Cotton Fabric-Supported Cationic Acrylate Polymer as an Efficient and Recyclable Catalyst for Williamson Ether Synthesis Reaction in Solid−Liquid−Liquid Phase Transfer Catalysis System

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ABSTRACT: Cotton-based catalytic fabric (CCF) was prepared by the simple padding-drying method with the copolymer of five functional monomers as the modifier and was applied in the solid−liquid−liquid phase-transfer catalysis (SLL-PTC) system. Effects of the structure of the function monomer, the content of the cation, and the loading amount on the catalytic activity of CCF were investigated. The lipophilicity, disperse extent of cationic center, and the accessibility to the ion for CCF were influenced by the structure and content of the function monomer. The organic phase was adsorbed on the surface of the catalytic fabric, and the novel catalytic cycle in the PTC system was initiated. The anion in the aqueous phase diffuses through the interfacial region to the site for ion exchange. Bond-forming reaction was initiated in the interfacial region between the organic phase on the fabric and the aqueous phase. The conversion rate for Williamson ether synthesis reaction reached 92%, and CCF could be reused five times in this SLL-PTC system.

1. INTRODUCTION
Phase transfer catalysis (PTC) is one of the most widely used synthetic techniques because of the advantage of simple and easy reaction procedure, mild conditions, and inexpensive reagents and has been widely applied in the synthesis of dyes, pigments, pharmaceuticals, perfumes, and polymers. Design of the efficient and green PTC system has been one of the topics in the PTC field. The introduction of the third phase to the common biphasic PTC system was considered as the efficient way to meet the requirement of the green chemistry, for example, third-liquid PTC (TL-PTC) with the catalyst-philic liquid phase, solid(catalyst)−liquid−liquid PTC (SLL-PTC) system with the immobilized catalyst phase, and the introduction to the solid-o-liquid PTC with the omega phase (water). In these third-phase PTC systems, the reaction rate and the reusability of the catalyst were increased. However, the introduction of the third liquid phase into the PTC system always induced that the emulsion between the liquid phases exited and the separation of the phase was more difficult than that in the biphasic PTC system, which limited the application in industry. The SLL-PTC system with the immobilized catalyst can overcome these drawbacks and exhibits excellent easy removal and subsequent reusability of the catalyst. The SLL-PTC system has been one of the most promising industrial systems.

In the existing SLL-PTC system, the catalyst support can be divided into two types: inorganic support and organic support. Silica gel, alumina, and clay were used as inorganic supports. The ammonium salt, phosphonium salt, macrocyclic polyether, or poly ethylene glycol was introduced by the reaction of hydroxyl in the surface. However, the size of the inorganic support was too small and the complicated separation processes, such as filtration and centrifugation, were required. Filtration and centrifugation of these immobilized catalyst commonly required much more time and energy. Polymer of styrene, alkyl methacrylate, or vinyl pyridine was used as the organic support. The catalytic center was introduced by the grafting reaction or the copolymerization of functional monomers. Microporous and macroporous polystyrene resins crosslinked with divinylbenzene were the most popular supports. However, the high specific surface area and the mass-transfer efficiency were hardly obtained at the same time. The catalytic activity would be reduced owning to the uncertain interfacial or the low mass transfer rate. Hence, an urgent requirement is the development of the much practical immobilized catalyst to overcome the disadvantage of higher initial cost of preparation and lower catalytic activity in the SLL-PTC system.

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Fabric has been used as a support for the catalyst immobilization because of the cheap cost, being facile, and high-specific surface area, such as acrylic fabric and nylon fabric.\textsuperscript{13,15} These immobilized catalysts with the fabric have exhibited excellent catalytic activity and reusability in the acid, basic, and noble metal catalytic reaction systems.\textsuperscript{16–25} However, there are few research studies on the immobilization of the phase-transfer catalyst on the fabric.\textsuperscript{26–28} In the preparation of the reported catalytic fabric, the pretreatment was required and the active group (NH\textsubscript{2} or OH) was introduced on the surface of the fiber. However, the pretreatment induced the high cost and complex preparation process. Cotton fabric is the most used textile owing to its numerous advantages such as good strength, easy processing, and relatively low cost. The hydroxyl group on the surface of cotton fiber can provide the site for functional modification. In real production and processing, the cationization of the cotton fiber has been one of the useful ways to increase the sustainability and green performance of the dyeing and finishing processes.\textsuperscript{29,30} The cationic center was introduced with the reaction of −OH and the modifier and had the similar structure to the phase transfer catalyst. In this paper, the cotton fabric was chosen as the supporter to prepare the catalytic fabric.

Surface grafting and coating are the common ways to modify the fiber. However, the surface grafting amount is insufficient because the amount of the accessory reaction group on the surface of the fabric is limited, especially for the bulky modifier molecule. Therefore, the simple and feasible coating method was used. Similar to the porous polystyrene resins, the modifier consisted of the long-chain alkyl, cross-linking, quaternary ammonium, and solvent resistant groups (Scheme 1).

Scheme 1. Preparation Route Scheme for the Catalytic Cotton Fabric

2. EXPERIMENTAL SECTION

2.1. Materials. All materials were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Scoured and bleached cotton woven fabric (118.2 gm\textsuperscript{−2}) was provided by Zhongheng Dayao Textile Technology Co., Ltd.

2.2. Synthesis of Quaternary Ammonium Monomers. In a typical procedure, N-[3-(dimethyl amino)propyl]-2-methyl-acrylamide (DMAPMA) (0.24 mol), n-butyl bromide (0.24 mol), hydroquinone (0.2 g), and acetone (120 mL) were added into a 250 mL round-bottom four-neck flask. The reaction solution was magnetic-stirred under a nitrogen atmosphere for 30 h at 60 °C. Then, the reaction mixture was cooled to 4 °C for 12 h. The precipitate was collected, washed with cold ethyl acetate, and dried under vacuum at 60 °C (86.23% yield).

2.3. Synthesis of the Polymers. In a typical procedure, butyl methacrylate (10.88 g, 0.077 mol), butyl acrylate (6.54 g, 0.051 mol), styrene (2.34 g, 0.023 mol), the cationic monomer (0.026 mol), N-methyl acrylamide (2.08 g, 0.021 mol), and 2,2′-azobisis(2-methylpropionitrile) (0.16 g, 1 mmol) were dissolved in ethanol (76 mL); 20 mL of the solution was added into the flask, and the rest was added into the constant-pressure dripping funnel. The reactor was degassed by purging with nitrogen gas for 30 min. The polymerization was then performed at 65 °C. The remaining solution gradually dropped (1 h). The reaction solution was incubated for 8 h.

2.4. Preparation of the Catalytic Fabric. The catalytic cotton fabric was prepared by the padding-drying method. The solid content of the polymer solution was adjusted to 24% with ethanol, and 0.2 g of phosphoric acid-ethanol solution (12 wt %) was added. The cotton fabric was dipped into the polymer solution and padded twice. The weight gain rate was regulated to 70%. The fabric was cured at 170 °C for 1.5 h and then washed with ethanol solution.

2.5. Williamson Ether Synthesis Reaction. Cresol (0.0042 mol), NaOH (0.0048 mol), and deionized water (14 mL) were placed into a 50 mL round-bottom flask. The solution of 4-nitrobenzyl bromide (0.0014 mol) and diphenyl (0.08 g) in 2,4-dimethyl-3-pentane (14 mL) was added. The catalytic fabric was cut in 4 mm widths (0.08 g) in 2,4-dimethyl-3-pentane (14 mL) was added. The catalytic fabric was immersed in 4 mm lengths and added into the flask. The reaction mixture was heated at 50 °C under magnetic stirring (600 rpm). With the completion of the reaction, the fabric was filtered and then washed twice with ethanol and water. After dried at 50 °C, the catalytic fabric was reused. The conversion of benzyl bromide derivates for Williamson reaction was determined by high-performance liquid chromatography (HPLC) analysis.\textsuperscript{31}

Samples (about 50 μL) of the reaction mixture were withdrawn at a regular time interval and put into a test tube. Subsequently, 0.2 mL of 10% (v/v) HCl solution was added to quench the reaction, and the solution was diluted to 10 mL with 50% (v/v) aqueous acetonitrile solution. The compositions of the sample were estimated with an internal standard method and diphenyl was used as an internal standard. HPLC
analysis was operated with a mobile phase consisting of 40:60 (v/v) water/acetonitrile and a flow rate of 1.0 mL/min. Detection wavelength was set at 260 nm, and the column temperature was 30 °C.

2.6. Adsorption Experiments. A quantity of 20 mL of dye (C.I. acid red 6) solutions (5 g/L) was placed into a conical flask and heated to 30 °C; 0.2 g of the fabric was added. With the adsorption saturation, the dye concentrations in the residual solutions were determined, and the equilibrium adsorption capacity \( Q_e \) could be calculated.

2.7. Characterization. HPLC analysis was performed using a Zorbax Eclipse XDB-C18 column (150 mm × 0.46 mm, 0.5 μm) on an Agilent 1260 system. Contact angle (CA) analysis was performed with an optical contact angle meter (12907666, Kruss, Germany). SEM analysis was carried out using a Phenom desktop scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of the Catalytic Fabric. The properties of the acrylic copolymer depend mainly on the monomers used and the possible modification. As shown in Scheme 1, five functional monomers were used. The long-chain alkyl methacrylate in the copolymer would endow the high lipophilicity and the solvent resistance. Styrene could increase solvent resistance. N-methylyl acrylamide had been used as the finishing agent for the cotton fabric and showed high reactivity with OH in the surface of the cotton fiber. Butyl methacrylate would improve the rigidity of the chain segment. NMR and DSC curves of the copolymers were characterized. NMR spectra of the products were in complete agreement with the expected structures and showed essentially no contaminants (Figure S1). DSC spectra showed the polymer could be crosslinked with itself with more than 130 °C (Figure S2).

The SEM picture of the catalytic fabric is shown in Figure 1a–f. It can be seen that the membrane is formed on the surface of the cotton fiber. The gap of the fibers in the yarn was filled with the modifier. However, the gap between yarns existed. Therefore, the specific surface area would be still high enough, which was certified in the following kinetics experiments. The FT-IR spectrum of the catalytic fabric and the polymer are shown in Figure 1g. For the polymer modifier, the absorption peaks 2954.9 and 2935.4 cm\(^{-1}\) are assigned to the \( \text{CH}_3 \) and \( \text{CH}_2 \) group in the long-chain alkyl, and peaks at 1741.1 and 1649.8 cm\(^{-1}\) are ascribed to the stretching vibration of the C=O. In addition, the peaks appearing at 1538.98 and 1455.9 cm\(^{-1}\) are attributed to N–H deformation vibration and the benzene skeleton vibration absorption, respectively. It should be noted that all the characteristic absorption peaks for the modifier could be observed on the spectrum of the catalytic fabric, which demonstrated that the modifier polymer was deposited on the fabric. Meanwhile, with the catalytic fabric reused five times, no change in the structure of the fiber and yarn on the catalytic fabric was observed (Figure 1c,f). The result shows that the catalytic fabric is enough firm to be reused, which also is certified in the following experiments.

The reaction conversion rate curve against time for the catalytic fabric is shown in Figure 2. Conversion rate curves against reaction time for blank experiments are shown in Figure S3. The blank experiments were carried out with no catalyst, and unmodified cotton fabric was used. The conversion rates were less than 3% after 10 h with the unmodified cotton or without the catalyst. With the increase in the stirring speed, the conversion rate for 10 h has little change. Without the catalyst, the reactant molecules hardly collided with each other because of the hindrance between the interface between the aqueous phase and the organic phase. However, the catalytic fabric can transfer the phenolic from the aqueous phase into the organic phase, which induced the bond-forming reaction. For the common phase-transfer catalyst, the lipophilicity and adsorption property are main aspects to ascertain the catalytic activity. The immobilized catalyst should exhibit the amphiphilicity, and the reactants can be adsorbed at the surface. Therefore, CA of the catalytic fabric with water...
was characterized. The acid dye was chosen as the adsorbate, and the corresponding equilibrium adsorption capacity ($Q_e$) was compared. Moreover, the reaction conversion rate curve could be fitted well with the first-order model (Figure 2). The first-order reaction rate constant ($k_{\text{fre}}$) was used to evaluating the catalytic activity.

### 3.2. Effect of the Stirring Speed on the Catalytic Activity

For exploring the influence of the mass transfer resistance and the interfacial region, Williamson ether synthesis reaction in the SLL-PTC system was carried out with various stirring speed for the catalytic fabric curing at 130 °C. According to the result in Figure 1, the modifier was not firm and would shed into the reaction mixture on first use. The solvent resistance for the modifier was not high enough because the cross-link bond for the copolymer molecule was not completely formed. However, the effect of the stirring speed on $k_{\text{fre}}$ on first use was same to that for the second use. The saturation value reached when the stirring speed was high than 600 rpm (Figure 3). In the common PTC system, the saturated value reached with higher than 200 rpm for the extract mechanism while with higher than 600 rpm for the interfacial mechanism. This is because the interfacial region area can reach the maximum value with higher than 600 rpm, and the mass transfer rate can reach the maximum value with higher than 200 rpm. Therefore, with the catalytic fabric, the reaction followed the interfacial mechanism and the formation of the interfacial region is also the vital process for the catalytic cycle. Interestingly, the shed of the modifier had no influence on the generation of the interfacial region. This result demonstrated that enough high interfacial region was also generated with the catalytic fabric used. Meanwhile, it was observed that the organic phase was adsorbed on the surface of the fabric with the addition of the catalytic fabric. Therefore, the generation process of the interfacial region in this SLLPTC system would be different from that of the common SLLPTC system.

### 3.3. Effect of the Structure for the Long-Chain Alkyl in the Modifier

The effect of the long-chain alkyl in the copolymer on the catalytic activity was first investigated. As shown in Figure 4, $k_{\text{fre}}$, $Q_e$, and CA increase with the increasing chain length. Except with octadecyl, $k_{\text{fre}}$ for the second time is lower than that for the first time.

As the chain length of the alkyl in the modifier increases, the lipophilicity of the modifier broadens, and then, the surface energy of the catalytic fabric drops. The long-chain alkyl in the modifier also can facilitate the dispersion of the cationic monomer in the synthesis process. Therefore, more cation is exposed and can enter into the aqueous phase. The increased adsorption property is observed. Moreover, the ion pair of the cation and the adsorbed anion should be more close to the substrate layer because of the hydrophobic force. The adsorption property and the transfer efficiency of the reactant anion are increased, thus inducing the higher catalytic activity. The dissolubility of the modifier molecule in the organic phase decreases with the increasing chain length. Therefore, the highest fitness is observed for the catalytic fabric with octadecyl.

### 3.4. Effect of the Cationic Monomer in the Modifier

Catalytic fabrics with different cationic monomers were prepared, and the catalytic activity is shown in Figure 5. It can be noticed that $k_{\text{fre}}$ and $Q_e$ for the dimethylbutyl cation ($M_1$) is higher than those of the dimethylbenzyl cation ($M_2$) and diethylbenzyl cation ($M_3$), while $k_{\text{fre}}$ and $Q_e$ for $M_2$ are same with those for $M_3$. The structure of the cationic monomer has no influence on CA.

For the quaternary ammonium phase transfer catalyst, the lipophilicity and accessibility of the catalyst are the main aspects influencing the catalytic activity. Similar CA also indicates that the catalytic fabric has the same "apparent" lipophilicity. The cationic monomer is the only hydrophilic component in the modifier, and the mole content is 15%. The
lipophilicity of the catalytic fabric is hardly influenced by the structure of the cation center. In other words, the lipophilicity of the catalytic fabric is mainly determined by the hydrophobic monomer. However, the accessibility to the anion is determined by the structure of the cation monomer. The content of the cationic monomer remains constant, and the density of the cation is same. The volume of the cation center for M1 is the smallest, and the cation is more visible than other cations (M2 and M3). The amount of the adsorbed anion increases, and the higher adsorption property and catalytic activity are observed for the catalytic fabric with M1. Therefore, the lipophilicity and accessibility for the catalytic fabric can be obtained by the adjustment of the structure of the cationic monomer and the lipophilic monomer, which is difficultly obtained for the common homogeneous phase transfer catalyst.

3.5. Effect of the Mole Percent of the Cationic Monomer in the Modifier. The effect of the cation content in the modifier molecule on the catalytic performance is shown in Figure 6. It can be seen that k_{cat} for the first time increased with the cationic monomer content varied from 6.67 to 26.67%, while k_{cat} for the second time decreases intensively with the cationic monomer content varied from 20 to 26.67%. The corresponding CA of the catalytic fabric gradually decreases, while Q_{e} remains constant as the cation content increases.

The hydrophilicity of the modifier increases with the content of the cationic monomer; thus, the decreasing contact angle is observed. The adsorption of the anion on the surface of the catalytic fabric is induced by the electrostatic interaction between the cation and anion. Normally, the adsorption property would increase with the increase in the amount of the cation charge. The modifier molecule not only reacts with the −OH in the surface of the cotton fabric but also with itself. The crosslink between the molecules causes the aggregation of the cation center. Therefore, the effective cation charge for the adsorption process is limited. Therefore, the content of the cationic monomer has no influence on the adsorption property. According to the results from Q_{e}, the catalytic fabric also has the same adsorption property to the phenolic anion and the catalytic activity remains constant.

Decreased k_{cat} for the second catalysis demonstrates that the polymer is not firm enough and sheds from the surface of the catalytic fabric. However, the shed polymer in this PTC system has no influence on the catalytic activity in the first time. Commonly with the dispersion of the catalyst in the reaction system, the mass transfer rate would increase and the catalytic activity would increase. Namely, the interfacial region and the mass transfer rate are not varied with the dispersion and insoluble of the polymer modifier. It is also found that the catalytic fabric can adsorb the organic solvent on its surface in the PTC system. The catalytic fabric is wetted by the organic phase. In this SLL PTC system, the interfacial region is formed between the wetted fabric and the aqueous phase. The aqueous phase must diffuse through the organic phase to the site for ion exchange.

3.6. Effect of the Loading Amount for the Modifier. Enough high superficial area is the main aspect to accelerate the mass transfer rate in the PTC system with the immobilization catalyst. With the fiber as the support, the specific surface area should be higher because of the relatively low fineness of fibril. However, the polymer modifier will form the membrane on the surface of the fabric; therefore, the surface area is easily influenced by the loading amount. The catalytic activity for the fabric with various loading amounts were studied (Figure 7). It can be seen that k_{cat} remains constant with the loading amount varied from 5 to 20%, while Q_{e} decreases dramatically. With the further increase in the loading amount to 30%, k_{cat} decreases, while Q_{e} remains constant.

For this SLL-PTC system, the catalytic fabric not only provides the cationic center but also induces the generation of the interfacial region. The area of the interfacial region is influenced by both the lipophilicity and specific surface area of the catalytic fabric. With 5% of the modifier loaded on the fabric, only the thin member is formed on the surface of the fiber. The micro/nanostructures exist and much cations are exposed. The solid–liquid interfacial free energy is reduced, and a higher contact angle is observed. However, the adsorption of the organic phase by the fabric is limited. The catalytic center is fixed on the fabric, and the area of the interfacial region is also limited. With the increase in the loading amount, the thickness of the membrane increases and the surface of the polymer becomes flatter. The micro–nanostructure disappears, and the amount of the exposed cationic center also decreases, leading to the decrease in CA and Q_{e}. The adsorbed amount of the organic phase for the catalytic fabric increases, and the interfacial region in the PTC
system increases. As a result, the catalytic activity also has little change. With further increase in the loading amount, the gap between fibers will be filled by the modifier and this fabric can be treated as the film. Both the area of the interfacial region and the amount of the active catalytic center decrease. Thus, the catalytic activity decreases intensively.

3.7. Williamson Ether Synthesis Reaction in LSL PTC System. Williamson ether synthesis reactions for other phonic derivates and benzyl bromide derivates were proceeded. The conversion rate and \( k_{\text{for}} \) are listed in Table 1. The conversion rates for all reactions are higher than 92%. With the increase in the electron-donating ability of the group in the phonic derivates and electron-withdrawing property of the group in the benzyl bromide derivates, the reaction rate constant increased, which is the same with that in the common PTC system. In this PTC system, the reaction rate constant for the catalytic fabric was three times of that for IRA-910 and six times of that for IRA-402. These results demonstrate that the catalytic fabric exhibit an excellent catalytic activity. For TBAB and TEBAB, the catalyst can easily enter the organic phase and the aqueous phase. However, for the support catalyst, the resistance for the mass transfer increase intensively. IRA-910 and 402 are the copolymer of styrene and divinylbenzene and have a tetramethyl ammonium cation and an ethyl trimethyl ammonium cation as functional group, respectively. These ion-exchange resins had been used as the catalyst for C-alkylation in the phase transfer catalyst system and exhibited a relatively high catalytic activity. In this PTC system, the reaction rate constant for the catalytic fabric was three times of that for IRA-910 and six times of that for IRA-402. For TBAB and TEBAB (common LLPTC system), the catalyst can easily enter into the aqueous phase and the organic phase. However, the catalytic center was fixed on the surface of the support catalyst. Therefore, the resistance for the mass transfer would be higher than that for TBAB. With the catalytic fabric, the organic phase was adsorbed on the catalytic fabric. The area of the interfacial region would be higher than that for ion-exchange resin, and mass transfer resistance also is lower than that for the ion-exchange resin. Therefore, the catalytic fabric shows a higher catalytic activity than the common ion-exchange resin.

3.8. Recyclability of the Catalytic Fabric. To evaluate catalyst recyclability, the catalytic fabric was reused for five consecutive cycles. Table 2 shows the conversion rate and reaction rate constant obtained in each cycle. Only a 5% loss of the reaction rate constant is observed, and the conversion rate does not change. SEM of the catalytic fabric after reusing five times was characterized (Figure 2). No significant change in the surface is observed when compared to the unused catalytic fabric. These results demonstrate that the catalytic fabric exhibits good recycling performance. The cross-linking monomer in the modifier can react with −OH on the surface of the cotton fabric. Moreover, the self-cross-linking of the modifier and long-chain alkyl can further enhance the solvent resistance. The slight loss of catalyst activity was mainly caused by the detachment of the polymer modifier.

3.9. Reaction Mechanism of the SLL-PTC System. According to the abovementioned research, it can be concluded that the catalytic fabric not only provides the support for the catalytic center but also induces the generation of the catalytic activity. As a result, the catalytic activity also has little change. With further increase in the loading amount, the gap between fibers will be filled by the modifier and this fabric can be treated as the film. Both the area of the interfacial region and the amount of the active catalytic center decrease. Thus, the catalytic activity decreases intensively.

Table 1. Reaction Rate Constant and the Conversion Rate for Williamson Ether Synthesis Reaction in the SLL-PTC System

| Product | Catalyst | \( k_{\text{for}} \) (L/(mol*min)) | Reaction conversion rate |
|---------|----------|-------------------------------|------------------------|
| \( \text{C}_6\text{H}_4\text{O} - \text{R} \) | 0.40 | 94% |
| \( \text{C}_6\text{H}_4\text{O} - \text{NO}_2 \) | 0.61 | 96% |
| \( \text{C}_6\text{H}_4\text{O} - \text{Cl} \) | 0.51 | 92% |
| \( \text{C}_6\text{H}_4\text{O} - \text{Cl} \) | 0.70 | 93% |
| \( \text{C}_6\text{H}_4\text{O} - \text{CN} \) | 0.32 | 92% |
| \( \text{C}_6\text{H}_4\text{O} - \text{NO}_2 \) | 0.54 | 95% |
| \( \text{C}_6\text{H}_4\text{O} - \text{Cl} \) | 0.43 | 96% |

Table 2. Reaction Rate Constant and the Conversion Rate with the Catalytic Fabric Reused

| Product | Reused times | \( k_{\text{for}} \) (L/(mol*min)) | Reaction conversion rate |
|---------|--------------|-------------------------------|------------------------|
| \( \text{C}_6\text{H}_4\text{O} - \text{NO}_2 \) | 1 | 0.61 | 96% |
| \( \text{C}_6\text{H}_4\text{O} - \text{NO}_2 \) | 2 | 0.59 | 95% |
| \( \text{C}_6\text{H}_4\text{O} - \text{NO}_2 \) | 3 | 0.59 | 95% |
| \( \text{C}_6\text{H}_4\text{O} - \text{NO}_2 \) | 4 | 0.58 | 94% |
| \( \text{C}_6\text{H}_4\text{O} - \text{NO}_2 \) | 5 | 0.58 | 93% |

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of the interfacial region. The whole catalytic cycle in this SLL-PTC system contains three steps, namely, adsorption, transfer, and regeneration (Figure 8).

![Figure 8. Mechanism of Williamson ether synthesis reaction in the SLL-PTC system with the catalytic cotton fabric.]

(1) Because of the lipophilicity of the catalytic fabric, the organic phase is adsorbed on the surface of the fabric. The interfacial region was generated between the organic phase and the aqueous phase. The cation center is prone to enter the aqueous phase because of the hydrophilicity. With the electronic interaction, the ion pairs of the cation and the ion are quickly generated in the interfacial region near the aqueous phase.

(2) After the generation of the ion pair, the catalytic center is more lipophilic than the ion pair with Br\(^-\). In this case, the ion pair can quickly return into the center of the interfacial region. Benzyl bromide also can diffuse into the interfacial region.

(3) The bond-forming reaction is initiated in the interfacial region and follows a SN\(_2\) bimolecular nucleophilic substitution mechanism. The phenolic ion acts as the nucleophile to attack the electrophilic carbon. Br\(^-\) is the leaving group and will quickly interact with the catalytic center. The product diffuses into the organic phase. The catalytic center is regenerated and can enter into the aqueous phase to catalyze the next cycle.

4. CONCLUSIONS

In conclusion, the cotton-based catalytic fabric immobilized with the phase transfer catalyst was successfully prepared by the padding-dry method with the copolymer containing the quaternary ammonium cation, long-chain alkyl, and crosslinking group as the modifier. The long-chain alkyl not only endowed solvent resistance but also acted as the spacer chain. However, the crosslink of the modifier molecule induced the aggregation of the cation center. The absorption property to the ion was determined by the accessibility of the cation and the disperse extent of the cationic center. The organic phase was adsorbed on the surface of the catalytic fabric. Interfacial region area was influenced by the amount of the organic phase adsorbed and specific surface areas of the fabric. For the Williamson reaction, the conversion rate can reach to 92% in this SLL-PTC system, and the catalytic fabric can be reused five times with no loss in the catalytic activity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01981.

NMR and DSC curves for the copolymer (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.
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