Short communication

Transesterification of dimethyl carbonate and phenol to diphenyl carbonate catalyzed by samarium diiodide

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Abstract

Samarium diiodide was found to be a novel and efficient catalyst for the transesterification of phenol and DMC. Compared with other catalysts, samarium diiodide can reach high activity with a very 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 0.2% (molar ratio to phenol), the conversion of phenol was 52.8%, the yield of MPC and DPC was 26.5% and 22.8%, respectively.
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1. Introduction

Polycarbonates (PCs) are achieving great importance due to their promising mechanical, optical, heat, engineering and electronic properties [1,2]. Diphenyl carbonate (DPC) has been regarded as a potential substitute material for highly toxic phosgene in the synthesis of PCs [3–5]. Several non-phosgene methods for the synthesis of DPC have been proposed, including oxidative carbonylation of phenol and transesterification between dimethyl carbonate (DMC) and phenol. Though the oxidative carbonylation is an attractive method for the production of DPC due to the cheap and easily available materials, the noble catalysts and the low yield of DPC limit its commercial utilization [6]. The best method as of now appears to be through the transesterification between DMC and phenol in spite of the fact that this reaction is slow and possesses unfavorable equilibrium and thermodynamics [7,8] (Scheme 1).

Various different catalysts have been studied for the transesterification reaction, including homogeneous catalysts such as Lewis acids [9], organometallic compounds [10–14] and heterogeneous catalysts such as TiO$_2$/SiO$_2$ [15], MoO$_3$/SiO$_2$ [16], Pb–Zn double oxides [6] and so on [17,18]. Though heterogeneous catalysts are easy to separate and recover for reuse, their low catalytic activities and selectivities impede their industrialization. And homogeneous catalysts are used in commercial production. 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 catalysts is desirable.

First introduced by Kagan and co-workers [19], samarium diiodide (SmI$_2$) has rapidly become a well-established reagent in organic chemical community due to its stability, reactivity, and availability [20]. SmI$_2$ is air sensitive but tolerant of water and some organic solvents and can be handled with standard techniques. At the same time, it is commercially available and can be conveniently prepared in THF solution at room temperature by the reaction of samarium metal and 1,2-diiodoethane [21]. Samarium diiodide has strong oxophilicity, high reduction potential, and high electropositivity and can be used as Lewis acids or as a powerful one electron-donating reagent. Therefore, most of substrates containing oxygen, halide or p-electrons are active toward SmI$_2$ [22]. Many important individual reactions found useful in organic synthesis have been promoted by SmI$_2$ [23], but up to now, to the best of our knowledge, samarium diiodide has not been used as a catalyst for the transesterification of DMC and phenol. Herein, we report our preliminary findings of samarium diiodide in this reaction.

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$$2PhOH + H_3CO-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 \rightleftharpoons PhO-\overset{\overset{\displaystyle O}{\|}}{C}-OPh + CH_3OH$$

Scheme 1.

2. Experimental

2.1. Chemical reagents

Ti(OBu)$_4$, BuSnO$_2$ and samarium diiodide were purchased from Aldrich Chemical Co. and used as received. Dimethyl carbonate, phenol, ZnCl$_2$ and FeCl$_3$ were obtained from local manufactures and were of laboratory reagent grade.

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 160 °C, DMC was added drop-wise. The reaction temperature was kept 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 for analysis. After the reaction, the mixture was cooled to room temperature and then analyzed by gas chromatograph.

2.3. Product analysis

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

3. Results and discussion

3.1. The catalytic activity of samarium diiodide

Conventional Lewis acid catalysts have played important roles in the transesterification of DMC and phenol. SmI$_2$ is a kind of Lewis acid and can work in aqueous media or in organic solvents, so we thought that SmI$_2$ should be suitable for this reaction. At the same time, Sm$_2$O$_3$ [24] and Sm(OTf)$_3$ [17] have been reported as catalysts for the transesterification of DMC and

phenol. In addition, SmI$_2$ has strong oxophilicity, so we thought it might coordinate with the oxygen atom and thus accelerate the reaction rate. Taking all these into consideration, we decided to explore the catalytic behavior of SmI$_2$ in the transesterification between DMC and phenol.

Lewis acid, tetrabutyl titanate and dibutyltin oxide are traditionally used as catalysts for the transesterification of DMC and phenol. For comparison, the catalytic activities of samarium diiodide, Lewis acids, Ti(OBu)$_4$ and Bu$_2$SnO were tested in a refluxing batchwise reactor. As shown in Table 1, the activities of FeCl$_3$ and ZnCl$_2$ were very low when the catalyst amount was only 0.2%. Ti(OBu)$_4$ and Bu$_2$SnO had higher activities than Lewis acids. Among all these tested catalysts, SmI$_2$ had the highest activity though a small quantity of by product, anisole, was formed. Mei et al. [18] reported that when the reaction was carried out at 190 °C with the molar ratio of phenol-to-DMC 4:1, the molar ratio of Sm-to-DMC 1:70 for 12 h, the conversion of DMC was 34.4%. It is obvious that the catalytic activity of SmI$_2$ was also much higher than that of Sm(OTf)$_3$. The high activity of SmI$_2$ might ascribe to its strong oxophilicity. SmI$_2$ might coordinate with oxygen atom in the reactant molecule and thus accelerate the reaction rate.

3.2. The effect of catalyst amount on the transesterification reaction

The effect of catalyst amount on the transesterification of DMC and phenol was studied. As shown in Table 2, the conversion of phenol increased rapidly when the molar ratio of SmI$_2$/phenol was below 0.002. When the molar ratio of SmI$_2$/phenol was above 0.002, the conversion of phenol kept almost unchanged while the yield of anisole kept increasing, so the optimal catalyst amount might be 0.002. The data also showed that SmI$_2$ could reach its high catalytic activity with a very low catalyst amount, while other catalysts including titanium esters and BuSnO$_2$ required a large amount in this reaction to reach the maximum catalytic activity (usually the catalyst amount was 1–5% of phenol or DMC) [7,8]. Therefore, SmI$_2$ is an economic and efficient catalyst for the transesterification of DMC and phenol.

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

The effect of molar ratio of phenol/DMC on the transesterification reaction was also studied. As shown in Table 3, when

Table 1
Transesterification of phenol and DMC catalyzed by SmI$_2$ and some other catalysts

Catalyst	Conversion of phenol (%)	Yield of MPC (%)	Yield of DPC (%)	Yield of AN (%)	Transesterification selectivity (%)
SmI$_2$	47.7	26.0	18.7	2.3	93.7
Bu$_2$SnO	21.4	14.7	6.7	–	100
Ti(OBu)$_4$	40.4	21.2	17.5	–	95.8
FeCl$_3$	4.5	3.6	0.6	Trace	93.3
ZnCl$_2$	6.7	5.1	1.4	Trace	97.0

MPC: methyl phenyl carbonate; DPC: diphenyl carbonate; AN: anisole. Reaction condition: temperature: 150–180 °C, the molar ratio of phenol/DMC: 1, the molar ratio of catalyst/phenol: 0.2%, reaction time: 8 h, the mole of phenol: 0.2 mol.

Table 2
The effect of molar ratio of SmI$_2$ to phenol on the transesterification reaction

Catalyst amount $n(SmI_2):n(PhOH)$	Conversion of phenol (%)	Yield of MPC (%)	Yield of DPC (%)	Yield of AN (%)	Transesterification selectivity (%)
0.0005	36.3	20.6	14.4	0.9	96.4
0.001	41.7	23.9	15.6	1.4	94.7
0.002	47.7	26.0	18.7	2.3	93.7
0.003	48.1	24.9	18.7	3.1	90.6
0.004	48.4	23.4	18.3	5.1	86.2

MPC: methyl phenyl carbonate; DPC: diphenyl carbonate; AN: anisole. Reaction condition: temperature: 150–180 °C, the molar ratio of phenol/DMC: 1, reaction time: 8 h, the mole of phenol: 0.2 mol.

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

n(Phenol):n(DMC)	Conversion of phenol (%)	Yield of MPC (%)	Yield of DPC (%)	Yield of AN (%)	Transesterification selectivity (%)
1:0.5	40.2	16.5	19.0	3.9	88.3
1:1	47.7	26.0	18.7	2.3	93.7
1:1.5	47.9	25.5	19.3	2.4	93.5
1:2	48.5	25.6	19.7	2.1	93.4
1:2.5	48.4	26.0	18.7	2.0	92.4
1:3	47.0	28.3	15.8	1.6	93.8

MPC: methyl phenyl carbonate; DPC: diphenyl carbonate; AN: anisole. Reaction condition: temperature: 150–180 °C, the molar ratio of catalyst/phenol: 0.2%, reaction time: 8 h, the mole of phenol: 0.2 mol.

Table 4
The effect of reaction time on the transesterification reaction

Reaction time (h)	Conversion of phenol (%)	Yield of MPC (%)	Yield of DPC (%)	Yield of AN (%)	Transesterification selectivity (%)
6	40.4	20.0	16.9	2.5	91.3
8	47.7	26.0	18.7	2.3	93.7
10	52.8	26.5	22.8	2.8	93.4
12	56.0	21.6	29.7	4.3	91.6
15	56.8	15.2	34.4	6.6	87.3
18	56.8	9.1	39.1	8.0	84.9

MPC: methyl phenyl carbonate; DPC: diphenyl carbonate; AN: anisole. Reaction condition: temperature: 150–180 °C, the molar ratio of phenol/DMC: 1, the molar ratio of catalyst/phenol: 0.2%, the mole of phenol: 0.2 mol.

phenol and DMC was added in the stoichiometric ratio, the conversion of phenol was very low. This might be ascribed to the evaporation of DMC under the reaction condition, thus the amount of phenol was actually in excess compared with the amount of DMC according to the stiochiometric reaction equation. When the molar ratio of phenol/DMC was increased to 1:1, the conversion of phenol increased sharply, but thereafter increased a little, so the optimal molar ratio of phenol/DMC should be 1:1. When the molar ratio of phenol/DMC was above 1:2, the conversion of phenol and the yield of DPC decreased slightly. This might be caused by the decrease of the reaction temperature. When a large amount of DMC was added to the reaction system, the temperature was difficult to reach to 170 °C because of the evaporation of DMC, and thus the reaction rate might be somewhat slow under the comparative low reaction temperature. In addition, the formation of anisole was suppressed slightly due to the comparative low temperature.

3.4. The effect of reaction time on the transesterification reaction

The transesterification reaction was also monitored by changing the reaction time. As shown in Table 4, the conversion of

phenol and the yields of MPC and DPC increased sharply within 10 h. After 12 h of reaction, the conversion of phenol kept almost unchanged while the yield of anisole kept increasing. When the reaction time was between 10 and 12 h, the conversion of phenol increased evidently while the total yield of MPC and DPC increased slightly, so the optimal reaction time should be 10 h. The yield of DPC kept increasing all the time whereas the yield of MPC decreased after 10 h reaction, which might be ascribed to the disproportionation of MPC to DPC when the reaction temperature reached approximately 180 °C.

4. Conclusion

In summary, samarium diiodide was firstly used as an efficient catalyst for the synthesis of DPC by transesterification of phenol and DMC. Samarium diiodide is commercially available and can be handled with standard techniques. The ease of the availability and the ease of the handling make this catalyst more promising for this reaction. Under the optimized reaction conditions, the reaction temperature between 150 and 180 °C, the molar ratio of phenol to DMC of 1:1, the reaction time 10 h and the catalyst amount 0.2% (molar ratio to phenol), the conversion of phenol was 52.8%, the yield of MPC and DPC was 26.5% and 22.8%,

respectively. Further work on the detail of this novel catalyst is under way in our laboratory.

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