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To cite this article: Pravin P. Upare , Anil K. Kinage , Savita K. Shingote & Sunil P. Gupte (2012) Environmentally benign synthesis of  $\beta$ -hydroxy sulfides using cyclic carbonates catalyzed by large-pore zeolites, Green Chemistry Letters and Reviews, 5:1, 19-26, DOI: [10.1080/17518253.2011.574295](https://doi.org/10.1080/17518253.2011.574295)

To link to this article: <https://doi.org/10.1080/17518253.2011.574295>



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Published online: 09 Aug 2011.



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## RESEARCH LETTER

### Environmentally benign synthesis of $\beta$ -hydroxy sulfides using cyclic carbonates catalyzed by large-pore zeolites

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(Received 02 December 2010; final version received 17 March 2011)

An efficient one-pot synthesis of  $\beta$ -hydroxy sulfides from thiophenol and cyclic carbonates catalyzed by large-pore zeolites has been reported. Reaction of thiophenol with ethylene carbonate in the presence of the Na-X zeolite catalyst gave the highest yield of 2-(phenylthio)ethanol (100%), while reaction with propylene carbonate a highest yield of regioselective product 1-(phenylthio)propan-2-ol was obtained (97%). Enantiomerically pure 1,2-propylene carbonate gave highly regioselective and stereospecific phenylthiopropanol, demonstrating that original chirality of propylene carbonate is retained. A plausible mechanism has been proposed for zeolite-catalyzed transformation involving a chemoselective nucleophilic attack of thiophenoxide ion onto the less-substituted carbon of cyclic carbonate. The Na-X zeolite catalyst is recyclable and provides advantages of green chemistry approach to the synthesis of  $\beta$ -hydroxy sulfides without the use of any solvent.

**Keywords:** zeolite;  $\beta$ -hydroxy sulfide; ethylene carbonate; propylene carbonate; thiophenol

#### Introduction

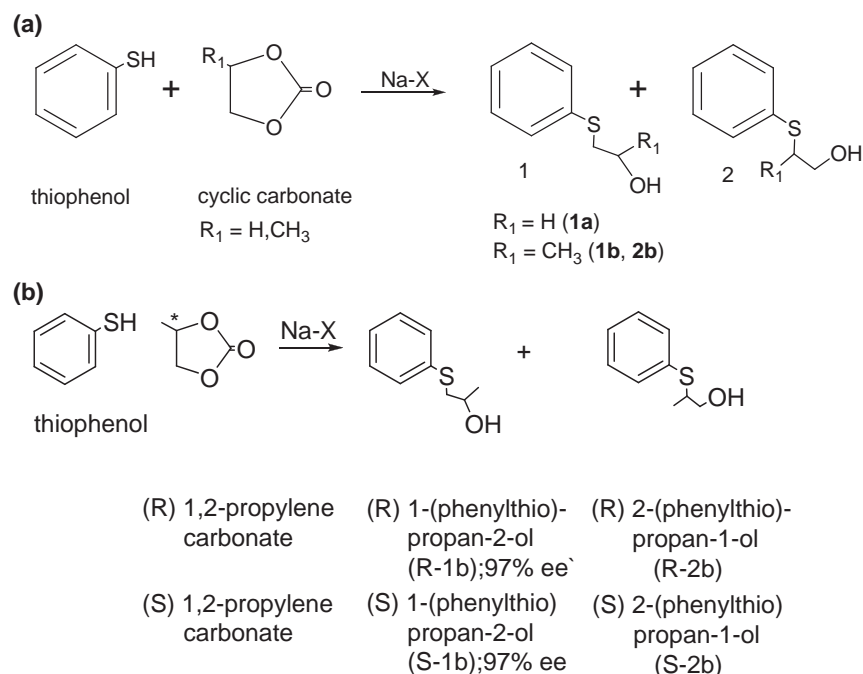
The demand for clean and efficient chemical reactions using a reusable catalyst and solvent-free conditions has received much interest in recent years. Most of organic transformations use an organic cosolvent to remove phase boundary limitations to facilitate the rate of reaction. Hence, the organic synthesis under solvent-free condition is attractive from the viewpoint of green chemistry. The green chemical processes, with the enhanced yield of the desired product and reduced workup cost and product recovery, are the requirements of an industrial production. The zeolite catalyst showing general superiority for many organic reactions is undoubtedly one of the most intriguing aspects and may have a considerable impact on the development of new catalytic systems (1). Recently, we found that large-pore zeolites are highly efficient catalysts in the synthesis of fine chemicals using cyclic carbonate (2, 3).

Since beta-hydroxy sulfides have increasing demand in synthetic organic and medicinal chemistry, the development of efficient and benign methods for their preparation is desirable.  $\beta$ -Hydroxy sulfides are useful in the field of pharmaceuticals (4) and natural products (5), especially for the synthesis of

leukotrienes such as LTC<sub>4</sub> and LTD<sub>4</sub>. It is also a versatile moiety for synthesizing benzoxathiepins (6), benzotiazepines (7),  $\alpha$ -thioketones (8) and  $\alpha$ -substituted and  $\alpha,\beta$ -unsaturated enones (9).  $\beta$ -Hydroxy sulfides are generally prepared by the nucleophilic ring opening of epoxides with thiols in the presence of typical Lewis acid catalysts such as InCl<sub>3</sub> (10), ZnCl<sub>2</sub> (11), alumina (12), polyethylene glycol (13), tertiary amines (14), ionic liquids (15) and aqueous NaOH (16). However, most of these preparations involve the use of toxic reagents, with poor regioselectivities, extended reaction times, poor yields and undesirable side products due to oxidation of thiol or rearrangement of oxiranes. To the best of our knowledge, only two reports that described the synthesis of phenylthioalcohols from thiophenol and ethylene carbonate, with ~70% conversion of thiophenol to the desired product, were found (17, 18). The catalysts used were alkali metal carbonate with or without crown ether; however, in this report the recycle and reuse of the catalyst is not described.

We report here on the efficient and selective catalytic synthesis of  $\beta$ -hydroxy sulfides by the reaction of thiophenol with cyclic carbonates in the absence of solvent (Scheme 1(a)).

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Scheme 1. (a) Chemoselective thiolysis of cyclic carbonate. (b) Thiolysis of chiral 1,2-propylene carbonate.

## Results and discussion

In the present paper, we report an efficient heterogeneous catalytic system for preparing phenylthioethanol from thiophenol and ethylene carbonate over large-pore zeolite catalysts such as FAU, BEA, MOR, Na-P and K-L. To the best of our knowledge, a systematic study on this simple but useful zeolite-assisted transformation is not available in the previous literature.

Before attempting a detailed catalytic screening work, a noncatalytic reaction between thiophenol and ethylene carbonate was examined and it was observed that under the experimental conditions, the formation of phenylthioethanol could not be detected at the end of 24 h reaction time and at 140°C, indicating that the reaction is not feasible in the absence of any catalyst (Table 1, entry 1). Hydroxyalkoxylation of thiophenol using MgO or ZnO as a solid base catalyst was also examined (Table 1, entries 2 and 4); the results indicated that ZnO shows excellent activity and yield for phenylthioethanol (98.2% and 90.1%, respectively) while MgO shows good activity (74.2%) as well as yield (70.3%). TEAB (tetraethyl ammonium bromide) as a homogeneous catalyst was also examined for this reaction (entry 3) and was found to give excellent activity (93.8%) and yield (89.2%). It may be noted that the activity and yield for 2 h contact time were, however, poor for these catalysts, e.g. less than ~20% (entries 2–4).

Further, the reaction of thiophenol and ethylene carbonate was carried out over different zeolites and

hydrotalcite (entries 5–11). It was found that except K-L and Na-X (Table 1, entries 10–11, yields 93.8% and 100%, respectively), other zeolite-based materials as catalysts showed rather moderate activities (0%–69%) and yields (0%–68%) (entries 5–9). Thus activity and yield decrease in the order Na-X > K-L > Na-P > Na-MOR > Na-Y > hydrotalcite > Na-ZSM-5, with Na-ZSM-5 showing no activity for the reaction. Unlike in the oxide catalysts wherein the activity of a catalyst largely depends on the strength of acid–base active sites, in zeolites due to three-dimensional channel structure the acid–base sites have charge distribution prevailing in the channels and cages arising from framework Si, Al and O atoms as well as occluded alkaline atom ions. These effects make the zeolites very special and thus each zeolite show a specific activity toward substrates. For example, in the present case, Na-X and K-L zeolites showed a significant enhancement in yields compared to other catalysts, especially Na-Y, which is similar in properties to Na-X but show poor activity. These aspects are further discussed later in the section under mechanism. Since the Na-X catalyst showed excellent activity at 2 h (entry 11, 100% yield of **1a**) as compared with K-L (entry 10, 21% yield of **1a**), further exploitation of this reaction was carried out using Na-X zeolite as a catalyst. In fact, the Na-X catalyst was so active that close to 100% conversion of thiophenol was obtained in just over 30 min of the reaction time at 140°C (Figure 1).

Table 1. Screening of catalysts for the synthesis of 2-(phenylthio)ethanol (**1a**) from thiophenol and ethylene carbonate.<sup>a</sup>

Entry no.	Catalyst	Al/(Si + Al) ratio	Thiophenol conversion <sup>b</sup> (%)	Yield <sup>b</sup> <b>1a</b> (%)
1	Nil	–	Nil	–
2	MgO	–	74.2 (20.1)	70.3 (20.0)
3	TEAB	–	93.8 (6.6)	89.2 (5.2)
4	ZnO	–	98.2 (20.2)	90.1 20
5	Na-ZSM-5	0.03	Nil	–
6	Hydrotalcite (Mg/Al; 3:1)	–	5.7 (nil)	4.8 (nil)
7	Na-Y	0.29	20 (19.6)	18.5 19
8	Na-MOR	0.15	30.9 (24.0)	30.2 (22.4)
9	Na-P	0.41	68.5 (41.4)	66.1 (40.2)
10	K-L	0.24	93.8 (22.7)	90.5 (21.1)
11	Na-X	0.46	100 (100)	100 (100)

<sup>a</sup>Thiophenol 50 mmol; ethylene carbonate 50 mmol; catalyst 100 mg; reaction time 24 h; temperature 140°C.<sup>b</sup>Figure in parentheses indicate conversion or yield at the end of 2 h.

It may be noted that the system with no solvent often results in poor yields due to deactivation of active sites by the adsorption of reactant and product molecules. However, in our reaction condition, high yield of 2-(phenylthio)ethanol is obtained without using any solvent; the carbonate itself is acting as a reactant as well as a solvent in the reaction system. The effect of temperature in the range 90–140°C on the activity and selectivity of the reaction over Na-X zeolite was studied (Figure 1). It was observed that at 140°C, the highest yield of 2-(phenylthio)ethanol is obtained; therefore, further reactions were carried out at 140°C for optimizing the other reaction conditions.

Table 2 compares the effect of substituted functional group on the thiophenol ring on the yield of phenylthio ethanol formation. Thiophenol and 4-methyl thiophenol were smoothly converted into 2-(phenylthio)ethanol (100% yield, entry 1) and

2-(4-methylphenylthio)ethanol (95% yield, entry 2), respectively. 4-Chlorothiophenol and 4-nitrothiophenol gave moderate yields of the corresponding phenyl thioethanols, viz. 2-(4-chlorophenylthio)ethanol and 2-(4-nitrophenylthio)ethanol, respectively, due to poor nucleophilicity of these thiophenol derivatives compared to thiophenol. Thus, 4-chlorothiophenol gave 35% yield of 2-(4-chlorophenylthio)ethanol (entry 3), while 4-nitrothiophenol gave 12% yield of 2-(4-nitrophenylthio)ethanol (entry 4).

It is interesting to compare the thiolysis of epoxide and ethylene carbonate as both reactions give rise to the same product thioalcohol. Since epoxide is a three-member ring compound, it is highly reactive toward ring opening by nucleophile as compared to ethylene carbonate, which is a more stable five-member ring compound. Usually, the oxygen of epoxide is activated by catalysts having acidic centers (10–13), and base catalysts, such as Na-X zeolite, are inactive for this purpose (19). On the contrary, ring-opening reaction of ethylene carbonate is preferably catalyzed by solid bases such as Na-X zeolite via activation of thiophenol. This is believed to be generating thiophenol anion partially

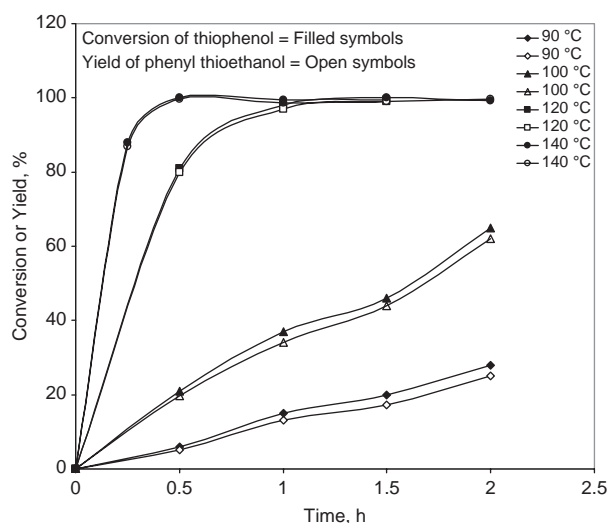


Figure 1. Effect of temperature on the activity of the Na-X catalyst.

Table 2. Screening of substrates for the synthesis of phenylthio ethanol using Na-X zeolite as the catalyst.

S. no.	Thiophenol	Conversion thiophenol (%)	Phenylthioethanol <sup>a</sup> (%)
1	R = H	100	100
2	R = 4-CH <sub>3</sub>	95	95
3	R = 4-Cl	36	35
4	R = 4-NO <sub>2</sub>	13 <sup>b</sup>	12

<sup>a</sup>Reaction conditions: thiophenol 50 mmol; ethylene carbonate 50 mmol; zeolite Na-X 100 mg; temperature 140°C; time: 2 h; yields based on phenol converted (by GC analysis).<sup>b</sup>Time: 12 h.

stabilized by Lewis acid centers of Na-X, thereby increasing the nucleophilicity of thiophenol anion. Also, ethylene carbonate has two types of electrophilic carbons, viz. carbonyl carbon and alkylene carbon. And, according to hard and soft acid–base theory, thiophenol being the softer nucleophile will preferably react with the soft alkylene carbon center of carbonate, yielding phenyl thioalcohol (3).

To further test the activity of the Na-X catalyst and applicability of the method, 1,2-propylene carbonate was examined for the synthesis of phenylthioalcohols (Table 3). Quantitative yields of phenylthioalcohol were obtained by regioselective ring-opening reaction of unsymmetrical cyclic carbonates by thiophenol. The corresponding regioisomers of hydroxy sulfides obtained from 1,2-propylene carbonate could not, however, be separated by column chromatography; hence, the regioselectivity was determined by gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS) analyses (Table 3, entries 1 and 2). As expected, an excellent regioselectivity of 97:3 (Scheme 1(b), 1(b):**2b**) in favor of a nucleophilic attack at the sterically less-hindered methylene carbon of carbonate was observed, affording 96.8% yield of 1-(phenylthio)propan-2-ol (**1b**) during the reaction with 1,2-propylene carbonate (Table 3, entry 1).

The reaction of thiophenol was also carried out either with optically pure enantiomer (*R*)-(+)-1,2-propylene carbonate (98% ee) or with (*S*)-(–)-1,2-propylene carbonate (98% ee)<sup>1</sup> at 110°C for 72 h, and the results are presented in Table 3. The GC analysis using a chiral column (see Experimental section for details) showed the formation of enantiomerically excess optical isomer showing that the racemization of either optically pure carbonate or thioalcohol is not taking place. For example, the reaction of (*S*)-(–)-1,2-propylene carbonate showed complete conversion of thiophenol and carbonate with the formation of (*S*)-(+)-1-(phenylthio)propan-2-ol (**S-1b**) in quantity ~98% (>97% ee) along with the other regioisomer 2-(phenylthio)-1-propanol (**S-2b**) in minor amount (~1%) and (*R*)-(–)-1-(phenylthio)propan-2-ol (**R-1b**) was also formed (due to the presence of small amount of (*R*)-(+)-1,2-propylene carbonate in the substrate). As expected, an excellent regioselectivity

for **S-1b** with >99% yield was realized (Table 3, entries 2 and 3). The enantiomeric excess was evaluated on the basis of chiral GC of **S-1b** and **R-1b**. The optical rotations of **S-1b** and **R-1b** were also measured for the determination of their configuration. For this purpose, a solution of the accurately known quantity of (*S*)- or (*R*)-1-(phenylthio)propan-2-ol was prepared in chloroform (*c* = 1.0, CHCl<sub>3</sub>) and the specific optical rotation  $[\alpha]_D$  was measured at 25°C, which was in agreement with the literature value of +54.7° and –54.7° for pure compounds, respectively (20, 21). It may be noted that enantiopure phenylthioalcohols are largely used as chiral-building blocks in the synthesis of drugs for pharmaceuticals industry (22).

In the synthesis of fine chemicals using zeolitic materials, it is often important to tune the acid–base strength of the catalyst with that of reactants and products in order to achieve optimal yields of products (23, 24). The importance of acid–base pairs of the Na-X catalyst was investigated by modifying these pairs in the original Na-X catalyst by exchanging with a solution of ammonium acetate (see Experimental section for details). The results show that by exchanging Na<sup>+</sup> of Na-X zeolite with H<sup>+</sup> Brønsted acidity, the substrate conversion and product selectivity decreases with increase in the extent of exchange (Table 4, entries 1–4); that is, increase in the Brønsted acidity of Na-X zeolite does not favor catalysis. These results are in agreement with our earlier work on N- and O-alkylation of aniline (2) and phenol (3) by using the zeolite catalyst (also see Selva et al. (25) on faujasites-catalyzed transesterification of ethylene carbonate followed by N-alkylation of aniline, wherein acid forms of Na-X and Na-Y zeolites were less active compared to basic). Comparison of our earlier results with those of the present study on S-alkylation show that in spite of a wide differences in p*K*<sub>a</sub> values of substrates (26), viz. aniline (p*K*<sub>a</sub> = 4.87), phenol (p*K*<sub>a</sub> = 9.99) and thiophenol (p*K*<sub>a</sub> = 6.62), Na-X demonstrates excellent activity. The results show that milder acid–base sites of these catalysts probably prevent irreversible strong adsorption of substrates on zeolites X, thereby demonstrating excellent activity, which is unlike oxide catalysts, e.g. Al<sub>2</sub>O<sub>3</sub>, MgO, ZnO and SiO<sub>2</sub>.

Table 3. Synthesis of 1-(phenylthio)propan-2-ol over Na-X zeolite.

Entry no.	Cyclic carbonate	Time (h)	Temperature (°C)	Thiophenol conversion (%) <sup>a</sup>	Yield <b>1b</b> (%)	Yield <b>2b</b> (%)
1	1,2-Propylene carbonate	15	140	99.5	96.8	2.7
2	( <i>R</i> )-1,2-Propylene carbonate	72	110	99.9	98.9	1.0
3	( <i>S</i> )-1,2-Propylene carbonate	72	110	100.0	99.0	1.0

<sup>a</sup>Conversion and yield are based on chiral GC and GC-MS analysis.

Table 4. Effect of sodium exchange on the activity of the NaX catalyst.<sup>a</sup>

Entry no.	Catalyst	Na <sup>+</sup> form (%)	Thiophenol conversion (%)	2-(Phenylthio) ethanol yield (%)
1	Na-X	100	100	100
2	25 HNa-X	75	98.5	98.5
3	48 HNa-X	52	89.6	89.6
4	67 HNa-X	33	83.5	82.8

<sup>a</sup>Thiophenol 50 mmol; ethylene carbonate 50 mmol; catalyst 100 mg; temperature 140°C; reaction time 2 h.

Further, it is worth mentioning here that the activity of the catalyst, e.g. Na-X zeolite is not proportional to the number of acidic and basic sites of framework alumina or oxygen, respectively, alone, but rather to a cooperative effect of acid–base pairs. Note that the systematic exchange of Lewis acidity to Brønsted acidity of Na-X zeolite has decreased the activity of the Na-X catalyst, but the effect is not proportional to the decreased number of Lewis sites (see Table 4), indicating that the nature of modified active sites is much complex than that expected based on the degree of exchange.

From the industrial point of view, one of the most important aspects is the reusability of the catalyst. The reaction parameters were chosen so that the catalyst deactivation during subsequent recycle can be noticed (high loading and longer contact time sometime mask the deactivation effect unless deactivation is strong). The catalyst recycle experiments carried out at a contact time of 0.5 h shows that the catalyst can be recycled up to five times, with minor loss in its catalytic activity (Figure 2; 99.6%–85% yield). In this study, the catalyst recycle experiments were also carried out till complete conversion of thiophenol (contact time of 2 h), and it was observed

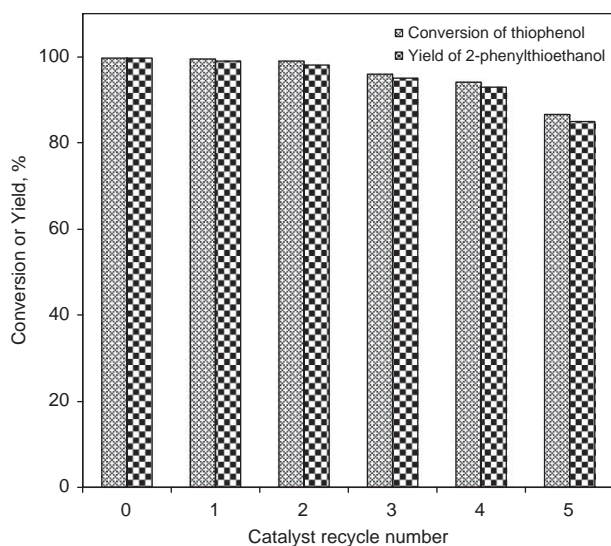


Figure 2. Catalyst recycle study (0.5-h contact time).

that at the end of the fifth recycle ~96% activity of the catalyst was retained with up to ~94% yields of **1a** (for the sake of convenience, these data are not shown in the figure). These two sets of experiments show that the catalyst is deactivated to some extent during the reaction; however, the loss in catalyst activity can be compensated by increasing the contact time of reaction.

In order to examine the cause of slight deactivation during recycle, the recycled catalyst at the end of the fifth recycle was recovered, washed with acetone and calcined (see Experimental section for details) and subjected to X-ray diffraction (XRD) analysis. The XRD pattern of Na-X zeolite before and after the fifth recycle is shown in Figure 3; the pattern shows no change in XRD even after fifth recycling. However, it is known that zeolite calcined several times may undergo dealumination and this type of dealumination is not seen in XRD. The activity of the catalyst may slightly go down because of the traces of unburned carbon deposition remaining in the pores of the zeolite even after calcination at 400°C during regeneration of the zeolite catalyst. Therefore, this carbon deposition may have retained on the active site of the zeolite due to which the catalyst shows a slight decrease in its activity at the end of the fifth recycle.

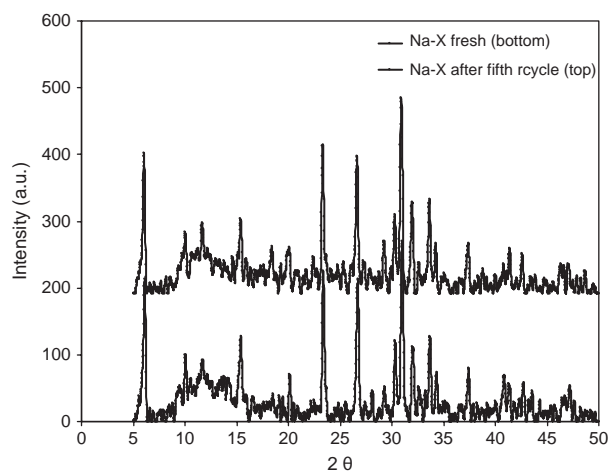
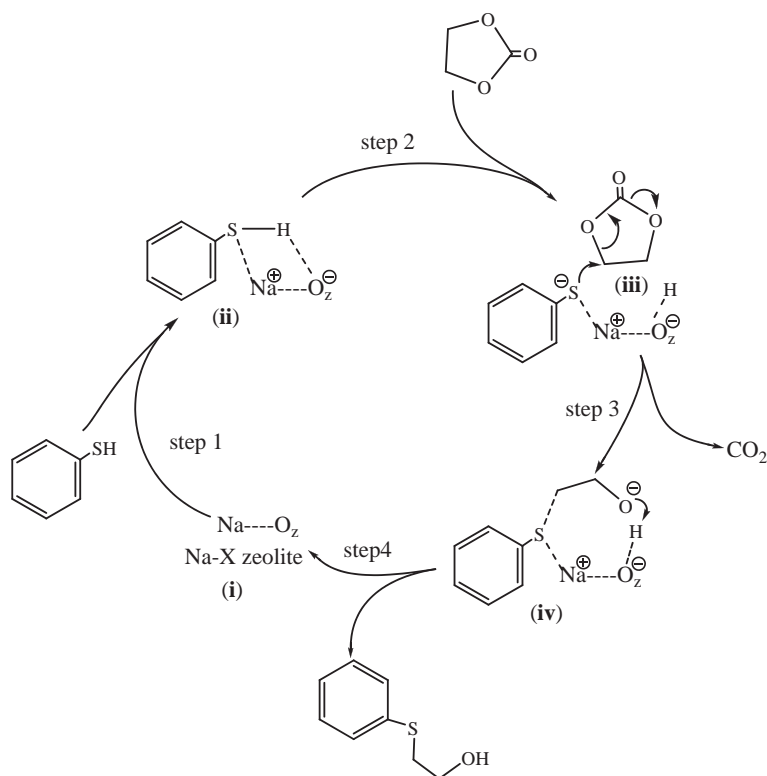


Figure 3. XRD pattern for Na-X zeolite before and after reaction.





Scheme 2. A plausible Na-X zeolite-catalyzed ring-opening mechanism of ethylene carbonate by thiophenol.

A mechanism of NaX-catalyzed synthesis of phenylthioalcohol from thiophenol and ethylene carbonate is speculated (Scheme 2). The zeolite X has a framework of cationic and anionic sites, which act as Lewis acid–base pairs. It is likely that the cations located in S-I, S-II and S-III sites of Na-X zeolites (27, 28) interact with aromatic ring of thiophenol, while acidic H ions of thiophenol are stabilized by slightly electronegative framework oxygen atoms. An earlier study showed that the adsorption of sulfur compounds (thiophene) is favored on Na-X zeolite compared to Na-Y zeolite (29). The mechanistic scheme is consistent with the above hypothesis of adsorption mechanism and it is shown that activated thiophenol (species **ii**) behaves like an effective nucleophile ( $\text{PhS}^-$ ). Thus, the methylene carbon of ethylene carbonate is now susceptible to a nucleophilic attack by phenylthiolate anion, resulting in liberation of  $\text{CO}_2$  as shown in step 3. In the final step,  $\text{O}^-$  of phenylthioethanolate abstract H atom of surface hydroxy species to liberate phenylthio ethanol (step 4), generating the original catalyst Na-X. This is a speculative mechanism and obviously more work needs to be done to confirm catalytic steps shown in the scheme.

In summary, it is shown that Na-X zeolite can be effectively used as a catalyst for the synthesis of  $\beta$ -hydroxy sulfides from thiophenol and cyclic carbon-

ate. The highest conversion of thiophenol and selectivity for 2-(phenylthio) ethanol and 1-(phenylthio)propan-2-ol obtained are 100% and 97%, respectively, at  $140^\circ\text{C}$ . The methodology can effectively produce enantiopure phenylthioalcohols from enantiopure 1,2-propylene carbonates, demonstrating regio- and stereospecificity of the protocol. This solvent-free reaction is a clean, safe and reproducible method and could be effectively used for the synthesis of wide range of  $\beta$ -hydroxy sulfide derivatives.

### Experimental

In a typical procedure, a 100-mL round-bottomed flask equipped with a magnetic stirring and reflux condenser was charged with 50 mmol of thiophenol, 50 mmol of ethylene carbonate and 0.10 g of the Na-X catalyst. The mixture was vigorously stirred at room temperature for 10 min and then mixture was heated at  $140^\circ\text{C}$  for 2 h (15 h for racemic 1,2-propylene carbonate). The liquid product was separated from catalysts and analyzed by gas chromatograph. The reactant (thiophenol) and product [2-(phenylthio)ethanol] were analyzed on a gas chromatograph (Hewlett Packard 6890 series equipped with autosampler, using HP-5 capillary column,  $30\text{ m} \times 320\text{ }\mu\text{m} \times 0.25\text{ }\mu\text{m}$  film, on a 5% phenyl methyl siloxane stationary phase), and these analytical data, after applying necessary

corrections for standardization, were used for calculating conversions and yields.

#### Reaction with enantiopure propylene carbonate

In a typical procedure, a 25-mL round-bottomed flask was charged with 10 mmol of thiophenol, 10 mmol of *S*-(–)-propylene carbonate, 10 mL of toluene and 0.05 g of the Na-X catalyst. The mixture was vigorously stirred at room temperature for 10 min and then mixture was heated at 110°C for 72 h. The reactants and products were analyzed by a gas chromatograph equipped with chiral column (see “Analysis of chiral carbonate and alcohol” section for details).

#### Isolation of product

The reaction crude diluted with acetone was coated on 3 g column-grade silica gel so that about 300 mg of compound is coated after evaporation of acetone on rotary vacuum drier. The products were separated by flash chromatography on a 4 g normal phase silica RediSep column employing *n*-hexane–ethyl acetate as the eluent with gradient programming. Liquid chromatography was performed using Combi-Flash Companion (Teledyne ISCO, USA). Products were characterized and confirmed by GC-MS, infrared and <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectroscopies. The regioselectivity of isomers was determined by GC and GC-MS analysis (Agilent, model 6890/5973N mass selective detector). Products **1a–1e** and **2b** are known and were characterized by comparing their reported spectral data (30–32).

#### Analysis of chiral carbonate and alcohol

Chiral substrates [*S*-(–)- and *R*(+)-propylene carbonates] and products [*S*(+)- and *R*(–)-phenylthiopropansols, **S-1b** and **R-1b**, respectively] were analyzed on a gas chromatograph using Supelco beta Dex 225 (catalog #24348) capillary column (30 m length, 250 µm diameter and 0.25 µm thickness) employing oven temperature program (40°C: 1 min; 40–90°C, ramp: 10°C/min keeping at 90°C for 18 min; 90–130°C, ramp: 20°C/min keeping at 130°C for 10 min; 130–200°C, ramp: 20°C/min keeping at 200°C for 11 min) under the column flow of 2 mL He/min. Standard enantiopure propylene carbonate was analyzed for identification of chiral isomers. The reaction solution of racemic propylene carbonate analyzed at an intermediate time showed two well-resolved peaks corresponding to (*R*)- and (*S*)-propylene carbonate (retention time 40.51 and 40.76 min, respectively) as well as (*R*)- and (*S*)-phenylthiopropansols (**R-1b** and **S-1b** having retention time 38.51 and 38.47 min,

respectively). The specific rotation of phenylthiopropansols was measured on a polarimeter autopol IV (M/s. Rudolph Research Analytical, UK).

#### Ion-exchange of NaX zeolite

One gram of Na-X zeolite was exchanged with 25 mL of 1 M ammonium acetate solution by stirring the mixture at 70°C for 1 h. The extent of exchange was monitored by number of exchanges carried out as desired. The exchanged form of zeolite was washed with distilled water several times, dried at 120°C overnight and calcined under the flow of air at 540°C for 12 h by increasing the temperature from room temperature to 540°C at a rate of 3°C/min. Three samples were thus prepared with degree of exchange, 25%, 48% and 67%, and designated as 25% HNaX, 48% HNaX and 67% HNaX, respectively.

#### Catalyst recycles experiments

At the end of each experiment, the catalyst was separated by decantation, washed with acetone three times, dried at 100°C for 2 h and calcined at 400°C for further 2 h, and reused after cooling to room temperature.

#### Notes

1. The reagents were purchased from Aldrich Chemical Co. Ltd., USA. (*S*)-Propylene carbonate: catalog number: 540005 (optical purity 98%); (*R*)-propylene carbonate: catalog number 540013 (optical purity 98%).

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