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Mesoporous silica-anchored organotin as heterogeneous catalyst for the transesterification of dimethyl carbonate with phenol

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Abstract A simple scheme for a mesoporous silica-anchored organotin catalyst was developed for the transesterification of dimethyl carbonate with phenol to diphenyl carbonate. N_2-sorption, TEM, UV–Vis, and elemental analysis combined with ^{29}Si and ^{13}C NMR measurements evidenced the formation of mesoporous organic–inorganic hybrid silica with a highly dispersed tetrahedral Sn species. The catalyst exhibited excellent activity and reusability in the transesterification. With a catalyst of 1.0 g, a reaction temperature of 150–180 °C, and a reaction time of 9 h, the phenol conversion and transesterification selectivity reached 51.1 and 99.9 %, respectively. The phenol conversion just decreased from 41.2 to 35.0 % after five runs with 0.5 g of catalyst. The improved stability was attributed to the strong covalent bonding between the organotin and mesoporous silica.

Keywords Organotin · Silica-anchored · Transesterification · Diphenyl carbonate · Phenol

Introduction

Diphenyl carbonate (DPC) is an important green chemical intermediate for the production of many organic chemicals, especially for the synthesis of polycarbonate by the melt polymerization process [1–3]. The transesterification of dimethyl

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carbonate (DMC) with phenol is considered to be the most suitable phosgene-free route to synthesize DPC [4–6]. This reaction is usually carried out in the liquid phase, and the organotin catalysts display excellent catalytic performance [7]. However, the organotin compounds are usually highly toxic, and difficult to be separated from the reaction system and recovered for reuse. A scientifically rewarding strategy to overcome the problems is to anchor the organotins onto an insoluble support, which is also a general trend nowadays in catalysis [8, 9].

In this context, anchored organotins on insoluble support have been successfully developed, especially in the use of polymers as carriers. With regard to transesterification reactions, excellent catalytic properties have been reported for cross-linked polystyrene-anchored dichlorobutyltins, distannoxanes, and trichlorotins [10–12]. For example, the polystyrene-anchored $(CH_2)_{11}$–$SnCl_3$ could display an average conversion degree of 76 % after 2 h in the transesterification between ethyl acetate and n-octanol. The catalyst was recycled at least nine times without loss of activity, and the residual tin content averaged just 5 ± 3 ppm [11]. Although the use of polymer supports may give advantages of facile functionalization and high loading, there are the disadvantages of poor mechanical stability, solvent swelling, and even decomposing at the relatively high temperature. Compared to polymer carriers, silica exhibits better thermal and chemical stabilities, so the silica-anchored organotin catalyst may provide better stability. The covalent anchoring of molecule catalysts on the silica surface is generally achieved by the reaction between surface silanols and a $Si(OEt)_3$ group of molecule-substituted triethoxysilane [13]. However, the organotin-silane is not a ready-made reagent, and often requires complex organic synthesis. For this reason, only a few silica-supported organotins have been reported so far, including dialkyl dimethoxyltin [14], dibutylpropyltin hydride [15], undecyltrichlorohexyltin [16], and propyl methoxyldichlorotin [17]. The use of silica-supported organotins to catalyze transesterification reactions of DMC and phenol has not yet been reported.

In this paper, one kind of organotin-substituted triethoxysilane was synthesized by a simple method, and then anchored on the mesoporous silica to yield a silica-anchored organotin catalyst. This catalyst was used as a heterogeneous catalyst to catalyze the liquid transesterification reaction between DMC and phenol, and the catalytic and recyclability properties was presented and discussed.

Experimental

Reagents

Pluronic P123 triblock polymer was purchased from Aldrich Chemical Co. 3-chloropropyl triethoxysilane was obtained from Sinopharm: $[CH_3^{(1)}CH_2^{(2)}O]_3SiCH_2^{(3)}CH_2^{(4)}CH_2^{(5)}Cl$, ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 3.67–0.77 (m, 2H, H_3), 1.20 (t, 9H, H_1), 1.81–1.92 (m, 2H, H_4), 3.47–3.55 (m, 2H, H_5), 3.79 (q, 6H, H_2); ^{13}C NMR (75 MHz, $CDCl_3$, 293 K): δ 8.1 (C_3), 18.2 (C_1), 26.5 (C_4), 47.4 (C_5), 58.4 (C_2). The other chemicals were obtained from local manufacturers. Diethyl ether was dried and distilled over Na prior to use, and the other chemicals were used as received.

Preparation of mesoporous silica-anchored organotin catalyst

The preparation of mesoporous silica-anchored organotin primarily involved the synthesis of organotin-silane and the anchoring of organotin on the mesoporous silica. Mesoporous silica was prepared using a reported procedure at 100 °C [18]. The template was removed by extraction using Soxhlet apparatus in ethanol, and dried at 120 °C overnight under vacuum.

Synthesis of organotin-silane

A suspension of magnesium powder (4.0 g), 3-chloropropyl triethoxysilane (8.0 g), and a small amount of iodine in 60 mL diethyl ether was heated to reflux with stirring under an inert atmosphere for 2 h. After cooling, the supernatant liquid was decanted into another container. Then, $SnCl_4$ (17.0 g) was added dropwise to the obtained liquid. The unreacted $SnCl_4$ was reduced by addition of excess magnesium, and reflux for 5 h. Some non-volatile solvents, such as toluene, could be added during this manipulation. The resulting mixture was filtered, and the filtrate was obtained as a colorless or faint yellow liquid. The atomic ratio of Cl:Sn:Si was 2.83:0.83:1 as determined by ICP-AES and Mohr titration.

Anchoring of organotin on mesoporous silica

The activated silica powder was suspended in the above solution, and refluxed under stirring for 12 h. A white solid was recovered by filtration, then washed with ethanol, and dried at 80 °C for 12 h. The sample was named as SiO_2–Sn, with a chemical formula of $C_{12.7}H_{47.0}O_{20.0}Cl_{2.5}Si_{8.3}Sn_{1.3}$. After each catalytic run, the catalyst was filtrated, washed with DMC, and dried at 80 °C overnight. The recovered samples were designated as SiO_2–Sn-*x*, where *x* indicated the recycle number.

Characterizations

The textural properties were measured from nitrogen sorption isotherms at −196 °C with a Builder SSA-4200 system. Prior to measurement, the samples were degassed at 200 °C for 6 h. The surface areas were calculated by the BET method, and the pore size distributions were calculated from the adsorption branch of the isotherms using the BJH method. A JEM-2010 high-resolution transmission electron microscope with an electron kinetic energy of 300 kV was used to scan the silica and catalysts on the Cu grid. The Sn and Si content were determined with an inductively coupled plasma-atomic emission spectrometer (IRIS 1000). Elemental analyses (C and H) were carried out with a Euro EA 3000 elemental analyzer. The chlorine was detected by the Mohr titration method [19]. The solid-state NMR spectra were recorded on a Bruker Avance 300 M solid-state spectrometer at resonance frequencies of 125 MHz for ^{13}C and 99 MHz for ^{29}Si.

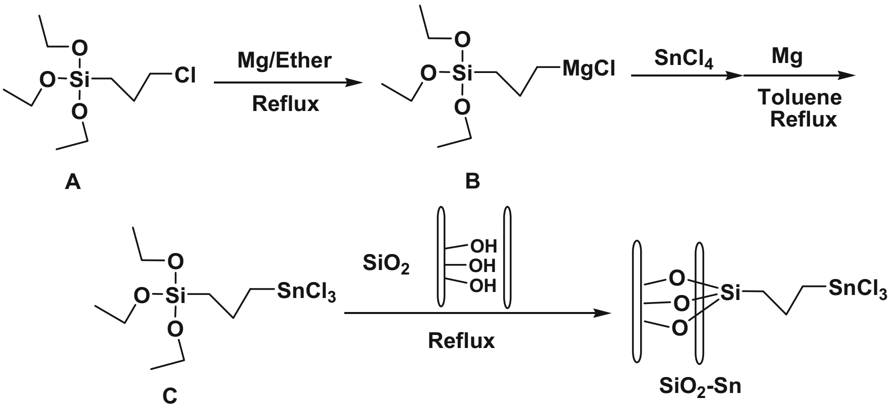
Reaction procedure

The reaction was carried out in a 100 mL glass flask equipped with a thermometer, a nitrogen inlet, a dropping funnel and a fractionating column connected with a liquid dividing head. Phenol and catalyst were charged into the flask under a nitrogen atmosphere. DMC was added drop-wise into the flask after the mixture was heated to 175 °C. The reaction temperature was kept at 150–180 °C during the period of reaction. The products were analyzed by a gas chromatograph equipped with a FID detector.

Results and discussion

Catalyst synthesis and characterization

The organotin-alkoxysilanes have been prepared through the hydrosilylation of alkenyl organotin by triethoxysilane [16], or the hydrostannylation of alkenyl trialkoxysilane by organotin hydride [15]. The former method used noble metal catalysts, and the latter method needed expensive active organotin hydride precursors. In this work, the propyltin-silane (C) was synthesized by the reaction between $SnCl_4$ and the Grignard reagent (B) of 3-chloropropyl triethoxysilane (A), as shown in Scheme 1. The organotin had connected with a $Si(OEt)_3$ group after organotin synthesis. This was simpler compared to that reported previously. The anchored organotin catalyst SiO_2–Sn was then prepared by the silylation of Compound C and mesoporous silica. The atomic ratio of Cl:Sn in Compound C was 3.41:1, but it was decreased to 1.97:1 after organotin immobilization on the silica,



Scheme 1 Synthetic pathway to the mesoporous silica-anchored organotin catalyst

due to the hydrolysis of some organotin chloride by moist air. Thus, not real propyltin trichloride (–CH_2–CH_2–CH_2–$SnCl_3$), as depicted in Scheme 1, was anchored on the mesoporous silica. The organotin was more likely to be immobilized in the form of organotin chloride derivatives, such as organotin hydroxide and dichlorodistannoxane.

The structural properties of the parent silica, fresh SiO_2–Sn, and the catalyst used five times with SiO_2–Sn-5, were investigated by N_2 adsorption/desorption techniques. As shown in Fig. 1a, the three samples all displayed type IV isotherms with a pronounced H3 hysteresis loop, which implied the mesoporous structure of SiO_2 was substantially maintained after either an organotin immobilization or a transesterification reaction. The pore size distributions of samples in Fig. 1b were from 5 to 13 nm, which were within the mesoporous size ranges. The textural data are summarized in Table 1. The BET surface area and pore volume of SiO_2–Sn were smaller than that of bare silica, ascribed to the organotin deposition inside the pore system of mesoporous silica. It is worthy to note that the surface area, pore volume, and pore diameter of SiO_2–Sn-5 showed little difference compared with that of SiO_2–Sn, once again proving that the mesoporous structure of SiO_2–Sn was stable in the reaction.

The TEM micrographs of the samples are shown in Fig. 2. The bare silica, SiO_2–Sn, and SiO_2–Sn-5 all presented parallel straight channels viewed along the pore direction, indicating the presence of the highly ordered mesopores. Hence, the TEM images further testified that the mesoporous structure was well maintained.

The DR UV–Vis spectrum of SiO_2–Sn is shown in Fig. 3. The absence of a band above 300 nm suggested that no SnO_2 was present in the catalyst [20]. The intense band at 215 nm indicated the presence of highly dispersed tetrahedral Sn species [21]. In addition to this band, an additional shoulder band at ~260 nm was observed, indicative of the presence of small amounts of hexacoordinated Sn species [21]. This could be attributed to the usually hexacoordinated distannoxane formed by organotin hydroxide adjacent to each other.

The successful anchoring of organotin on the surface of the mesoporous silica was further confirmed by the solid state ^{29}Si and ^{13}C MAS NMR spectra of SiO_2–Sn. In the ^{29}Si MAS NMR spectrum shown in Fig. 4a, the resonances at -113 and

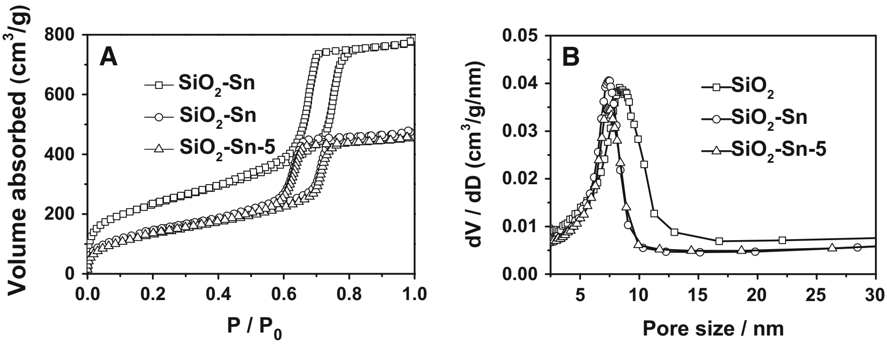


Fig. 1 N_2 adsorption–desorption isotherms (**a**) and the pore size distributions (**b**) of samples

Table 1 Textural properties of the samples

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SiO_2	843	1.225	8.38
SiO_2–Sn	535	0.756	7.46
SiO_2–Sn-5	500	0.719	7.36

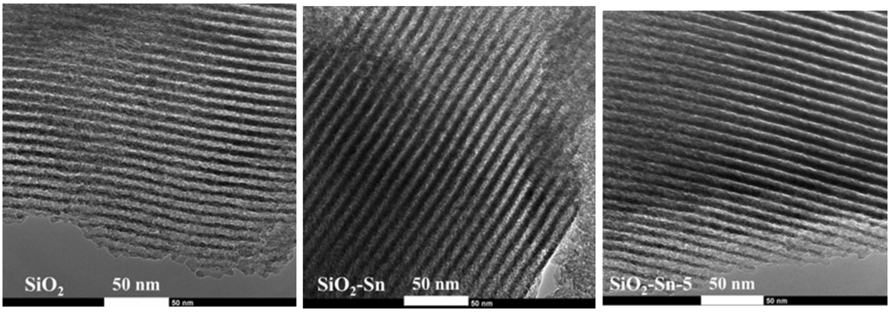


Fig. 2 TEM images of the samples

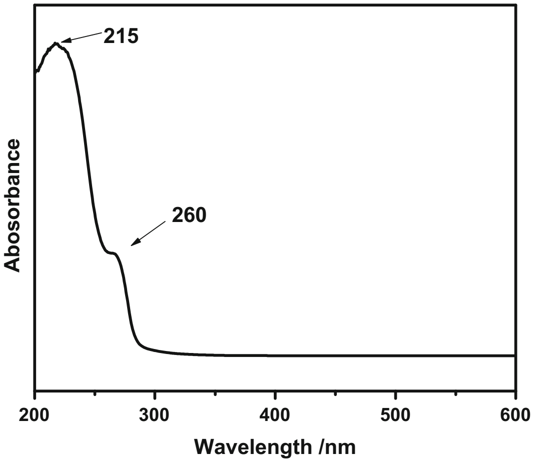


Fig. 3 Diffuse reflectance UV–Vis spectrum of SiO_2–Sn

−104 ppm were associated with $Si(OSi)_4$ (Q^4) and $Si(OSi)_3OH$ (Q^3) species of the silica framework. The upfield peaks at −68, −60, and −49 ppm were assigned to C–$Si(OSi)_3$ (T^3), C–$Si(OSi)_2OEt$ (T^2) and C–$Si(OSi)_1(OEt)_2$ (T^1) [22, 23]. The intense resonance of T species indicated that a large amount of organotin was anchored on the silica, which would be in favor of the catalytic activity. It also could be seen that T^2 and T^3 were the predominant T species, indicating the organotin was mostly anchored on the silica surface through two or three siloxane bonds (Si–O–Si). In the ^{13}C MAS NMR spectrum (Fig. 4b), the peaks observed at 26.5 and 48.0 ppm were assigned to the unreacted 3-chloropropyl triethoxysilane (Compound A) anchored on the silica

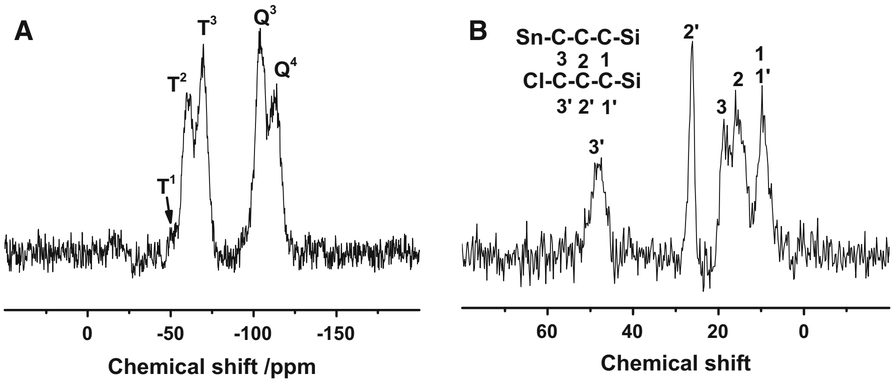


Fig. 4 Solid state ^{29}Si (**a**) and ^{13}C (**b**) MAS NMR spectra of SiO_2–Sn

[24]. The resonances at 9.4, 15.1, and 18.6 ppm were assigned to the C1, C2, and C3 carbons of the anchored organotin group, $(–O–)_3SiC^{(1)}–C^{(2)}–C^{(3)}Sn$ [17]. Therefore, the ^{13}C MAS NMR spectrum revealed that no structural change had happened in the carbon chain of organotin after immobilization onto mesoporous support.

Catalytic performance

The catalytic performance of anchored catalyst SiO_2–Sn for the transesterification reaction of DMC with phenol was investigated. For the sake of comparison, the activity of SiO_2–Sn was compared with that of soluble Compound C, with identical molar fractions, i.e., 0.40 mmol. The results are shown in Table 2. Blank tests had shown that no reaction occurred in the absence of catalyst or just in the presence of bare silica. The transesterification reaction is a two-step process, involving the transesterification of phenol and DMC to methyl phenyl carbonate (MPC), followed by further transesterification of MPC and phenol to DPC or disproportionation of MPC to DPC. Thus, MPC is usually considered as a desired product [25, 26]. It can be seen from Table 2 that the two samples showed the same transesterification selectivity of up to 99 %. Trace anisole was detected as the only by-product. SiO_2–Sn presented a little low phenol conversion compared to the soluble Compound C, but not to a very large extent. When considering the easy recycling of the anchored catalyst, the slightly lower conversion was only a minor drawback.

Table 2 Catalytic performance of Compound C and SiO_2–Sn

Sample	Phenol conversion (%)	Yield (%)		Transesterification selectivity (%)
		MPC	DPC	
Compound C	38.3	20.7	17.6	99.9
SiO_2–Sn	32.2	17.0	15.1	99.9

Reaction conditions: 160–180 °C, n(phenol) = n(DMC) = 160 mmol, n(Sn) = 0.40 mmol

The effect of the amount of SiO_2–Sn on the transesterification was explored, and the results are given in Table 3. The phenol conversion increased with the increase the amount of catalyst from 0.4 to 1.0 g, and reached 50.4 % at 1.0 g, which was close to the equilibrium conversion under this reaction condition [27]. Thus, SiO_2–Sn was an excellent catalyst for the transesterification of DMC with phenol.

Recyclablity

In addition to the catalytic activity, reusability and metal leaching are obviously critical features for the anchored catalyst. Figure 5 displays the reusability of SiO_2–Sn with a catalyst of 0.5 g. The phenol conversion decreased obviously to 36.9 % at the second run from 41.2 % of fresh catalyst, but the decrease was not significant afterwards, and a conversion of 35.0 % was obtained at the fifth run. Correspondingly, the tin content decreased sharply from 15.1 to 12.3 % after the first run, then decreased slowly to 9.9 % (not shown in Fig. 5) after five runs. The residual tin content in the reaction products was 0.042 wt % at the end of the first run. After five runs, the catalyst presented a chemical formula of $C_{22.9}H_{51.8}O_{22.3}Cl_{0.8}Si_{6.7}Sn_{0.8}$. The atomic ratio of Cl:Sn decreased to 1.02:1, indicating the organotin chloride of the fresh SiO_2–Sn was further hydrolyzed in the course of experimental operation. However, this was not responsible for the decline of catalytic activity, because the hydrolysis products of organotin chloride, such as organotin hydroxides or oxides, exhibited better activity in the transesterification than the organotin chloride [28]. Hence, the leaching of tin should be the main reason for the decline of catalytic activity, as the decreases of phenol conversion were approximately in coincidence with the decreases of tin content. The remarkable tin leaching in the first run could be attributed to the physisorption of some organotin on the silica surface, which was inefficient to anchor organotin species that easily desorbed and migrated into the liquid phase under the reaction conditions. Even allowing for the remarkable tin loss in this case, the metal leaching of SiO_2–Sn occurred to a much lower extent compared with some supported or mixed metal oxide catalysts, which was found to be corroded by the phenol [29, 30]. The high stability of SiO_2–Sn could be attributed to the strong siloxane bonds (Si–O–Si) between organotin and silica, and to the inertness of the silica towards the reaction media.

Table 3 Catalytic performance of SiO_2–Sn with different amounts

Catalyst amount/g (tin amount/mmol)	Phenol conversion (%)	Yield (%)		Transesterification selectivity (%)
		MPC	DPC	
0.4 (0.51)	36.5	27.8	8.60	99.9
0.6 (0.76)	43.5	25.7	17.7	99.8
0.8 (1.02)	47.5	24.4	23.0	99.7
1.0 (1.27)	50.6	22.3	28.3	99.9
1.2 (1.53)	51.1	24.8	26.3	99.9

Reaction conditions: 160–180 °C, 9 h, n(phenol) = n(DMC) = 160 mmol

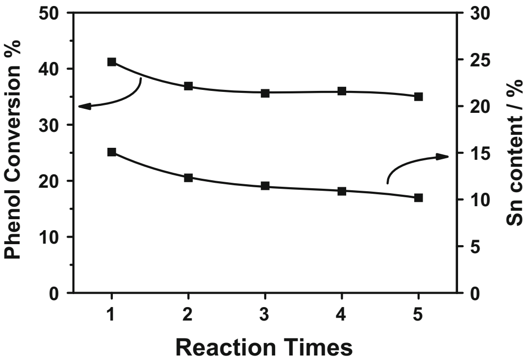


Fig. 5 Recyclability and Sn content of SiO_2–Sn. Reaction conditions: 160–180 °C, 9 h, n(phenol) = n(DMC) = 160 mmol, amount of catalyst = 0.5 g

Conclusions

A heterogeneous organotin catalyst was prepared via anchoring organotin on the mesoporous silica. The key step involved the synthesis of organotin-substituted triethoxysilane by the reaction between $SnCl_4$ and Grignard reagent of 3-chloropropyl triethoxysilane. The characterizations showed that the organotin chloride derivatives were anchored on the silica in mostly four coordinated geometry. The resulting catalyst showed a satisfactory catalytic performance in the transesterification reaction of DMC with phenol. Under the optimal conditions, the phenol conversion and transesterification selectivity reached 50.6 and 99.9 %, respectively. After five recycles, the phenol conversion just decreased from 41.2 to 35.0 % with 0.5 g of catalyst. The high stability could be attributed to the strong siloxane bonds between organotin and silica.

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