Catalytic study on the transesterification of dimethyl carbonate and phenol to diphenyl carbonate

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Abstract

Transesterification of dimethyl carbonate and phenol to diphenyl carbonate and catalysts were investigated. The results showed that the transesterification was the reaction of soft base binding to hard acid, and hard acid catalysts had higher transesterification selectivity than the soft and border acid catalysts. When the hard acid n-Bu$_2$SnO and bases constituted acid–base complex catalysts, it was found that Cu$_2$O, as a promoter, could enhance the activity of n-Bu$_2$SnO outstandingly. The conversion of dimethyl carbonate was up to 50.8% with 99.9% transesterification selectivity. A plausible mechanism was also suggested.
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1. Introduction

Diphenyl carbonate (DPC) can be used to synthesize many organic compounds, especially to produce polycarbonates by the melt transesterification [1,2]. The synthetic methods of DPC include phosgene processes, carbonylation of phenol and CO$_2$, oxidative carbonylation of phenol and transesterification [3–5]. The transesterification of dimethyl carbonate (DMC) with phenol is considered as a green route because DMC is nontoxic to human and environment [6].

The reactions of DMC with phenol involved in the transesterification (shown in Eqs. (1)–(3)) and *O*-methylation (shown in Eq. (4)).

For the transesterification of DMC and phenol to DPC, most of the catalysts were acidic, for example, homogeneous catalysts like Lewis acids [5], titanium esters [7] and organotin compounds [8], and heterogeneous catalysts like MoO$_3$/SiO$_2$ [9], TiO$_2$/SiO$_2$ [10–12] and V$_2$O$_5$/SiO$_2$ [13]. Up to now, there is no report on how to choose acid catalysts for the transesterification. Alkaline catalysts were seemed to be avoided because they are in favor of the *O*-methylation [14]. However, Mei and co-workers [15] reported alkaline Mg–Al–hydrotalcite was active for the transesterification, and the yield and transesterification selectivity were 26.3% and 82.4%, respectively. In addition, Zhou and co-workers [16] reported Pb$_3$O$_4$–ZnO was an active catalyst for transesterification, but deactivated easily. Cao and co-workers [17] also reported the conversion of phenol was 36.8% with the 99.5% transesterification selectivity when O$_2$-promoted PbO/MgO was used. The common feature of Pb$_3$O$_4$–ZnO and O$_2$-promoted PbO/MgO was each of catalysts was composed of an acid species (Pb$_3$O$_4$ or O$_2$-promoted PbO) and base species (ZnO or MgO). This result showed that the acid–base bi-component catalyst was very effective for the synthesis of DPC. In this article, we investigated firstly how to choose acid catalysts, and reported a new and efficient acid–base complex catalyst for the transesterification of DMC and phenol to DPC under atmosphere pressure.

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2. Experimental

2.1. Chemical reagents

n-Bu$_2$SnO was purchased from Aldrich Chemical Co. Other chemicals with A.R. purity were purchased from local manufacturers and used without further purification.

2.2. Reaction procedure

The reaction was carried out in a flask, equipped with a thermometer, a nitrogen inlet, a dropping funnel and a fractionating column connected to a liquid dividing head. Phenol and catalyst were charged into the flask under nitrogen atmosphere. When the mixture was heated to 176 °C, DMC was added drop-wise, and the reaction was continued for a certain period of time. During the reaction, a distillate of DMC and methanol was collected slowly in a receiver flask. After the reaction was finished, the reaction mixture was cooled and analyzed.

2.3. Product analysis and catalyst characterization

Qualitative and quantitative analyses of the reaction mixture were carried out on a HP 6890/5973 GC–MS spectrometer and a Shimadzu GC-14B equipped with a SE-30 capillary column and a FID, respectively.

IR spectra were recorded on a NICOLET MX-1E FT-IR spectrometer.

3. Results and discussion

3.1. The analysis for the reaction of DMC with phenol

In the DMC molecule, there are two active centers: a sp^2-hybridized carbonyl carbon and sp^3-hybridized methyl carbon. The former may be regarded as a hard acid center, correspondingly the latter is the soft acid center. Because the conjugation of lone-pair electrons in oxygen atom with benzene ring decreases the nucleophilic nature of phenol, phenoxy is a soft base. Therefore, the transesterification of DMC and phenol belongs to a reaction of soft base binding to hard acid, while the O-methylation is the reaction of soft base binding to soft acid (Fig. 1). According to hard–soft acid–base principle, the O-methylation is much easier than the transesterification.

Xing and co-workers [18] have reported that the standard Gibbs free energy ($\Delta_r G^0$) of reaction (1), (2) and (4) (Scheme 1) is 1.83×10^4, 1.56×10^4 and -6.12×10^4 J mol^{-1} at 453 K, respectively. This indicates that the O-methylation is thermodynamically favorable and the transesterification is thermodynamically unfavorable. But the transesterification may proceed when the equilibrium is broken by continuously removing methanol from the reaction system, and is still difficult because of the thermodynamic limitation. On the contrary, the O-methylation is easy. The result is in agreement with the above analysis,
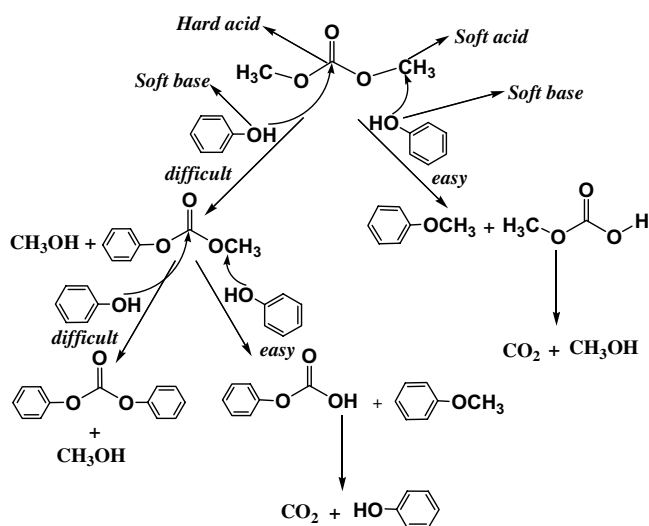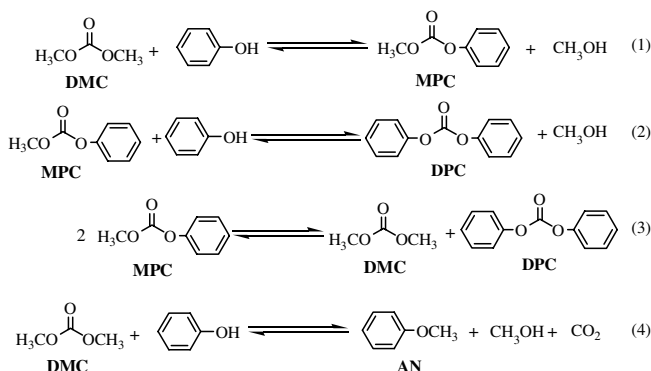

Fig. 1. The reaction of DMC with phenol.

Scheme 1.

and confirms the transesterification is the reaction of soft base binding to hard acid.

On basis of this analysis, hard acids should be selected as the transesterification catalysts in order to increase the transesterification selectivity, because they activated only the carbonyl of DMC to form the carbocation, promoting phenol to react with it and yielding the transesterification products.

3.2. Choice of acid catalysts for the transesterification

To identify the above principle, the activities of a series of catalysts (soft acid: Cu$^+$; border acids: Co^{2+}, Cu^{2+}, Zn^{2+} and Fe^{2+}; hard acids: Fe^{3+}, Sn^{4+}, Al^{3+}, Ti^{4+} and (CH$_3$)$_2$Sn^{2+} [19]) were tested.

As shown in Table 1, CuCl (soft acid), CuCl$_2$ and Co-(OAc)$_2$ (border acids) had no activity (entries 1, 2 and 3). The transesterification selectivity was 90.7% and 97.9% over ZnCl$_2$ and FeCl$_2$, respectively (entries 4 and 5). However, when hard acids, FeCl$_3$, SnCl$_4$, Ti(OBu)$_4$ and n-Bu$_2$SnO, were used as catalysts, the transesterification selectivity was nearly 100% (entries 6, 7, 9 and 10). These results showed hard acids have higher transesterification

Table 1
Effect of various catalysts on the transesterification

Entry	Catalyst	X (DMC) (%)	Yield (%)			Transesterification selectivity (%)
			AN[a]	MPC[b]	DPC	
1	CuCl	0	0	0	0	
2	CuCl$_2$	0	0	0	0	
3	Co(OAc)$_2$	0	0	0	0	
4	ZnCl$_2$	5.4	0.5	4.9	0	90.7
5	FeCl$_2$	9.4	0.2	6.5	2.7	97.9
6	FeCl$_3$	6.6	Trace	6.6	0	99.9
7	SnCl$_4$	11.4	Trace	10.2	1.2	99.9
8	AlCl$_3$	18.2	1.5	13.8	2.9	91.8
9	Ti(OBu)$_4$	20.2	Trace	18.7	1.5	99.9
10	n-Bu$_2$SnO	29.7	Trace	27.6	2.2	99.9

Reaction conditions: n(DMC):n(phenol) = 1:2, n(catalyst):n(DMC + phenol) = 0.012:1, t = 8 h, T = 150–180 °C.
[a] AN: anisole.
[b] MPC: methyl phenyl carbonate.

Table 2
Effect of acid–base complex catalysts on the transesterification

Entry	Catalyst	X (DMC) (%)	Yield (%)			Transesterification selectivity (%)
			AN	MPC	DPC	
11	n-Bu$_2$SnO + Cu$_2$O	50.8	Trace	35.4	15.4	99.9
12	n-Bu$_2$SnO + CaO	62.1	50.2	9.5	2.4	19.2
13	Cu$_2$O	0	0	0	0	–
14	CaO	61.3	47.3	9.6	4.4	22.8
15	[n-Bu$_2$Sn(OPh)OsnBu$_2$(OPh)]$_2$ + Cu$_2$O	50.6	Trace	36.4	14.2	99.9

Conditions: n(DMC):n(phenol) = 1:2, n(catalyst):n(DMC + phenol) = 0.012:1, n(Sn):n(Cu/M) = 1:1, t = 8 h, T = 150–180 °C.

selectivity than the others. But 1.5% yield of anisole was produced when AlCl$_3$ (hard acid) was used as the catalyst (entry 8). The reason might be ascribed to the decarboxylation of MPC [9].

Among hard acids, FeCl$_3$, SnCl$_4$ and AlCl$_3$ cannot be applied to the large-scale production of DPC due to the low activity and corrosion from the chloric ion. Ti(OBu)$_4$ is easily hydrolyzed and deactivated (entry 9). Although n-Bu$_2$SnO had more activity than Ti(OBu)$_4$, and could overcome the disadvantage brought by titanium esters (entry 10), its activity was not high enough for industrial purpose.

3.3. Choice of the complex catalyst and the reaction mechanism

As remarked in the introduction, the acid–base bi-component catalyst was very effective for the transesterification, so we selected Cu$_2$O (weak base) and CaO (strong base) as base species, and studied the performance of the complex catalyst, which was composed of n-Bu$_2$SnO and Cu$_2$O/CaO. The results are listed in Table 2.

When Cu$_2$O was used in conjunction with equimolar n-Bu$_2$SnO, the complex (n-Bu$_2$SnO–Cu$_2$O) not only remained the nearly 100% transesterification selectivity, but also exhibited far higher activity than n-Bu$_2$SnO: the conversion of DMC was increased from 29.7% to 50.8% (entry 11). However, when Cu$_2$O was replaced with CaO, the new catalyst gave rather low transesterification selectiv-

ity though it had high activity (entry 12). The results suggest the base strength of metal oxide affect the activity and transesterification selectivity.

In order to understand the role of metal oxides, we investigated the effect of Cu$_2$O and CaO on the transesterification (Table 2). It was found that Cu$_2$O was not active
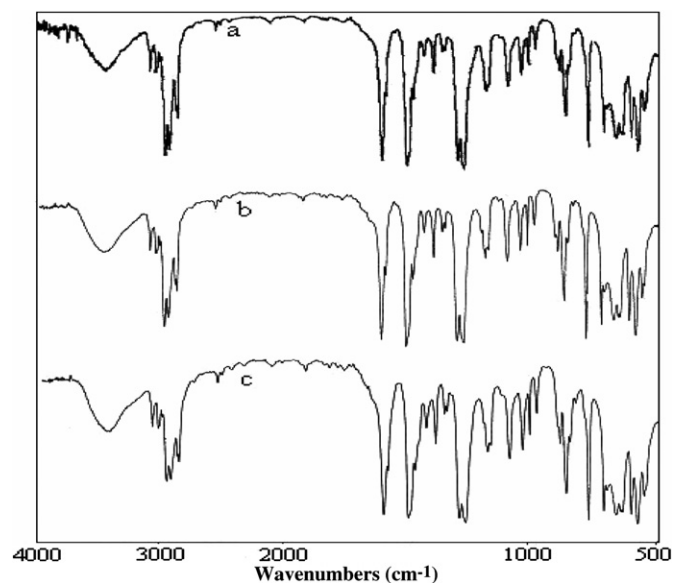

Fig. 2. FT-IR spectra of the catalysts (a) [n-Bu$_2$Sn(OPh)OSnBu$_2$(OPh)]$_2$; (b) the catalyst separated from the reaction catalyzed by n-Bu$_2$SnO–Cu$_2$O; (c) the catalyst separated from the reaction catalyzed by n-Bu$_2$SnO–CaO.

(entry 13), while n-Bu$_2$SnO–Cu$_2$O presented high activity. This shows Cu$_2$O is an excellent promoter.

Wang and co-workers [20] have found that [n-Bu$_2$Sn(O-Ph)OSnBu$_2$(OPh)]$_2$, which was in situ synthesized from phenol and n-Bu$_2$SnO, was the real active species when n-Bu$_2$SnO was used as the catalyst for the transesterification. We also separated [n-Bu$_2$Sn(OPh)OSnBu$_2$(OPh)]$_2$ from the reaction mixture when n-Bu$_2$SnO was used, and its infrared spectra are shown in Fig. 2. A weak peak at 3074 cm^{-1} and strong bands at 1591 and 1489 cm^{-1} are assigned to v(Ar–H) and skeletal vibration of benzene ring, respectively. Strong absorption at 2955 and 2929 cm^{-1} is attributed to

v(C–H). Peaks at 1281 and 1256 cm^{-1} are ascribed to v(Ar–O). Strong bands at 641 and 621 cm^{-1} are assigned to v(Sn–O–Sn). The absorption bands at 550 and 524 cm^{-1} are attributed to v(Sn–C) and v(Sn–O), respectively. When n-Bu$_2$SnO–Cu$_2$O and n-Bu$_2$SnO–CaO were used as catalysts, respectively, new catalysts were separated from the corresponding reaction mixture. As shown in Fig. 2, new the catalyst had the same infrared characters as [n-Bu$_2$Sn(OPh)OSnBu$_2$(OPh)]$_2$. This shows that they are [n-Bu$_2$Sn(OPh)OSnBu$_2$(OPh)]$_2$. In addition, it was found that the activity of [n-Bu$_2$Sn(OPh)OSnBu$_2$(OPh)]$_2$-Cu$_2$O was the same as that of n-Bu$_2$SnO–Cu$_2$O (entry 15).
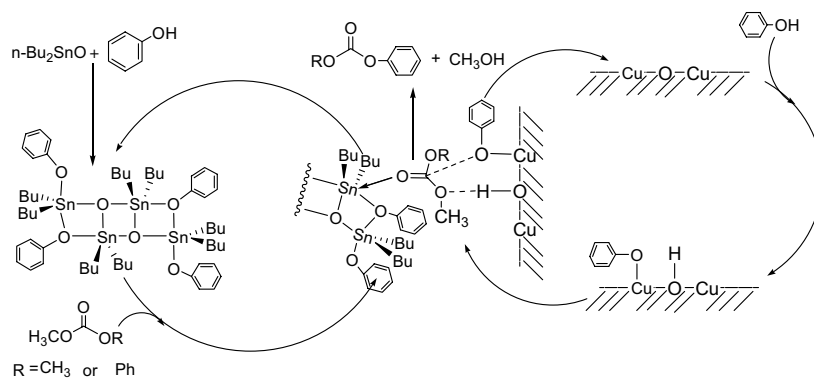
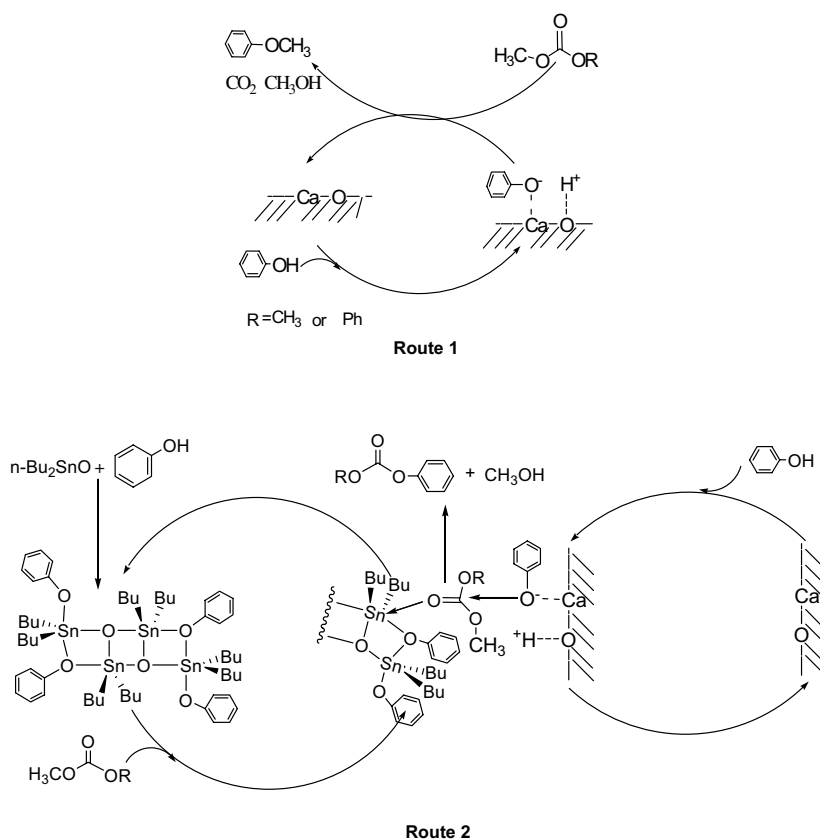Fig. 3. Plausible mechanism over n-Bu$_2$SnO–Cu$_2$O.

Route 1

Route 2

Fig. 4. Plausible mechanism over n-Bu$_2$SnO–CaO.

Table 3
Effect of the molar ratio of *n*-Bu$_2$SnO to CaO on the transesterification

Entry	n(n-Bu$_2$SnO):n(CaO)	X (DMC) (%)	Yield (%)			Transesterification selectivity (%)
			AN	MPC	DPC	
16	1:1	62.1	50.2	9.5	2.4	19.2
17	4:1	60.8	25.9	26.0	8.9	57.4
18	8:1	54.9	11.3	34.4	9.2	79.4
19	16:1	51.5	9.16	35.2	7.2	82.2

Conditions: n(DMC):n(phenol) = 1:2, n(catalyst):n(DMC + phenol) = 0.012:1, t = 8 h, T = 150–180 °C.

For *n*-Bu$_2$SnO–Cu$_2$O, *n*-Bu$_2$SnO is reacted initially with phenol to form [*n*-Bu$_2$Sn(OPh)OSnBu$_2$(OPh)]$_2$, acting as acid activation. Cu$_2$O can strengthen the nucleophilicity of phenol though it is not active, acting as base activation, so the acid–base complex catalyst shows the higher activity. According to the adsorption of phenol on the oxides [21] and the esterification mechanism over tetraorganodistannoxane [22], we suggested a plausible mechanism for the transesterification of phenol and DMC over *n*-Bu$_2$SnO–Cu$_2$O (Fig. 3).

As distinct from Cu$_2$O, CaO is a strong base and easily promotes phenol to form phenoxide anion. Phenoxide anion gives priority to the methyl carbon of DMC according to the hard–soft acid–base principle, so the transesterification selectivity over CaO was very low (entry 14). When the equimolar of CaO and *n*-Bu$_2$SnO constituted the acid–base complex catalyst, the forming rate of phenoxide anion is far quicker than that of the carbocation from DMC activated by *n*-Bu$_2$SnO, so the transesterification selectivity was still very low (entry 12). The plausible mechanism is shown in Fig. 4, and route 1 is dominant.

According to the above mechanism, the forming rate of phenoxide anion is slowed with the decrease of the CaO amount, and more phenoxide anions react with the carbonyl carbon activated by *n*-Bu$_2$SnO, so the transesterification selectivity increases. Route 2 in Fig. 4 gradually plays a dominant role. As shown in Table 3, the transesterification selectivity was certainly enhanced with the decrease of the molar ratio of CaO to *n*-Bu$_2$SnO. This shows that the mechanism analysis is reasonable.

4. Conclusions

It was firstly found that the transesterification of DMC and phenol to DPC was the reaction of soft base binding to hard acid by the analysis of the reaction and thermodynamic data, and hard acids were in favor of the transesterification. Among hard acids chosen in the experiment, *n*-Bu$_2$SnO exhibited the most activity.

When the hard acid *n*-Bu$_2$SnO and the weak base Cu$_2$O constituted the acid–base complex catalyst, the new catalyst gave the 50.8% conversion of DMC with 99.9% transesterification selectivity.

The study of the reaction mechanism showed the performance of the base in the acid–base complex affected the catalytic activity and transesterification selectivity. Cu$_2$O was the weak base, so it did not affect the transesterification selectivity, but could improve the activity of *n*-Bu$_2$SnO. By contrast, CaO was the strong base, so the transesterification selectivity was very low, and could be enhanced with the decrease of the molar ratio of CaO to *n*-Bu$_2$SnO.

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