SBA-15 supported quaternary ammonium salt: an efficient, heterogeneous phase-transfer catalyst

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Abstract

The immobilization of an ammonium salt on the pore surface of highly hydrothermally stable inorganic mesoporous material SBA-15 provided an efficient phase-transfer catalyst (PTC) that could easily be recovered and recycled. Compared with the corresponding polymer supported phase-transfer catalyst, it need not swell before use and shows relative high and sustained catalytic activity.
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*Keywords:* SBA-15; Mesoporous material; Homogeneous; Catalyst

Heterogeneous phase reaction is of significant importance in organic chemistry. By using phase-transfer catalysts (PTC), the reactants in different phases can react with each other and much milder reaction conditions can be employed. Since being discovered, phase-transfer catalyst has been in use for more than three decades and is an established technique nowadays in organic synthesis [1]. However, the drawbacks associated with the recovery and reuse of expensive phase-transfer catalyst from the liquid phase were somewhat neglected in the earlier period perhaps due to the success achieved across the broad spectrum of reactions that could be conducted using PTC. This problem can be overcome by immobilizing the phase-transfer catalyst to a solid support, which was first mentioned by Regen [2]. He reported that ammonium salts immobilized on cross-linked polystyrene resins are as effective as corresponding phase-transfer catalysts. Meanwhile, polymer supported phosphonium salts, macrocyclic polyethers, polar solvent residues, and poly (ethylene glycol) were also reported [3]. Compared to the traditional homogeneous PTC, this technique is more attractive due to its easy recovery of the catalyst from the reaction product mixture by filtration, potential use in flow reactors, and recycling. However, this kind of immobilized PTC does not at present enjoy indus-

trial acceptance mainly for the following reasons. Among the support matrixes, the most popular are microporous (gel) polystyrene resins, minimally (1–4%) cross-linked with divinylbenzene (DVB) or macroporous supports, highly cross-linked with more than 10% DVB [4]. The microporous resins have low specific surface areas, the polymeric chains shrink in a dry state and must swell to extend the polymeric chains before use. The resin may gelatinize in the swell agent if being reused for several times and they always show the reduced activity compared to its homogeneous analog in a two-phase system due to diffusional retardation. The macroporous resins have high specific surface areas and need not to swell before use, but they have lower activity compared to the microporous minimally cross-linked resins due to its less hydrophilic character, although spacer chains can be linked on the support to enhance their activity [5,6].

Compared to the polymer, inorganic mesoporous material is the excellent support for the heterogenization of molecular catalysts due to its excellent thermal and chemical stability. There also have some reports about silica- and alumina gel supported PTC [7–9]. But highly hydrothermally stable mesoporous material not only has all the virtues of inorganic material but also has a large specific surface area, well-defined tunable pore sizes and adjustable hydrophobic or hydrophilic character [10], which will provide great opportunities for immobilization of large catalytic species and catalytic conversion of bulky organic substrates.

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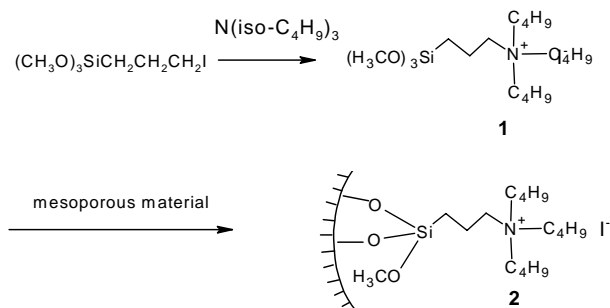
Scheme 1. Synthesis process and immobilization of alkaloid phase-transfer catalyst on the pore surface of SBA-15.

Fig. 1. TG–DSC diagram of SBA-15 supported quaternary ammonium salt catalyst.

In this paper, we prepared quaternary ammonium iodine salts phase-transfer catalyst immobilized on highly hydrothermally stable SBA-15 mesoporous material following the procedure described in Scheme 1. This kind of heterogeneous phase-transfer catalyst shows exceptionally high activity in the multiphase substitution reaction.

A highly hydrothermally stable mesoporous material SBA-15 was synthesized using P123 ($EO_{20}PO_{70}EO_{20}$) as template in acidic conditions [11]. Zeolite precursor seeds,[1] P123, hydrochloric acid, and deionized water were mixed to give a reaction mixture with a molar composition of $1Al_2O_3$:$100SiO_2$:$1.8P123$:$10TPAOH$:$10Na_2O$:$590HCl$: $17,680H_2O$. The mixture was aged at $60\,^{\circ}C$ for 24 h and afterward heated at $100\,^{\circ}C$ for 48 h. The resultant solid was filtered, extensively washed with deionized water, and then dried at $100\,^{\circ}C$. The organic template was removed from the as-synthesized product after calcination at $550\,^{\circ}C$ in air for 10 h to obtain highly hydrothermally stable mesoporous material SBA-15.

Quaternary ammonium salt **1** was readily prepared from commercially available 1-iodo-3-trimethoxysilylpropane with tri-isobutylamine in toluene solution at $70\,^{\circ}C$. Immobilization of quaternary ammonium salt **1** in the pore channels of SBA-15 was carried out through refluxing it with SBA-15 in the *N,N*-dimethylformamide (DMF) solution under nitrogen atmosphere.

The anchoring of quaternary ammonium salt **1** in SBA-15 was confirmed by using a TG–DSC–MS technique. Fig. 1 presents TG–DSC spectra for as-synthesized PTC-SBA-15 material; there is an endothermic peak at $230\,^{\circ}C$ in the DSC curve, and after this temperature a big mass loss can be found. At this temperature in TG–MS curve (Fig. 2), $N(C_4H_9)_3^+$ ($m/z = 185$) ion peak appears, indicating the decomposition of the covalently anchored quaternary ammonium salt according to Scheme 2. Above this temperature, there are several small endothermic peaks due to the decomposition of the halide; this also can be proved in the
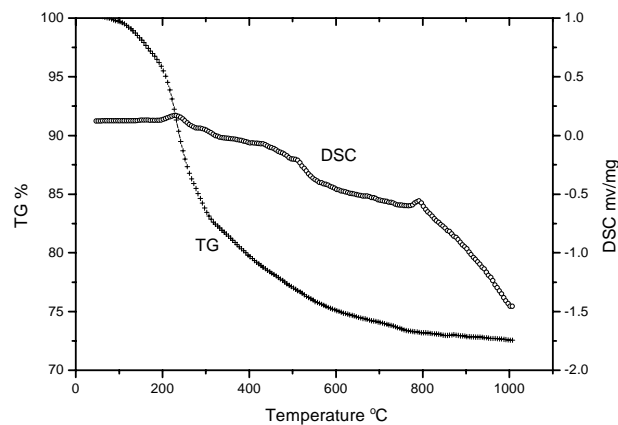
TG–MS spectra. The calculated loading content of quaternary ammonium salt **1** is about 20 wt.%, in agreement with the titration of halogen ion analysis (19.8%).

After the immobilization, the hexagonal pore structure of SBA-15 remained intact. Fig. 3 shows an HRTEM image of the sample after immobilization with the electron beam parallel to pore channels. The mesoporous channels are well ordered with a characteristic hexagonal structure as suggested by the electron diffraction pattern. As high surface area of SBA-15 material is almost totally contributed by its open pore system, the catalytic functional group prepared via this scheme should have been evenly confined in the pores.

The N_2 adsorption–desorption isotherms of these materials are shown in Fig. 4. The type IV isotherm curves with a well-defined step clearly indicate that these materials possess mesoporous structure. After immobilization, the BET surface area of SBA-15 decreased from 665 to 311 m^2/g and the average pore size decreased from 6.0 to 5.1 nm due to the loading of the quaternary ammonium salt in the mesopores. However, the pore size is still large enough to permit the diffusion of large organic molecule in it.
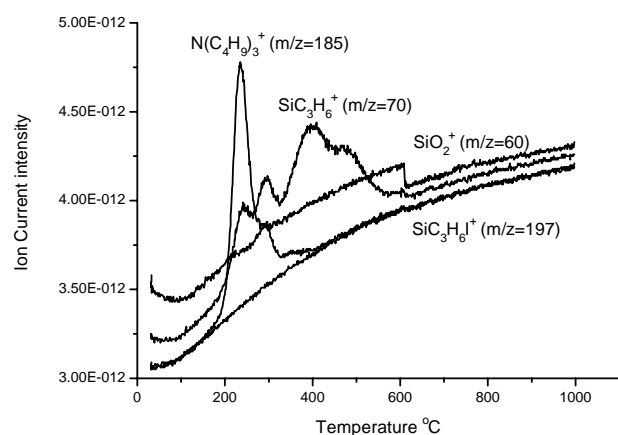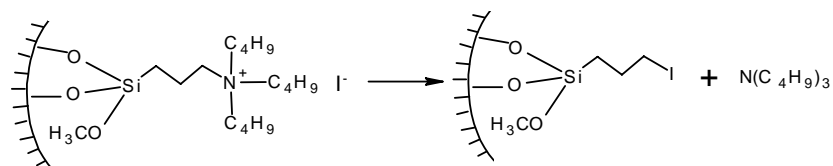

Fig. 2. TG–MS diagram of SBA-15 supported quaternary ammonium salt catalyst.

Scheme 2. Pyrolytic decomposition of the SBA-15 supported quaternary ammonium salt catalyst.
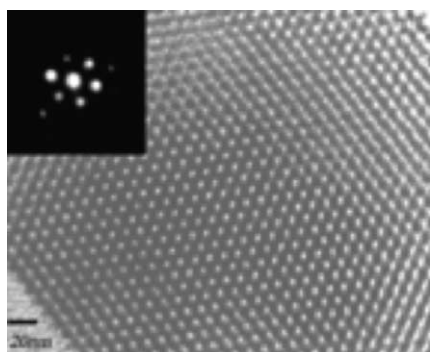

Fig. 3. HRTEM image of SBA-15 after immobilization with quaternary ammonium salt.

Scheme 3. Substitution reaction between sodium phenolate and *n*-butyl bromide.

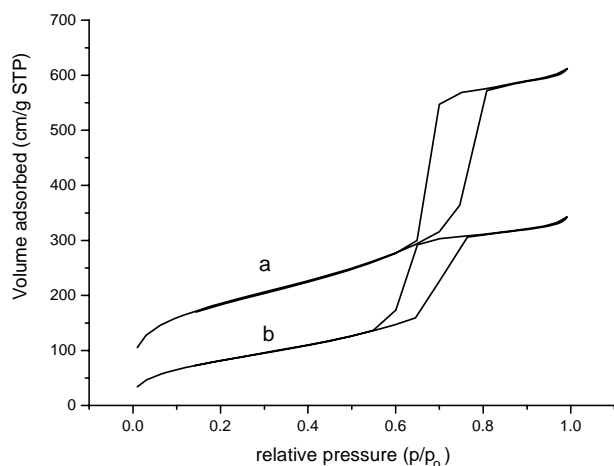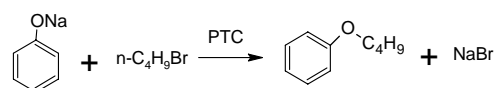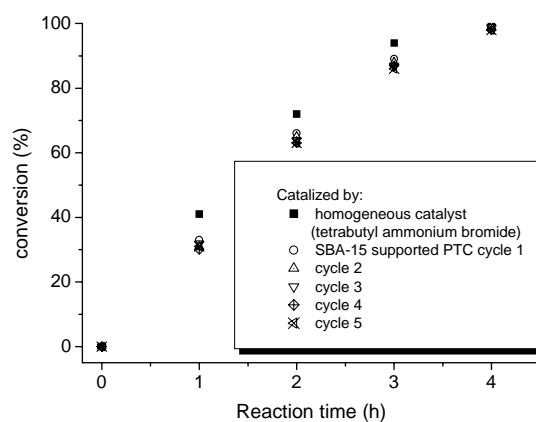Fig. 5. Effect of reaction time on the conversion of *n*-BuBr.

Fig. 4. Nitrogen adsorption–desorption isotherms of SBA-15 before (a) and after (b) immobilization with quaternary ammonium salt.

The catalytic activity of **2** was tested for the substitution reaction between sodium phenolate and *n*-butyl bromide (Scheme 3). Typical experiments were conducted by mixing 0.03 mol of *n*-butyl bromide in toluene (25 ml) and 0.03 mol of sodium phenolate in water (20 ml), and a suit-

able quantity of SBA-15 supported PTC **2** (contain 0.003 molar equiv quaternary ammonium salt) at 70 °C for 4 h. In order to test its recycling and reusing capability, after the first reaction, all the catalysts were separated by filtration and thoroughly washed, and then reused under the same conditions. The reaction process was monitored by means of a GC–MS technique.

In this reaction the phenyl butyl ether was the only organic product formed in the reaction mixture. The reaction conversion data (Fig. 5) illustrates that the immobilized catalyst has efficiently high catalytic activity just the same as the heterogeneous PTC (4 h, conversion 99%) although the initial reaction speed is somewhat slower than the homogeneous one due to the retarded diffusion of the reactants in the pore channels. It also shows that the SBA-15 immobilized PTC can be repeatedly used with only a very slight

Table 1
Phase-transfer reactions catalyzed by SBA-15 supported phase-transfer catalyst

Substrate	Reagent	Condition	Product	Time and temperature	Conversion (%)
n-C$_4$H$_9$Br	NaI	H$_2$O/toluene	*n*-C$_4$H$_9$I	4 h; 50 °C	62
CH$_3$(CH$_2$)$_7$H=CH$_2$	KMnO$_4$	H$_2$O/benzene	CH$_3$(CH$_2$)$_7$CO$_2$H	4 h; 70 °C	95
PhCH$_2$Br	PhONa	H$_2$O/toluene	PhOCH$_2$Ph	4 h; 70 °C	98

decrease after reused for several times. We believe that the open pore system with quaternary ammonium salts in pore channel remain effective when recycled.

Table 1 lists the results of the other heterogeneous phase reactions catalyzed by SBA-15 supported phase-transfer catalyst.

In conclusion, the immobilization of an ammonium salt on the pore surface of highly hydrothermally stable inorganic mesoporous material SBA-15 provided an efficient phase-transfer catalyst that could be easily recovered and recycled. Compared with the corresponding polymer supported phase-transfer catalyst, it need not swell before use and shows relative high and sustained catalytic activity. It has a potential use in industrial application.

Acknowledgements

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