



Reusable and efficient polystyrene-supported acidic ionic liquid catalyst for esterifications

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ABSTRACT

Polystyrene (PS)-supported 1-(propyl-3-sulfonate) imidazolium hydrosulfate acidic ionic liquid (PS-CH₂-[SO₃H-pim][HSO₄]) catalyst was prepared by supporting the ionic liquid onto highly cross-linked chloromethylated polystyrene (PS-CH₂Cl). FT-IR, SEM and TG-DSC were employed to characterize the structure and property of the catalyst. Results suggested that acidic ionic liquid was supported onto the surface of PS-CH₂Cl by covalent bond. The original rough surface of PS-CH₂Cl was covered with acidic ionic liquid, forming a compact and thin surface layer, and its size had no obvious change. Moreover, the PS-CH₂-[SO₃H-pim][HSO₄] catalyst showed a better thermal stability than that of PS-CH₂Cl support. It also exhibited high catalytic activity for a series of esterifications. After the catalyst was reused for 13 times in the synthesis of n-butyl acetate, the yield only decreased 7.3%. A reaction mechanism of esterification over this new catalyst was proposed as well.

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1. Introduction

Carboxylic esters as important intermediates for the synthesis of dopes, adhesives, plasticizers, flavors, and pharmaceuticals, had attracted much attention. Typically, they were synthesized by Fischer esterification of carboxylic acids and alcohols [1–4]. The popular catalysts in this esterification reaction were inorganic liquid-phase acids including hydrochloric acid and sulfuric acid [5,6]. Although these homogeneous mineral acids presented high catalytic performance in this reaction, they suffered from some problems, such as tedious purification procedure of the product, large amount of acidic wastes, and corrosion of equipments. These could cause environmental pollution and reduce the economic benefit [7–9]. Therefore, there was an urgent need to develop the environmentally friendly and highly efficient catalysts for this esterification reaction. In recent years, ionic liquids as novel catalysts had received particular interests due to their unique properties (thermal stability, negligible vapor pressure and selective solubility). Acidic ionic liquids including the Lewis and the Brønsted ones had proved to be effective catalysts in esterification [10–12]. However, their high costs and unendurable viscosities restricted their industrial applications [13,14].

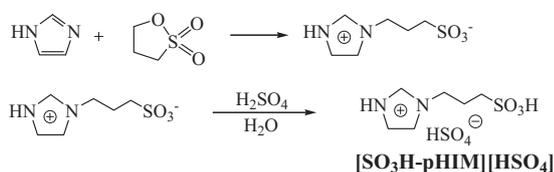
In order to solve these problems mentioned above, chloroaluminate ionic liquids had been supported onto the surface of

ZrO₂, TiO₂, Al₂O₃ and silica materials firstly [15]. Particularly, many researchers focused on the investigation of supporting ionic liquids onto the surface of silica [16–21]. The supported ionic liquid catalysts had many advantages over their unsupported counterparts, such as separation, reusability, and the ability to provide practical conveniences in a continuous system. In 2004, Kim and Chi [22] developed PS-supported ionic liquid catalysts for a series of nucleophilic substitution reactions. In 2006, this research group further [23] investigated the structural modified PS-supported ionic liquids and examined their catalytic activities in nucleophilic fluorination and other substitution reactions. Recently, PS-supported basic ionic liquid catalysts had been used for the hydrolysis of propylene carbonate [24] and the aldol-type coupling of a variety of aldehydes with ethyl diazoacetate in water [25]. Furthermore, Sun et al. [26] investigated the immobilization of ionic liquids which had both acidic and basic characteristics onto PS resin and the application in the synthesis of cyclic carbonates. All the reported PS-supported ionic liquid catalysts mentioned above could catalyze the organic reactions efficiently, and give high yield, high selectivity and good reusability.

The previous reports showed that PS-supported ionic liquid catalysts were potential candidates for catalyzing organic reactions such as CO₂ cycloaddition reaction [27,28], Henry reaction [29] and acetalization reaction [30,31]. However, there were few studies on PS-supported acidic ionic liquid catalyst for Fischer esterifications. In this paper, we focused on investigating the synthesis of PS-supported acidic ionic liquid (PS-CH₂-[SO₃H-pim][HSO₄]) catalyst and its catalytic performance for Fischer esterification. FT-IR,

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Scheme 1. Synthesis of ionic liquid.

SEM and TG–DSC were employed to characterize the structure and property of the catalyst. A reaction mechanism of esterification over this new catalyst was proposed as well.

2. Experimental

2.1. Chemical reagents

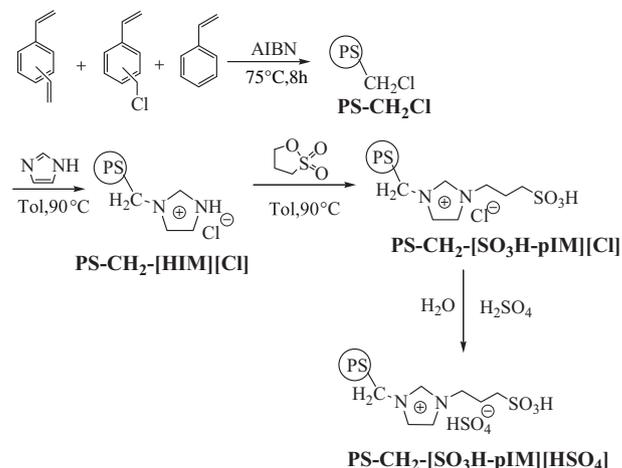
Divinylbenzene (DVB, mixture of isomers, 78–80% grade, Kehua Laboratory Instruments Sales Department, China) and styrene (St, >99%, Sinopharm Chemical Reagent Co. Ltd., China) were extracted with 5% (w/w) hydroxyl sodium solution to remove the inhibitor (*p*-hydroquinone), respectively, and then washed with deionized water until the pH was equal to 7.0. Vinyl benzyl chloride (VBC, 95%, mixture of *m*- and *p*-isomers, Changzhou Wujin Linchuan Chem. Co. Ltd., China), 2,2-azo-bis-isobutyronitrile (AIBN, Shanghai NO.4 Reagent & H.V. Chem. Co. Ltd.), polyvinyl alcohol (PVA, degree of polymerization: 1788), dichloromethane, toluene, imidazole, 1,3-propane sultone (99%) and other corresponding chemicals were commercially available and used without further purification.

2.2. Preparation of ionic liquid [SO₃H-pHIM][HSO₄]

The synthetic process of [SO₃H-pHIM][HSO₄] was shown in Scheme 1 [32]. First, imidazole was dissolved in ethanol and an equal mole of 1,3-propane sultone was slowly added. The mixture was stirred at room temperature for 24 h. After the reaction was completed, the reaction mixture was filtered to get the white precipitate which was washed with ethanol and dried under vacuum at 60 °C for 12 h. Second, the obtained white precipitate was dissolved in water and an equal mole of sulfuric acid was added slowly. Then the mixture was slowly heated to 60 °C for 12 h. After that, water was removed under vacuum at 60 °C for 12 h, resulting in [SO₃H-pHIM][HSO₄] as a viscous and colorless liquid.

2.3. Preparation of PS-CH₂Cl

The PS-CH₂Cl was synthesized by the polymerization of conventional free radical suspension according to the previous reports [33,34] and the synthetic process was shown in Scheme 2. First, 3.5 g PVA (1.0% wt), 10.5 g sodium chloride and 1.75 g AIBN (0.5 wt% of total water phase) were gradually added into the glass reactor containing 350 mL deionized water, and stirred to be a transparent solution. Second, the organic phase composed of 20 mL of the monomer mixture (volume ratio of VBC:DVB:St = 12:4:4) and 24 mL of porogen (toluene) were mixed in the beaker and regularly stirred until this organic phase became homogeneous. Third, the polymerization of conventional free radical suspension was conducted by adding the uniformed organic phase into the transparent solution mentioned above at 75 °C for 8 h under the protection of nitrogen atmosphere. Fourth, the synthesized PS-CH₂Cl was collected by means of pumping filtration and washed with hot water and methanol for three times, respectively, to remove the dispersant (PVA). Then, the product was extracted with dichloromethane for 10 h in a Soxhlet to remove the porogen (toluene) and residual monomers, and washed with ethanol for twice to ensure the



Scheme 2. Synthesis of PS-CH₂Cl and PS-CH₂-[SO₃H-pIM][HSO₄] catalyst.

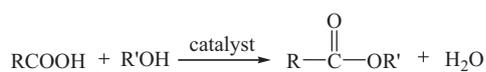
removal of other impurities. Finally, the product was dried under vacuum at 50 °C for 24 h to obtain the cross-linked PS-CH₂Cl. The cross-link degree of PS-CH₂Cl was 93.5%.

2.4. Preparation of PS-CH₂-[SO₃H-pIM][HSO₄] catalyst

The synthetic process of PS-CH₂-[SO₃H-pIM][HSO₄] catalyst was shown in Scheme 2. First, PS-CH₂Cl (10.5 g) was suspended into a 250 mL three-necked flask reactor containing 100 mL anhydrous toluene and an excess of imidazole (10.5 g). Then the mixture was reacted with stirring at 90 °C for 24 h. After the completion of the reaction, the mixture was filtered to get the solid product named as PS-supported imidazolium chloride (PS-CH₂-[HIM][Cl]). The obtained PS-CH₂-[HIM][Cl] was washed with toluene, ethanol and methanol, separately, and dried under vacuum at 50 °C for 4 h. Second, PS-CH₂-[HIM][Cl] (10.5 g) reacted with 1,3-propane sultone (10.5 g) at 90 °C for 24 h, using anhydrous toluene as a solvent. The product named as PS-supported 1-(propyl-3-sulfonate) imidazolium chloride (PS-CH₂-[SO₃H-pIM][Cl]) was repeatedly washed with toluene, ethanol and acetone, respectively, and dried under vacuum at 50 °C for 4 h. Finally, the prepared PS-CH₂-[SO₃H-pIM][Cl] (10.5 g) was directly acidified with sulfuric acid solution composed of sulfuric acid (14.0 g) and water (35.0 g) under stirring condition at 60 °C for 24 h. The target catalyst PS-CH₂-[SO₃H-pIM][HSO₄] was collected by filtration and washed with large amount of diethyl ether and ethanol, repeatedly, and dried under vacuum at 50 °C for 12 h.

2.5. Characterization

The amount of ionic liquid supported on the PS-CH₂Cl was determined by elemental analysis (Vario EL III, Elementar, Germany). The nitrogen analysis of PS-CH₂-[SO₃H-pIM][HSO₄] (N, 5.32%) indicated that its loading amount was 1.90 mmol/g. The content of chlorine of PS-CH₂Cl (12.2 wt%) was achieved by oxygen flask combustion method with AgNO₃ potentiometric titration. Fourier transform infrared (FT-IR) spectroscopy was carried out on a Thermo Nicolet 870 spectrophotometer with anhydrous KBr as standard (Nicolet, America). Thermogravimetric and differential scanning calorimetry (TG-DSC) analysis was performed using STA 449F3 (Netzsch, Germany) in a nitrogen atmosphere between 25 °C and 800 °C with a heating rate 10 °C/min. Average diameters and surface morphologies of PS-CH₂Cl and PS-CH₂-[SO₃H-pIM][HSO₄] were characterized by a scanning electron microscope (SEM) QUANTA200 (FEI, Holland).



Scheme 3. Esterifications of various acids and alcohols.

2.6. Procedure for esterification reactions

Taking the esterification of acetic acid with n-butanol as an example, the typical procedure was performed as follows (Scheme 3): acetic acid (4.80 g, 80 mmol), n-butanol (7.12 g, 96 mmol), cyclohexane (8 mL) and catalyst (0.95 g, 8% of the total mass of alcohol and acid) were added into a round-bottomed flask with a water segregator (cyclohexane as the water-carrying agent). The resulting mixture was refluxed at 92 °C for 3 h with magnetic stirring. The content of produced ester was determined by a gas chromatograph equipped with an FID detector (SP6800A, SE-54 capillary column 30 m × 0.25 mm × 0.3 μm). For other esterification reactions, the procedure was carried out accordingly.

In a recycling experiment, the catalyst was recovered by filtration and washed with acetone, and then dried under vacuum at 50 °C for 2 h. The procedure for recycling reaction was the same as described above.

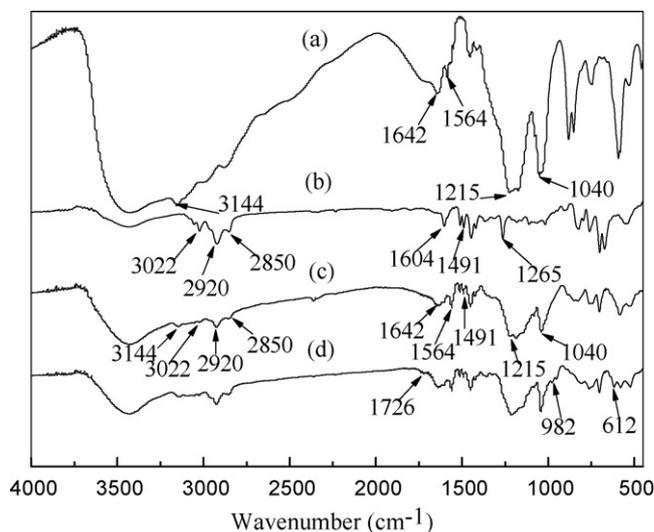


Fig. 1. Comparisons of FT-IR spectra of $[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ (a), PS- CH_2Cl (b), PS- CH_2 - $[\text{SO}_3\text{H-pIM}][\text{HSO}_4]$ catalyst (c) and PS- CH_2 - $[\text{SO}_3\text{H-pIM}][\text{HSO}_4]$ catalyst reused for 13 times (d).

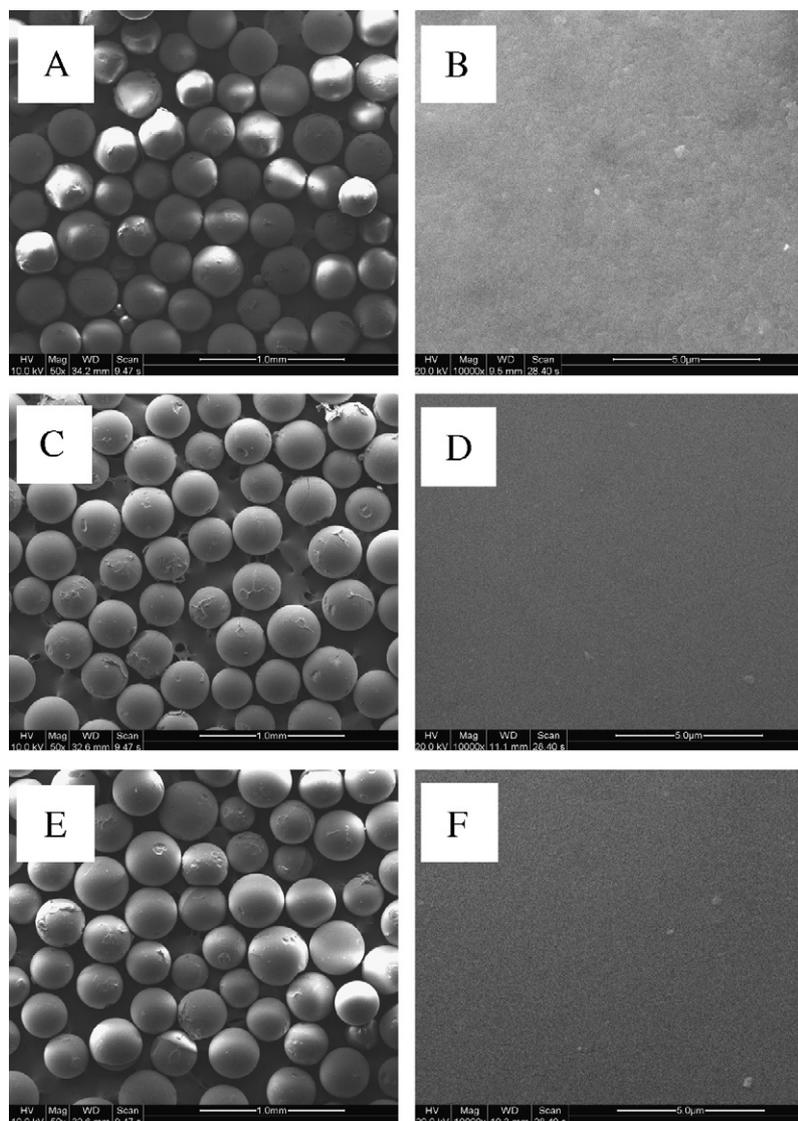


Fig. 2. The whole and magnified SEM images of PS- CH_2Cl (A and B), PS- CH_2 - $[\text{SO}_3\text{H-pIM}][\text{HSO}_4]$ catalyst (C and D) and PS- CH_2 - $[\text{SO}_3\text{H-pIM}][\text{HSO}_4]$ catalyst reused for 13 times (E and F).

3. Results and discussion

3.1. FT-IR

To confirm the immobilization of the active component $[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ on the support $\text{PS-CH}_2\text{Cl}$ and the stability of $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst, FT-IR spectroscopic studies were carried out. For $[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ (Fig. 1a), the characteristic peaks at 3144 cm^{-1} , 1642 cm^{-1} and 1564 cm^{-1} were due to the C–H, C=C, and C=N stretching vibration of imidazole ring, respectively [35,36], and the bands at 1215 cm^{-1} and 1040 cm^{-1} were assigned to the S=O asymmetric and symmetric stretching vibrations of $-\text{SO}_3\text{H}$ group. For $\text{PS-CH}_2\text{Cl}$ (Fig. 1b), the characteristic peaks of polystyrene exhibited the C–H stretching vibration of aromatic ring at 3022 cm^{-1} , and C–H asymmetric and symmetric stretching vibrations of methylene at 2920 cm^{-1} and 2850 cm^{-1} . The peaks at 1604 cm^{-1} and 1491 cm^{-1} were due to the C–C skeleton vibration of aromatic ring of polystyrene [37]. These above-mentioned peaks were also observed in $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst (Fig. 1c). Comparatively, a typical peak at 1265 cm^{-1} for stretching frequency of the functional group $-\text{CH}_2\text{Cl}$ disappeared in the spectrum of $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst (Fig. 1c). This observation suggested that $[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ had been supported on $\text{PS-CH}_2\text{Cl}$ surface through covalent bond. In addition, compared with the fresh $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst, these above characteristic bands also appeared in the reused $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst (Fig. 1d). This indicated that $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst was very stable. However, three new peaks appeared at 1726 cm^{-1} , 982 cm^{-1} and 612 cm^{-1} , which were attributed to the C=O, C–O stretching vibrations, and the C=O wagging vibration of n-butyl acetate, respectively. This phenomenon may be caused a little n-butyl acetate adhered on the surface of catalyst during the recycling experiments.

3.2. SEM

SEM was performed to characterize the morphology of $\text{PS-CH}_2\text{Cl}$, $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst and $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst reused for 13 times as shown in Fig. 2. It was seen that uniform $\text{PS-CH}_2\text{Cl}$ was in the size of $250\text{--}300\text{ }\mu\text{m}$ (Fig. 2A). After the introduction of $[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$, the size of $\text{PS-CH}_2\text{Cl}$ had no obvious change (Fig. 2C). At high magnifications, the surface of $\text{PS-CH}_2\text{Cl}$ (Fig. 2B) was rough, whereas the surface of $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst (Fig. 2D) was much plain. This finding demonstrated that the surface of $\text{PS-CH}_2\text{Cl}$ was bonded with $[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ ionic liquid, forming a compact and thin surface layer. Moreover, in comparison with fresh $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst (Fig. 2C, 2D), the size of reused catalyst (Fig. 2E, 2F) had a little change and the surface was rough slightly. This indicated that there was little ionic liquid falling off the surface of $\text{PS-CH}_2\text{Cl}$.

3.3. TG-DSC

TG-DSC analysis was carried out to investigate the thermal stability of $\text{PS-CH}_2\text{Cl}$ and $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst, as shown in Fig. 3.

Comparatively, in the range of $25\text{--}200\text{ }^\circ\text{C}$, there was more weight loss over $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst (Fig. 3b) than that over $\text{PS-CH}_2\text{Cl}$ (Fig. 3a). The weight loss was mainly ascribed to the physical adsorbed water. The hydrophilic structure of ionic liquid $[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ facilitated its adsorption of more water. Another aspect, some residual imidazole might be adhered to the surface of $\text{PS-CH}_2\text{Cl}$ by electrostatic adsorption. These two reasons could cause the difference in the weight loss. Correspondingly, for $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst (Fig. 3b'), a

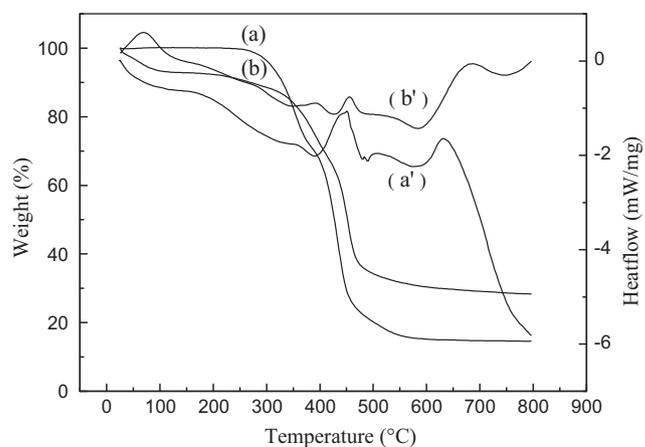


Fig. 3. TG-DSC patterns of $\text{PS-CH}_2\text{Cl}$ (a, a') and $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst (b, b').

small obvious exothermic peak appeared around $50\text{ }^\circ\text{C}$. However, it disappeared in the DSC curve of $\text{PS-CH}_2\text{Cl}$ (Fig. 3a'). When the temperature further increased up to $300\text{ }^\circ\text{C}$ and $350\text{ }^\circ\text{C}$, weight loss obviously displayed in TG curves of both $\text{PS-CH}_2\text{Cl}$ and $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$. The reason may be that their structures were destroyed and disordered or the chloromethyl group and the ionic liquid separated from the surface of $\text{PS-CH}_2\text{Cl}$. Correspondingly, sharp exothermic peaks at $440\text{ }^\circ\text{C}$ and $450\text{ }^\circ\text{C}$ appeared, respectively. Finally, it was observed that the residue weight of $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ and $\text{PS-CH}_2\text{Cl}$ was about 35% and 22% at $460\text{ }^\circ\text{C}$, respectively. These observations indicated that the immobilization of ionic liquid onto the $\text{PS-CH}_2\text{Cl}$ surface could improve the thermal stability of $\text{PS-CH}_2\text{Cl}$.

3.4. Catalytic activity of $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst for esterifications

To evaluate the $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst described here, the catalytic activities of various catalysts for the esterification reaction of n-butyl alcohol and acetic acid were examined under the same reaction conditions (Table 1).

Obviously, the yields of n-butyl acetate over $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ (Table 1, sample 4) and acidic ionic liquid (Table 1, sample 3) were much higher than that over the support (Table 1, sample 2) and no catalyst (Table 1, sample 1). This meant that the reaction hardly carried out without catalyst and the support almost had no influence on the yield. The pure ionic liquid was considered as the active component and the $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst had obvious catalytic activity. The TON of $[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ (Table 1, sample 3) and $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ (Table 1, sample 4) were almost the same. However, the heterogeneous catalyst facilitated the separation of the product.

Table 1

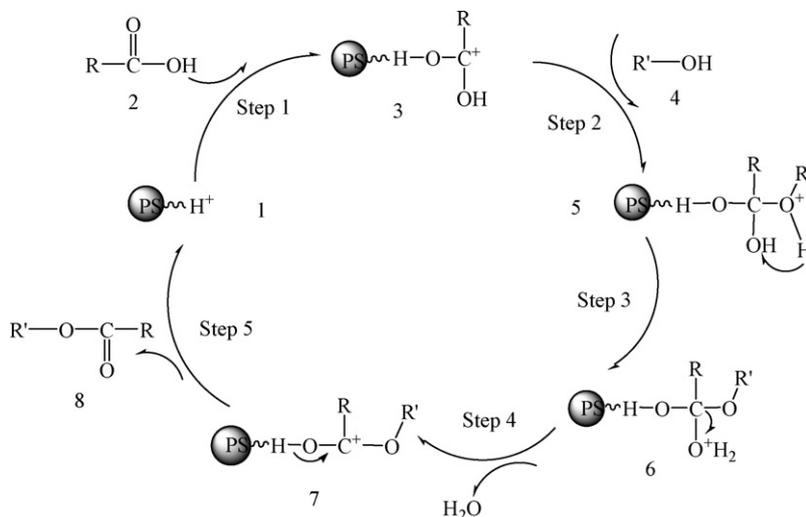
Activities of various catalysts for the esterification of n-butyl alcohol and acetic acid^a.

Samples	Catalysts	Active sites (mmol)	Yields (%)	TON ^b
1	Blank	0	22.6	–
2	$\text{PS-CH}_2\text{Cl}$ ^c	0	35.8	–
3	$[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$	0.0018	98.2	43.4
4	$\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$	0.0018	99.1	43.8

^a Reaction conditions: $n_{\text{n-butyl alcohol}}:n_{\text{acetic acid}} = 1.2:1$, (wt)% catalyst = 8%, cyclohexane (8 mL), $92\text{ }^\circ\text{C}$, 3 h.

^b Turnover number as mole of product/mole of acidic ionic liquid in catalyst.

^c Prepared via $\text{PS-CH}_2\text{Cl}$ acidified with the same concentration of sulfuric acid solution in the preparation of $\text{PS-CH}_2\text{-}[\text{SO}_3\text{H-pHIM}][\text{HSO}_4]$ catalyst.



Scheme 4. Mechanism of esterification catalyzed over PS-CH₂-[SO₃H-pIM][HSO₄] catalyst.

In order to further investigate the application of PS-CH₂-[SO₃H-pIM][HSO₄] catalyst for various systems of esterification, different systems were carried out and the results were displayed in Table 2. It was concluded that yields of various esters were all higher than 86.8%, even up to 99.4%. It indicated that the PS-CH₂-[SO₃H-pIM][HSO₄] catalyst possessed good catalytic activity for a series of esterification reactions of different alcohols and acids.

3.5. Recycling experiments

The reusability of PS-CH₂-[SO₃H-pIM][HSO₄] catalyst was evaluated in the esterification reaction of n-butyl alcohol and acetic acid. As shown in Fig. 4, the reused PS-CH₂-[SO₃H-pIM][HSO₄] catalyst still showed high activity for the yield of n-butyl acetate, and only decreased 7.3% after reusing for 13 times. As indicated by the FT-IR and SEM characterizations, the size and surface of reused catalyst changed slightly. Moreover, FT-IR analysis showed that there was a little n-butyl acetate adhering on the surface of reused catalyst, which might cover the active site of the catalyst. The slight decrease of catalytic activity in the recycles may be caused by this reason. All these results indicated that PS-CH₂-[SO₃H-pIM][HSO₄] catalyst was efficient and reusable.

3.6. Mechanism of esterification

It was well known that the classical esterification mechanism usually had two key steps, one was the protonation of acid, and the other was the nucleophilic attack of the protonated acid by the alcohol [38–40]. In the present work, the catalytic mechanism of esterification over PS-CH₂-[SO₃H-pIM][HSO₄] catalyst was consis-

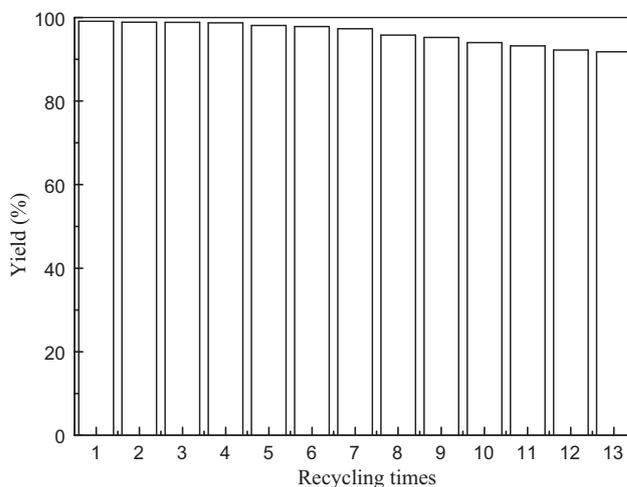


Fig. 4. Recycling of PS-CH₂-[SO₃H-pIM][HSO₄] catalyst for the synthesis of n-butyl acetate.

tent with the reported one. As displayed in Scheme 4, acid was first protonated to generate a carbocation. Then, the O atom of R'-OH made a nucleophilic attack as a result of producing the middle product 5 (as shown in Step 2). The protonated hydroxyl in product 6 had been formed when H⁺ of product 5 transferred, and then one molecule water took off the backbone of product 6. Finally, this catalyst was recovered when the bond of hydrogen and oxygen of product 7 had been broken.

4. Conclusions

The PS-supported acidic ionic liquid catalyst PS-CH₂-[SO₃H-pIM][HSO₄] was prepared and applied in the synthesis of carboxylic ester. Acidic ionic liquid was successfully supported onto the PS-CH₂Cl surface by covalent bond, and the original rough surface of PS-CH₂Cl was covered with acidic ionic liquid, forming a compact and thin surface layer, and its size had no obvious change. Moreover, the PS-CH₂-[SO₃H-pIM][HSO₄] catalyst showed a better thermal stability than that of PS-CH₂Cl, and it also exhibited high catalytic activity in a series of esterification reactions. The PS-CH₂-[SO₃H-pIM][HSO₄] catalyst could be recovered by simple filtration, and the yield only decreased 7.3% for the synthesis of n-butyl acetate after reusing for 13 times. In conclusion, the

Table 2
Catalytic activity of PS-CH₂-[SO₃H-pIM][HSO₄] catalyst for different esterifications^a.

Samples	R ^b	R' ^b	Yields (%)	Selectivity (%)
1	CH ₃	n-C ₄ H ₉	99.1	100
2	CH ₃	n-CH ₃ (CH ₂) ₅	99.3	100
3	CH ₃	i-CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)CH ₂	98.1	100
4	CH ₃	C ₆ H ₅ CH ₂	99.3	100
5	CH ₃	CH ₃ (CH ₂) ₃ OCH ₂ CH ₂	97.5	100
6	CH ₃ CH ₂	n-C ₄ H ₉	99.4	100
7	CH ₃ CH ₂	C ₆ H ₅ CH ₂	86.8	100
8	CH ₃ (CH ₂) ₂	n-C ₄ H ₉	87.9	100

^a Reaction conditions: $n_{\text{alcohol}}:n_{\text{acid}} = 1.2:1$, (wt)% catalyst = 8%, cyclohexane (8 mL), 92 °C, 3 h.

^b R and R' represented different groups in acid or alcohol shown in Scheme 3.

PS-CH₂-[SO₃H-pIM][HSO₄] catalyst prepared in this paper was an excellent recyclable catalyst for the synthesis of carboxylic esters and showed potential application in industry.

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