

Synthesis of unsymmetrical organic carbonates catalyzed by a sulfonic acid-functionalized zirconium phosphonate*

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Abstract: Synthesis of unsymmetrical organic carbonates by transesterification of various alcohols with diethyl carbonate (DEC) is an interesting topic in green chemistry. In this work, we synthesized a kind of zirconium phosphonate functionalized with pendent *N*-SO₃H group by the reaction of ZrOCl₂·8H₂O with *N,N*-bis(phosphonomethyl)-sulfamic acid, which was formed from sulfamic acid through a Mannich-type reaction. The functionalized zirconium phosphonate was characterized by Fourier transform/infrared (FT/IR), N₂ adsorption and desorption, scanning electron microscopy (SEM), and powder X-ray diffraction (XRD) techniques, and was used as the heterogeneous catalyst for the synthesis of unsymmetrical organic carbonates by transesterification of various alcohols with DEC. It was demonstrated that the catalyst is very active and selective for the reactions, and very high yields of the desired products could be obtained. In addition, the catalyst could be easily recovered and the decrease in catalytic activity and selectivity was minor after three-fold usage. The mechanism for the transesterification reactions is discussed.

Keywords: diethyl carbonate; Mannich-type reaction; transesterification; unsymmetrical organic carbonates; zirconium phosphonate.

INTRODUCTION

Organic carbonates represent an important class of compounds in organic chemistry because they can be used as intermediates in the production of pharmaceuticals and fine chemicals, as monomers for organic glass, synthetic lubricants, plasticizers, and as excellent polar aprotic solvents [1]. Most of the catalytic procedures for the synthesis of organic carbonates require phosgene or halo compounds as reagents [2]. However, these reagents have negative impacts on global environment (e.g., ozone layer depletion and climate change) and health (e.g., toxicity and ecotoxicity). Therefore, significant contributions to alternative solutions have been provided by research devoted to the systematic substitution of halogens. To avoid the use of the toxic halogens, in recent years, symmetrical organic carbonates, especially dimethyl carbonate (DMC) and diethyl carbonate (DEC), have been synthesized by CO₂, epoxides, and alcohols [3], or synthesized directly from CO₂ and alcohols [4].

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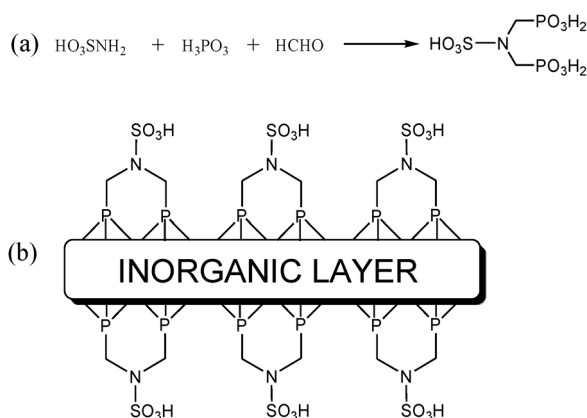
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Compared to symmetrical organic carbonates, unsymmetrical organic carbonates are more useful than the symmetrical ones, but the synthetic routes are more complex. Several methods have been developed for the production of unsymmetrical organic carbonates. For example, some unsymmetrical organic carbonates have been produced by the coupling of alcohols, CO_2 , and alkyl halides in the presence of Cs_2CO_3 [5]. Furthermore, carbonates have been synthesized from primary or secondary alcohols and CO_2 via unstable methanesulfonyl carbonates [6]. Recently, Chi and co-workers reported the synthesis of organic carbonates via alkylation of metal carbonate with various alkyl halides and sulfonates in ionic liquids [7].

DMC and DEC are versatile building blocks in organic synthesis because they are substitutes for dangerous reagents such as phosgene and halo compounds [8]. In recent years, the synthesis of unsymmetrical organic carbonates by transesterification of various alcohols with DEC has attracted much attention. Several heterogeneous catalysts, including MCM-41-TBD [9], Mg/La metal oxide [10], $\text{CsF}/\alpha\text{-Al}_2\text{O}_3$ [11], nanocrystalline MgO [12], and metal–organic frameworks [13] have been successfully developed. However, the development of highly efficient and reusable catalysts for the synthesis of unsymmetrical organic carbonates is still a very interesting topic.

Recently, zirconium phosphonates with porous structure have wide potential applications in catalysis, adsorption, ion exchange, and functional materials [14]. In addition, organics with different functional groups can be introduced into the zirconium phosphonates structure by converting desired organic compounds into a phosphonic acid. Among various applications, using zirconium phosphonates as catalysis is very attractive. Many reactions have been conducted using zirconium phosphonates as the catalysts or the supports of catalysts, such as asymmetric hydrogenation of β -keto esters [15] and aromatic ketones [16], ZnEt_2 additions to aldehydes [17], ethene polymerizations [18], asymmetric epoxidation of unfunctionalized olefins [19], polymerization of cyclic esters [20], hydroformylation [20], asymmetric Mukaiyama Aldol reaction [21], Knoevenagel condensation [22], and preparation of pyrroles [23].

In this work, we synthesized zirconium phosphonate functionalized with pendent $N\text{-SO}_3\text{H}$ group (b in Scheme 1, ZrBPMSA hereafter) based on N,N -bis(phosphonomethyl)-sulfamic acid (H_5BPMSA), which was formed from sulfamic acid by a Mannich-type reaction (a in Scheme 1) [24], for the transesterification of various alcohols with DEC to synthesize unsymmetrical organic carbonates. It was found that ZrBPMSA was very active, selective, and stable for the transesterification, and could be easily separated and reused.



Scheme 1 (a) Mannich-type reaction for the synthesis of N,N -bis(phosphonomethyl)-sulfamic acid. (b) Structure of zirconium phosphonate functionalized with pendent $N\text{-SO}_3\text{H}$ group.

RESULTS AND DISCUSSION

Catalyst characterization

Fourier transform/infrared (FT/IR) technique was used to study whether the SO_3H group was grafted onto the surface of ZrBPMSA, and the IR spectrum is shown in Fig. 1. There was a peak at 1646 cm^{-1} that is assigned to a characteristic peak of the SO_3H group, indicating that a SO_3H group existed on the surface of ZrBPMSA.

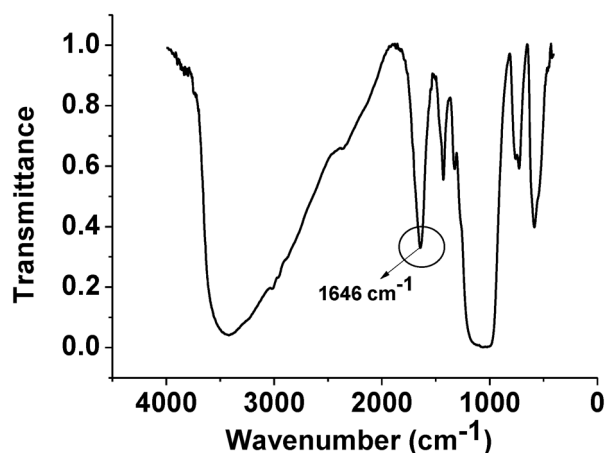


Fig. 1 FT/IR spectrum of ZrBPMSA.

The textural parameters of ZrBPMSA obtained from N_2 adsorption and desorption isotherms are presented in Fig. 2 and Table 1. The results indicate that ZrBPMSA synthesized was porous with an average pore diameter of 8.9 nm. ZrBPMSA exhibited a total Brunauer–Emmett–Teller (BET) surface area of $474\text{ m}^2/\text{g}$ with a pore volume of $0.67\text{ cm}^3/\text{g}$.

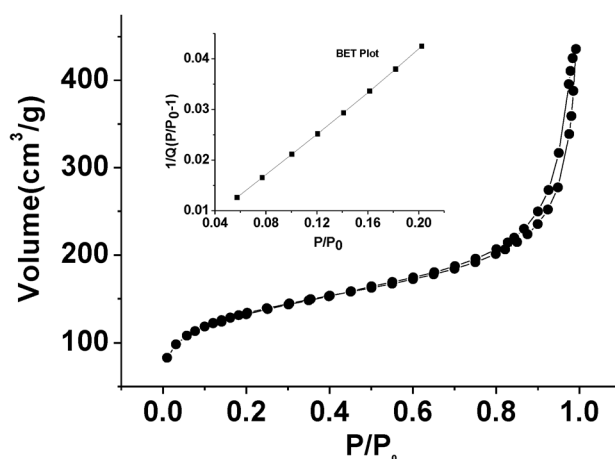


Fig. 2 N_2 adsorption/desorption isotherm for ZrBPMSA.

Table 1 Physical properties of ZrBPMSA.

Sample ^a	BET surface area (m ² /g) ^b	Pore volume (cm ³ /g) ^c	Pore diameter (nm) ^d
ZrBPMSA	474	0.67	8.9

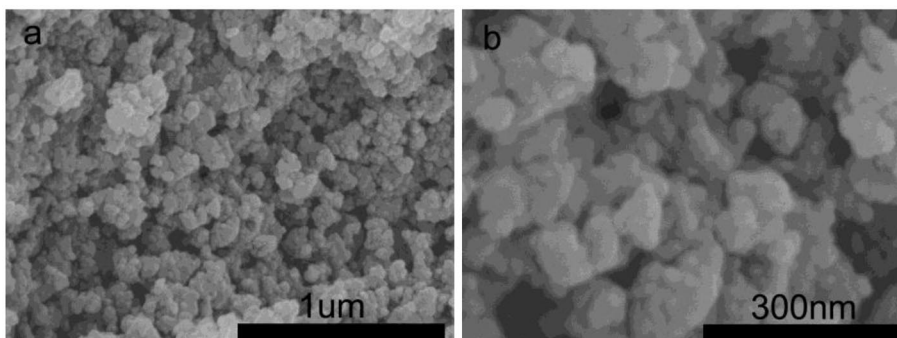
^aThe samples were degassed at 100 °C for 12 h.

^bSurface based on multipoint BET method.

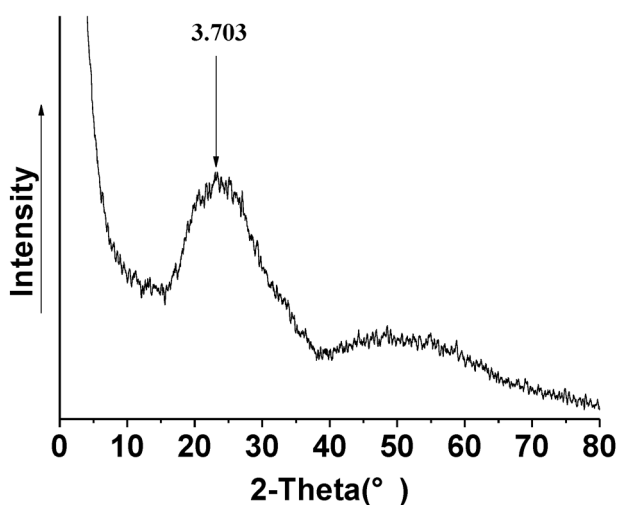
^cPore volume based on BJH method.

^dPore diameter based on BJH method.

Scanning electron microscopy (SEM) was used to characterize ZrBPMSA. It can be seen from the SEM images shown in Fig. 3 that the material was featureless with a size of submicron.

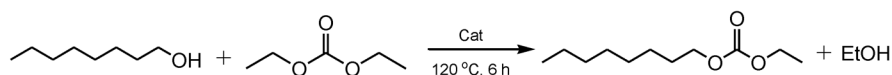
**Fig. 3** SEM images of ZrBPMSA prepared.

The powder X-ray diffraction (XRD) result (Fig. 4) showed that ZrBPMSA synthesized had no X-ray crystal structure with a d spacing of 3.703 Å obtained from the Bragg equation.

**Fig. 4** Powder XRD pattern of ZrBPMSA.

Reaction with different catalysts

In this work, various catalysts were tested by transesterification of 1-octanol and DEC (Scheme 2). The results are summarized in Table 2. It can be known from the table that no product was detected without catalyst (entry 1). When the sulfamic acid was used as the catalyst, there was no desired product produced although the conversion of the alcohol approached 100 % (entry 2). Various catalysts containing Zr were screened for the reaction (entries 3–6), and the zirconium phosphonate functionalized with pendent *N*-SO₃H group (ZrBPMSA) was the most effective (entry 6). This can be explained by the fact that ZrBPMSA has the highest acidity because of the group of SO₃H. At the same time, the amount of ZrBPMSA had great influence on the reaction (entries 6–8) and the amount of 0.2 g gave the best result (entry 6). The reusability of ZrBPMSA was also studied at the same experimental conditions of entry 6, and the results are also presented in Table 2 (entries 9, 10). Obviously, the decrease in the activity of the catalyst was not considerable after it was used three times.



Scheme 2 Synthesis of organic carbonate by the reaction of 1-octanol and DEC.

Table 2 Reaction of 1-octanol and DEC catalyzed by different catalysts^a.

Entry	Catalyst	Amount of catalyst (g)	Conversion (%) ^b	Yield (%) ^b	Selectivity (%) ^c
1	None	0	0	0	–
2 ^d	HO ₃ SNH ₂	0.2	100	0	0
3	ZrOCl ₂ ·8H ₂ O	0.2	10.5	10.4	99
4	ZrO ₂	0.2	0	0	0
5	Zr(HPO ₄) ₂	0.2	1	0.6	60
6	ZrBPMSA	0.2	99.8	97.9	98
7	ZrBPMSA	0.1	81.3	80.5	99
8	ZrBPMSA	0.05	51.0	50.4	99
9	ZrBPMSA(2 nd)	Recovered from entry 6	98.7	96.7	98
10	ZrBPMSA(3 rd)	Recovered from entry 6	95.5	94.5	99

^aReaction conditions: a flask of 10 mL, 4 mL DEC, 2 mmol 1-octanol, reaction temperature 120 °C, reaction time 6 h.

^bThe conversion and yields were determined by GC.

^cThe by-product was mainly octanoyl ethyl ether, corresponding di-ether, and the product of the alcohol oxidation.

^dThe by-product was unidentified.

Effect of reaction temperature

Table 3 shows the effect of temperature on the transesterification of 1-octanol with DEC catalyzed by ZrBPMSA in the temperature range of 100–130 °C, and the reaction time was 6 h. The yield of the product increased with increasing temperature below 120 °C. At 120 °C, the yield of product reached 97.9 %. However, the yield was nearly unchanged with further increasing temperature.

Table 3 Effect of reaction temperature on the reaction of 1-octanol and DEC^a.

Entry	Reaction temperature (°C)	Conversion (%) ^b	Yield (%) ^b	Selectivity (%) ^c
1	100	55.7	55.1	99
2	110	75.4	74.5	99
3	120	99.8	97.9	98
4	130	100	98	98

^aReaction conditions: a flask of 10 mL, 4 mL DEC, 2 mmol 1-octanol, 0.2 g ZrBPMSA, reaction time 6 h.

^bThe conversion and yields were determined by GC.

^cThe by-product was mainly octanoyl ethyl ether, corresponding di-ether, and the product of alcohol oxidation.

Catalyst leaching test

To exclude the possible leaching of catalytic species in the solution, the effect of reaction time on the transesterification of 1-octanol with DEC catalyzed by ZrBPMSA at 120 °C was compared with that of another reaction where the reaction was stopped after 2 h, and then continued after filtering out the solid catalyst. The results are shown in Fig. 5. It is obvious that there was no further increase in the product yield after the solid catalyst was separated out, confirming that the active site in ZrBPMSA was not soluble in the reaction mixture.

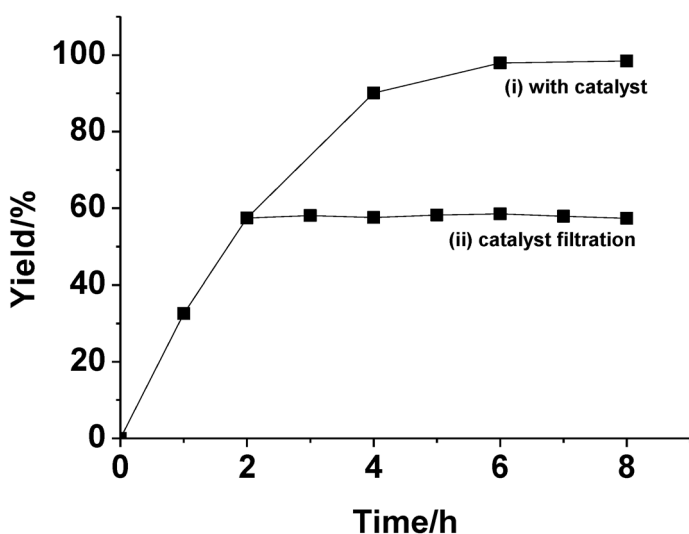
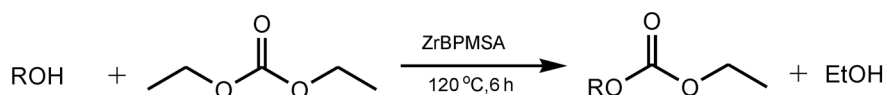


Fig. 5 The result of the leaching test of the catalyst. (i) Without filtration of the catalyst and (ii) catalyst was filtrated out after 2 h.

Other substrates

The transesterification reactions of DEC with various alcohols including alkyl and aryl (Scheme 3) were also studied, and the results are summarized in Table 4. The data in the table showed that the catalytic system could convert all alcohols to the corresponding unsymmetrical organic carbonates under the optimized conditions. From Table 4, it can be known that all the alkyl alcohols could be transformed to unsymmetrical organic carbonates with excellent yield and selectivity. However, the aryl alcohols had lower yields than the alkyl ones owing to the electric effect of the benzene ring.



Scheme 3 Transesterification of DEC with various alcohols.

Table 4 Unsymmetrical organic carbonates synthesis catalyzed by ZrBPMSA^a.

Entry	Alcohol	Product	Conversion (%)	Yield (%) ^b	Selectivity (%) ^c
1			98.4	97.4	99
2			99.6	98.6	99
3			99.8	97.9	98
4			97.2	96.2	99
5			98.3	96.3	98
6			95.3	93.4	98
7			92.7	91.8	99
8			95.6	92.7	97
9			92.3	91.4	99

^aTypical reaction conditions: a flask of 10 mL, 4 mL DEC, 2 mmol alcohol, 0.2 g ZrBPMSA, reaction temperature 120 °C, reaction time 6 h.

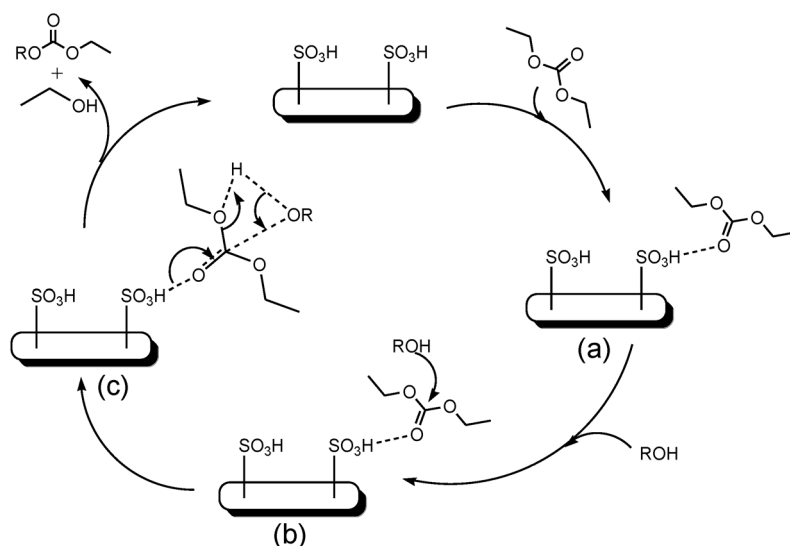
^bThe yields were determined by GC.

^cThe by-product was mainly corresponding ether, di-ether, and the product of the alcohol oxidation.

Reaction mechanism

A plausible mechanism was proposed based on a typical transesterification process (Scheme 4), where the more nucleophilic reagent displaces the less nucleophilic one or the less volatile compound displaces the more volatile one when both the reagents have similar nucleophilicity. In the present process, the nucleophilic displacement of the ethoxy group by a second molecule of the alcoholic reagent leads to the corresponding unsymmetrical carbonate. As shown in Scheme 4, the catalytic cycle is initiated by activation of DEC through hydrogen binding formed between the SO₃H group on ZrBPMSA and

carbonyl group of DEC (a in Scheme 4). Then, the alcohol attacked the activated carbonyl group of DEC (b in Scheme 4). Finally, the corresponding unsymmetrical carbonates were formed through an intermediate (c in Scheme 4). From the discussion above, we think that the SO_3H groups on the surface of ZrBPMSA play the key role for the catalytic activity.



Scheme 4 Plausible mechanism for synthesis of unsymmetrical organic carbonates catalyzed by ZrBPMSA.

CONCLUSIONS

In summary, we have successfully synthesized a porous zirconium phosphonate functionalized with pendent *N*- SO_3H group (ZrBPMSA). ZrBPMSA has been used for heterogeneous transesterification of different alcohols with DEC. The catalyst is very active, selective, and stable, and can be reused after simple separation. At the optimized conditions, the yields of the unsymmetrical organic carbonates can be higher than 98 %. We believe that the simple, efficient, and easily recyclable catalyst has potential application for producing unsymmetrical organic carbonates from DEC and alcohols.

EXPERIMENTAL

Materials

DEC was purchased from Alfa Aesar. Other reagents, such as various alcohols, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, ZrO_2 , sulfamic acid, H_3PO_3 , formaldehyde (37–40 % water solution), hydrochloric acid (38 % water solution) were A. R. grade and purchased from Beijing Chemical Reagents Company. All chemicals were used as received.

Methods

FT/IR spectra were recorded on Bruker Tensor 27 IR spectrometer, and the sample was prepared by the KBr pellet method. SEM images were taken using a Hitachi S-4300 instrument (Japan) operated at 15 kV. The BET surface area measurement and pore analysis were carried out by N_2 adsorption at 77 K with Micromeritics ASAP 2020 V3.00 H (USA) surface area analyzer. XRD measurements were con-

ducted on an X-ray diffractometer (D/MAX-RC, Japan) operated at 40 kV and 200 mA with Cu K α ($\lambda = 0.154$ nm) radiation.

Catalyst synthesis

N,N-Bis(phosphonomethyl)-sulfamic acid [(H₂O₃PCH₂)₂NSO₃H]

The diphosphonic acid with a functional SO₃H group was prepared by a Mannich-type reaction. In the reaction, sulfamic acid (9.7 g, 0.1 mol) was mixed with hydrochloric acid (30 mL), deionized water (30 mL), and phosphorous acid (32.8 g, 0.4 mol). The mixture was allowed to reflux at 120 °C for 0.5 h, then formaldehyde (50 g) was added over a period of 1 h, and the mixture was then refluxed for an additional hour. The water was removed under reduced pressure to get a white powder, which was dissolved in 10 mL of water and recrystallized by adding 300 mL of acetone. The diphosphonic acid was collected by filtration and washed using acetone and dried at room temperature.

Preparation of Zr[(O₃PCH₂)₂NSO₃H] (ZrBPMSA)

N,N-Bis(phosphonomethyl)-sulfamic acid (5.7 g, 20 mmol) was dissolved in DMSO (300 mL) at 40 °C with stirring, and ZrOCl₂·8H₂O (6.44 g, 20 mmol) was added to this solution. Immediately, white precipitate was formed and the reaction mixture was stirred for three days. The white precipitate was separated by filtration, thoroughly washed with H₂O, ethanol, ethyl ether, and dried at 80 °C under vacuum for 12 h.

Catalytic reaction

In a typical experiment, DEC (33 mmol, 4 mL), alcohol (2 mmol), and catalyst (0.2 g) were charged into a flask of 10 mL equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was stirred at 120 °C until the completion of the reaction. After the reaction, the reaction mixture was centrifuged to separate the catalyst. The products were analyzed by gas chromatography (GC, Agilent 6820) and identified by GC-MS (Shimadzu QP2010). In the experiments to test the reusability of the catalyst, the catalyst was recovered by centrifugation and washed using ethyl ether to remove the reactants and products. After being dried under vacuum for 12 h at 60 °C, the catalyst was reused under the same reaction conditions as the fresh catalyst.

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