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Novelties of selective triphasic synthesis of bis-(p-chlorobenzyl) sulfide using hydrogen sulfide and reusable phase transfer catalyst

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GRAPHICAL ABSTRACT



Highlights

- Methyldiethanolamine was used for selective absorption of toxic H₂S gas
- The product bis-(para-chlorobenzyl) sulfide was synthesized with 100% selectivity.
- The green PTC catalyst was regenerated and reused up to 2 cycles.
- The catalyst used was found to perform better than other catalysts tested.
- A generalized empirical kinetic model was developed and validated.

ABSTRACT

The present investigation is based on the advancement in hydrogen sulfide (H₂S) capture and utilization (HSCU). Commercially H₂S is absorbed efficiently using alkanolamines such as methyldiethanolamine (MDEA). Aqueous H₂S-rich MDEA is proposed to act as a sulfiding agent for aromatic halides such as pchlorobenzyl chloride (p-CBC) to synthesize value-added thioethers. The objective of the present investigation is to synthesize bis-(p-chlorobenzyl) sulfide (BPCBS), a value-added thioether, selectively using p-CBC and H₂S-laden aqueous MDEA. For the immiscible bi-phasic system, reusable solid phase transfer catalyst, polymer-bound tributylmethylammonium chloride (PBTBMAC) was employed under liquid-liquid-solid (L-L-S) mode in the presence of solvent toluene to enhance the reaction rate and product selectivity. Full conversion of p-CBC was obtained with 100% selectivity towards the desired product BPCBS at optimized specific level of process parameters. The catalyst has shown substantial activity even after three times of reuse, which leads to waste minimization and economic benefits. A generalized empirical kinetic model was developed and successfully validated against the experimental results. The triphasic reaction thus leads to process intensification, waste minimization and selectivity enhancement. The process can be utilized as an alternative to many other HSCU processes to utilize the sour gas in synthesizing value-added chemicals.

Keywords: bis-(p-chlorobenzyl) sulfide, liquid-liquid-solid phase transfer catalyst, hydrogen sulfide, kinetics, modeling

Nomenclature

MDEA	N-Methyldiethanolamine	
MEA	monoethanolamine	
TEA	triethanolamine	
DEA	diethanolamine	
DIPA	diisopropanolamine	

BC	benzyl chloride
DBS	dibenzyl sulfide
p-CBC	para- chlorobenzyl chloride
p-CBM	para- chlorobenzyl mercaptan
BPCBS	bis-(para-chlorobenzyl) sulfide
РТС	phase transfer catalyst
TBMAC	tributylmethyammonium chloride

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1. Introduction

Hydrogen sulfide (H_2S) is a very poisonous and corrosive colorless gas. Most of the H_2S emission in the earth's atmosphere is from the natural sources like volcanoes, sulfur spring, lakes, and saline marsh, etc. but 10% of the total H_2S emission has an anthropogenic source. Petroleum refining and Kraft pulping industries are the primary sources of H_2S emission whereas other industries like natural gas and heavy crude oil industry, viscose rayon production plant, wastewater treatment plants, and wood pulp industry contribute some. In the era of human health effects, the concentration of H_2S at the level greater or equal to 10.76 ppm causes conjunctival irritation, a concentration greater than 161.42 ppm or 150 ppm has a paralyzing effect on olfactory perception and concentration around 286 ppm can cause pulmonary edema [1]. In the industries, the presence of H_2S gas in pipelines may lead to severe corrosion as it reacts directly with the metals contained in the pipe. Therefore, the prime objective of the investigation is to utilize H_2S gas in synthesizing fine chemicals so that H_2S emission can be minimized.

Due to stringent environmental pollution regulations as well as above mentioned reasons, the level of H_2S in the by-product streams, needs to be brought down to the safer limit before releasing it into the atmosphere. There are various laboratory methods as well as industrial scale based processes available for H_2S recovery and utilization. Claus process is an industrially important process that produces elemental sulfur from H_2S gas. But the process is accompanied by many disadvantages [2,3]. There are some

processes corroborated in the literature for the removal of H_2S gas via absorption. H_2S is soluble in various liquids including water, ammonia, various alkanolamines like monoethanolamine, diethanolamine, diglycolamine, and N-methyldiethanolamine (MDEA). The removal and recovery of hydrogen sulfide (H_2S) from the streams by aqueous ammonium hydroxide solution are well documented [4,5]. Ammonium hydroxide was used by Hamblin in 1973 for the removal for removal of H_2S from the gas stream. Triethanolamine (TEA), monoethanolamine (MEA) [6], diethanolamine (DEA) [7], Diisopropanolamine (DIPA) [8] and N-methyldiethanolamine (MDEA) [9] are the alkanolamines that have been used for H_2S absorption in industry. Now a days MDEA is replacing the other absorbent because of its better selectivity towards the H_2S in presence of CO_2 [9]. Therefore, the present work has been carried out using MDEA for the absorption of H_2S gas, and H_2S -laden MDEA has been used for the synthesis of value-added fine chemicals like bis-(p-chlorobenzyl) Sulfide.

Thioethers like dibenzyl sulfide (DBS) and bis-(p-chlorobenzyl) sulfide (BPCBS) are some of the fine chemicals that can be synthesized using H₂S-laden amines. These fine chemicals have found a wide range of applications like use as additives for extreme pressure lubricants, anti-wear additives for motor oils, stabilizers for photographic emulsions, in refining and recovery of precious metals, and in different anticorrosive formulations [10]. DBS can be oxidized to prepare some useful synthetic intermediates like dibenzyl sulfoxide and dibenzyl sulfone formulations [11]. Synthesis of DBS and BPCBS in L-L and S-LPTC mode using sodium sulfide has been done by using benzyl chloride and p-chlorobenzyl chloride (p-CBC) respectively [12]. Kinetic study of DBS has also been done using solid sodium sulfide in S-LPTC in the presence of solid catalysts, basic alumina and Amberlyst A27 (Cl⁻ form) anion exchange resin [10]. DBS has been successfully synthesized by reducing corresponding disulfides in the presence of Zn powder and AlCl₃ in aqueous media [14-15]. Reduction of sulfoxide using Al-NiCl₂-6H₂O as reducing agents was also performed for the synthesis of DBS [16]. But due to long reaction time,

expensive reagents and extreme reaction conditions, the reduction is not found to be an economical method [16].

All of the catalysts used so far for the synthesis of thioethers like DBS are soluble in nature, and it is, therefore, tough to reclaim back and reuse. In the case of L-L PTC, disposal of the used catalyst is also an issue because of its hazardous nature. So, in the field of utilization of hydrogen sulfide for the synthesis of thioethers like BPCBS, the use of a reusable polymer-supported catalyst is still awaited. In this case, polymer-supported PTC is a 'green' option because it is insoluble and therefore easy to reclaim and environment-friendly. In this type of PTC (also known as triphase L-L-S catalyst), the catalyst is impregnated with some polymers like polystyrene and polyacrylamide. The support can either be soluble or insoluble as well [17]. Ambelite IRA-400 has been used as L-L-S PTC for the synthesis of dibenzyl disulfide by Singh et al. [18].

Biphasic reactions have always been very difficult to carry out because of their immiscible nature. The reaction between two immiscible phases can be enhanced with the aid of a phase transfer catalyst (PTC) that can act as a carrier of ions between both the phases. PTC has got worldwide acceptance because of its effectiveness, mild operating conditions, and versatility in the field chemical reaction engineering. PTC is now being utilized for the synthesis of many value-added chemicals. Ido and Susaki studied the effect of the third phase in a phase transfer catalytic system where tetrahexylammonium bromide acts as a PTC and BC as a reactant [19]. Wang used tetrabutylammonium bromide as a PTC in higher concentration to form a third phase and its effect on the rate of the reaction was studied [20].

The synthesis of thioethers like BPCBS demands two reactants - H_2S -laden aqueous alkanolamine and p-chlorobenzyl chloride (organic). This reaction system is a biphasic one that needs a good solvent and a suitable phase transfer catalyst. According to Stark's mechanism, a quaternary onium halide dissolved in the aqueous phase (Q⁺X⁻), undergoes anion exchange with the anion (Y⁻) of the organic phase reactant (MY). The ion-pair formed (Q⁺Y⁻) crosses the liquid-liquid interface due to its lipophilic nature, diffuses from the interface into the organic phase (phase transfer step). Now in the organic phase, the anion (Y⁻) of

the ion-pair, being nucleophilic in nature, undergoes a nucleophilic substitution reaction with the organic reagent (RX) forming the desired product (RY). The catalyst subsequently recycles back to the aqueous phase and the cycle continues [21]. The reaction rate is a function of various parameters like organic group structure, the activity of the leaving group X⁻, nucleophilicity of the displacing group Y⁻, relative ease of transfer of X⁻ and Y⁻ between the phases, solvent types, reagent concentrations, agitation intensity, temperature, and catalyst structure. For triphase catalysis (TPC), the catalyst structure is more accountable for the determination of the rate of the reaction than in any other phase transfer catalysis.

The mechanism for polymer-supported catalyst was firstly developed and explained by Desikan and Doraiswamy [22]. Contrary to the assumption made in Stark's mechanism (the catalyst moves freely in both the phases), in this mechanism, the movement of polymer-supported catalyst was stated to be confined in the interphase. Therefore, organic and aqueous phase need to be brought into contact with the catalyst in a sequential manner. The reaction takes place through the attachment and detachment of ions of aqueous and organic phase on the active sites of the catalyst that is better explained in the diagram of the reaction mechanism of TPC system (Fig.1).

The reaction occurs in different steps which comprise of diffusion, attachment, detachment and again diffusion of ions [23].

- Nucleophile from the aqueous phase (HS⁻ and S²⁻) travels from bulk to the vicinity of the inactive site of the catalyst through diffusion.
- 2. Attachment followed by ion-exchange reaction between the nucleophile and the inactive site of the catalyst leaving the catalyst site active (Q⁺HS⁻) for further ion exchange. (The catalyst is marked as inactive when attached to its original anion).
- Diffusion of the organic substrate (RX) from bulk to the active site of the catalyst, followed by ion exchange to form the product (RSH). During this ion-exchange, the inactive form of the catalyst also gets regenerated to Q⁺X⁻.

2. Experimental

2.1. Chemicals

Toluene (>99%), MDEA (>99%) and p-CBC (>99%), all of analytical reagent grade, were procured from Sigma-Aldrich, Mumbai, India. The catalyst tributylmethylammonium chloride polymer-bound is procured from Fluka, Switzerland. Ferrous sulfide (FeS) stick, used for H₂S production, has been purchased from Rankem, India.

2.2. Experimental set-up

All the experiments have been performed in fully baffled three-necked 150 cm³ glass reactor, which was connected to a direct-drive digital stirrer with a six-bladed glass turbine impeller and a reflux condenser. The whole reaction set-up was assembled in an isothermal water bath (\pm 1°C) having PID temperature controller.

2.3. Preparation of H₂S-laden MDEA

35 wt. % of aqueous MDEA was prepared as an optimum concentration for MDEA by dissolving sufficient raw MDEA in Millipore ultrapure water in an ice bath. H₂S gas was bubbled through the aqueous MDEA solution kept in a gas bubbler. The gas bubbler was kept immersed in an ice bath to prevent oxidation of sulfide ion. The process of chemisorption was continued until the desired concentration of sulfide or desired sulfide/MDEA mole ratio, ideal for sulfidation reaction, has been achieved. The concentration of sulfide was estimated by iodometric titration method [21].

2.4. Experimental procedure

The measured quantity of catalyst was first introduced into the reactor, followed by 25 cm³ of aqueous sulfide solution of known sulfide concentration. The organic phase, prepared by dissolving p-CBC

in the solvent toluene in a definite proportion, was then poured into the three-necked batch reactor, and the stirrer was turned on at a definite rpm to start the reaction provided the temperature of the water bath reaches its set point. The samples were collected after certain time interval using micropipette from both the phases after turning the stirrer off and allowing the phases to separate to stop the reaction between the phases.

2.5. Sample analysis

Samples from the organic phase were analyzed in Agilent GC-MS, (Model 7890B/5977A) to identify the products using a capillary column DB-5MS, $2m \times 3m$. GC with FID detector was used for the quantification of all the reactants and products.

3. Result and discussion

Two products were identified namely BPCBS and p-chlorobenzyl mercaptan (p-CBM) by GC-MS. The following sensitivity study was performed by varying the range and levels of different process parameters as shown in Table 1 and the effect of variations in those parameters on conversion of p-CBC and selectivity of BPCBS and PCBM was investigated. The optimum values of range and levels were chosen based on some preliminary studies [10,13,25]. The process parameters that can affect the kinetics of reactions are reaction time, stirring speed, p-CBC concentration, sulfide concentration, MDEA concentration, catalyst concentration, different PTC catalysts, and temperature.

3.1 Proposed Mechanism

In this investigation, polystyrene supported tributylmethylammonium chloride catalyst has been used which can be regenerated using NaCl solution. H₂S-laden MDEA solution with the known concentration of sulfide and p-CBC were reacted.

The whole mechanism of L-L-S was found to be very complex. The reaction among H₂S, MDEA and H₂O forms ionic complexes like RNH⁺HS⁻ and (RNH)₂S that react with the organic reactant p-CBC to form p-CBM as an intermediate product and BPCBS as shown in Scheme 1. The intermediate p-CBM also

combines with the excess organic reactant p-CBC to form the final product BPCBS as shown in stoichiometric Eq. (12).

3.1.1. Reaction in aqueous phase

The aqueous phase contains, MDEA and H₂S absorbed in it. The reaction among H₂S, MDEA and H₂O forms ions like HS⁻, S²⁻ and OH⁻ as shown in the Eq. (1), (2), (3)and (4) [18]. These nucleophiles migrate from bulk of the aqueous phase to the catalytic interface, then attachment of nucleophile occurs at the inactive site of the catalyst followed by the ion exchange reaction as shown in the reaction Eq. (5)- (7). This ion exchange reaction is very fast and always considered to be in equilibrium.

3.1.2. Non-catalytic contribution

The presence of the solvent and the rigorous stirring of both phases trigger the onset of the reaction. The reaction between the organic and inorganic phase in the absence of the catalyst was also found to be enough to be taken into the consideration (Fig.3). The ionic complex RNH^+HS^- reacts with the organic reactant p-CBC to form p-CBM (Eq. (11)), which can again react with the organic reactant p-CBC to form the final product BPCBS. The S²⁻ plays a significant role in the synthesis of product BPCBS as it forms the complex (RNH)₂S with MDEA that combines with two molecules of p-CBC to form BPCBS. This reaction is a two steps process as shown in the Eq. (13) and (14). The products p-CBM and BPCBS diffuse back to the organic phase when reaction stops.

3.1.3 .Catalytic contribution

These nucleophilic ions migrate from bulk of the aqueous phase to the catalytic interface where attachment of nucleophile to the inactive site of the catalyst occurs, followed by the ion exchange reaction as shown in the reaction Eq. (5) - (7). This ion exchange reaction step is very fast and so always considered to be in equilibrium. As the active sites are immobilized on the catalyst itself, reactants sequentially come in the contact of the catalyst, as shown in the Eq. (8)-(10). The reactant, p-CBC travels to the active site and ion exchange takes place between to form p-CBM and BPCBS. The whole mechanism is shown in

Scheme 1. The overall stoichiometric equation of the reaction between p-CBC and H_2S -laden MDEA is shown as Eq. (15).



3.2. Sensitivity study

3.2.1 Effect of catalyst concentration

The catalyst concentration was varied from 0.0 to 2.4 x 10^{-2} kmol/m³ and its effect on p-CBC conversion, and BPCBS selectivity was plotted against time as shown in Fig.2 (a) and (b). The selectivity of BPCBS and conversion of p-CBC were found to be 30% and 40% respectively without catalyst and both of them shoot up to 100% for the catalyst concentration of 2.4 x 10^{-2} kmol/m³. The S²⁻ and HS⁻ ions form catalyst active intermediates QSQ and QSH that combine with p-CBC to form BPCBS and p-CBM respectively. Upon increasing the catalyst concentration, the concentrations of these intermediates increase and hence the conversion of p-CBC and selectivity of BPCBS also increase [6]. The enhancement of reaction rate with catalytic loading can also be observed in terms of enhancement factor as shown in Table 1. For minimizing the catalyst consumption for each run, the optimum catalytic concentration was chosen as 6.0×10^{-3} kmol/m³ for rest of the reactions.

The order of the reaction with respect to the catalyst concentration was calculated by plotting a graph of ln (initial rate) vs. ln (catalyst concentration). From Fig. 3, the slope of the graph was found to be 0.63 which is the order of the reaction with respect to catalyst concentration.

3.2.2. Comparison with different catalysts

For the establishment of the superiority of the catalytic activity of the catalyst, polymer-bound tributylmethylammonium chloride (PBTBMAC) over the other catalysts, insoluble PTC like Amberlite IR-400 and soluble PTC like Tetrabutylphosphonium bromide (TBPB) and Ethyltriphenylphosphonium bromide (ETPB) were chosen. All catalysts were used at same concentration i.e. 6.0 x 10⁻³ kmol/m³ keeping all the parameters at optimized values. The best result was observed in the case of PBTBMAC (Fig. 4). From the past literature, we have found that the activity of the polymer-supported catalyst is greater than the soluble catalyst due to reasons like increase in its lipophilicity due to its polymer backbone, the microphase effect of catalyst, and substrate selectivity [23, 26]. For both the soluble catalysts, their distribution in both the phases is necessary for which again more amount of catalyst is required. But polymer-supported catalyst PBTBMAC doesn't get distributed in both of the phases, its active sites which get activated and deactivated time and again throughout the reaction, are responsible for the reaction. So, it is effective at very low concentration. Thus, the results imply that the catalyst PBTBMAC is not only reusable but also gives an excellent conversion of the reactant at remarkably low concentration.

3.2.3. Effect of reactant concentration

The effect of reactant concentration on conversion of p-CBC and selectivity of BPCBS was observed by varying the p-CBC concentration from 1.6 to 3.9 kmol/m³ as shown in Fig. 5. It is clearly visible from Fig.5. (a), that conversion of p-CBC decreases with increase in p-CBC concentration. Decrease in consumption of the reactant p-CBC with more p-CBC is due to the presence of a limited amount of S²⁻ and HS⁻ ions in the aqueous phase. On the other hand, the selectivity of BPCBS increases with increasing reactant concentration as the undesired product i.e. p-CBM, recombines with the excess unreacted p-CBC to form more BPCBS (Fig.5. (b)). For simultaneous optimization of conversion of reactant along with the selectivity of the product, an intermediate value of p-CBC concentration i.e. 2.4 kmol/m³ was taken for all other reactions.

The order of the reaction with respect to the p-CBC concentration was calculated by plotting a graph of ln (initial rate) vs. ln (reactant concentration). From the slope of the graph of Fig. 6, the order of the reaction was found to be 1.58 with respect to catalyst concentration.

3.2.4. Effect of sulfide concentration

The sulfide concentration was varied between 2.0 kmol/m³ to 1.25 kmol/m³ keeping other parameters at an optimum value. The effect of the sulfide concentration on conversion of p-CBC and selectivity of BPCBS are shown in the Fig. 7 (a) and (b) respectively. From the graph, it can be interpreted that conversion of p-CBC decreases with a decrease in sulfide concentration as S²⁻ and HS⁻ ions present in limiting quantity. Selectivity of the BPCBS was found to decrease with increasing sulfide concentration because an increase in total sulfide concentration, results in an increase in HS⁻ ion concentration in comparison to that of S²⁻ ions, that leads to higher rate of formation of p-CBM and not BPCBS [25]. As per the stoichiometry of Eq. (6)-(9) and (13)-(14) in Scheme 1, S²⁻ is more responsible for the formation of BPCBS than HS⁻.

The order of the reaction with respect to the sulfide concentration was calculated by plotting a graph of ln (initial rate) vs. ln (sulfide concentration). The slope of the straight line in Fig. 8 was calculated as 1.72, which is the order of the reaction with respect to sulfide concentration.

3.2.5. Effect of MDEA concentration

To study the effect of MDEA concentration on the kinetics of the reaction, MDEA concentration was varied keeping the sulfide concentration same for each case Fig.9. For this experiment, a fixed H₂S-laden MDEA was taken, and the concentration of MDEA was managed by adding the proper quantity of raw MDEA. Distilled water was used to make up the volume of aqueous phase if needed.

Even though MDEA doesn't take part in the reaction, the change in concentration of MDEA affects the conversion of p-CBC as well as the selectivity of BPCBS. By changing the MDEA concentration, the equilibrium between the MDEA, H_2O , S^{2-} and HS^- gets affected. When MDEA concentration is increased keeping H_2S concentration fixed, the equilibrium shifts towards the product side according to Le-Chatelier's principle, and that results in more RNH⁺HS⁻ and (RNH)₂S. Therefore, the conversion of p-CBC as well as the selectivity of BPCBS increase due to a rise in S^{2-} ion in comparison to HS⁻ with an increase in MDEA concentration [13].

3.2.6. Effect of temperature

To study the effect of temperature, four set of experiments have been performed at different temperatures like 313, 323, 333 and 343 K, keeping the other parameters constant. The graphical representation of p-CBC conversion and BPCBS selectivity vs. time at different temperatures are shown in the Fig. 10. From the graph, it is clearly understandable that the conversion (and rate of reaction) increases with increasing temperature as the number of particles colliding with sufficient energy (i.e. more than the activation energy) increases by increasing the temperature. But no significant effect on the selectivity of product BPCBS due to temperature change was observed.

The effect of temperature on chemical reactions is explained in the terms of activation energy present in the Arrhenius equation. The colliding molecules should have sufficient energy to overcome the threshold energy i.e. activation energy for a successful reaction. The apparent activation energy was calculated from the slope of the Arrhenius plot (Fig. 9) as 34.86 kJ/mol.

3.2.7. Effect of stirring speed.

Stirring speed was varied in the range 500 - 2000 rpm keeping other parameters fixed at the optimized condition and the impact of the variation in the conversion of p-CBC and the selectivity of BPCBS is shown in Fig. 12. The conversion of p-CBC and the selectivity of BPCBS after 30, 60 and 120 min were plotted against different stirring speed. From the Fig. 12, it is visually clear that role of mass

transfer on conversion of p-CBC is negligible in the stirring speed ranges from 1000-2000 rpm. The conversion of p-CBC as well as the selectivity of BPCBS is comparatively less in 500 rpm than in 1000, 1500 and 2000 rpm. The relation between ln (initial rate of the reaction) and stirring speed is also plotted in Fig. 12(c) that shows, there is no effect of agitation intensity on the initial rate of reaction. Therefore, to avoid mass transfer resistance, 1500 rpm was chosen as stirring speed for all above reactions conditions.

3.2.8. Reusability of the catalyst

The major advantages of polymer-supported insoluble catalyst over the other soluble L-L PTC catalysts are manifold. It is reusable in nature whereas the other L-L PTC are not, so the polymer-bound catalyst can be used multiple times without much loss of its catalytic activity. It is also environment-friendly in nature. In the present study, after each run, the catalyst was separated using filtration and regenerated by washing it with NaCl solution. The reusability of the catalyst was investigated up to two cycles and a little decrement in the conversion of p-CBC was observed i.e. from 100% for a fresh catalyst to 95% for 1st reuse and 91% for 2nd reuse. The conversion of p-CBC for 1st and 2nd cycle of reuse is as shown in the Fig.13. The reduction in the conversion can be attributed to the loss of little catalyst during filtration and regeneration.

3.3. Kinetic modelling

3.3.1. Development of kinetic model

The model for the synthesis of DBS in L-L mode of reaction is also not found to be applicable in L-L-S mode of reaction because solid catalyst does not get distributed in both the phases [25]. There is various literature available for different the type of reaction of L-L [27,28], L-L-L [29,30], L-L-S PTC-driven reactions [18] where authors have developed and applied their kinetic model. But the model for L-L-S mode of synthesis of any thioethers or ethers is not available in the literature.

From Fig.2, it can easily be interpreted that non-catalytic contribution in this reaction rate is unavoidable. The rate equation (Eq. (16)) thus comprises of two terms - first one is accountable for catalytic reaction and dependents on concentration of reactant (C_{R1}), sulfide (C_{S1}) and catalyst (C_C) and second term

is for non-catalytic reaction and dependents on concentration of reactant (C_{R2}) and sulfide (C_{S2}) only [Eq. (16)]. Non-catalytic reactions at different temperatures - 313, 323, 333 and 343 K were carried out to estimate k_2 from Eq. (16). The effect of temperature change in the catalytic as well as non-catalytic part of the reaction is shown in terms of Arrhenius plot in the Fig. 15(a) and (b) respectively. Here it was assumed that the contribution of reactant concentration and sulfide concentration to rate of reaction for non-catalytic reaction. Thus, order of reaction with respect to the reactant and sulfide for catalytic and non-catalytic reaction are assumed to be same.

$$-r = k_1 C_{R1}^{1.58} C_{S1}^{1.72} C_C^{0.62} + k_2 C_{R2}^{1.58} C_{S2}^{1.72}$$
(16)

The overall mass balance for sulfide can be obtained from the stoichiometric equations Eq. (8), (9), (10) and (12) and is given by Eq. (17).

$$C_S = C_{S0} - 1/2f(C_{R0} - C_R) \tag{17}$$

Where, C_{R0} and C_{S0} are initial concentration of p-CBC and sulfide and *f* is the ratio of volume of organic phase to that of aqueous phase.

A nonlinear regression algorithm is used for the estimation of parameters. The optimum values of the rate constants, k_1 and k_2 was estimated by minimizing the objective function (*E*) as given by the following equation:

$$E = \sum_{i=1}^{n} [\{(-r_R)_{pred}\}_i - \{(-r_R)_{expt}\}_i]^2$$
(18)

The optimum values of rate constant k_1 and k_2 of the reaction for different temperatures were listed the table below:

From its slope of Fig. 15 (a) and (b), the activation energies for catalytic and non-catalytic reaction were found to be 28.89 kJ/mol and 49.96 kJ/mol respectively, which also shows the effectiveness of the catalyst.

3.3.2. Validation of kinetic model

From the regression of the model, the predicted values for reaction rate were found. Using those values, the predicted conversions are compared with experimentally calculated values of conversion. Excellent agreement between the predicted and experimental conversion was obtained as shown in the Fig.16.

4. Conclusion

Toxic H_2S gas has been utilized for the preparation of BPCBS with a final selectivity of 100% against p-Chlorobenzyl Mercaptan. Polymer-supported tributylmethylammonium chloride was found to be better than other catalysts like TBPB, Amberlite IRA-400, and ETPB in terms of enhancement of reaction rate and product selectivity. Also, the catalyst is green and can be reused several times with a little compromise in its activity. The reaction is found to be more optimum in the sense of selectivity when agitation speed is 1500 rpm, but the conversion was found to be undisturbed through the range of variation of agitation speed. The synthesis of BPCBS is a success with minimal side product formation i.e. p-CBM which was identified by mass spectroscopy. Based on the detailed kinetic study, a general empirical kinetic model was developed that was found to predict conversions reasonably well. The present process can be used as a possible alternative to energy-expensive Claus Process for better utilization of downstream toxic by-product H_2S .

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Associated content

Supplementary Information

Condition for GC-FID and GC-MS, Gas Chromatographs and MS spectra.

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Fig. 1: The mechanism of L-L-S catalysis



(b)

Fig. 2. The effect of catalyst concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS. Thermochemical condition: Volume of aqueous and organic phase 2.5×10^{-5} m³ each, temperature: 323 K, MDEA concentration: 3.0 kmol/m³, stirring speed- 1500 rpm, reactant concentration: 2.4 kmol/m³, sulfide concentration of aqueous phase: 2.0 kmol/m³.



Fig. 3. Plot between ln (initial rate) and ln (catalyst conc.) (All conditions are same as mentioned under Fig. 2.)



Fig. 4. Effect of the different catalysts on conversion of p-CBC

Thermochemical condition: Volume of aqueous and organic phase: 2.5×10^{-5} m³ each, MDEA concentration: 3.0 kmol/m³, temperature: 323 K, stirring speed: 1500 rpm, all catalyst concentration: 6.0×10^{-3} kmol/m³, reactant concentration: 2.4 kmol/m³, sulfide concentration: 1.29 kmol/m³.



(b)

Fig. 5. The effect of reactant concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS. Thermochemical condition: Volume of aqueous and organic phase: 2.5×10^{-5} m³ each, temperature: 323 K, MDEA concentration: 3.0 kmol/m³, stirring speed: 1500 rpm, catalyst concentration: 6.0×10^{-3} kmol/m³, sulfide concentration: 2.0 kmol/m³.



Fig.6. Plot of ln (initial rate) vs. ln (reactant conc.) All conditions are same as mentioned under Fig. 4.



Fig. 7. Effect of sulfide concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS. Thermochemical condition: Volume of aqueous and organic phase: 2.5×10^{-5} m³, temperature: 323 K, MDEA concentration: 3.0 kmol/m³, stirring speed: 1500 rpm, catalyst concentration: 6.0 x 10^{-3} kmol/m³, reactant concentration: 2.4 kmol/m³.



Fig.8. Plot between ln (initial rate) and ln (sulfide conc.) All conditions are same as mentioned under Fig. 6.



Fig. 9.The effect of MDEA concentration on (a) conversion of reactant and (b) selectivity of the product. Thermochemical condition: Volume of aqueous and organic phase: 2.5×10^{-5} m³, temperature: 323 K, stirring speed: 1500 rpm, catalyst concentration: 6.0×10^{-3} kmol/m³, reactant concentration: 2.4 kmol/m³.sulfide concentration: 1.29 kmol/m³.



(b)

Fig. 10. The effect of Temperature on (a) conversion of reactant and (b) selectivity of the product. Thermochemical condition: Volume of aqueous and organic phase: 2.5×10^{-5} m³ each, MDEA concentration: 3.0 kmol/m³, stirring speed- 1500 rpm, catalyst concentration: 6.0 x 10^{-6} kmol/m³, reactant concentration: 2.4 kmol/m³, sulfide concentration: 1.29 kmol/m³.



Fig. 11. Arrhenius plot of ln (rate of reaction) and 1/Temperature. All conditions are same as mentioned under Fig. 9.



Fig. 12. The effect of stirring speed on (a) conversion of p-CBC (b) selectivity of BPCBS (c) ln (initial rate of the reaction). Thermochemical condition: Volume of aqueous and organic phase: 2.5×10^{-5} m³ each, temperature: 323 K, MDEA concentration: 3.0 kmol/m³, catalyst concentration: 6.0×10^{-6} kmol/m³, reactant concentration: 2.4 kmol/m³, sulfide concentration of aqueous phase: 2.0 kmol/m³.



Fig.13. Conversion of p-CBC with the number of cycle reuse.

Thermochemical condition: Volume of aqueous and organic phase: 2.5×10^{-5} m³ each, MDEA concentration: 3.0 kmol/m³, temperature: 323 K, stirring speed- 1500 rpm, sulfide concentration: 1.29 kmol/m³, catalyst concentration: 6.0×10^{-3} kmol/m³, reactant concentration: 2.4 kmol/m³.



(a)



Fig.15. Arrhenius plot, (a) ln (rate constant, k_1) vs temperature (1/T) and (b) ln (rate constant, k_2) vs temperature (1/T)



Fig. 16. Comparison of Model-predicted p-CBC conversion with the experimental p-CBC conversion.



Scheme 1. The proposed mechanism for synthesis of BPCBS via L-L-S reaction

Parameters (units)	Optimized values
Stirring speed (rpm)	1500
Temperature (K)	323
Catalyst concentration (kmol/m ³)	0.006
Reactant concentration (kmol/m ³)	2.4
Sulfide concentration (kmol/m ³)	2.0
MDEA concentration (kmol/m ³)	3.0
Volume of aqueous and organic phase (m ³)	2.5 ×10 ⁻⁵

Table 1: Optimized conditions for each run

 Table 2

 Effect of catalyst loading on initial rate of reaction and enhancement factor ^a

Catalyst Loading ×	Initial Rate of Reaction	Enhancement Factor
10 ⁵ (kmol/m ³)	\times 10 ³ (kmol/m ³ .s)	
0.0	0.217	1.0
0.6	3.135	14.4
1.2	3.700	17.1
1.8	4.638	21.4
2.4	5.200	24.0

^a All other conditions are same as Fig.2

Table 2

Rate Constants of the Model

Temperature (k)	Rate constant (with catalyst) $k_1((kmol/m^3)^{-4}.s^{-1})$	Rate constant (without catalyst) $\mathbf{k_2} \times 10^5 ((kmol/m^3)^{-4}.s^{-1})$
313	0.001264	3.496
323	0.005190	7.439
333	0.010246	11.542
343	0.013381	20.333