

# Cp<sub>2</sub>TiCl<sub>2</sub> used as a catalyst for the transesterification between dimethyl carbonate and phenol to diphenyl carbonate

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## Abstract

Titanocene dichloride (Cp<sub>2</sub>TiCl<sub>2</sub>) was found to be a novel and efficient catalyst for the transesterification between dimethyl carbonate (DMC) and phenol to diphenyl carbonate (DPC). Compared with other titanium esters, Cp<sub>2</sub>TiCl<sub>2</sub> is more stable in air and can reach maximum catalytic activity at low catalyst amount. When the reaction was carried out between 150 and 180 °C, with a molar ratio of phenol to DMC of 1:1, a reaction time 10 h, a catalyst amount 0.5% (molar ratio to phenol), the conversion of phenol was 46.8%, and the selectivity of DPC and MPC was 54.9 and 43.4%, respectively.

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**Keywords:** Titanocene dichloride; Transesterification; Diphenyl carbonate; Dimethyl carbonate; Titanium ester

## 1. Introduction

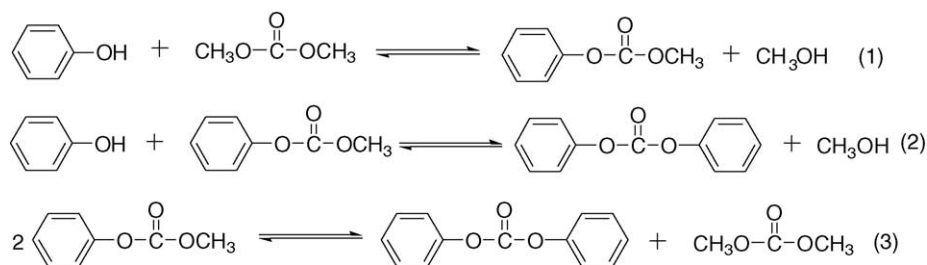
Polycarbonates (PCs) are important engineering thermoplastics with good mechanical and optical properties as well as electrical and heat resistance useful for many applications [1]. However, the commercial PCs have been produced mostly by reacting bisphenol-A with phosgene (COCl<sub>2</sub>). This conventional COCl<sub>2</sub> process has serious environmental and safety problems such as the use of highly toxic phosgene, the formation of a stoichiometric amount of NaCl or HCl, and the use of a copious amount of methylene chloride as solvent [2]. In recent years, there has been an increasing demand for safer and more environmentally friendly processes for PCs synthesis, and non-phosgene process has been proposed to replace the traditional phosgene process [3,4]. The most practical non-phosgene process for the production of PCs is the melt polymerization of bisphenol-A with diphenyl carbonate (DPC), so DPC is an essential starting material for the green production of PCs.

Several alternative non-phosgene methods for the manufacturing of DPC have been proposed, including oxidative carbonylation of phenol and transesterification between phenol and dimethyl carbonate (DMC). Though the oxidative carbonylation of phenol is considered to be a prospective route for the synthesis of DPC, the use of noble catalyst such as palladium complex and the low yield of DPC limit its industrialization [5]. So the transesterification between DMC and phenol seems to be the most promising and practical candidate for DPC synthesis without using phosgene and is now used in a pilot-plant.

The synthesis of DPC is usually performed in two steps. In the first step, phenol is converted into methyl phenyl carbonate (MPC) (Eq. 1), and in the second step, MPC is converted into DPC by the reaction with phenol or by disproportionation (Eq. (2) and (3), Scheme 1).

But the reaction suffers from low yield and selectivity even at elevated temperature due to a critical thermodynamic limitation in the formation of MPC ( $3 \times 10^{-4}$  at 453 K) and the reaction rate is somewhat slow. So active catalyst systems are important for the transesterification of DMC and phenol.

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Scheme 1.

A variety of catalyst systems have been developed for the transesterification between DMC and phenol, which include homogeneous catalysts such as titanium esters [6,7], tin compounds [8,9], conventional Lewis acids [10], and heterogeneous catalysts such as  $\text{MoO}_3/\text{SiO}_2$  [11],  $\text{TiO}_2/\text{SiO}_2$  [12], lead and zinc double oxide [5] and so on [13]. Although heterogeneous catalysts have drawn more and more attention because they are easy both to separate from products and to recover for reuse, their low activities impede them from industrialization. And the homogeneous catalysts are used in commercial applications. Unfortunately, these homogeneous catalysts require a large amount in the transesterification reaction to reach the maximum catalytic activity, which, to some extent, may impair their values in commercial applications. Consequently, the development of more efficient catalyst is desirable.

Titanocene dichloride,  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{Ti}(\text{OR})_4$  are active components in Ziegler–Natta catalyst for  $\alpha$ -olefins polymerization and copolymerization [14–16]. Since  $\text{TiCl}_4$  and  $\text{Ti}(\text{OR})_4$  are active catalysts for the transesterification of DMC and phenol, we thought that titanocene dichloride would also be an active catalyst in this reaction. At the same time, titanocene dichloride is much more stable in air condition than titanium esters and can be handled in air directly. Thus we decided to examine the employment of titanocene dichloride in the transesterification of DMC and phenol. We thought it would be interesting to compare the activity of the well known  $\text{Ti}(\text{OR})_4$  with titanocene dichloride, especially on the basis of the different Lewis acidities, coordinating properties as well as steric factors of these Ti(IV) catalysts. Furthermore, to the best of our knowledge, there have been no reports on the application of  $\text{Cp}_2\text{TiCl}_2$  as a catalyst for the transesterification of DMC and phenol to DPC.

## 2. Experimental

### 2.1. Chemical reagents

Dimethyl carbonate (Huasheng Co. Ltd., Shandong University of Petroleum, China) was fractionally distilled and stored over molecular sieve (4A). Phenol was of laboratory reagent grade.  $\text{Ti}(\text{OR})_4$  and  $\text{BuSnO}_2$  were purchased

from Aldrich Chemical Co. and used as received. Titanocene dichloride was purchased from Hubei Huabang Reagent Co. (China) and was used without any pretreatment.

### 2.2. General procedure

The reaction was carried out in a 100 mL three-neck round-bottomed flask, equipped with a magnetic stirring bar, a nitrogen inlet, a dropping funnel, and a fractionating column connected to a liquid dividing head. Under nitrogen gas, phenol and a catalyst were introduced into the flask. After the mixture was heated to 150 °C, DMC was added drop-wise. The reaction temperature was kept between 150 and 180 °C and the reaction mixture was under refluxing condition between 150 and 180 °C. During the reaction, a distillate of DMC and methanol was collected slowly in a receiver flask attached to the liquid dividing head and for analysis. After the reaction, the mixture was cooled to room temperature and the catalyst was filtrated and then the filtrate was analyzed by gas chromatograph.

### 2.3. Product analysis

The azeotrope of DMC and methanol and the reaction system were analyzed by gas chromatograph equipped with a capillary column (30 m) and a flame ionization detector (FID). Identification analysis of the reaction system was conducted on a 6890/5973 GC-Mass spectrometer.

## 3. Results and discussion

### 3.1. The catalytic activity of titanocene dichloride

Titanium esters such as tetrabutyl titanate, tetraethyl titanate and tetraisopropyl titanate have been reported as efficient catalysts for the transesterification of DMC and phenol as well as  $\text{Bu}_2\text{SnO}$ . For comparison, the catalytic activity of titanocene dichloride, titanium esters and  $\text{Bu}_2\text{SnO}$  were tested in a refluxing batchwise reactor. The results are shown in Table 1.

As shown in Table 1, titanocene dichloride has the highest activity of the tested catalysts. The reason for the enhancement of titanocene dichloride than titanium esters

Table 1  
Transesterification of DMC and phenol catalyzed by  $\text{Cp}_2\text{TiCl}_2$  and some other catalysts

Catalyst	Phenol conc. (%)	Yield of MPC (%)	Yield of DPC (%)	Transesterification selectivity (%)
$\text{Cp}_2\text{TiCl}_2$	46.8	20.3	25.7	98.3
$\text{Ti}(\text{O}i\text{Bu})_4$	38.9	21.9	16.0	97.4
$\text{Ti}(\text{O}Et)_4$	36.8	13.2	22.9	98.1
$\text{Ti}[\text{O}i\text{Pr}]_4$	30.0	17.2	12.4	97.7
$\text{BuSnO}_2$	28.7	18.1	10.5	99.7

MPC: methyl phenyl carbonate, DPC: diphenyl carbonate. Reaction condition: temperature: 150–180 °C, the molar ratio of phenol/DMC: 1, the molar ratio of catalyst/phenol: 0.005, reaction time: 10 h, the mole of phenol: 0.3 mol.

can be ascribed to the electrophilicity of Ti atom and the steric factors. First, the Ti atom becomes highly electrophilic or Lewis acidic in titanocene dichloride molecule than in titanium ester molecule because of the electron withdrawing of the atom Cl, thereby coordination of DMC to electron-deficient Ti center, the first step of the transesterification, would take place more easily. At the same time, the bulk of atom Cl is smaller than that of the alkoxys and thus lower the steric hindrance, this made the Ti atom become more attackable or coordinating on other atom.

### 3.2. The effect of catalyst amount on the transesterification reaction

The effect of molar ratio of titanocene dichloride to phenol on the transesterification of DMC with phenol was studied at 150–180 °C. As shown in Table 2, yield of MPC and DPC increased rapidly with molar ratio of titanocene dichloride/phenol below 0.005. Above 0.005, however, the yield of MPC and DPC remained almost unchanged, so the optimal catalyst amount may be 0.005. The data shows that the reaction can reach high yield of DPC and MPC at low catalyst amount using titanocene dichloride, while other catalysts including titanium esters and  $\text{BuSnO}_2$  require a large amount in this reaction to reach the maximum catalytic activity (usually the catalyst amount is 1–5% of phenol or DMC) [7,8]. So titanocene dichloride is an economic catalyst for the transesterification of DMC and phenol.

Table 2  
The effect of molar ratio of titanocene dichloride to phenol on the transesterification reaction

Catalyst amount $n(\text{Cp}_2\text{TiCl}_2):n(\text{phOH})$	Phenol conc. (%)	Yield of MPC (%)	Yield of DPC (%)
0.001	27.4	13.0	14.4
0.0025	39.2	18.5	20.7
0.005	46.8	20.3	25.7
0.0075	47.5	21.5	25.3
0.01	48.0	22.3	23.9

MPC: methyl phenyl carbonate, DPC: diphenyl carbonate. Reaction condition: temperature: 150–180 °C, the molar ratio of phenol/DMC: 1, reaction time: 10 h, the mole of phenol: 0.3 mol.

Table 3  
The effect of molar ratio of phenol/DMC on the transesterification reaction

$n(\text{Phenol}):n(\text{DMC})$	Phenol conc. (%)	Yield of MPC (%)	Yield of DPC (%)
2:1	29.9	13.6	16.3
1:1	46.8	20.3	25.7
1:2	47.8	22.0	25.1
1:3	48.5	22.8	25.0

MPC: methyl phenyl carbonate, DPC: diphenyl carbonate. Reaction condition: temperature: 150–180 °C, the molar ratio of catalyst/phenol: 0.005, reaction time: 10 h, the mole of phenol: 0.3 mol.

### 3.3. The effect of molar ratio of phenol/DMC on the transesterification reaction

The effect of molar ratio of phenol/DMC was also studied during 150–180 °C in the presence of titanocene dichloride. The molar ratio of phenol to DMC was varied in the range of 2–1/3 and the results are listed in Table 3.

As shown in Table 3, when phenol and DMC was added as stoichiometrically according to the reaction equation, the conversion of phenol is fairly low. This may be ascribed to the evaporation of DMC with methanol under the reaction condition, and thus the amount of phenol is slightly in excess compared with the amount of DMC, according to the stoichiometric reaction equation. When the molar ratio of phenol/DMC was increased to 1:1, the conversion of phenol increased greatly, but thereafter remained almost constant. In addition, with the increase of the molar ratio of phenol/DMC, the yield of MPC kept increasing while the yield of DPC became slightly decreasing when the molar ratio of phenol/DMC was above 1:1. This illustrates that the excess of phenol is in favor of the formation of DPC.

### 3.4. The effect of reaction time on the transesterification reaction

The yield of MPC and DPC was also monitored with the reaction time because the transesterification of DMC and phenol is reversible and the reaction rate is slow. The results are given in Table 4.

As shown in Table 4, the formation of DPC continuously increased with reaction time, whereas the formation of MPC increased with the reaction time up to 15 h and then decreased thereafter. After 15 h of reaction, the conversion of phenol

Table 4  
The effect of reaction time on the transesterification reaction

Time (h)	Phenol conc. (%)	Yield of MPC (%)	Yield of DPC (%)
10	46.8	20.3	25.7
15	52.1	21.8	29.6
20	53.3	21.6	31.7
25	53.5	15.7	37.8
30	53.9	11.1	41.6

MPC: methyl phenyl carbonate, DPC: diphenyl carbonate. Reaction condition: temperature: 150–180 °C, the molar ratio of catalyst/phenol: 0.005, the molar ratio of phenol/DMC: 1, the mole of phenol: 0.3 mol.

reached 53.3% and did not change much thereafter, this indicated that the transesterification reaction almost reached equilibrium within 15 h. The decrease of the MPC yield after 15 h may be ascribed to the disproportionation of MPC to DPC when the reaction temperature reached approximately 180 °C. The data indicates that the optimal reaction time for the transesterification of DMC and phenol with the catalyst  $\text{Cp}_2\text{TiCl}_2$  is from 10 to 15 h.

#### 4. Conclusions

For the transesterification of DMC and phenol,  $\text{Cp}_2\text{TiCl}_2$  was found to be a novel and efficient catalyst. To the best of our knowledge, we have got the best results of all the catalysts at normal pressure with the reaction temperature under 200 °C. When the reaction was carried out between 150 and 180 °C, with a molar ratio of phenol to DMC of 1:1, a reaction time 10 h, a catalyst amount 0.5% (molar ratio to phenol), the conversion of phenol was 46.8%, and the selectivity of DPC and MPC was 54.9 and 43.4%, respectively. Compared with other titanium esters,  $\text{Cp}_2\text{TiCl}_2$  is more stable in air condition and can reach maximum catalytic activity at low catalyst amount.  $\text{Cp}_2\text{TiCl}_2$  is commercial available and inexpensive, and needn't any pretreatment before the reaction, so it is a convenient and economic catalyst in this reaction. Moreover, although the catalyst is soluble at the reaction condition, it is immiscible when the reaction mixture is cooled to ambient temperature,

and thus it has high activity under reaction condition and can be separated from the reaction system easily. So it is a promising catalyst for the transesterification of DMC and phenol and further study on the detail of this novel catalyst is underway in our laboratory and will be reported separately.

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