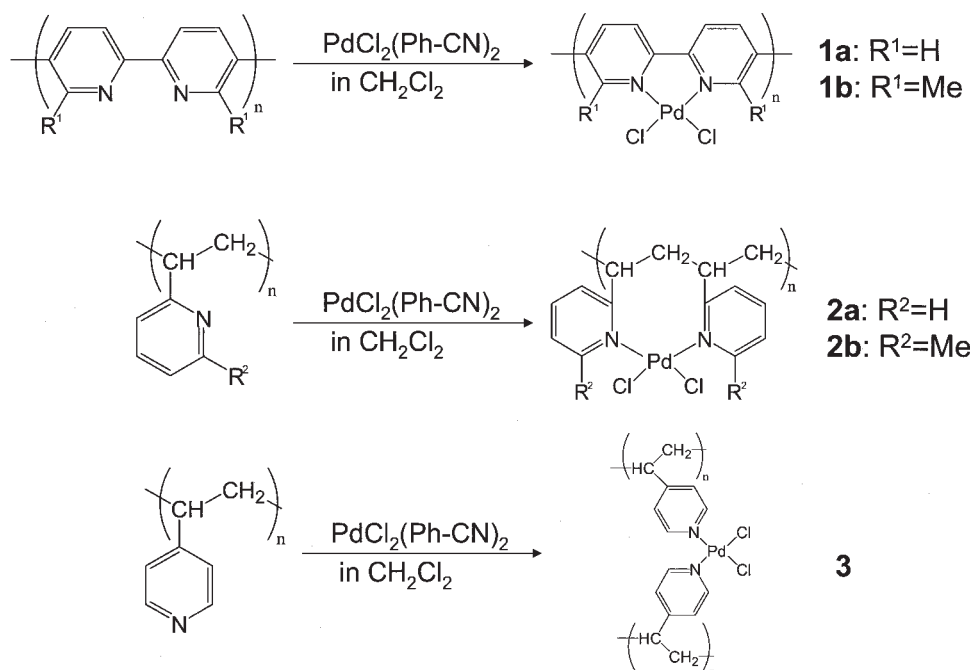
Polymer-supported catalyst

As the Pd-supporting polymer, polybipyridyl and polyvinylpyridine were examined. The heterogeneous Pd catalysts were prepared according to Scheme 3. Poly(2,2'-bipyridine-5,5'-diyl) did not dissolve in dichloromethane. However, when it was stirred at room temperature for 18 h in a dichloromethane solution of PdCl₂(PhCN)₂, the brown color of the solution gradually disappeared. This implies that the complex is formed. On the contrary, poly(2-vinylpyridine) and poly(4-vinylpyridine) dissolved in dichloromethane and the reaction progressed quickly. The color of the solution disappeared completely in 15 min. The structures of the complexes (Scheme 3) were not identified.

Then, using these polymer-supported catalysts, oxidative carbonylation of BPA to PC was examined. The results are summarized in Table I. Also, **1b**, which is a derivative of **1a** with methyl groups at the 6,6'-position of 2,2'-bipyridine-5,5'-diyl moiety, was examined. According to previous reports,^{4,6} when using the homogeneous catalyst, the Pd/6,6'-dimethyl-2,2'-bipyridyl complex is more effective than the Pd/2,2'-bipyridyl complex that lacks the substituents at the 6,6'-position. When using the heterogeneous catalyst, however, the substituent effect



Scheme 2 Formation of carbonate bond by Pd catalyst.



Scheme 3 Preparation of Pd complexes.

was not generated while, with the Pd/poly(2,2'-bipyridyl) complex, PC was produced. In this reaction, when Pd(II) is reduced to Pd(0), palladium comes off the ligand forming the cluster and its activity is lost. It is considered that when using the homogeneous catalyst, the substituents of the carbon neighbor to the nitrogen disturb the palladium coming off the ligand. On the contrary, with the heterogeneous catalyst, palladium originally has a difficulty coming off the ligand. With the use of Co(OAc)₂·H₂O, the inorgano-redox catalyst, all of the polymer-supported catalysts gave good PC yields (58% or more). This result is the same as the case of the homogeneous catalysts using propylene carbonate as a halogen-free solvent.⁶

After polymerization, the polymer-supported catalyst was collected with synthetic zeolite that is a

dehydration agent to confirm the recycling potential of the catalyst. After they were dried *in vacuo* at 110°C for 12 h, polymerization was executed again using them. The results are summarized in Table II. Both **1a** and **2a** gave low PC yields (about 10%) with Co(OAc)₂·H₂O.

Inorganic layered compound-supported catalyst

As inorganic layered compounds that support Pd, smectite, and hydrotalcite were examined. Using PdCl₂-SWN or Pd(OAc)₂-SWN, oxidative carbonylation of BPA to PC was conducted and the recycling potential of the catalyst was examined. The results are summarized in Table III. Both PdCl₂-SWN and Pd(OAc)₂-SWN were found to give catalytic activity when using Co(OAc)₂·4H₂O, Ce(OAc)₃·H₂O,

TABLE II
Recycling Potential of Polymer-Supported PdCl₂ Catalyst^a

Run	Pd complex	Redox catalyst	PC yield (%)	GPC ^b		
				M _n	M _w	M _w /M _n
2-1	1a	Co(OAc) ₂ ·4H ₂ O	58	2,470	3,970	1.61
2-2	1a (Recycling)	Co(OAc) ₂ ·4H ₂ O	11	1,970	2,740	1.39
2-3	2a	Co(OAc) ₂ ·4H ₂ O	60	2,850	4,620	1.62
2-4	2a (Recycling)	Co(OAc) ₂ ·4H ₂ O	14	2,050	2,970	1.45
2-5	2a	Ce(OAc) ₃ ·H ₂ O	65	2,790	4,900	1.76
2-6	2a (Recycling)	Ce(OAc) ₃ ·H ₂ O	4	–	–	–

^a Reaction conditions: BPA (4.16 mmol), Pd (0.025 mmol), redox catalyst (0.125 mmol), 1,4-benzoquinone (0.625 mmol), (*n*-Bu)₄NBr (0.625 mmol), synthetic zeolite (1 g), propylene carbonate (10 mL), CO (6.0 MPa), O₂ (0.3 MPa), 100°C, 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by adding excess methanol.

^b Calculated by using calibration curve for polystyrene.

TABLE III
Oxidative Carbonylation of BPA Catalyzed by Smectite-Supported Pd^a

Run	Pd complex	Redox catalyst	PC yield (%)	GPC ^b		
				M_n	M_w	M_w/M_n
3-1	PdCl ₂ -SWN	Co(OAc) ₂ ·4H ₂ O	66	3,300	6,340	1.92
3-2	PdCl ₂ -SWN (1st recycling)	Co(OAc) ₂ ·4H ₂ O	60	2,890	4,320	1.49
3-3	PdCl ₂ -SWN (2nd recycling)	Co(OAc) ₂ ·4H ₂ O	46	2,370	3,500	1.48
3-4	PdCl ₂ -SWN	Ce(OAc) ₃ ·H ₂ O	57	2,920	4,580	1.57
3-5	PdCl ₂ -SWN (1st recycling)	Ce(OAc) ₃ ·H ₂ O	32	2,360	4,450	1.89
3-6	PdCl ₂ -SWN (2nd recycling)	Ce(OAc) ₃ ·H ₂ O	5	2,150	3,070	1.43
3-7	PdCl ₂ -SWN	Mn(OAc) ₂ ·4H ₂ O	74	3,450	6,150	1.78
3-8	PdCl ₂ -SWN (1st recycling)	Mn(OAc) ₂ ·4H ₂ O	3	Insoluble	Insoluble	–
3-9	PdCl ₂ -SWN	Mn(TMHD) ₃ ^c	50	3,100	4,900	1.58
3-10	PdCl ₂ -SWN (1st recycling)	Mn(TMHD) ₃	18	Insoluble	Insoluble	–
3-11	Pd(OAc) ₂ -SWN	Co(OAc) ₂ ·4H ₂ O	61	2,870	4,670	1.63
3-12	Pd(OAc) ₂ -SWN (1st recycling)	Co(OAc) ₂ ·4H ₂ O	51	2,300	3,620	1.57
3-13	Pd(OAc) ₂ -SWN (2nd recycling)	Co(OAc) ₂ ·4H ₂ O	23	2,510	3,880	1.55
3-14	Pd(OAc) ₂ -SWN	Ce(OAc) ₃ ·H ₂ O	71	3,130	5,540	1.77
3-15	Pd(OAc) ₂ -SWN (1st recycling)	Ce(OAc) ₃ ·H ₂ O	0	–	–	–
3-16	Pd(OAc) ₂ -SWN	Mn(OAc) ₂ ·4H ₂ O	68	3,330	5,980	1.80
3-17	Pd(OAc) ₂ -SWN (1st recycling)	Mn(OAc) ₂ ·4H ₂ O	6	Insoluble	Insoluble	–
3-18	Pd(OAc) ₂ -SWN	Mn(TMHD) ₃	39	3,290	5,840	1.78
3-19	Pd(OAc) ₂ -SWN (1st recycling)	Mn(TMHD) ₃	19	Insoluble	Insoluble	–

^a Reaction conditions: BPA (4.16 mmol), Pd (0.025 mmol), redox catalyst (0.125 mmol), 1,4-benzoquinone (0.625 mmol), (*n*-Bu)₄NBr (0.625 mmol), synthetic zeolite (1 g), propylene carbonate (10 mL), CO (6.0 MPa), O₂ (0.3 MPa), 100°C, 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by adding excess methanol.

^b Calculated by using calibration curve for polystyrene.

^c TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionate.

Mn(OAc)₂·4H₂O, or Mn(TMHD)₃ (TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionate), each of which is an inorgano-redox catalyst. However, when testing the recycling potential for these inorgano-redox catalysts, an insoluble compound was produced in the case of the manganese cocatalyst (Run 3-8, 3-10). This insoluble compound seems to be a crosslinked

polymer. When using Ce(OAc)₃·H₂O, the recycling potential was obtained for PdCl₂-SWN, but not for Pd(OAc)₂-SWN (Run 3-15). When using Co(OAc)₂·4H₂O, both PdCl₂-SWN and Pd(OAc)₂-SWN showed recycling potential. They gave a PC yield also in the second recycling process although the yield decreased gradually (Run 3-3, 3-13).

TABLE IV
Oxidative Carbonylation of BPA Catalyzed by Hydrotalsite-Supported Pd^a

Run	Pd complex	Redox catalyst	PC yield (%)	GPC ^b		
				M_n	M_w	M_w/M_n
4-1	PdCl ₂ -KW-500	Ce(OAc) ₂ ·H ₂ O	0	–	–	–
4-2	PdCl ₂ -KW-500	Mn(OAc) ₂ ·4H ₂ O	0	–	–	–
4-3	PdCl ₂ -KW-500	Co(OAc) ₂ ·4H ₂ O	54	2,550	4,040	1.58
4-4	PdCl ₂ -KW-500 (recycling)	Co(OAc) ₂ ·4H ₂ O	24	2,450	3,880	1.58
4-5	PdCl ₂ -KW-500	Mn(TMHD) ₃ ^c	48	3,240	5,910	1.82
4-6	PdCl ₂ -KW-500 (recycling)	Mn(TMHD) ₃	31	Insoluble	Insoluble	–
4-7	PdCl ₂ -KW-1000	Ce(OAc) ₂ ·H ₂ O	0	–	–	–
4-8	PdCl ₂ -KW-1000	Mn(OAc) ₂ ·4H ₂ O	0	–	–	–
4-9	PdCl ₂ -KW-1000	Co(OAc) ₂ ·4H ₂ O	54	2,620	4,190	1.60
4-10	PdCl ₂ -KW-1000 (recycling)	Co(OAc) ₂ ·4H ₂ O	44	2,450	3,580	–
4-11	PdCl ₂ -KW-1000	Mn(TMHD) ₃	54	3,070	5,840	1.90
4-12	PdCl ₂ -KW-1000 (recycling)	Mn(TMHD) ₃	8	Insoluble	Insoluble	–

^a Reaction conditions: BPA (4.16 mmol), Pd (0.025 mmol), redox catalyst (0.125 mmol), 1,4-benzoquinone (0.625 mmol), (*n*-Bu)₄NBr (0.625 mmol), synthetic zeolite (1 g), propylene carbonate (10 mL), CO (6.0 MPa), O₂ (0.3 MPa), 100°C, 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by adding excess methanol.

^b Calculated by using calibration curve for polystyrene.

^c TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionate.

Pd can be supported on hydrotalcite as it is on smectite. Using PdCl₂-KW-500 or PdCl₂-KW-1000, oxidative carbonylation of BPA to PC and its recycling potential were examined. The results are summarized in Table IV. When using Co(OAc)₂·4H₂O or Mn(TMHD)₃, each of which is an inorgano-redox catalyst, PC was produced. However, it was not produced when using Ce(OAc)₃·H₂O or Mn(OAc)₂·4H₂O. With Co(OAc)₂·4H₂O, both of PdCl₂-KW-500 and PdCl₂-KW-1000 showed recycling potential. When using Mn(TMHD)₃, an insoluble compound was produced similar to the smectite-supported Pd catalyst.

CONCLUSIONS

Using propylene carbonate that is a halogen-free solvent, PCs were prepared by oxidative carbonylation of BPA and CO, catalyzed by the Pd-polybipyridyl complex, Pd-polyvinylpyridine complex, smectite-supported Pd complex, or hydrotalcite-supported Pd

complex as a heterogeneous Pd compound to separate the PC solution and Pd catalyst after the reaction. When using Co(OAc)₂·4H₂O as the inorgano-redox catalyst, all of the Pd compounds showed a good PC yield with a recycling potential of the catalyst.

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