Catalytic Synthesis of Propylene Carbonate from Propylene Oxide and Carbon Dioxide in the Presence of Rhodium Complexes Modified with Organophosphorus Ligands and Chitosan

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Abstract—The reaction between CO_2 and propylene oxide to produce propylene carbonate in the presence of rhodium complexes modified with organophosphorus ligands and chitosan has been studied. Highly effective catalysts mediating the reaction with almost a 100% yield and 100% selectivity have been prepared using rhodium compounds modified with triphenylphosphine and chitosan.

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Propylene carbonate is an important intermediate in the chemical industry; it is strongly sought for by a number of advanced technologies. It is used as a coolant in booming laser technology and as a precursor for the synthesis of monomers, polymers, plasticizers, modifiers, plant protection agents, etc. Furthermore, it is a starting material in the synthesis of 1,2-propylene glycol.

At present, the demand for this chemical material is tens of tons per year, and this figure will increase in the coming years.

Propylene carbonate is produced from propylene oxide and CO_2 through the reaction:

$$CO_2 + CH_3 - CH_- CH_2 \rightarrow CH_3 - CH_- CH_2$$

The synthesis is conducted at a high pressure of CO_2 (5.0–10.5 MPa) and high temperatures (100–200°C) in the presence of quaternary ammonium salts and alkali metal halides (commercial versions of Jefferson Chemical Company, BASF (Ludwigshafen, Germany) [1], and Chimei-Asahi Corporation (Taiwan) [2]). The catalyst (quaternary ammonium salt) can be reused; however, it is necessary to feed it with a fresh batch in an amount of 30%, and the purification of the product from the spent catalyst is fraught with the formation of large amounts of wastewater.

Recently, many studies focused on the use of complexes of transition metals, in particular ruthenium, for this process have been carried out [3, 4]. In the presence of ruthenium complexes, the synthesis of propylene carbonate occurs under milder conditions than in the case of catalysis by quaternary ammonium salts [4]. The best results were obtained for the reaction conducted in an ionic liquid (in cetyltrimethy-lammonium chloride) using a ruthenium chloride bipyridine complex as a catalyst [3]. The complete conversion of propylene oxide is achieved at 3.0 MPa and 75° C within 4 h.

It is of great interest to study the catalytic properties of rhodium complexes in this reaction, because it is known from [5, 6] that rhodium exhibits a high activity in syntheses involving CO₂. Modification of rhodium complexes with ligands of different nature can lead not only to a significant change in the dynamics of the process and the composition of the reaction products, but also to an increase in the lifetime of the catalyst. Therefore, the aim of this study was to examine the interaction between propylene oxide and CO₂ in the presence of a catalyst system based on rhodium complexes and search for ways to improve its efficiency.

EXPERIMENTAL

The rhodium precursors of the catalyst system were rhodium chloride RhCl₃, complex RhCl(PPh₃)₃, carbonyl-containing acetylacetonate complex acacRh(CO)₂, and dirhodium tetracarbonyl dichloride Rh₂Cl₂(CO)₄. The rhodium precursors were modified with organophosphorus ligands and chitosan.

The series of organophosphorus ligands, along with conventional triphenylphosphine (the P–C bond), was composed of a cyclic phosphite ligand (the P–O–C bond) and phosphonite (containing both the P–C and P–O–C bond). Chitosan was used as a nitrogen-containing ligand.

Table 1. S	tructure	of the	rhodium	compounds	and	modifying	ligands
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Rhodium compound/ligand	Structure	Molecular weight	Reference to synthesis technique	
Triphenylphosphine	PPh ₃	262	"Fluka"	
Bicyclocresol phosphite (BCCP)	O O O O O O O O O O O O O O O O O O O	376	[7]	
Phosphonite		4000	[8]	
Chitosan	H = O = O = O = O = O = O = O = O = O =	60000	VNIT Bioprogress	
Rhodium(III) trichloride	$RhCl_3 \not P 4 \hat{l}_2 \hat{l}$	281	"Fluka"	
hodium dicarbonyl acetylacetonate $Me \xrightarrow{O} CO$ cacRh(CO) ₂ $Me \xrightarrow{O} CO$		259	[9]	
Wilkinson's complex	RhCl(PPh ₃) ₃	924.5	[10]	
Dirhodium tetracarbonyl dichloride	OC Rh Cl Rh CO	389	[11]	

The structure of the rhodium precursors and modifying ligands, as well as references to their preparation techniques, are given in Table 1.

The synthesis of propylene carbonate from propylene oxide and CO_2 was conducted in a 250-mL steel autoclave equipped with an electromagnetic stainless steel stirrer and placed in the unit furnace. Pressure was measured using standard manometers with an accuracy of ± 0.04 MPa.

To obtain active rhodium sites, the catalytic synthesis was conducted in a reducing environment (with hydrogen added to the gas mixture).

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The reactor was charged with a solvent (45 mL) and catalyst system components, i.e., a catalyst precursor and modifying ligands. Phosphorus- and nitrogencontaining ligands were taken in an amount corresponding to P/Rh and N/Rh molar ratios of 9 and 12, respectively. The rhodium concentration was 1.8×10^{-3} g-at/L. The reactor was purged with hydrogen and checked for leaks; after that, the catalyst solution was heated to a desired temperature under stirring. Next, propylene oxide (prepurified by distillation) was fed into the heated reactor from a batcher 9 with a volume of 15 mL). After that, CO₂ and hydrogen were successively introduced into the autoclave to a given pressure. The synthesis was conducted at a constant

Num- ber	Rhodium complex	Induction period, h	Ligand	Propylene oxide conver- sion, %	Pagation rata	Product composition, %	
					mol $L^{-1} h^{-1}$	propylene carbonate	propylene glycol
1	RhCl ₃	1.5	_	80	0.28	78	22
2	RhCl ₃	1.0	BCCP	95	0.32	100	0
3	RhCl ₃	0.2	Phosphonite	90	0.1	100	0
4	RhCl ₃	0	PPh ₃	100	0.32	82	18
5	RhCl ₃	0	Chitosan	100	0.21	100	0
6	RhCl ₂ (CO) ₄	0	PPh ₃	100	0.33	90	10
7	$acacRh(CO)_2$	0	PPh ₃	100	0.20	90	10
8	RhCl(PPh ₃) ₃	0	—	85	0.20	82	18
9	RhCl(PPh ₃) ₃	0	Chitosan	100	0.27	100	0

Table 2. Catalytic properties of rhodium complexes in the reaction between propylene oxide and CO₂ (140°C, 5 MPa of CO₂, 5 MPa of H₂, dimethylsulfoxide solvent, 15 h)

temperature for 15 h. The occurrence of the reaction was monitored according to the pressure drop in the reactor (by recording the pressure using a manometer).

Liquid products were analyzed by gas—liquid chromatography using a Chrom-5 chromatograph equipped with a flame ionization detector and a capillary column (with a length of 50 m) coated with the PEG-20 liquid phase.

RESULTS AND DISCUSSION

The effect of the structure of the rhodium-containing complex and the modifying ligand on the reaction rate and the composition of the reaction products was studied at first.

The results are shown in Table 2. It is evident from the data that the reaction between propylene oxide and CO_2 in the presence of unmodified RhCl₃ occurs with an induction period (1.5 h), yet at a fairly high rate (Table 2, entry 1). However, the conversion of propylene oxide after the termination of the reaction (cessation of the absorption of the gas mixture) is no more than 80%. Since a black precipitate is observed in the reactor after the experiment, the loss of catalytic activity is most probably attributed to the deactivation of the rhodium complex. The liquid reaction product contains 78% of propylene carbonate and 22% of propylene glycol.

Modification of rhodium chloride with an organophosphorus ligand, regardless of its structure, or with chitosan leads to a decrease in the induction period and an increase in the conversion of propylene oxide and the selectivity for propylene carbonate (Table 2, entries 2-5). Consequently, modifying ligands facilitate the transition of the inactive form of rhodium (RhCl₃) to catalytically active particles and stabilize them. PPh₃ and chitosan are most efficient: the reaction in their presence occurs without an induction period and with the complete conversion of propylene oxide (Table 2, entries 4, 5).

The replacement of rhodium chloride with the $Rh_2Cl_2(CO)_4$ dimer complex (modified with triphenylphosphine) does not lead to any significant change in the overall picture, whereas the catalytic activity decreases in the case of an acetylacetonate complex free from Cl⁻ (Table 2, entries 6, 7). Apparently, the presence of chlorine in the composition of the starting complex is a necessary condition for providing a high activity of the catalyst.

The reaction between propylene oxide and CO_2 using RhCl(PPh₃)₃ as a starting rhodium complex also occurs at a fairly high rate (Table 2, entry 8); however, the catalyst activity is lower than in the case of using the RhCl₃–PPh₃ system (P/Rh = 12) (Table 2, entry 4). This is apparently attributed to the fact that the stable occurrence of the reaction requires excess organophosphorus ligand. In addition, the conversion of propylene oxide achieves as little as 85% with the selectivity for propylene of 78%. The RhCl(PPh₃)₃ complex in the presence of chitosan mediates the reaction with a 100% conversion and 100% selectivity (Table 2, entry 9); however, its rate is slightly lower than that of the RhCl₃–PPh₃ system (Table 2, entry 4).



Fig. 1. Effect of reaction time on the conversion of propylene oxide and the composition of the reaction products ($RhCl_3$ -PPh_3, 140°C, 5 MPa of CO₂, 5 MPa of H₂, dimethylsulfoxide solvent).

Thus, catalysts based on rhodium complexes and phosphorus-containing ligands and chitosan exhibit a high activity in the reaction between propylene oxide and CO_2 . Both chlorine and carbonyl-containing rhodium complexes can be used for the reaction. In some cases, the reaction catalyzed by rhodium complexes, along with propylene carbonate, yields propylene glycol (Table 2, entries 4, 6–8). This by-product is most probably a product of the secondary hydrogenation of propylene carbonate. Transition metal complexes, such as ruthenium complexes, catalyze this reaction [12]. For a rhodium catalyst, the conversion of propylene carbonate to propylene glycol apparently occurs by the same scheme.



Scheme. Assumptive mechanism for the reaction of formation of propylene glycol.

Since the reactions of formation of propylene carbonate and propylene glycol are consecutive, the duration of synthesis has a great effect on the selectivity of the process. In fact, the data in Fig. 1 show that only propylene carbonate is detected in the reaction solution after 12 h. If the synthesis is conducted for 15 h,

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propylene glycol appears in the product in an amount of 18%, and the content of propylene glycol in the reaction product achieves almost 40% after 20 h. Note that the formation of propylene glycol begins only after the complete conversion of propylene oxide. Therefore, by fixing the reaction time, it is possible to produce propylene carbonate with 100% selectivity at a 100% conversion of propylene oxide.

Taking into account the availability of RhCl₃ and PPh₃, a phosphine system was selected for further studies aimed at searching for ways to improve its efficiency.

The effect of the solvent and operating parameters on the catalytic properties of the RhCl₃–PPh₃ system has been studied.

Dimethylformamide and methanol, along with dimethylsulfoxide, were used as a solvent. It is evident from Table 3 that the best solvent is dimethylsulfoxide. The reaction in it occurs at the highest rate. The rate in dimethylformamide and methanol is significantly lower. This is probably attributed to the insufficiently high solubility of the reaction components in these solvents.

The effect of temperature on the rate and selectivity of the reaction between propylene oxide and CO_2 in the presence of RhCl₃ modified with triphenylphosphine was studied in a temperature range of 125– 155°C (Figs. 2, 3).

These data show that the reaction rate significantly increases with increasing temperature (Fig. 2). However, at 155°C, propylene glycol, in addition to propylene carbonate, is detected in the reaction products (Fig. 3); this is apparently associated with an increase in the hydrogenation function of the rhodium complex. At 125°C, the reaction occurs at a low rate; therefore, the optimum temperature was assumed to be 140°C.



Fig. 2. Effect of temperature on the rate of reaction between propylene oxide and CO_2 ($T = 140^{\circ}C$, 5 MPa of CO_2 , 5 MPa of H_2 , dimethylsulfoxide solvent).

Table 4 represents the results of studying the effect of the total pressure and composition of the gas mixture on the activity and selectivity of the catalyst system. The data show that a decrease in the total pressure has little effect on the reaction rate and selectivity, whereas the composition of the gas mixture has a significant effect on the occurrence of the process. Thus, a decrease in the pressure of hydrogen leads to a decrease in the reaction rate; in the absence of hydrogen, the reaction does not occur at all. This fact suggests that the catalytically active site of the reaction

Table 3. Effect of solvent on the rate of reaction between propylene oxide and CO_2 ($T = 140^{\circ}C$, 5 MPa of CO_2 , 5 MPa of H_2O , 15 h)

Solvent	Propylene oxide conversion, %	Reaction rate, mol $L^{-1} h^{-1}$	
Dimethylsulfoxide	100	0.32	
Dimethylformamide	30	0.13	
Methanol	20	0.10	



Fig. 3. Effect of temperature on the product composition of the reaction between propylene oxide and CO_2 (5 MPa of CO_2 , 5 MPa of H_2 , dimethylsulfoxide solvent, 12 h).

between propylene oxide and carbon dioxide is a rhodium hydride complex.

Thus, this study gives the possibility to determine the best parameters of the synthesis of propylene carbonate from CO₂ and propylene oxide in the presence of RhCl₃–PPh₃ as follows: the reaction temperature is 140°C; the pressure and the composition of the gas mixture is 10 MPa (5 MPa of CO₂ and 5 MPa of H₂); the solvent is dimethylsulfoxide. Under these conditions, the RhCl₃–PPh₃ catalyst system mediates the reaction at a rate of 0.32 mol L⁻¹ h⁻¹ with 100% selectivity; the conversion of propylene oxide achieves 100% after 12 h of the reaction. The turnover number of the catalyst is 163 h⁻¹.

It can be concluded that a system based on $RhCl_3$ and PPh_3 is an effective catalyst for the synthesis of propylene carbonate from CO_2 and propylene oxide. It should also be noted that the use of chitosan as a ligand (Table 2, entries 5, 9) makes it possible to prepare an efficient catalyst system which is slightly inferior in activity to rhodium triphenyl-containing systems; however, the modification of rhodium complexes with chitosan provides the preparation of heterogenized

Table 4. Effect of total pressure and gas composition on the synthesis of propylene carbonate from CO₂ and propylene oxide ($T = 140^{\circ}$ C, dimethylsulfoxide solvent, 12 h)

Pressure of CO ₂ , MPa	Pressure of H ₂ , MPa	Propylene oxide conversion, %	Reaction rate	Product comp	osition, mol %
			mol $L^{-1} h^{-1}$	propylene carbonate	Propylene glycol
5	5	100	0.32	100	0
3	3	94	0.30	95	5
5	1.5	30	0.12	100	0
5	0	0	0	0	0

* To a 100% conversion of propylene oxide.

catalysts that are superior in selectivity to systems with PPh_3 .

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