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ORIGINAL PAPER

Study on the transesterification and mechanism of bisphenol A and dimethyl carbonate catalyzed by organotin oxide

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Abstract

$(CF_3C_6H_4)_2SnO$, $(CH_3C_6H_4)_2SnO$ and Ph_2SnO were successfully synthesized for the transesterification of DMC with BPA. The products of mono-methylcarbonate-ended-BPA (MmC(1)) and two-methylcarbonate-ended-BPA (DmC(1)) were selectively synthesized over them. The catalysts were characterized by FT-IR, TG and XPS. When Ph_2SnO was used as the catalyst at 170 °C, the BPA conversion reached to 28.60% and the transesterification selectivity reached to 98.35%. As for $(CF_3C_6H_4)_2SnO$, BPA conversion and transesterification selectivity declined to 12.48% and 64.74%, respectively. The BPA conversion increased to 42.83%, but the transesterification selectivity declined to 44.55% over $(CF_3C_6H_4)_2SnO$. Notability, the higher transesterification selectivity of Ph_2SnO was due to its lowest electron binding energy of Sn^{4+}. More importantly, the DMC adsorption, activation and decomposition process over $(CF_3C_6H_4)_2SnO$, $(CH_3C_6H_4)_2SnO$ and Ph_2SnO were characterized by TG–MS and in situ DRIFT techniques, which provided more information about the mechanism of transesterification and methylation.

Keywords Bisphenol A · Dimethyl carbonate · Phenyl tin oxide catalysts · TG–MS · In situ DRIFT

Introduction

PC is the fastest growing general engineering plastic among the five engineering plastics (Artham and Doble 2008). It is usually prepared through interfacial polycondensation of phosgene and bisphenol A (BPA). However, a large amount of toxic phosgene and methylene chloride was used as raw material and solvent in this method uses a large amount of toxic phosgene and methylene chloride as raw material and solvent. (Fukuoka et al.2003). To avoid the use of highly toxic reagents in the preparation of PC, diphenyl carbonate (DPC) (Fukuoka et al. 2003; Curtius et al. 1969; Kim and Lee 2010; Kim et al. 1992; Kim and Choi 1993; Turska and Wróbel 1970), CO (Goyal et al. 1999a, b; Hallgren and Lucas 1981; Ishii et al. 2000; Moiseev et al. 1996; Song et al. 2000; Takagi et al. 1998), and DMC (Bolon and Hallgren 1984; Deshpande et al. 1995; Haba et al. 2015; Pokharkar and Sivaram 1995; Shaikh et al. 1994) were used as carbonylation agents to replace phosgene. The synthesis of PC by oxidative carbonylation of BPA with CO requires expensive noble metal palladium as a catalyst; this method of preparing PC is difficult to industrialize because the low average molecular weight of PC produced can be obtained (Goyal et al. 1999a, b, 2000; Wang et al. 2004). High-molecular weight PC can be obtained by melting polycondensation of DPC with BPA, but the obtained byproduct phenol can only be removed in high temperature (higher than 300 °C) and low vacuum (less than 13 Pa). Furthermore, the high temperature always leads to more side reactions, which resulted in the discoloration of the PC resin (Schnell 1964). DMC can react with BPA to prepare precursor of polycarbonate. The catalyst used in this method is cheaper than the oxidative carbonylation of carbon monoxide. Moreover, DMC is completely qualified for a green reagent, and the byproduct methanol can be easily removed at low temperature (Huang et al. 2015). It is reported that high-molecular weight PC

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can be obtained by melt-polycondensation of two-methyl carbonate-ended oligomers (DmC (1)) or one-methylcarbonate-ended-BPA (MmC (1)) (Haba et al. 2015; Shaikh et al. 1994). Therefore, the transesterification of BPA with DMC is particularly important for the synthesis of DmC (1). Kim and Lee (2010) investigated the activity of TiO_2/SiO_2 with small specific surface area and they found that the conversion of BPA was only reached to 11% within 55 h at the reaction temperature of 160 °C, and the yield of MmC(1) was only 10%. Su et al. (2010) synthesized TiO_2/SBA-15 to catalyze the transesterification of DMC with BPA. It was found that the conversion of BPA reached to 30.33%; the yield of DmC(1) and MmC(1) achieved 25.3% and 3.6% under the optimized conditions, respectively. Organotin oxide has been widely used in catalytic transesterification (Shaikh and Sivaram 1996). Li et al. (2011) grafted organotin oxide onto SBA-15 molecular sieve for transesterification of BPA and DMC, but the yield of DmC (1) and MmC (1) was still very low compared with $(C_4H_9)_4SnO$. Liang et al. (2019) catalyzed the transesterification of DMC and BPA with lithium-doped titanium dioxide, but the selectivity of alkylation was still unsatisfactory. Haba et al. (2015) reported that DmC(1) could be synthesized by transesterification of BPA with excess DMC. They found that the yield of DmC(1) reached 22% over $(Bu_2SnCl)_2O$/DMAP, but a large amount of 4 A molecular sieve was added to remove byproduct methanol. Furthermore, it was found that alkyltin oxide, such as $(C_4H_9)_2SnO$, $(C_6H_{11})_2SnO$, and $(PhCH_2)_2Sn$ exhibited higher BPA conversion but lower DmC(1) selectivity in our previous work (He et al. 2013).

In this work, $(CF_3C_6H_4)_2SnO$, $(CH_3C_6H_4)_2SnO$ and Ph_2SnO were successfully synthesized and characterized by various techniques, and the transesterification of DMC with BPA was carried out over them. It was found that Ph_2SnO displayed the outstanding catalytic performance in the transesterification, and the transesterification selectively reached 98.35%. The adsorption–activation–desorption mechanism of DMC on Ph_2SnO was characterized by TG–MS and in situ drift, and the suitable mechanism of transesterification between DMC and BPA was proposed.

Experimental

Chemical reagents

Dimethyl carbonate (DMC) (99.9 wt%) was purchased from Macklin Biochemical Co., Ltd., Shanghai, China. BPA (Tianjin Chemical Reagent Co. (III)) was analytic reagent (AR) grade and used without further purification.

Catalyst preparation

Ph_2SnO was synthesized as the following steps. The synthesis of Grignard reagents was performed in a three-neck flask equipped with a thermometer, dropping funnel and a reflux condensing tube. Magnesium ribbon (2.4 g) and anhydrous ether (150 mL) were charged into flask under nitrogen atmosphere. When the temperature increased to 40 °C, the ether solution of bromobenzene (15.7 g) began to drop slowly, and after at least 2 h, the Goliath reagent was obtained.

Stannic tetrachloride (5.85 mL) and toluene (50 mL) were charged into flask under nitrogen atmosphere. The Goliath reagent was slowly dripped at 110 °C. The ether was removed after 3 h of reaction. The rest of mixture was transferred into a PTFE-lined reactor to continue reacting for 4 h at 150 °C. After the reactor cooled down, the filtered filtrate was precipitated by NaOH (1 mol/L), and the solid was refluxed in NaOH for 2 h. The solid was washed to neutral by deionized water and dried in vacuum oven at 120 °C for 12 h to obtain Ph_2SnO. The preparation process of $(CF_3C_6H_4)_2SnO$ and $(CH_3C_6H_4)_2SnO$ (see supporting information) is detailed.

Characterization

Fourier-transform infrared spectroscopy of catalysts was measured by KBr Compression method with BRUKER FT-IR Analyzer. The surface chemical information and elemental analysis of the catalysts were characterized by X-ray photoelectron spectroscopy (XPS) with Mg kα (1253.6 e V) X-ray source from Thermo Fisher Company, USA. The samples of 2–8 mg were put into TG (STA449F3, Netzsch Instruments) crucible, volatilized or decomposed under temperature-programmed conditions, and detected by MS (QMS403C, Netzsch Instruments) detector. The heating rate was 2 °C/min and the carrier gas was high-purity nitrogen with flow velocity of 60 mL/min. In situ infrared spectra were obtained by diffuse reflectance instrument with Nicolet 6700 detector. In addition, in situ DRIFT spectra were collected on a Nicolet 6700 spectrometer supplied with a diffuse reflectance attachment. The catalysts were put into the PIKE DRIFT reaction cell which could work under high temperature and high pressure. Ph_2SnO was treated at 200 °C with high-purity Ar for 0.5 h before entering DMC, then cooled to room temperature to test the background of the sample. Subsequently, the catalyst kept adsorbing DMC at room temperature until the spectrum of the signal was constant. The spectra were collected under different backgrounds of mirror and sample, respectively. When the catalyst was saturated with DMC, argon was injected to remove excess DMC. In situ adsorption spectra were measured with the desorption of DMC as temperature increased and obtained in mirror background and sample background.

Reaction procedure

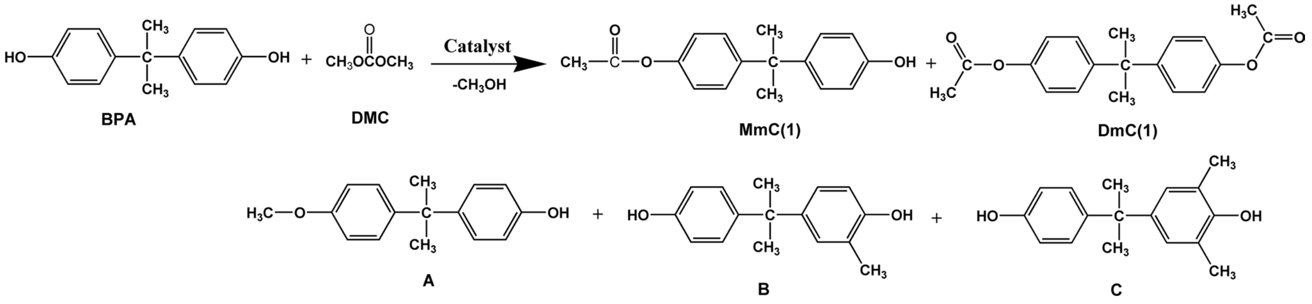
The interaction of Ph_2SnO with DMC was performed in a three-neck flask, equipped with a thermometer and a reflux condensing tube. 0.5 g catalyst and 70 mL DMC were loaded into the flask. The interaction lasted for 10 h at 90 °C to guarantee DMC was saturated and adsorbed by Ph_2SnO. After that, Ph_2SnO/DMC was air-dried for 24 h and then tested by TG–MS.

Transesterification was carried out in a three-neck flask, equipped with a thermometer, a controlled volume pump and fractionating column connected to a liquid dividing head under atmospheric pressure. BPA and catalyst were charged into flask under nitrogen atmosphere. When the mixture was reheated to 170 °C under rigorous stirring, DMC was added drop-wise by a controlled volume pump and the feeding rate of DMC during the reaction is 30 μL/min. During the reaction, the mixture of DMC and methanol was collected slowly in a receiver flask. After reaction, mixture was cooled and analyzed by GC–MS. The products were mainly one-methylcarbonate-ended-BPA (MmC(1)) and two-methylcarbonate-ended-BPA (DmC(1)), *O*-methylation of BPA (A), and from ortho-methylation of BPA with DMC (B and C) (Scheme 1). The selectivity of products to MmC(1) and DmC(1) was defined as the moles of MmC(1) and DmC(1) produced per 100 mol of consumed BPA.

$$\text{Conversion }\% = \frac{(\text{initial moles of BPA} - \text{final moles of BPA}) * 100}{\text{inital moles of BPA}}, \tag{1}$$

$$\text{Selectivity of products }\% = \frac{(\text{moles of product formed}) * 100}{\text{moles of BPA reacted}}, \tag{2}$$

$$\text{Yield }\% = \text{conversion of BPA*selectivity of products.} \tag{3}$$



Scheme 1 The main products of reaction between BPA and DMC

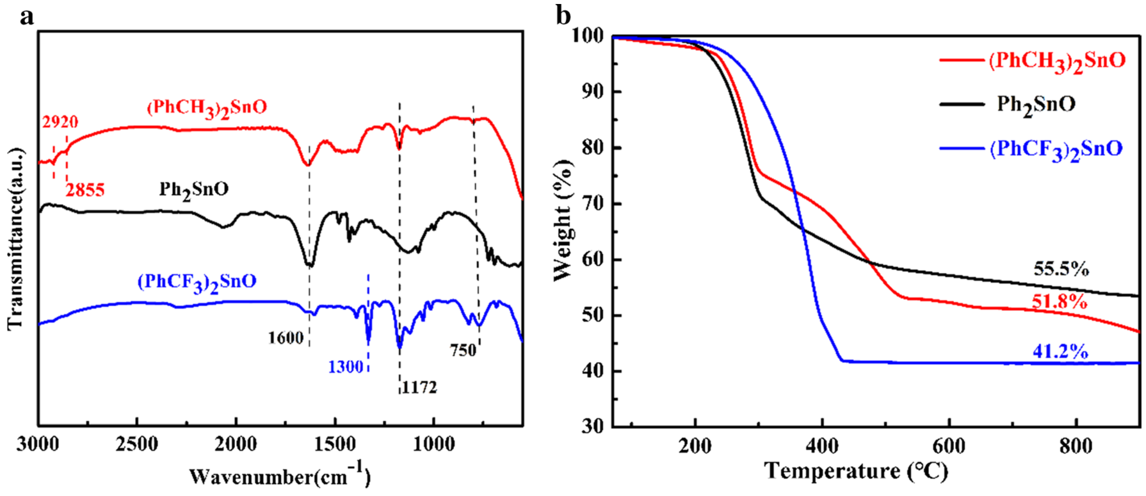


Fig. 1 **a** FT-IR spectra of phenyl tin oxide catalysts, **b** TG of phenyl tin oxide catalysts

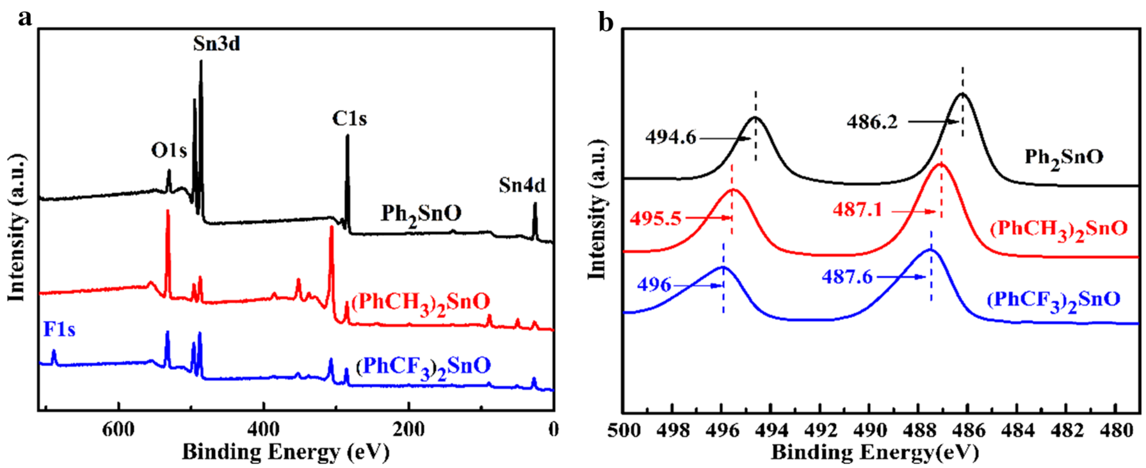


Fig. 2 The full scan (**a**) and Sn 3d (**b**) XPS of phenyl tin oxide catalysts

Results and discussion

Catalyst characterization

Figure 1a shows the FT-IR spectrum of the catalyst. The absorption peak near 1600 cm^{-1} was mainly attributed to the stretching vibration of the benzene ring skeleton. The IR peak at 750 cm^{-1} for $(CH_3C_6H_4)_2SnO$ and $(CF_3C_6H_4)_2SnO$ was assigned to P-substituted of the benzene ring. The IR bands appeared at 1172 cm^{-1} were ascribed to Sn=O bond stretching vibration, which was in agreement with the published results (He et al. 2013). At the same times, two weak bands located at 2920 cm^{-1} and 2855 cm^{-1} for $(CH_3C_6H_4)_2SnO$ were mainly attributed to the presence of –CH_3. Additionally, the IR bands that appeared at 1300 cm^{-1} for $(CF_3C_6H_4)_2SnO$ were due to the asymmetric stretch of the C–F bond. Figure 1b shows TG curves of different catalysts. The weights of $(CH_3C_6H_4)_2SnO$, $(CF_3C_6H_4)_2SnO$ and Ph_2SnO remained almost constant up to 200 °C. The decomposition of phenyl tin oxide occurred at about 200 °C, which was much higher than the transesterification temperature. In a wide temperature range of 200–550 °C, the catalyst weight residual was 51.8%, 41.2% and 55.5% for $(CH_3C_6H_4)_2SnO$, $(CF_3C_6H_4)_2SnO$ and Ph_2SnO, respectively. These results were attributed to the decomposition of organic groups. The results of the experiment were very close to the theoretical values 47.5%, 37.4% and 51.9%, respectively. Above 550 °C, the weight loss was attributed to the decomposition of oxides of Sn (Song et al. 2011).

The surface chemical state of solid catalyst could be detected by XPS (Jing et al. 2003). Figure 2 indicates the full scan and the high-resolution XPS spectra of phenyl tin oxide. The results of full spectrum scanning analysis of XPS demonstrated that the elements of O, C, Sn could be detected in all samples (Fig. 2a). But only F could be observed for $(CF_3C_6H_4)_2SnO$, which was in agreement with the above FT-IR results. Figure 2b reveals Sn 3d peaks of phenyl tin oxide catalysts. Sn 3d peaks of $(CF_3C_6H_4)_2SnO$ appeared at 496 eV and 487.6 eV, which were higher than those of $(CH_3C_6H_4)_2SnO$ and Ph_2SnO. Sn 3d electron binding energy of Ph_2SnO was the lowest among the three phenyl tin oxide catalysts. It indicated that Sn cation activity among the three phenyl tin oxide catalysts was as follows: $(CF_3C_6H_4)_2SnO>(CH_3C_6H_4)_2SnO>Ph_2SnO$ (Xia et al. 2014).

Adsorption–activation–desorption mechanism

The different active sites of DMC on the surface of Ph_2SnO were characterized by TG–MS techniques. The appearance of DMC (Fig. 3a) and CH_3OH (Fig. 3b) was observed in TG–MS curves of DMC–Ph_2SnO. The desorption or decomposition signals of the adsorbed DMC were detected at about 68, 87, 132, 156 and 170 °C, respectively. The desorption signals at 68–87 °C were attributed to the physical and weak chemisorption of DMC on the Ph_2SnO surface. The desorption or decomposition signals at 132, 156 and 170 °C indicated the formation of different adsorption types of DMC on the surface of the catalyst at high temperature. (Gao et al. 2016). The escapement peak of methanol was also detected in the TG–MS curves, due to the decomposition of DMC at high temperatures (Raab et al. 2001; Vilela et al. 2010). According to the results of TG–MS, five temperature points of 68, 87, 132, 156 and 170 °C were selected, and the adsorption types of DMC were determined by in situ drift.

The mechanism of adsorption–activation–desorption of DMC on Ph_2SnO surface was characterized by in situ DRIFT. Figure 4a and c shows in situ infrared spectra of DMC adsorbed on Ph_2SnO at selected temperatures under mirror background and sample background, respectively.

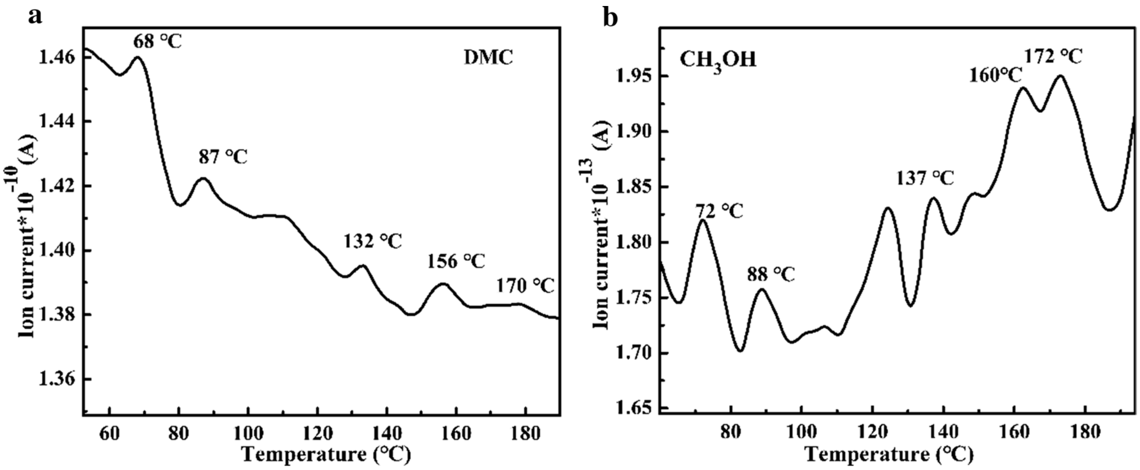


Fig. 3 TG–MS curves of DMC–Ph_2SnO: **a** DMC, **b** CH_3OH

The characteristic absorption peak at 3054 cm^{-1} was attributed to the stretching vibration of C–H on the benzene, while the peak at 1072 cm^{-1} was caused by the stretching vibration of the Sn=O bond. In addition, the absorption peaks at 1293 cm^{-1} and 1765 cm^{-1} were attributed to the stretching vibration of O–C–O and C=O bonds, respectively. With the increase of temperature from 68 to 170 °C, the stretching vibration peaks of O–C–O and C=O split into 1305–1263 cm^{-1} and 1800–1764 cm^{-1}, respectively. That was attributed to the conformation of different DMC adsorption types on the surface of Ph_2SnO [*cis–cis* (I)and *cis–trans* (II) and cis–cis species III (Scheme 2)]. The positive charge of the carbonyl carbon atom increased because the Sn atom in Sn=O interacted with the carbonyl oxygen atom, which leads to the red shift of C=O (1764 cm^{-1}) and the blue shift of O–C–O (1305 cm^{-1}). After that, hydroxyl oxygen atoms in BPA reacted with carbonyl carbon atoms to form transesterification products. The intensity of the blue shift peak at 1800 cm^{-1} increased with the temperature rose, (Fig. 4b), which was attributed to the interaction of the Sn atom in Sn=O bond with the methyl oxygen atom. Meanwhile, the positive charge of the carbon atom in the CH3O increased. Moreover, the negative peak of CH_3O^- was measured, which indicated that the interaction of carbonyl oxygen with Sn weakened the bond energy of O–CH_3 in DMC. Oxygen atoms in BPA mainly reacted with the methyl of DMC to form alkylation products (Scheme 1). Therefore, the coordination between carbonyl oxygen atoms and Sn resulted in the activation of the carbonyl group and the O–CH_3 moieties of the organic carbonate (Bonino et al. 2005; Distaso and Quaranta 2008). The degree of activation of CH_3O^- increased as the temperature increases (Fig. 4c). An experimental supporting evidence is presented in Table 2, which compared the effect of the temperature on the reactivity of DMC under otherwise analogous reaction conditions (time, Ph_2SnO loading, etc.). The stretching vibrational peaks of methyl in liquid DMC appeared at 2962 and 2852 cm^{-1} (Fig. 4d.). However, the methyl peak appeared and shifted to 2904 and 2825 cm^{-1} when the temperature was higher than 156 °C, which further indicated that high temperature led to methyl activation to form alkylation products.

Figure 5 shows the corresponding MS curves of $(CH_3C_6H_4)_2SnO$. It was observed that there were a large number of DMC and CH_3OH escape before 200 °C. There are five desorption temperature points for DMC: 71 °C, 108 °C, 121 °C, 142 °C, 175 °C. The adsorption type could be further determined by situ DRIFT and the product distribution between BPA and DMC at these temperature points could be detected by GC.

The in situ DRIFT spectra of DMC adsorbed on $(CH_3C_6H_4)_2SnO$ at various temperatures in mirror background are shown in Fig. 6a. The absorption band at 1765 cm^{-1} was caused by stretching vibration of C=O bond, but it could not obtain more information as temperature rises near 1765 cm^{-1}. Therefore, in situ DRIFT of DMC adsorbed on $(CH_3C_6H_4)_2SnO$ at various temperatures in sample background is shown in Fig. 6b. The position of υ(C=O) almost unchanged when the temperature rises to 71 °C, 108 °C and 121 °C, while the peak splits into two major components at 1774 cm^{-1} and 1744 cm^{-1} as temperature increases to 142 °C and 175 °C (Fig. 6c). The blue-shifted peak at 1774 cm^{-1} was stronger than the red-shifted peak at 1744 cm^{-1}, suggesting methylation products were easier to form with the catalysis of $(CH_3C_6H_4)_2SnO$. In addition, stretching vibration of –CH_3 appearing at 2863 cm^{-1} implies that methylation activities were obvious at 153 °C and 175 °C.

The TG–MS curves of $(CF_3C_6H_4)_2SnO$ are shown in Fig. 7. As shown in Fig. 7, the desorption of a small amount of DMC probably comes from physical adsorption or weak

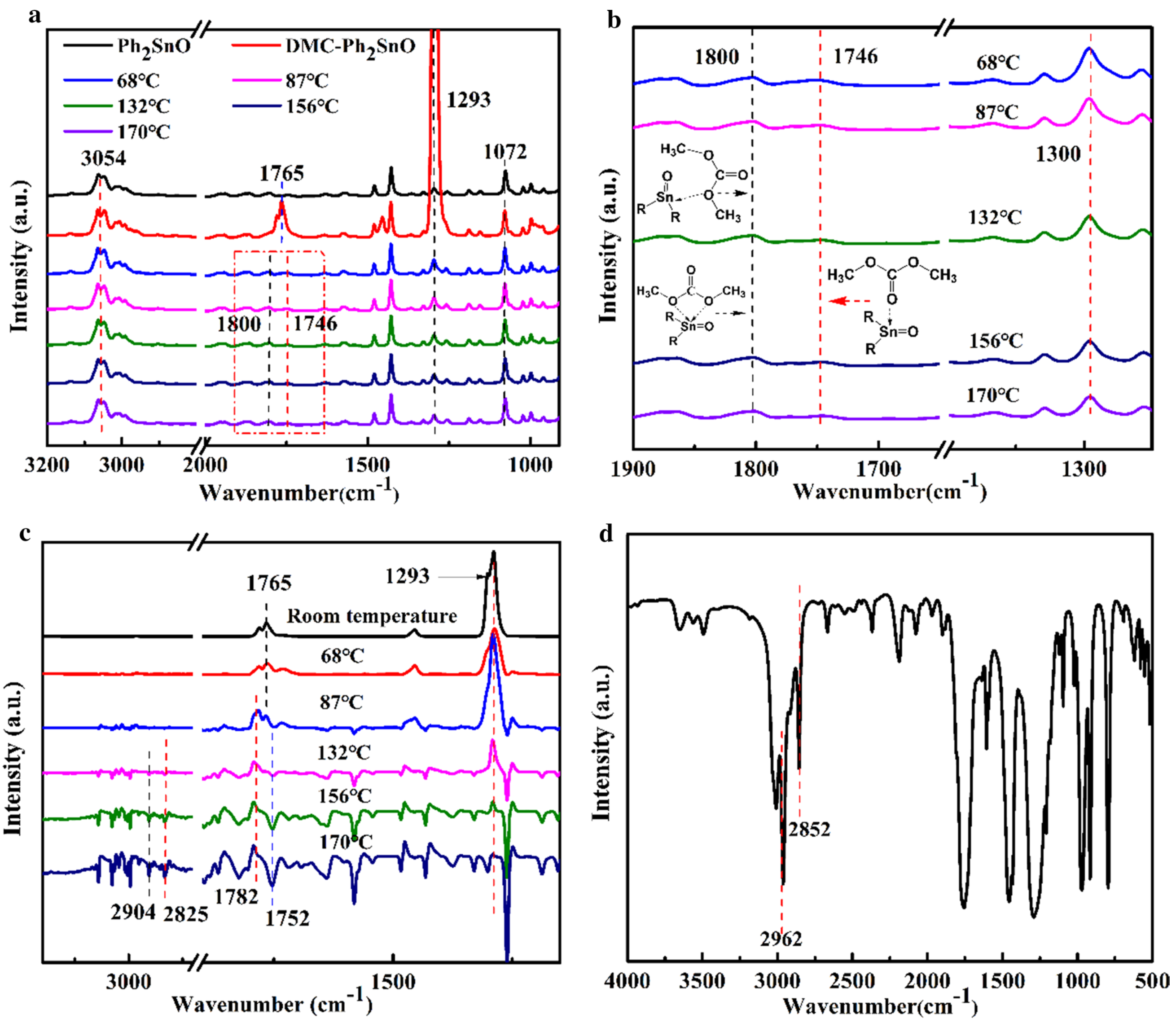
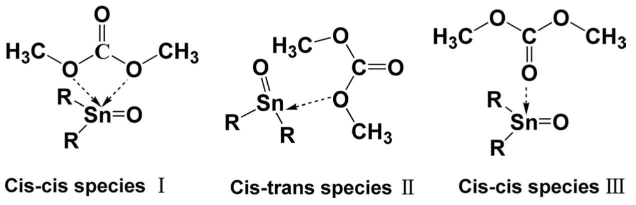


Fig. 4 **a** In situ DRIFT spectra of DMC adsorbed on Ph_2SnO at various temperatures in mirror background, **b** corresponding magnification of selected area. **c** In situ DRIFT spectra of DMC adsorbed on Ph_2SnO at various temperatures in a sample background, **d** FT-IR spectra of DMC



Scheme 2 DMC absorbs over phenyl tin oxide (*Cis–cis* species I, *Cis–trans* species II, *Cis–cis* species III)

chemisorption before 140 °C. Temperature above 140 °C may be attributed to chemisorption. Therefore, the three temperature points at 74 °C, 135 °C, and 168 °C were selected to analyze DMC adsorption type by in situ DRIFT and then to catalyze BPA and DMC to determine the composition of its product by GC.

In situ DRIFT spectra of DMC adsorbed on $(CF_3C_6H_4)_2SnO$ at various temperatures in mirror background and sample background are presented in Fig. 8. The

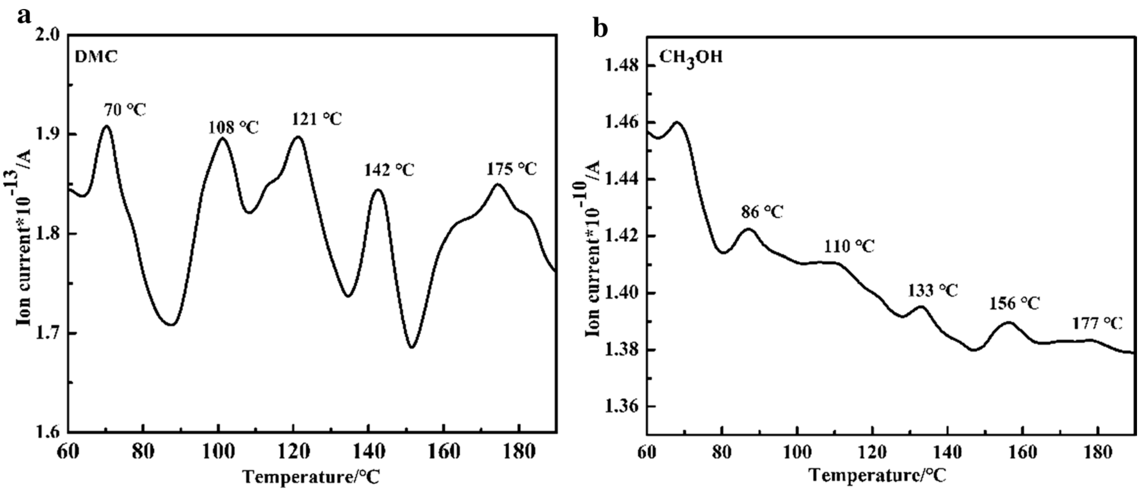


Fig. 5 TG–MS curves of DMC–$(CH_3C_6H_4)_2SnO$: **a** DMC, **b** CH_3OH

stretching vibration at 2855 cm^{-1} was caused by CH_3- of DMC which becomes clear at 165 °C; it was indicated that methylation activity was obvious at this temperature (Table 4 entry 3). Therefore, the higher temperature, the more methylated product. From 74 to 165 °C, the peak shape changed from positive to negative, which illustrated methylation that activity at 96 °C and 165 °C was different from 74 °C. The negative peaks of O–C–O move to 1275 cm^{-1} under 96 °C and 165 °C, but the peak at 74 °C was still positive, which indicates the difference between chemisorption at 165 °C and physisorption at 74 °C.

Catalytic activity

$(CF_3C_6H_4)_2SnO$, Ph_2SnO and $(CH_3C_6H_4)_2SnO$ were used as catalysts to test transesterification between BPA and DMC, and the results are shown in Table 1. Ph_2SnO exhibited the best performance for transesterification, BPA conversion achieved 28.60%, and transesterification selectivity [MmC (1) and DmC (1)] was 98.35%. When $(CF_3C_6H_4)_2SnO$ was used as catalyst, the BPA conversion and methylation selectivity increased to 42.83% and 55.4%, respectively. But the transesterification selectivity decreased to 44.6%. Besides, the methylation selectivity and the conversion of BPA declined to 35.26% and 12.48% over $(CH_3C_6H_4)_2SnO$. Based on the above discussion results, the lower activity of $(CF_3C_6H_4)_2SnO$ in transesterification was caused by the stronger electron withdraw which came from the trifluoromethyl benzene group (see XPS analysis). The high transesterification selectivity of Ph_2SnO may be related to its confined region effects (see Supporting information) (Li et al. 2011).

The effects of different reaction temperatures on the catalytic activity of Ph_2SnO were tested, and the results are listed in Table 2. The reaction temperature was varied from 68 to 170 °C, and BPA conversion increased from 0.2 to 28.60%, while transesterification selectivity decreased from 100 to 98.35%, and only 1.65% methylation products were detected. In addition, based on the in situ DRIFT, TG–MS and FT-IR characterization, high temperature might destroy the adsorption type of *cis–cis* species (I) or *cis–trans* species (II), which also results in the increase of methylated products.

Table 3 shows the catalytic activity of $(CH_3C_6H_4)_2SnO$ at different reaction temperatures. It can be seen from the results that the transesterification selectivity was 100 when the reaction temperature was lower than 121 °C. When the reaction temperature was 175 °C, the conversion of BPA increased 60.49%, but the selectivity of methylation increased sharply to 88.13%, and the selectivity of transesterification decreased to 11.87%. None DmC(1) was detected.

The effect of reaction temperature on the catalytic activity of $(CF_3C_6H_4)_2SnO$ is listed in Table 4. According to the selected temperature, the conversion of BPA increases from 0 to 40.92%, and the selectivity of transesterification was 93.43% when the reaction temperature was 132 °C. However, when the reaction temperature was 165 °C, the transesterification selectivity decreased to 46.6 °C.

Figure 9 shows the effects of the amount of Ph_2SnO on the transesterification of DMC and BPA. When the amount of Ph_2SnO was 0.05 g, the yields of MmC(1) and DmC(1) were 14.3% and 1.31%. As the amount of catalyst increased to 0.25 g, the yields of MmC(1) and DmC(1) increased to 25.8% and 2.3%, respectively. Meanwhile, methylation

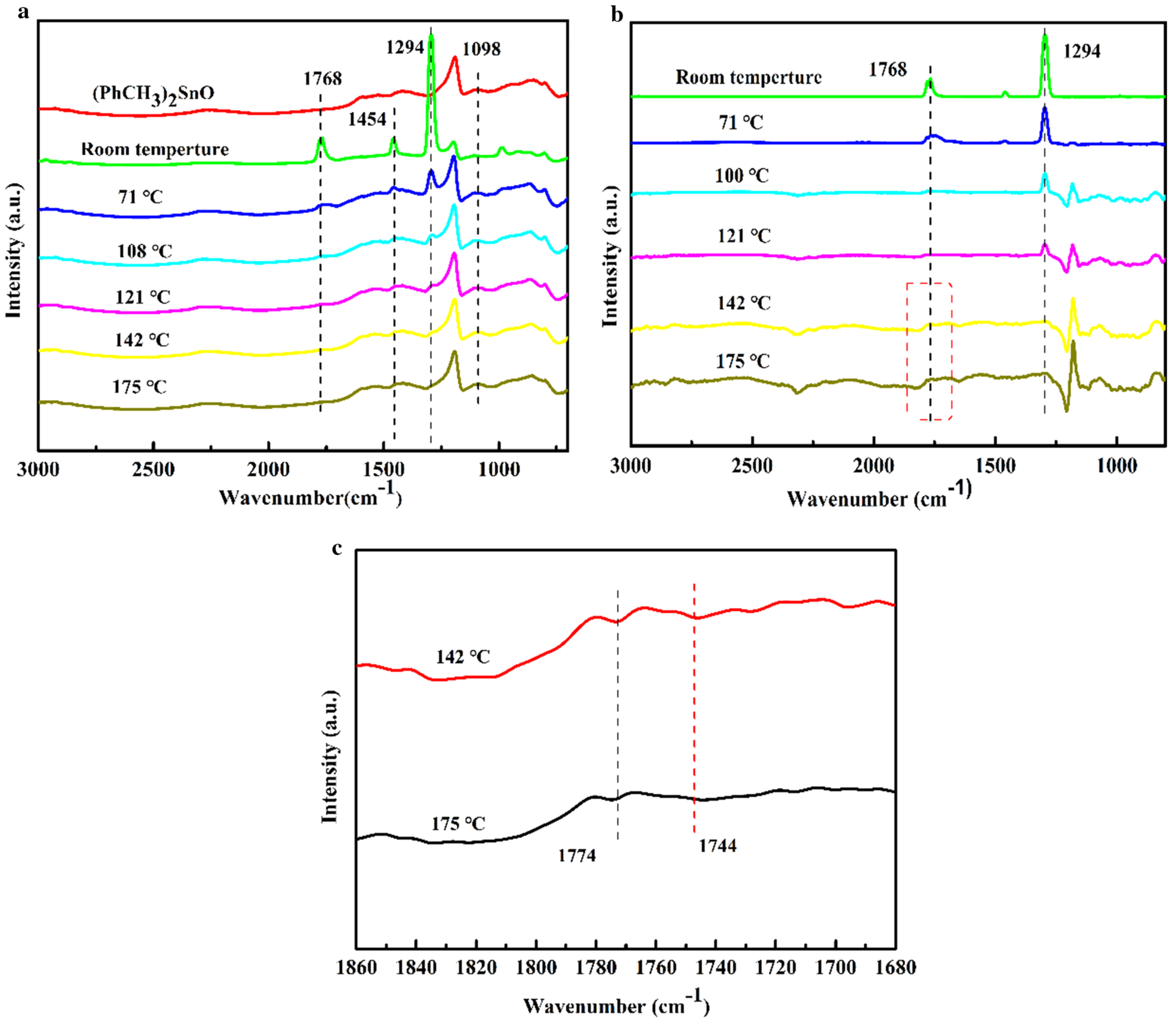
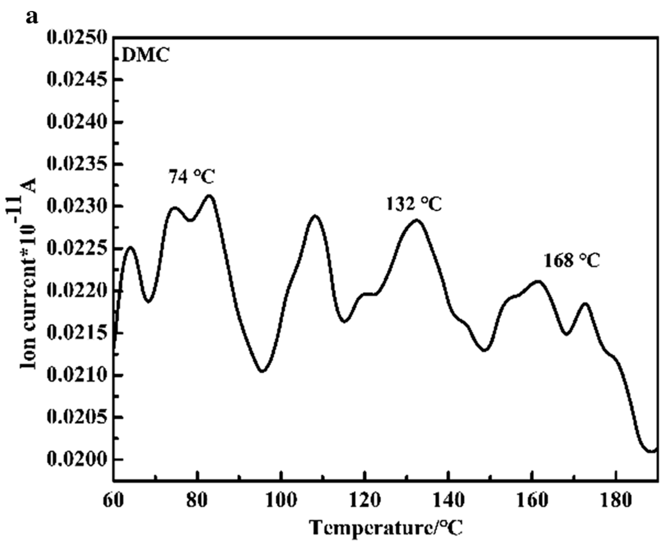


Fig. 6 **a** In situ DRIFT spectra of DMC adsorbed on $(CH_3C_6H_4)_2SnO$ at various temperatures in a mirror background, **b** Corresponding magnification of selected area. **c** In situ DRIFT spectra of DMC adsorbed on $(CH_3C_6H_4)_2SnO$ at various temperatures in sample background

selectivity reached to the minimum of 1.65%. When the catalyst amount was 0.4 g, MmC(1) and DmC(1) yields decreased to 15.28% and 1.06%, while the methylation selectivity increased to 7.64%. The excessive catalyst could lead to the decarboxylation of MmC(1) and DmC(1) (Bae 2015Query). Therefore, the optimal catalyst amount was 0.25 g.

Suggested mechanism

The plausible mechanism of the carboxymethylation of DMC with BPA over Ph_2SnO catalyst is shown in Scheme 3. When the transesterification of DMC with BPA was catalyzed by Ph_2SnO, the interaction between Sn cations in



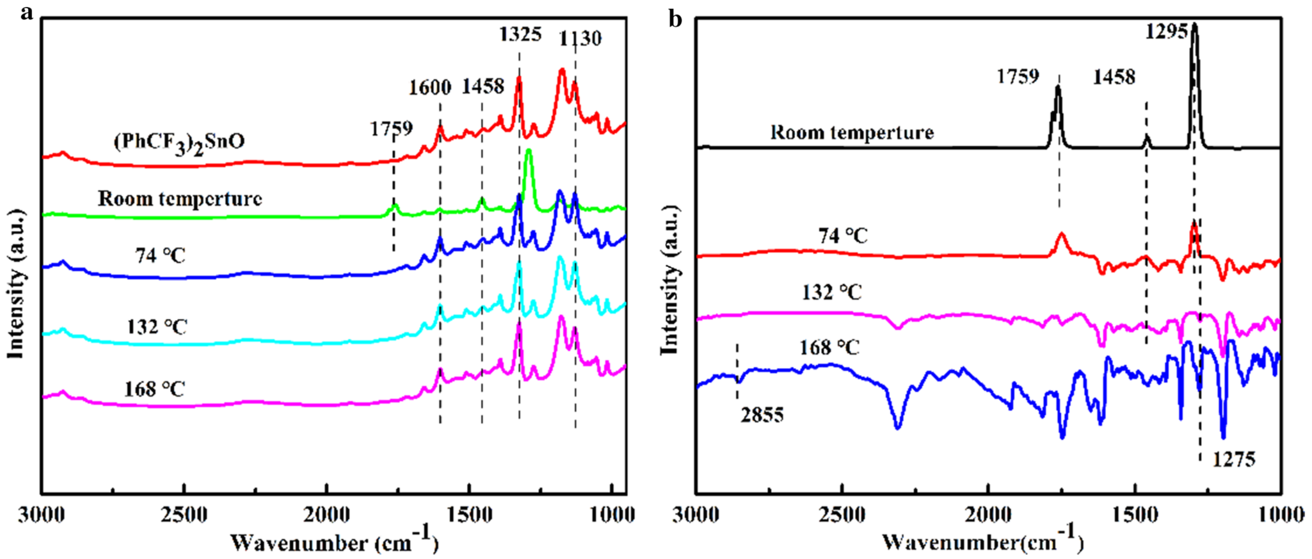


Fig. 7 TG–MS curves of DMC–$(CF_3C_6H_4)_2SnO$: **a** DMC, **b** CH_3OH

Fig. 8 **a** In situ DRIFT spectra of DMC adsorbed on $(CF_3C_6H_4)_2SnO$ at various temperatures in mirror background, **b** in situ DRIFT spectra of DMC adsorbed on $(CF_3C_6H_4)_2SnO$ at various temperatures in sample background

Table 1 The effects of different phenyl tin oxide catalysts on the selective carboxylation of BPA with DMC at the same temperature

Catalyst	Conversion (%)	Selectivity distribution (mol %)		
		Methyl	MmC (1)	DmC (1)
$(CF_3C_6H_4)_2SnO$	42.83	55.40	41.34	3.26
Ph_2SnO	28.61	1.65	90.33	8.02
$(CH_3C_6H_4)_2SnO$	12.48	35.26	63.57	1.17

Reaction conditions: BPA 2.28 g, DMC 17 mL, catalyst 0.25 g, *T* 170 °C, *t* 10 h

Table 2 The effects of Ph_2SnO on the selective carboxylation of BPA with DMC in different temperatures

Catalyst	Temperature (°C)	Conversion (%)	Selectivity distribution (mol %)		
			Methyl	MmC (1)	DmC (1)
Ph_2SnO	68	0.2	0	100	0
	87	1.71	0	100	0
	130	8.04	0	100	0
	156	14.03	0.83	99.17	0
	170	28.60	1.65	90.33	8.02

Reaction conditions: BPA 2.28 g, DMC 17 mL, catalyst 0.25 g, *t* 10 h

Table 3 The effects of $(CH_3C_6H_4)_2SnO$ on the selective carboxylation of BPA with DMC in different temperatures

Catalyst	Temperature (°C)	Conversion (%)	Selectivity distribution (mol %)		
			Methyl	MmC (1)	DmC (1)
$(CH_3C_6H_4)_2SnO$	71	0.16	0	100	0
	108	1.77	0	100	0
	121	3.59	0	100	0
	142	10.35	32.47	65.78	1.75
	175	60.49	88.13	11.87	0

Condition: BPA 2.28 g, DMC 17 mL, catalyst 0.25 g, 10 h

Table 4 The effects of $(CH_3C_6H_4)_2SnO$ on the selective carboxylation of BPA with DMC in different temperatures

Catalyst	Temperature (°C)	Conversion (%)	Selectivity distribution (mol %)		
			Methyl	MmC (1)	DmC (1)
$(CF_3C_6H_4)_2SnO$	74	0	0	0	0
	132	12	6.57	82.67	10.75
	165	40.92	53.40	45.34	1.26

Condition: BPA 2.28 g, DMC 17 mL, catalyst 0.25 g, 10 h

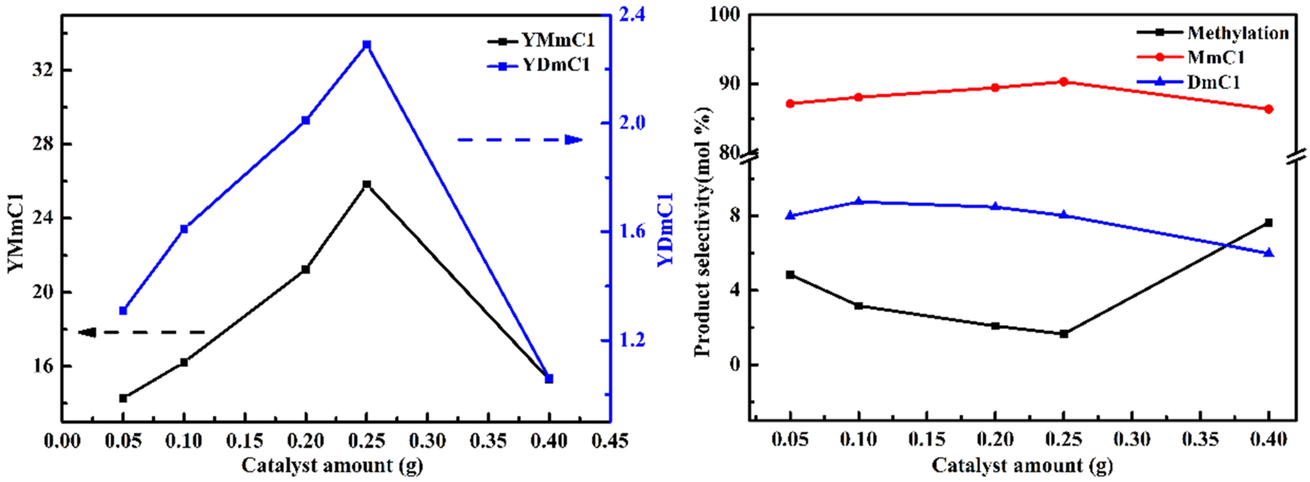
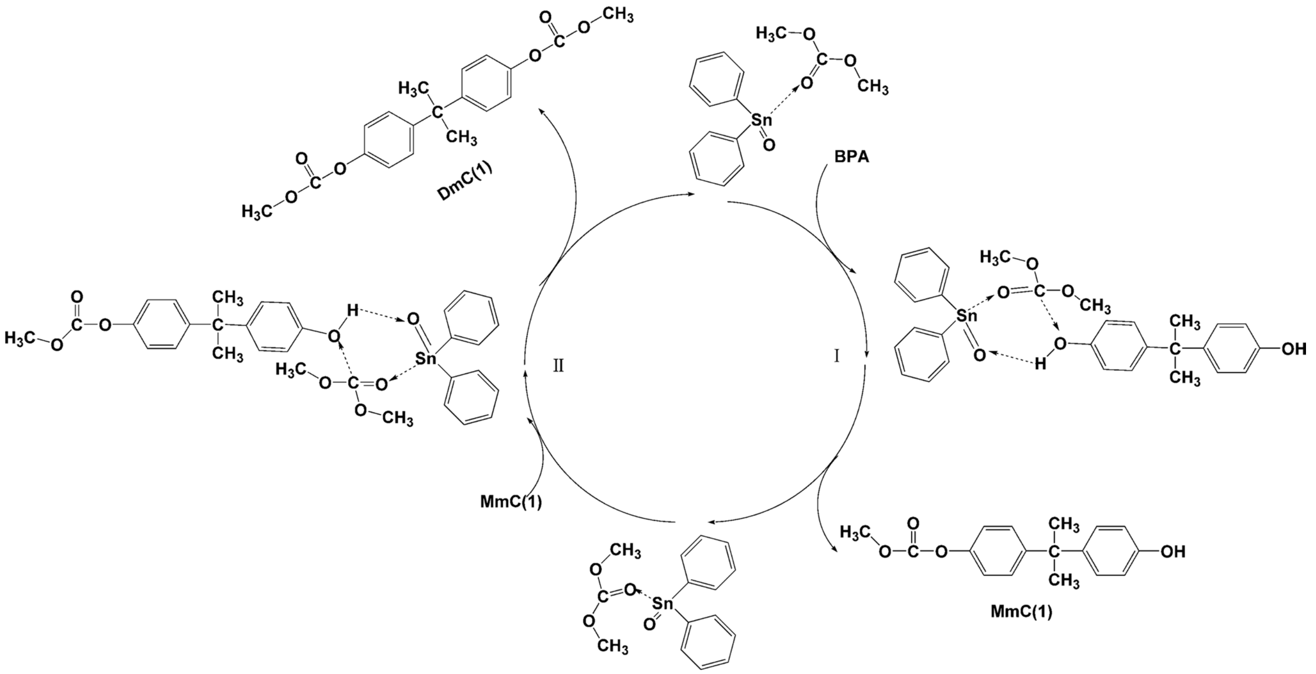


Fig. 9 Effect of Ph_2SnO amount on transesterification of BPA with DMC (reaction conditions: BPA 2.28 g, DMC 17 mL, T 170 °C, t 10 h)

Sn=O and O atoms in C=O increased the positive electrical of carbonyl carbon atoms to form the type of *cis–cis* species (III) adsorption. At the same time, hydrogen atoms of BPA reacted with oxygen atoms in Sn=O to form hydrogen bonds. Carbonyl carbon of DMC was attacked by hydroxyl oxygen in BPA to form transesterification products.

Conclusion

Ph_2SnO showed the best catalytic performance in the reaction of BPA with DMC at 170 °C, the conversion of BPA reached 28.6%, and the selectivity of transesterification came up to 98.35%. The blue-shift peak of in situ DRIFT spectra at 1800 cm^{-1} indicated that the oxygen atoms provided by CH_3–O of DMC combined with Sn in Sn=O to form *cis–cis* species (I) or *cis–trans* species (II), and this process was accompanied by the formation of methylation products. When Sn in Sn=O interacted with the oxygen of the C=O to form *cis–trans* species (III), the oxygen of BPA attacked the carbonyl carbon to form carboxymethylation



Scheme 3 The plausible mechanism of the carboxymethylation of DMC with BPA over Ph_2SnO catalyst

products, resulting in red-shift υ (C=O) at 1746 cm^{-1} on the in situ DRIFT spectra. In addition, regional effects can also affect the selectivity of ester exchange reactions.

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