

Chemical Structure and Catalytic Activity of Quaternary Onium Salt-Type Triphase Catalysts Based on CPS Microspheres

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ABSTRACT: In this work, diversified quaternary onium salt-type triphase catalysts (TPC) were prepared based on crosslinked polystyrene (CPS) microspheres, and the relationship between their chemical structures and catalytic activities in liquid-solid-liquid reaction system were investigated in depth by using the esterification reaction of benzyl chloride with sodium acetate as a model system. The experimental results indicate that the chemical structures of the TPC affect their catalytic activity greatly and there are four basic points: (1) the quaternary phosphonium-type TPC have higher activity than quaternary ammonium-type catalyst; (2) the TPC with more lipophilic substitutes at N atom have higher catalytic activity;

(3) the TPC with longer spacer arm, which links quaternary onium salt group to the matrix microsphere, have higher catalytic activity; (4) the bonding density of quaternary onium salt group on the polymeric carrier affects the hydrophilic and hydrophobic property of the TPC, and consequently, influences the catalytic activity significantly. For a given triphase catalysis system, there is an optimal bonding density of quaternary onium salt group on the solid catalysts. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 824–832, 2012

Key words: phase transfer catalysis; triphase catalyst; quaternary onium salt; structure and catalytic activity

INTRODUCTION

Phase-transfer catalysis (PTC) is an effective tool for accelerating the reactions between two immiscible reactants, which are present in two immiscible phase, liquid-liquid or liquid-solid, in organic synthesis.^{1–4} There are many types of phase transfer catalysts, such as quaternary onium salts (quaternary ammonium salt and phosphonium salt), crown ethers, cryptands (aza-macrobicyclic ethers), and open chain polyethers (polyethylene glycols, PEGs, and their derivatives).^{5–8} Among these phase transfer catalysts, quaternary onium salts are the most cost-effective and feasible PTC catalysts in terms of integrated properties,⁹ and are often the selected catalysts in organic synthesis. However, the reaction system of using a two-phase phase-transfer catalyst always encounters two major problems, the separation and purification of the final product, and the recovery and reuse of the catalyst.^{10–12} Solid-supported phase transfer catalysts, also known as triphase catalysts (TPC), offer many advantages associated with heterogeneous catalysts such as easily recovering and reusing of the cata-

lyst, and conveniently using continuous reactors as well as separating the product. For the TPC, phase-transfer catalysts (more precisely, phase-transfer catalytic groups) are chemically bound onto solid supports, such as silica gel, zeolites, polymers microsphere, etc.^{13–16} Among various solid supports, polymeric supports are received much attention and are widely used.^{17–19} The advantages of polymeric supports are that their chemical structures are easy to be designed and controlled, the polymer backbones can increase the organophilicity of catalysts, and this character is in favor of the enhancement of the catalytic activity to a certain degree.^{13,16}

In the phase-transfer catalytic systems using polymer-supported TPC, namely, in the reaction system of liquid-solid-liquid, the catalytic activity of the TPC is intensively influenced by their chemical structure, namely, the microenvironment of the TPC played a crucial role in accelerating the reaction rate. However, to date, there have been a few instances in the literature that discuss the relationship between the chemical structure and catalytic activity of TPC,^{14,20} whereas to understand the effects of the chemical structure on the catalytic activity of TPC is very important for the preparation and application of TPC. In this work, the modified crosslinked polystyrene (CPS) microspheres by introducing the exchangeable chlorine atoms on their surface were

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used as support in the synthesis of diversified polymer-supported TPC with onium salt type. These catalysts were used in the esterification reaction of benzyl chloride with sodium acetate in a three phase system of water-solid catalyst-organic solvent so as to investigate in detail the influence of the structure factors on the catalytic activity of quaternary onium salt-type TPC. The main aim of this work is to research the relationship between the structure and catalytic activity of quaternary onium salt-type TPC, and such fundamental research is very important and significant for the organic synthesis, in which TPC are used.

EXPERIMENTAL

Material and equipment

CPS microspheres (a crosslinking degree of 4% and a grain size of 0.32–0.45 mm, Tenlong Chemical Ltd., Changchou, Jiangsu Province, China), namely cross-linked styrene/divinylbenzene copolymer microspheres, was received. Chloroacetyl chloride (CAC, Anyang Yonghe Chemical Plant, Henan Province, China) was of reagent grade. Chlorobutyryl chloride (CBC, Jingchun Chemical Ltd., Shanghai, China) was of analytical grade. 1,4-Bis(chloromethoxy)butane (BCMB) was self-synthesized,²¹ and it has no carcinogenic toxicity. Triethylamine (TEA, Fuchen Chemical Reagent, Tianjin City, China) was of analytical grade. Triisopropylamine (TPA, Nanjing Dongfang Mingzhu Chemical Engineering Ltd., Nanjing City, China) was of analytical grade. Tri-*n*-butylamine (TBA, Shanghai Tianlian Chemical Ltd., Shanghai, China) was analytical grade. Triphenylphosphine (TPP, Beijing Chemical Reagent Ltd., Beijing, China) was analytical grade. Other chemicals were all commercial reagents with analytical pure and were purchased from Chinese companies.

The instruments used in this study were as follows: Perkin–Elmer 1700 infrared spectrometer (FTIR, Perkin–Elmer Company, USA), Unic UV/vis-2602 spectrophotometer (Unic Company, USA); HP 6890 gas chromatograph (GC, Beijing Analytical Instrument Plant, Beijing, China); DZ3310 calorimetric meter of oxygen-bomb type (Nanjing Yongyan Electronic limited liability Company, Nanjing City, China).

For the gas chromatograph analysis, a HP 6890 GC with flame ionization detector was used, and a packed column with a length of 2.0 m and a diameter of 0.32 cm was used. The determination conditions were as follows: the column temperature was at 150°C, the temperature of injection port was maintained at 250°C, the temperature of the detector port was maintained at 300°C, and the analysis was carried out with internal standard method.

Preparation and characterization of quaternary onium salt-type triphase catalyst

Surface modification of CPS microspheres

CPS microspheres were first surface-modified to introduce exchangeable chlorine atoms onto their surfaces, and three kinds of surface-modified CPS microspheres bearing exchangeable chlorine atoms were prepared¹: Two kinds of ω -chloroacyl chlorides, CAC, and CBC, were used as chloroacylation reagent, respectively, and two kinds of chloroacylated CPS microspheres, CACPS microspheres, and CBCPS microspheres, were prepared via Friedel-Crafts acylation reaction (here it was chloroacylation reaction) in the presence of Lewis acid catalyst SnCl₄²; 1,4-bis(chloromethoxy)butane (BCMB) was used as chloromethylation reagent, and chloromethylated CPS microspheres, CMCPs microspheres, were obtained via chloromethylation reaction²¹ also in the presence of Lewis acid catalyst SnCl₄. The typical procedure is demonstrated as follows by taking the preparation of CACPS microspheres for an example.

Two grams of CPS microspheres were placed into a reactor equipped with a mechanical agitator, followed by adding 20 mL of solvent chloroform (CHCl₃), and the microspheres were allowed to be soaked and sufficiently swelled for 12 h. CAC (1.5 mL) and Lewis acid catalyst SnCl₄ (1.2 mL) were added, and the chloroacylation reaction was carried out with stirrer at room temperature for 4 h. After finishing the reaction, the mixture was treated with diluted hydrochloric acid to destroy the Lewis acid catalyst. The resultant microspheres were collected by filtering, washed repeatedly with distilled water until without chloride ion in the cleaning solution, and dried in vacuum, obtaining CACPS microspheres.

According to the above process, CBCPS microspheres were also prepared with CBC as chloroacylation reagent, and as reported elsewhere,²¹ CMCPs microspheres were prepared with BCMB as chloromethylation reagent. By controlling the reaction conditions, the chlorine contents of the two microspheres were also controlled to be about 2.48 mmol/g (dry weight), and namely, for the three modified CPS microspheres, the amount of the exchangeable chlorine atoms were nearly identical.

The infrared spectra of CACPS, CBCPS, and CMCPs microspheres were determined with KBr pellet method. The sample of CACPS microspheres was burned out in an oxygen bomb and then the chlorine content (mmol/g) of the sample was analyzed with Volhard method.²¹ This chlorine content stands for the content of the chloroacetyl group on the CACPS microspheres. The chlorine content of CACPS microspheres prepared and used in this work was 2.48 mmol/g.

Quaternization reaction of preparing quaternary onium salt-type TPC

The quaternization reactions of three trialkylamines (TEA, TPA, and TBA) and TPP with three kinds of modified microspheres, CACPS, CBCPS, and CMCPs microspheres, were performed, respectively, diversified quaternary onium salt-type TPC were prepared, and they have different chemical structures. The typical preparation process is described below by taking the formation of a quaternary phosphonium salt (QPS)-type catalyst for example.

Two grams of CACPS microspheres were placed into a four-necked flask equipped with a mechanical agitator, a reflux condenser and a thermometer, followed by adding 20 mL of solvent dichloromethane (CH_2Cl_2), and the added microspheres were allowed to be swelled for 12 h. Subsequently, 10 mL of CH_2Cl_2 solution in which 2.28 g of TPP was dissolved were added into the flask, and the quaternization reaction (here is quaternary phosphonium reaction) was carried out with stirrer at 35°C for 1 h. After finishing the reaction, the product microspheres were washed repeatedly with ethanol to remove residual solvent and reagent TPP. By drying in vacuum, the solid catalyst QP-CACPS, on which QPS groups were bound (or immobilized), was obtained, and it belonged to QPS-type triphase catalyst. By adopting the similar experimental procedure, another two QPS-type TPC, QP-CBCPS, and QP-CMCPs, were also prepared with CBCPS and CMCPs microspheres as starting microspheres, respectively. The infrared spectra of this QPS-type TPC were determined to confirm their formation. The bonding amounts (or bonding density, mmol/g) of QPS group on these solid catalysts were determined via measuring the content of residual TPP in the final solution with UV spectrophotometry at 261 nm. By controlling the reaction conditions, these QPS-type TPC with different bonding densities of QPS group were prepared.

The quaternization of three trialkylamines, TEA, TPA, and TBA, with three kinds of modified microspheres, CACPS, CBCPS, and CMCPs microspheres, were performed, respectively, and diversified quaternary ammonium salt (QNS)-type TPC were prepared, for example, QN-CACPS (TEA), QN-CBCPS (TPA), and QN-CMCPs (TBA), and so on. The bounded amount of QNS group on various solid catalysts was determined with Volhard titrimetric method.²² Similarly, by controlling the reaction conditions, these quaternary ammonium salt-type TPC with different bonding densities of QNS group were prepared.

Esterification reaction of benzyl chloride with sodium acetate catalyzed by TPC

The above various TPC were used in the esterification reaction of benzyl chloride in organic phase

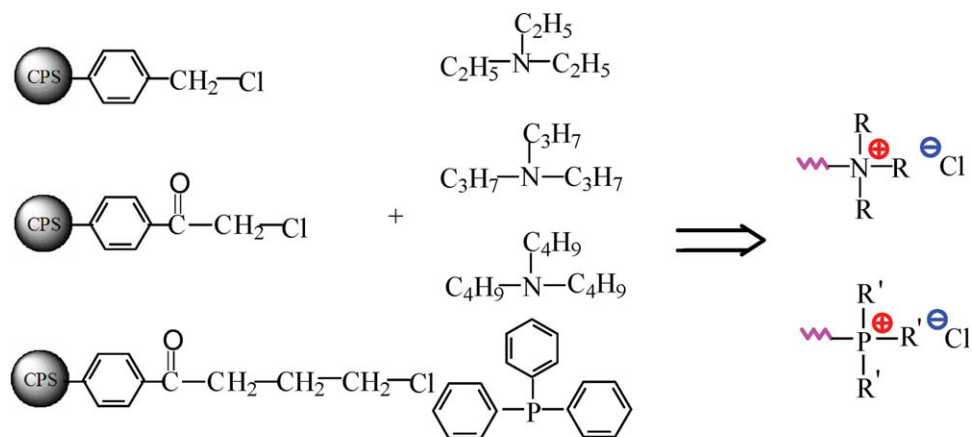
with sodium acetate in water phase to investigate the relationship between the chemical structure and the phase-transfer catalytic activity of TPC. The esterification reaction procedures are explained as follows by taking the reaction system with QP-CACPS for example.

Ten milliliters of benzyl chloride were dissolved in 40 mL of CHCl_3 , constituting organic phase, The organic phase was added into a four-necked flask equipped with a mechanical agitator, a reflux condenser and a thermometer, followed by adding 100 mL of aqueous solution of sodium acetate with a concentration of 4 mol/L (in the system, sodium acetate is largely excessive with respect of the added amount of benzyl chloride). Then, a given amount of the triphase catalyst QP-CACPS was added, so that the actual added amount of the catalytic group, QPS group, remained 8 mmol generally. The contents were agitated sufficiently at an agitation rate of 550 rpm to disperse fully the mixture. The triphase-transfer catalysis reaction of liquid-solid-liquid was carried out at 57°C . The reaction mixture (1 mL) was withdrawn periodically through the sampling port of the flask, and the organic phase was thoroughly separated by centrifugalization and filtered using a microporous filter. The content of benzyl chloride in the organic phase sample was quantitatively analyzed by gas chromatograph with internal standard method, and the conversion of benzyl chloride was further calculated.

RESULTS AND DISCUSSION

Reaction process to prepare various TPC

The chloroacylation reaction and chloromethylation reaction of CPS microspheres were conducted with CBC, CAC, and 1,4-bis (chloromethoxy) butane as reagents, respectively, obtaining three kinds of modified microspheres, CBCPS, CACPS, and CMCPs. For the three kinds of modified microspheres, exchangeable chlorine atoms had been introduced onto their surfaces. Moreover, they have the spacer arms with different lengths. For CBCPS, CACPS, and CMCPs microspheres, the spacer arms contain four carbon atoms, two carbon atoms, and one carbon atom, respectively, (to see the following Scheme 1). Via respective quaternization reactions of the three kinds of modified microspheres with three trialkylamines (TEA, TPA, and TBA) and triphenyl phosphine (TPP), the diversified quaternary onium salt-type TPC with different chemical structures were prepared. The process to prepare these diversified TPC through quaternization reactions can summarily expressed in Scheme 1, and the chemical structures for the diversified TPC can be also found from Scheme 1.



R: Various alkyl substitutes: ethyl group; propyl group; butyl group

R': Phenyl

↗: Various spacer arms

Scheme 1 Preparation process of various quaternary onium-type TPC.

Infrared spectra of TPC

Since the quaternary ammonium groups do not display characteristic IR absorption bands,²³ the formation of the quaternary onium salt-type TPC is confirmed by observing the spectrum of the QPS-type triphase catalyst QP-CACPS. Figure 1 gives the spectra of CPS, CACPS, and QP-CACPS microspheres.

In the spectrum of CPS microspheres, all characteristic absorption bands of CPS are displayed as shown in the spectrum. In the spectrum of CPCPS microspheres, four new bands at 670, 810, 1242, and 1680 cm^{-1} have appeared. The bands at 1680 cm^{-1} is attributed to the characteristic absorption of carbonyl group C=O of chloroacetyl groups, the bands

at 670 cm^{-1} is ascribed to C—Cl bond of chloroacetyl groups, the bands at 1242 cm^{-1} should correspond to C—O stretching bond of chloroacetyl group and the strengthened bending vibration (in-plane) absorption of C—H bond on the benzene ring after doubly substituting at position 1 (main chain) and position 4 due to the introducing of chloroacetyl group, and the bands at 810 cm^{-1} is corresponding to the bending vibration (out-of-plane) absorption of C—H bond on the benzene ring after doubly substituting. The above absorption band changes indicate that chloroacetyl groups have been introduced onto the surfaces of CPS microspheres via chloroacylation reaction, forming CACPS microspheres.

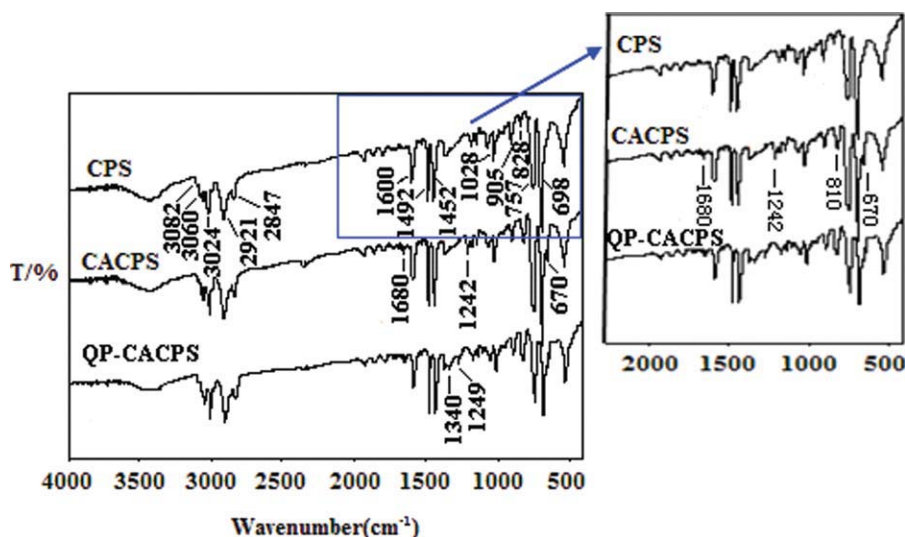


Figure 1 FTIR spectra of three kinds of microspheres. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

In the QP-CPCPS microspheres, the absorption bands of C—Cl bond of chloroacetyl groups at 670 cm^{-1} has been weakened greatly, and two new bands at 650 and 1249 cm^{-1} have appeared. The former is attributed to the stretching vibration absorption of C—P bond, and the latter should be corresponding to the bending vibration absorption of C—H bond associated with P atom. The above facts suggest that the quaternary phosphonium reaction between CACPS microspheres and TPP has occurred, and the triphase catalyst QP-CACPS have been obtained.

Phase-transfer catalytic activity and mechanism of TPC

In the reaction system between benzyl chloride (in organic solvent CHCl_3) and sodium acetate (in water), the triphase catalyst QP-CACPS with 1.17 mmol/g of the bonding density of QPS group was added. The added amount of the solid catalyst QP-CACPS was changed in series, leading to the variation of the actual added amount of QPS group in the system, and the esterification reactions were performed under other fixed conditions. Figure 2 gives the variations of benzyl chloride conversion with reaction time for various systems in which the added amounts of QPS group are different.

It can be observed from Figure 2 that as there is no triphase catalyst in the reaction system, the reaction rate is very slow, and the conversion of benzyl chloride is very low, or rather there is nearly no reaction to occur because the reaction only occurs at the limited interface between two liquid phases. However, as the solid catalyst QP-CACPS was added, the reaction rate speeds up and the benzyl chloride conversion is enhanced rapidly with increasing the added amount of QP-CACPS (expressed as the added amount of QPS group). This result fully displays that the solid catalyst QP-CACPS has high catalytic activity for the nucleophilic substitution reaction between benzyl chloride and sodium acetate. The phase-transfer catalytic mechanism for the liquid-solid-liquid system can be explained as follows. In the water phase, the solid catalyst QP-CACPS is swelled, and the negative chloride ions on the solid catalyst QP-CACPS are exchanged by acetate ions, and the positive quaternary phosphonium ions on QP-CACPS combine with acetate ions to form active ion pairs. The QP-CACPS microsphere bearing the active ion pairs enters into the organic phase, and releases the nucleophilic species acetate ions. The nucleophilic substitution reaction of benzyl chloride with the detached acetate ion as attacking reagent is allowed to be carried out, resulting in the product, benzyl acetate. At the same time, Cl atoms (in a form of anion)

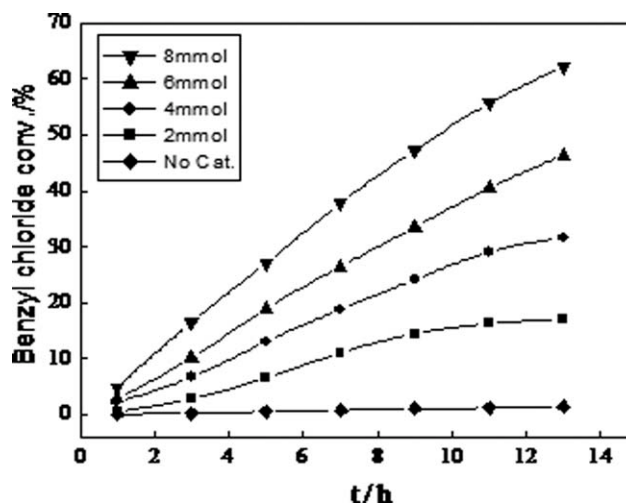


Figure 2 Variation of benzyl chloride conversions with time by using different amounts of QP-CACPS catalyst at 57°C .

detached from benzyl chloride molecules are combined by the positive quaternary phosphonium ions of QP-CACPS microspheres and are carried into water phase. Like this, the triphase catalyst QP-CACPS circularly plays a role in transferring negative acetate ions from water to organic phase. The overall reaction process of benzyl chloride and sodium acetate and the mechanism of the PTC can be schematically expressed in Scheme 2.

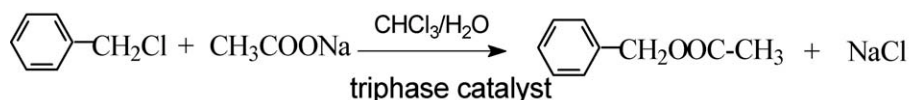
Effects of various structure factors on catalytic activity

Effects of group species having catalytic function

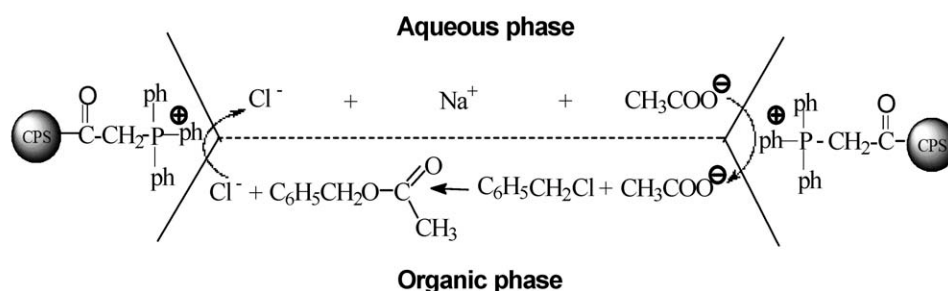
Two kinds of TPC, QN-CACPS (TBA) with quaternary ammonium salt type and QP-CACPS with QPS type, were selected. They have the same bonding density of quaternary onium salt group (about 1.17 mmol/g), but have different groups with catalytic function. The investigation results of some triphase catalysis systems,^{13,24} in which polymer-supported phase transfer catalyst were used, showed that there is no significant increase in conversion at agitation rates higher than 500 rpm . Therefore, to eliminate the external mass transfer resistance and to evaluate intrinsic kinetics, all experiments in this work were carried out at an agitation rate of 550 rpm . Figure 3 presents the benzyl chloride conversion curves.

It can be seen clearly that the triphase catalyst with QPS type has higher catalytic activity than the quaternary ammonium salt-type catalyst, and the benzyl chloride conversion for the system with QP-CACPS gets up to 60% in 13 h , whereas for the system with QN-CACPS (TBA), the conversion in 12 h is only about 35% . This result is consistent with the reported result.⁹ This is attributed probably to the

Overall reaction:



Mechanism of triphase-transfer catalysis



Scheme 2 Mechanism of triphase-transfer catalysis for benzyl acetate formation reaction.

higher lipophilic character of the cation (triphenylphosphonium) supplied by the catalyst QP-CACPS. The ion-pairs formed by the cations with a higher lipophilic character with acetate ions are easy to enter the less polar organic media in which the displacement reaction takes place, resulting in the acceleration of the esterification reaction.

Effects of the kinds of alkyl substitute

Three quaternary ammonium salt-type catalysts, QN-CACPS (TEA), QN-CACPS (TPA), and QN-CACPS (TBA), were selected. They have the same bonding density of QNS group (about 1.17 mmol/g) but have different alkyl substitutes at N atom. Under the same reaction conditions, the three catalysts

were used in the phase-transfer catalytic esterification reaction, respectively, and Figure 4 presents the benzyl chloride conversion curves.

Figure 4 shows that the activity sequence of the three catalysts is : QN-CACPS (TEA) < QN-CACPS (TPA) < QN-CACPS (TBA), fully displaying the effect of alkyl substitute on the catalytic activity of the TPC. For QN-CACPS (TEA), the substitute at N atom is ethyl group, and the shorter alkyl group makes the lipophilicity of the surface of the catalyst QN-CACPS (TEA) to be poorer than that of QN-CACPS (TPA) whose substitute at N atom is longer isopropyl group. The poorer lipophilicity of QN-CACPS (TEA) negatively affects its swelling property in the organic phase and the ability to release acetate ions, so that

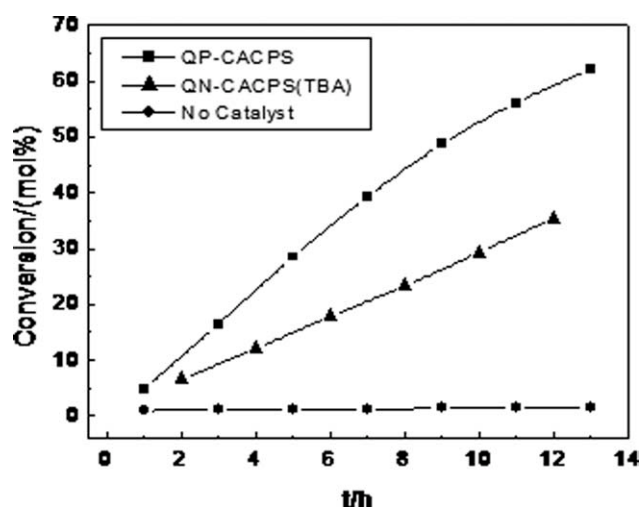


Figure 3 Variation of benzyl chloride conversions with time for QP-CACPS and QN-CACPS (TBA) catalyst systems at 57°C in the presence of 8 mmol onium salt group.

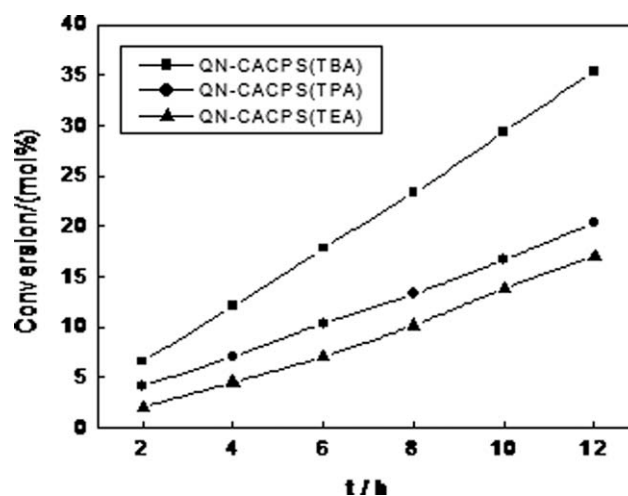


Figure 4 Variation of benzyl chloride conversions with time for QN-CACPS (TEA), QN-CACPS(TPA), and QN-CACPS(TBA) catalyst systems at 57°C in the presence of 8 mmol QNS group.

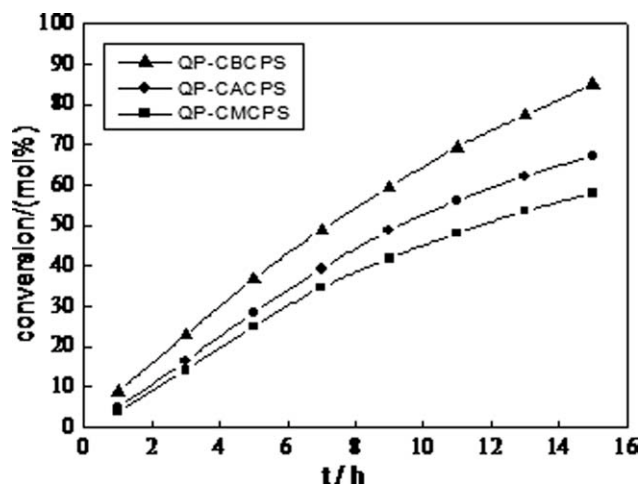


Figure 5 Variation of benzyl chloride conversions with time for QP-CMCPS, QP-CACPS, and QP-CBCPS catalyst systems at 57°C in the presence of 8 mmol QPS group. Reaction temperature: 57°C; Added amount of QPS group: 8 mmol.

the rate of the nucleophilic substitution reaction is influenced obviously. Therefore, the conversion of benzyl chloride catalyzed by QN-CACPS (TEA) is lower than that catalyzed by QN-CACPS (TPA). For the same reason, the conversion catalyzed by QN-CACPS (TPA) is lower than that catalyzed by QN-CACPS (TBA). Among the three catalysts, QN-CACPS (TBA) is the most active due to the lipophilicity imparted by the long chain alkyl (butyl). The stronger lipophilicity of QN-CACPS (TBA) affords it fine swelling property in the organic phase, and this will be greatly beneficial to the release of acetate ions from the ion-pairs. By the way, tetrabutyl ammonium halide has a high partition coefficient in the organic phase due to its higher lipophilic nature and is an effective and widely used PT catalyst.^{9,25}

Effects of length of spacer arm

Two groups of TPC were selected: one group consists of QP-CMCPS, QP-CACPS, and QP-CBCPS, which are the QPS-type catalysts with different lengths of spacer arm; another group consists of QN-CMCPS (TEA), QN-CACPS (TEA), and QN-CBCPS (TEA) which are the QNS-type catalysts with different lengths of spacer arm but with the same alkyl substitute at N atom. Besides, for the two groups of TPC, the binding densities of quaternary onium group are similar, about 1.17 mmol/g. Under the same reaction conditions, the two groups of TPC were used in the catalytic esterification reaction. The conversion curves of benzyl chloride are shown in Figures 5 and 6, respectively.

Figure 5 shows that the activity sequence of the three QPS-type catalysts is : QP-CMCPS < QP-

CACPS < QP-CBCPS, fully displaying the effect of the length of spacer arm on the catalytic activity of the TPC. For the three catalysts, the number of C atom contained in the spacer arm that link QPS group with the matrix microsphere are 1, 2, and 4, respectively, (to see Scheme 1). For the catalyst QP-CMCPS, the spacer arm is the shortest and bigger steric hindrance of the matrix microsphere negatively affects the combination of QPS group on QP-CMCPS with the acetate ion in water, leading to lower catalytic activity. For the catalyst QP-CBCPS with the longest spacer arm, the steric hindrance of the matrix microsphere is relatively smaller, and the acetate ions in water are easy to be close to surfaces of the catalyst QP-CBCPS. Therefore, the combination ability of QPS group on QP-CBCPS towards the acetate ion in water is stronger, resulting in higher catalytic activity. For the catalyst QP-CACPS with the spacer arm of middle length, the steric hindrance of the matrix microsphere is also placed in the middle, bringing on the middle catalytic activity.

Figure 6 displays that the activity sequence of the three quaternary ammonium salt-type catalysts is : QN-CMCPS (TEA) < QN-CACPS (TEA) < QN-CBCPS (TEA), and the length of the spacer arm should be responsible for this result like as the result shown in Figure 5.

Effects of bonding density of quaternary onium group

Two groups of TPC were selected: one group consists of QP-CACPS catalysts with different bonding densities of QPS group; another group consists of QN-CACPS (TEA) catalysts with different bonding

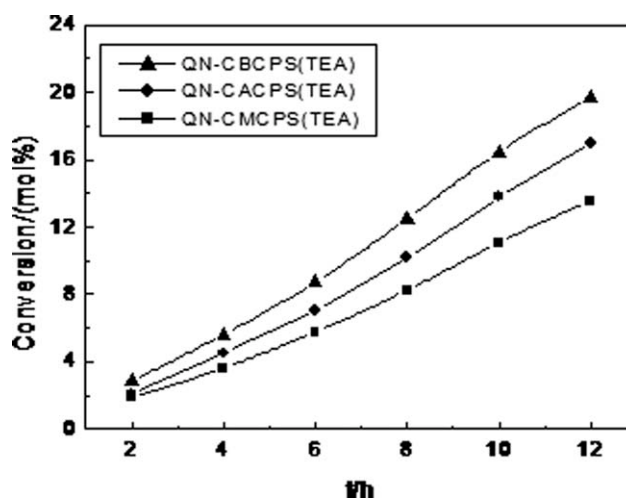


Figure 6 Variation of benzyl chloride conversions with time for QN-CMCPS (TEA), QN-CACPS (TEA), and QN-CBCPS (TEA) catalyst systems at 57°C in the presence of 8 mmol QNS group. Reaction temperature: 57°C; Added amount of QNS group: 8 mmol.

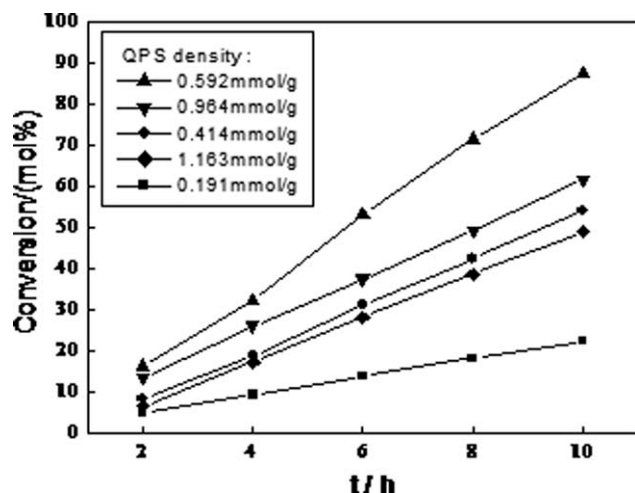


Figure 7 Variation of benzyl chloride conversions with time for QP-CACPS catalyst systems at 57°C in the presence of 8 mmol QPS group.

densities of QNS group. Under the same reaction conditions, the two groups of TPC were used in the catalytic esterification reaction, respectively. It needs to be pointed that for these reaction systems, the added amount of quaternary onium group is identical, and was 8 mmol. It means that for these reaction systems, the added amounts of the various solid catalysts are different. For the catalysts of the first group, the conversion curves of benzyl chloride are shown in Figure 7.

It can be found from Figure 7 that for the first group catalysts, the catalytic reaction results are different as QP-CACPS catalysts with different bonding densities of QPS group are used. To more clearly display the effect of bonding densities of QPS group on the catalytic activity, by taking the data in 10 h in Figure 7, the benzyl chloride conversion as a function of bonding density of QPS group is figured, as shown in Figure 8. It is shown clearly in Figure 8 that the conversion of benzyl chloride first rises and then decreases with the increase of the bonding density of QPS group on QP-CACPS microspheres, and there is a maximum conversion as the bonding density of QPS group is 0.592 mmol/g. This fact reflects the effect of the bonding density of QPS group on the catalytic activity. As the bonding density of QPS group is low, the hydrophobicity of QP-CACPS microspheres is stronger. Here, the microspheres cannot be fully swelled in water phase, and the QPS groups can not be exposed sufficiently but enwrapped inner the microsphere. This will lead to the decrease of the ability to carry the acetate ions for the triphase catalyst and slow down the substitution reaction in the organic phase. However, if the bonding density of the QPS groups is too high, the hydrophilicity of QP-CACPS microspheres is stronger, so that the swelled extent of the microspheres in

organic phase will become poorer. This will leads to that the acetate ions carried by the triphase catalyst are wrapped and cannot be released favorably. It also will slow down the substitution reaction in the organic phase.

For the catalysts of the second group, the benzyl chloride conversion in 12 h as a function of bonding density of QNS group is also figured, and shown in Figure 8. The displayed facts are identical with that of the first group: The conversion of benzyl chloride first rises and then declines with the increase of the bonding density of QNS group on QN-CACPS (TEA) microspheres, and there is a maximum conversion as the bonding density of QNS group is 1.373 mmol/g.

Therefore, via this work, an important status is found for the quaternary onium salt-type triphase catalyst prepared using polymeric microspheres as carrier, and it is that the phase-transfer catalytic group (more specifically, the density of phase-transfer catalytic group) on the carrier will change the hydrophilic and hydrophobic property of the triphase catalyst greatly, and will affect the catalytic activity markedly. For a given triphase-transfer catalysis system, there is an optimal bonding density of the catalytic group on the triphase catalyst, that is, there is an appropriate hydrophilic and hydrophobic property for the triphase catalyst.

Recycle and reuse property of TPC

After use, the catalyst microspheres were sufficiently soaked and washed with ethanol and distilled water to remove the adsorbed substances, and then dried under vacuum. The recovered catalysts were reused in the esterification reaction of benzyl chloride and

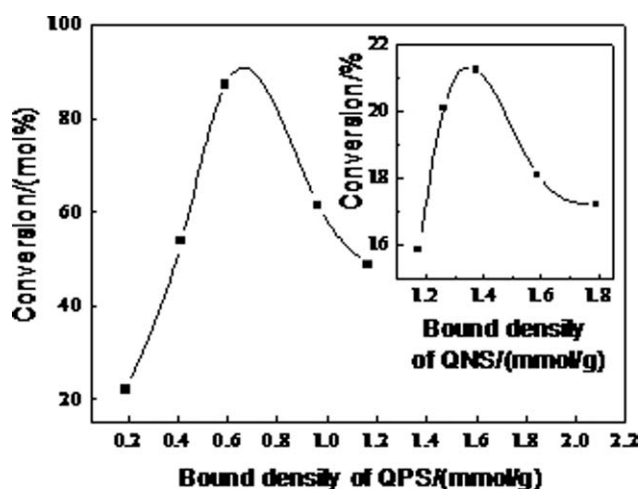


Figure 8 Benzyl chloride conversion as a function of bonding density of QPS group for QP-CACPS catalysts and QNS group for QN-CACPS (TEA) catalysts. Reaction time: 10 h (QPS system) and 12 h (QNS system).

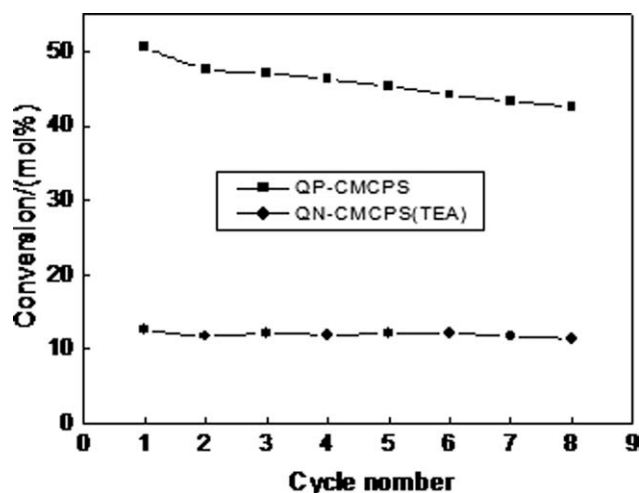


Figure 9 Effect of cycle number of reusing on catalyst activity. Temperature: 57°C; Solvent: CHCl₃; Reaction time: 12 h; Added amount of onium salt group: 8 mmol.

sodium acetate, respectively. In each recycle experiment, the reaction conditions were fixed (57°C, 12 h, CHCl₃ as organic solvent and 550 rpm of agitation rate, and so on). Here, the recycle and reuse property of two kinds of TPC, QP-CMCPS, and QN-CMCPS (TEA) are discussed.

Figure 9 shows the conversion of benzyl chloride as a function of recycle number. It can be seen clearly that during the eight recycle experiments, the activity of the triphase catalyst QN-CMCPS is not nearly changed, whereas the activity of QP-CMCPS declines slightly and gradually. The facts indicate that in the present system, quaternary phosphonium-type TPC are slightly unstable, whereas quaternary ammonium-type TPC have excellent reuse property and high stability. In general, quaternary phosphonium-type phase-transfer catalysts not only have high catalytic activity but also have high stability in comparison with ammonium-type phase-transfer catalysts.⁹ However, under alkaline condition, quaternary phosphonium-type phase-transfer catalysts are usually unstable.^{9,10} This system is just alkaline, and the alkaline property is caused by the hydrolysis of sodium acetate, leading to the slight instability of quaternary phosphonium-type catalysts.

CONCLUSIONS

The modified CPS microspheres on that the exchangeable chlorine atoms were introduced were used as the supports and diversified quaternary

onium salt-type TPC with different chemical structures were prepared. The relationship between their chemical structures and catalytic activities in liquid-solid-liquid reaction system were investigated in depth by using the esterification reaction of benzyl chloride with sodium acetate as a model system. The chemical structure affects the catalytic activity of the TPC greatly. QPS-type catalysts have higher activity than QNS-type catalysts; the TPC with more lipophilic substitutes at N atom have higher catalytic activity; the TPC with longer spacer arm, which links quaternary onium salt group to the matrix microsphere, have higher catalytic activity; the bonding density of quaternary onium salt group on the polymeric carrier affects the hydrophilic and hydrophobic property of the TPC, and consequently, influences the catalytic activity significantly.

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