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Carbomethoxylation of Propylene Catalyzed by Sulfonated Resin-supported Cationic Palladium Catalysts

BIAU-HUNG CHANG*

Ashland Chemical Company, Ventures Research and Development, P.O. Box 2219, Columbus, Ohio 43216, U.S.A.

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Abstract

The cationic palladium complex, $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$, has been supported onto sulfonated resins. The carbomethoxylation of propylene catalyzed by sulfonated resin-supported cationic palladium catalyst precursors has been carried out at temperatures of 100 ~ 160 °C and at pressures of 1500 ~ 2000 psi. The supported cationic Pd^{2+} complex precursors have higher catalytic activity than the supported $Pd(NO_3)_2$ and $Pd(PPh_3)_4$ catalyst precursors.

Introduction

The carbonylation of olefins to the esters of carboxylic acids with carbon monoxide and alcohols, in the presence of palladium compounds or other transition metal catalysts, is a process of considerably industrial importance [1]. Recently, the cationic palladium complexes with weakly bonded ligands such as $[Pd(CH_3CN)_4](BF_4)_2$ and its triphenylphosphine derivative, $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$, have been found to differ very significantly in catalytic reactions from those observed with analogous neutral Pd(II) compounds such as $PdCl_2$ and $Pd(OAc)_2$ [2, 3]. Waller [4–6] has reported that the catalytic activity of palladium complexes such as $Pd(PPh_3)_4$ and $Pd(NO_3)_2$ in the carbomethoxylation of olefins can be enhanced by the use of perfluoroalkane sulfonic acid resin as co-catalysts. The cationic palladium complexes with weakly bonded ligands supported onto sulfonated resins have not been reported before. We now wish to report the use of sulfonated resin-supported cationic palladium complex in the catalysis of carbomethoxylation of propylene.

Results and Discussion

Preparation of Sulfonated Resin-supported Cationic Palladium Catalysts

Several sulfonated resins have been used as supports such as perfluorinated ion exchange polymer powder (Nafion) and its acid form (Nafion-H), macroreticular sulfonated polystyrene ion exchange resin (Amberyst) and sulfonated polystyrene ion exchange resin (Dowex). The cationic palladium complex, $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ can be easily supported onto the resins by carrying out the exchange reactions at room temperature. However, much longer reaction time is needed to support $Pd(PPh_3)_4$ onto the resins.

Carbomethoxylation of Propylene

Propylene can be carbomethoxylated to two isomeric esters, methyl butyrate and methyl isobutyrate. The carbomethoxylation reactions were carried out in an autoclave at 100 ~ 160 °C under 1500 ~ 2000 psi pressures of carbon monoxide. Triphenylphosphine was added to prevent the catalyst decomposing to metallic palladium. Table I shows the effects on turnover rate and ratio of linear/branched products using a series of sulfonated resin-supported palladium catalyst precursors.

With the catalytic system described here, the cationic Pd^{2+} species, $[Pd(CH_3CN)(PPh_3](BF_4)_2$, supported onto Nafion-H gave higher catalytic activity than the same complex supported onto the other sulfonated resins such as Amberyst and Dowex by a factor of 2.4. Similar rate enhancement by a factor of 3.6 ~ 4.2 was observed for Nafion-H supported $Pd(PPh_3)_4$ catalyst precursor as reported by Waller [4–6]. Under the same reaction conditions, the supported cationic Pd^{2+} catalysts are more active than the supported Pd^0 catalysts by a factor of 1.8 ~ 3.0 depending on the sulfonated resins used. The Nafion-H supported cationic Pd^{2+} catalyst is also slightly more active than the supported $Pd(NO_3)_2$ complex precursor by a factor of 1.3. However, the catalytic activity of cationic Pd^{2+} complex was reduced by a factor of 2.8, when the support was changed from Nafion-H to Nafion. The selectivity to linear/branched products only changed slightly with the different sulfonated resins used.

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*Present address: Quantum Chemical Corp., USI Division, Research Division, 1275 Section Road, Cincinnati, Ohio 45222, U.S.A.

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TABLE I. Carbomethoxylation of Propylene Catalyzed by Sulfonated Resin-supported Palladium Complex Precursors

Catalyst (weight (g))	Temperature (℃)	Pressure (psig)	Yield (%)	Selectivity linear/ branched	Turnover rate (mole ester/ mole Pd/h)
Nafion-H–Pd^{2+} (1.18)	100	1500	7.0	1.60	221
Nafion-H–Pd^{2+a} (1.18)	100	1500	6.6	1.63	209
Nafion-H–Pd^{2+} (1.18)	100	2000	9.2	2.02	291
Nafion-H–Pd^{2+} (1.18)	135	1500	25.3	2.57	803
Nafion-H–Pd^{2+} (1.18)	160	1500	22.4	2.58	710
Nafion–Pd^{2+} (0.95)	100	1500	1.8	1.11	78
Nafion-H–Pd^0 (1.41)	100	1500	4.0	1.81	126
Nafion-H–Pd^0 (1.41)	135	1500	10.1	2.40	320
Nafion-H–$Pd(NO_3)_2$ (0.88)	100	1500	5.5	2.62	174
Dowex–Pd^{2+} (1.34)	100	1500	3.0	1.25	95
Dowex–Pd^0 (1.82)	100	1500	1.1	1.92	35
Amberyst–Pd^{2+} (1.25)	100	1500	2.8	1.32	89
Amberyst–Pd^0 (1.61)	100	1500	0.9	2.12	30

[a] Catalyst used was recycled from preceeding reaction.

Both temperature and pressure have also shown some effects on turnover rate as well as selectivity to linear/branched products. At constant temperature, the turnover rate for the Nafion-H supported Pd^{2+} complex increased as pressure increased. Similarly, the linear/branched selectivity increased slightly with increasing pressure. At equal pressures, the turnover rate increased by a factor of 3.6 and the selectivity increased by a factor of 1.6 as temperature increased from 100 to 135 ℃. The catalyst can be reused without loss of much activity; however, the turnover rate decreased and the selectivity remained unchanged as temperature further increased from 135 to 160 ℃, possibly due to partial decomposition of the catalyst to metallic palladium.

The active catalytic intermediates of the above catalyst systems are not known. Waller [4–6] has proposed a cationic palladium intermediate in the catalytic processes enhanced by perfluoroalkane sulfonic acid resin. Similarly, the cationic palladium intermediate would be mostly favorable for these carbomethoxylation reactions catalyzed by the sulfonated resin-supported palladium complexes, especially the supported dicationic species. These catalyst systems should be very interesting for industrial application. These sulfonated resins are also noncorrosive.

Experimental

Materials

Carbon monoxide and propylene were Matheson purified grade. Perfluorinated ion exchange polymer (Nafion 501) was obtained from DuPont Company. The acid form (Nafion-H) was prepared by acidification of Nafion with aqueous nitric acid. The sulfonated polystyrene ion exchange resins (Amberyst 15 and Dowex) were obtained from Aldrich Chemical Co. Absolute reagent grade methanol was used. Tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$, was obtained from Strem Chemicals. Palladium(II) nitrate $Pd(NO_3)_2 \cdot xH_2O$ was obtained from Morton Thiokol, Inc., Alfa Products. $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ was prepared by the previously published methods [2, 7].

General Procedures

In the general carbomethoxylation procedure, a 330 ml stainless steel autoclave was used. Carbon monoxide pressure was maintained approximately constant throughout the experiments. Units for the turnover rate are mol ester/mol Pd/h. Yields and the isomeric composition of the reaction products were determined by GLC, using a Hewlett-Packard gas chromatograph Model 5830A equipped with a Hewlett-Packard GC terminal Model 3388. Analyses were carried out using a 12 ft long column of Carbowax 10% on Chromosorb W.

Preparation of Sulfonated Resin-supported Palladium Catalysts

(a) Nafion-H–Pd^{2+} catalyst. In a typical reaction, 30.0 g of Nafion-H resin was suspended in 200 ml of chloroform and 6.65 g of $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ was added. The reaction mixture was stirred at room temperature under argon for one day. The resin was then filtered off, washed thoroughly with chloroform, and dried under vacuum to give an orange material having 0.127 mmol Pd/g of resin.

(b) Nafion–Pd^{2+} catalyst. A suspension of Nafion resin (30.0 g) in 200 ml of chloroform and 6.43 g of $[Pd(CH_3CH)(PPh_3)_3](BF_4)_2$ was stirred at room temperature under argon for one day. The resin was then filtered off, washed thoroughly with chloroform, and dried under vacuum to give a reddish-orange material having 0.158 mmol Pd/g of resin.

(c) Nafion-H–Pd^0 catalyst. A suspension of Nafion-H resin (20.0 g) and $Pd(PPh_3)_4$ (7.92 g) in 200 ml chloroform was stirred at room temperature under argon for one day. The reaction mixture was then allowed to stir at 60 °C for 6 h and at room temperature for seven days. The resin was then filtered off, washed thoroughly with chloroform, and dried under vacuum to give a brown material having 0.106 mmol Pd/g of resin.

(d) Nafion-H–Pd(NO$_3$)$_2$ catalyst. Following a literature procedure [6], a slurry of Nafion-H (300 g) in 200 ml distilled water containing 1.589 g of $Pd(NO_3)_2 \cdot xH_2O$ was stirred at 60 °C for 1 h. The reaction mixture was allowed to stir at room temperature for six days. The resin was separated by filtration and dried under vacuum to give a reddish-black material having 0.171 mmol Pd/g of resin.

(e) The Dowex and Amberyst catalysts. The Dowex–Pd^{2+} (0.112 mmol Pd/g of resin), Dowex–Pd^0 (0.0824 mmol Pd/g of resin), Amberyst–Pd^0 (0.093 mmol Pd/g of resin) and Amberyst–Pd^{2+} (0.120 mmol Pd/g of resin) catalysts were prepared by procedures similar to those described in (a) and (c).

Carbomethoxylation of Propylene

In a typical reaction, 1.18 g of Nafion-H–Pd^{2+} catalyst (0.127 mmol/g of resin), 0.590 g (2.25 mmol) of triphenylphosphine and 80 ml absolute methanol were placed into a 330 ml stainless steel autoclave. The autoclave was sealed and flushed three times with nitrogen. Propylene (20 g, 476 mmol) was introduced through a sampling tube. The reactor was pressurized with 1000 psig of carbon monoxide and heated to 100 °C with stirring. Carbon monoxide pressure was then maintained at 1500 psig. The reaction was allowed to proceed for 1 h. The reaction was cooled and the reaction products were drawn out and analyzed with GLC. It was found that 20.5 mmol of methyl butyrate and 12.7 mmol of methyl isobutyrate were obtained.

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