Short communication

# Novel fluorination of polystyrene sulfonic acid resin by CF$_3$SO$_3$H for high stability and strong acidity

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## ARTICLE INFO

## ABSTRACT

A novel fluorination method derived from CF$_3$SO$_3$H was employed to the polystyrene sulfonic acid resin, to enhance its acid strength and stability. The as-prepared CF$_3$SO$_2$-resin was characterized by FT-IR, XPS, $^{31}$P MAS NMR, and chemical titration, and its catalytic performance was tested. It was found that CF$_3$SO$_2$-resin exhibited higher selectivity to benzyltoluene in the Friedel–Crafts alkylation of toluene with benzyl alcohol, excellent catalytic activity with 96% conversion and a good recyclability over seven times in esterification of 1, 6-hexanedioic acid with 2-ethylhexanol.

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## 1. Introduction

The acid catalysts have the wide application in many reactions such as olefin hydration, biomass transformation [1,2], esterification [3] and alkylation of phenols [4]. Nevertheless, the liquid acid catalysts like H$_2$SO$_4$ are hazardous to the environment, difficult to recycle and severely corrosive to reactors [5]. Particularly, some reactions utilizing H$_2$SO$_4$ as the catalyst may release SO$_2$. Hence the replacement of mineral acids by solid acids has been intensively focused on, to develop environmentally-friendly, safe and sustainable catalysts. During the past decades, various types of solid acid catalysts have been developed such as zeolites, heteropolyacid, and sulfated metal oxides. Among these solid acid catalysts, polystyrene sulfonic acid resin (PS-SO$_3$H) turned out to give the great catalytic performance in the industry [6, 7]. Sulfonated polystyrene resin generally exhibits the high concentration of acid sites and is convenient for recycling [8]. However, PS-SO$_3$H has some disadvantages, the relatively low acid strength and the poor thermal stability which limit their potential application.

The substitution of additional electron withdrawing groups on phenyl ring has attracted many researchers' interests. Halogen has been known as a kind of efficient electron withdrawing group [9], thus the introduction of Cl onto phenyl ring of PS-SO$_3$H resin could strengthen its resistance to thermal de-sulfonation and improve acidity [10]. Siril et al. [11] had claimed that the chlorinated commercial Amberlyst 70 could keep stable up to 190 °C. Likewise, fluorinated polymers possess

a series of unique properties, including high chemical- and thermo-stability, and good barrier properties. [12]. The fluorination by F$_2$ is a common method to modify the resin for the strongest electronegativity of F, whereas the direct fluorination using F$_2$ needs harsh conditions and is easy to explode. Especially, even a trace of F$_2$ may be a threat to human [13]. Accordingly, a host of alternative fluorinating agents had been reported, such as TbF$_4$ [14], NF$_3$, KF, SF$_6$, SF$_4$, HF, CF$_4$ plasma and CoF$_3$. However, they could not meet the requirements for modern green chemistry, e.g. HF is highly corrosive and toxic [15], and SF$_6$ had been evaluated as a potential greenhouse gas (GWP = 23,900). Driven by increasingly strict environmental legislation and safety concerns, it becomes urgent to develop another new fluorinating agent.

In this paper, CF$_3$SO$_3$H is perfectly employed as fluorinating agent, based on its moderate chemical properties and less perniciousness. The prepared CF$_3$SO$_2$-resin was characterized by FT-IR, XPS techniques, to verify the fact that the CF$_3$SO$_2$ group can be successfully introduced onto the phenyl ring of sulfonic resin. It is worth noting that FT-IR was also used to optimize the fluorination conditions like temperature and concentration of CF$_3$SO$_3$H. Additionally, TG and $^{31}$P MAS NMR were performed to study the stability and acidity of CF$_3$SO$_2$-resin. Finally, CF$_3$SO$_2$-resin was performed as a solid acid catalyst for the Friedel–Crafts alkylation of toluene with benzyl alcohol and esterification of 1, 6-hexanedioic acid with 2-ethylhexanol.

## 2. Experimental

For the sample preparation, characterization and catalytic activity test see the experimental section in the Supporting Information.

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## 3. Results and discussions

X-ray photoelectron spectroscopy (XPS) technique was used for characterization of PS-Cl-CF$_3$SO$_2$-SO$_3$H, to verify the fact that parent resin (PS-Cl-SO$_3$H) was successfully fluorinated by CF$_3$SO$_3$H. The corresponding XPS spectra for the various elements are shown in Fig. S1 (Supporting Information). Clearly, the fluorinated resin showed a signal of F$_{1s}$ (b) at 687.8 eV (Insert of Fig. S1), indicating the presence of CF$_3$SO$_2$-group. The deconvolutions of C$_{1s}$ spectra for fluorinated and parent resin are shown in Fig. 1. For the parent resin (a), the high re-solved XPS spectrum of C$_{1s}$ shows at around 284.7 eV, 285.8 eV ($\alpha$) and 290.2 eV ($\beta$), associated with C–C, C–S, and C–Cl bond of PS-Cl-SO$_3$H, respectively [16,17]. Except for C–C, the new signals at around 291.2 eV ($\gamma$) and 287.2 eV ($\delta$) attributed to the C–F [18] and C–S bond can also be observed in CF$_3$SO$_2$-resin, confirming successfully graft of –SO$_2$CF$_3$ onto the network of parent resin [19]. Compared with the parent resin, the binding energy associated with the C–Cl bond ($\beta$) shifted from 290.2 eV to 289.3 eV, and the binding energy of S$_{2p}$ region shifted from 168.2 eV to 169.6 eV (Fig. S2). These are attributed to the presence of electron withdrawing group of –SO$_2$CF$_3$ in fluorinated resin [20]. Thus, this showed a successful introduction of CF$_3$SO$_2$-groups into PS-Cl-SO$_3$H [21,22]. In other words, the parent resin can be successfully fluo-rinated by CF$_3$SO$_3$H.

Herein, the concentration of CF$_3$SO$_3$H plays an important role in the preparation of PS-Cl-CF$_3$SO$_2$-SO$_3$H. Kharitonov et al. [12,23] re-ported the effect of the concentration of fluorinating agent on parent resin, and the excessive fluorination may cause the breakage of poly-mer backbone. But the low concentration of fluorinating agent may not get the ideal result. Fig. S3 shows the effect of concentration of CF$_3$SO$_3$H on acid exchange capacity. With increasing volume of CF$_3$SO$_3$H per gram resin from 2 to 4 ml g$^{-1}$, the initial acid exchange capacity of PS-Cl-CF$_3$SO$_2$-SO$_3$H reduced slightly (changing from 2.8 to 2.6 mmol g$^{-1}$). When the concentration of CF$_3$SO$_3$H was over 5 ml g$^{-1}$ the acid exchange capacity drastically dropped, which was lower than 1.5 mmol g$^{-1}$. Hence, the optimized CF$_3$SO$_3$H con-centration in the range of 2 to 4 ml g$^{-1}$ is fit for the preparation of PS-Cl-CF$_3$SO$_2$-SO$_3$H resin.

Fig. 2 shows the FT-IR spectra of fluorinated resin treated with dif-ferent concentrations of CF$_3$SO$_3$H. As shown in Fig. 2, the bands at
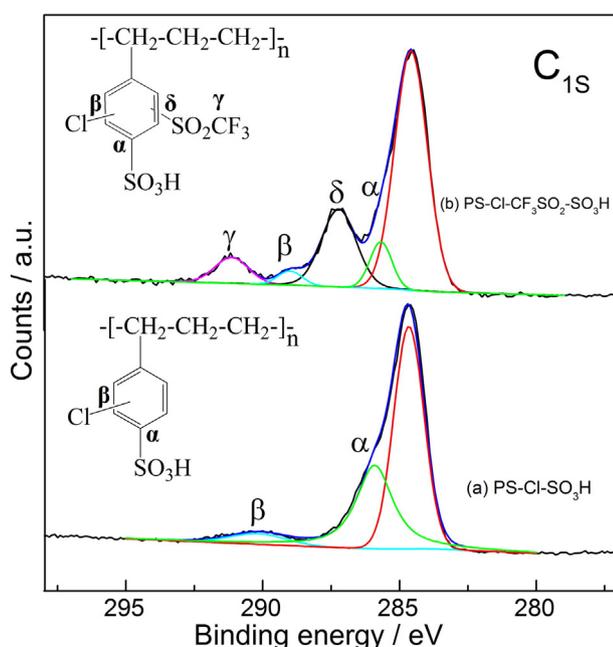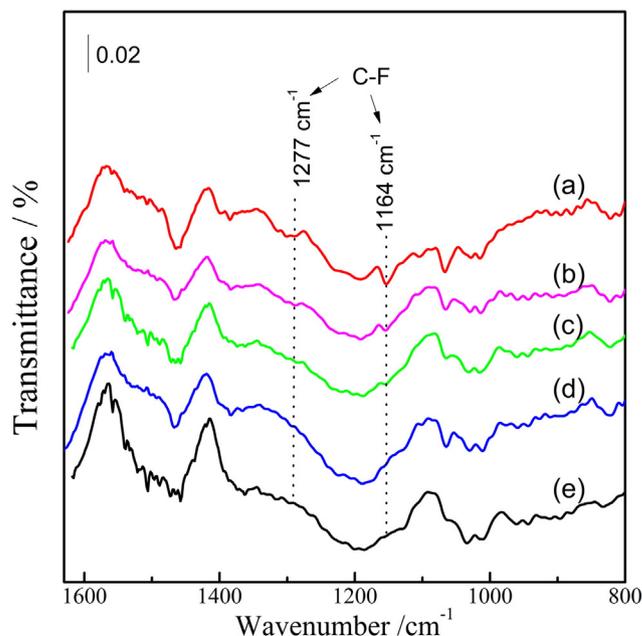
Fig. 2. FT-IR spectra of fluoridated resin modified by different concentrations of CF$_3$SO$_3$H. (a) 5 ml g$^{-1}$, (b) 4 ml g$^{-1}$, (c) 3 ml g$^{-1}$, (d) 1 ml g$^{-1}$, and (e) parent resin.

1006 cm$^{-1}$ and 1024 cm$^{-1}$ are associated with symmetric stretching vibration of –SO$_3$H [24,25]. The chlorinated resins are characterized by 1087 cm$^{-1}$ band, stretching vibration of C–Cl. Particularly, the asym-metric stretching vibration at 1277 cm$^{-1}$ and symmetric stretching vibration at 1164 cm$^{-1}$ are typical bands of CF$_2$ [26]. Due to the fact that the processed resin was washed many times, the absorbed CF$_3$SO$_3$H on it has been removed thoroughly. As for the same group, its FT-IR peak intensity is proportional to its amount, thus the higher intensity of C–F bond indicates more CF$_3$SO$_2^-$ in phenyl ring of resin. As shown in Fig. 2, the intensity of two peaks related to the C–F bond became stronger with the concentration of CF$_3$SO$_3$H added to the resin increasing when the concentration of CF$_3$SO$_3$H was over 4 ml g$^{-1}$, the peaks of the C–F bond can be observed obviously. It is generally known that the more electrons withdrawing groups resin has, the higher the acid strength is. Therefore, a relatively high concentration of CF$_3$SO$_3$H added to resin can give the resin a better performance in acid strength.

As known to all, the fluorination temperature is an important factor during the preparation of fluorinated resin [27]. Therefore, the effect of fluorination temperature on resin properties was investigated, shown in Fig. 3. The intensity of the C–F bands at 1279 cm$^{-1}$ and 1163 cm$^{-1}$ in-creased with increasing fluorination temperature. In addition, the peak assigned to the C–Cl band shifted from 1063 to 1044 cm$^{-1}$ when fluori-nation temperature reached 100 °C, which can be explained by the fact that the CF$_3$SO$_2$-group with strong electron-withdrawing results in the red shift of the C–Cl band.

$^{31}$P MAS NMR was performed to figure out the fluorinated influence on acid strength by using TEPO (triethylphosphine oxide) as probe mol-ecule. Fig. 4 shows the $^{31}$P MAS NMR spectra of fluorinated and parent resin. It is suggested that $^{31}$P chemical shift of TEPO chemisorbed on the acid site is related to acid strength [28,29]. As seen from Fig. 4, the peak at 87 p.p.m of weak acidic sites derived from the TEPO absorbed on –SO$_3$H [28], while the characteristic peak at 89 p.p.m was attributed to strong acidic sites. The single peak at 89 p.p.m was observed in the spectra of CF$_3$SO$_2$-resin (Fig. 4), and its peak intensity was stronger in comparison to the parent resin. This indicates that PS-Cl-CF$_3$SO$_2$-SO$_3$H has more strong acidic sites than the parent resin.

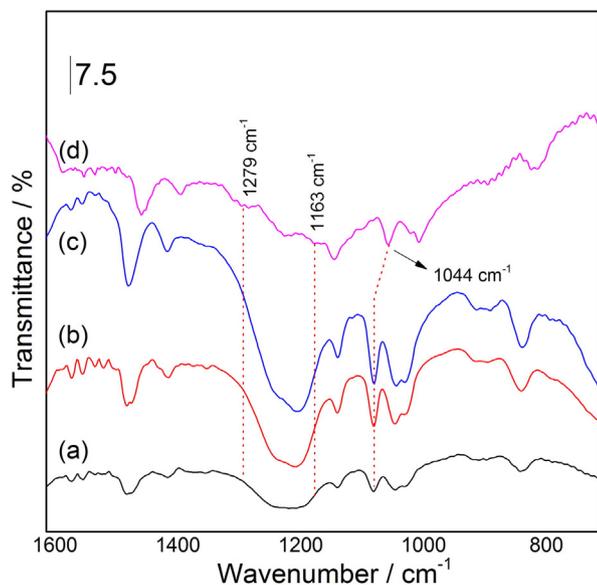Besides, it is worthwhile to note that the peak due to weak acid sites almost can't be detected in Fig. 4, indicating that PS-Cl-CF$_3$SO$_2$-SO$_3$H

Fig. 1. The C$_{1s}$ spectra of (a) resin and (b) fluorinated resin.

**Fig. 3.** FT-IR spectra of PS-Cl-CF$_3$SO$_2$-SO$_3$H with different fluorination temperatures. (a) Parent resin, (b) fluorinated at room temperature, (c) fluorinated at 50 °C, and (d) fluorinated at 100 °C.

possesses less weak acid sites. This may explain the fact about the slight drop of acid exchange capacity during the fluorination (Fig. S3). It is obvious that the treatment by CF$_3$SO$_2$H can dramatically enhance the acidic strength and make the acid dispersion more uniform in PS-Cl-CF$_3$SO$_2$-SO$_3$H, which is beneficial for promoting its catalytic activities in various reactions.

Thermal stability of fluorinated resin was characterized by TG-DTA, and the analysis results were shown in Fig. S4. The decline of TG curves shown in the temperature ranging from 100 to 150 °C is assigned to surface dehydration of resin [3,30]. Parent resin exhibited the weight loss at 226 °C while PS-Cl-CF$_3$SO$_2$-SO$_3$H at 273 °C, which is related to the decomposition of functional –SO$_3$H group [30]. As seen from Fig. S4, the weight loss temperature of acidic group of fluorinated resin (346 °C) is higher than that of parent resin (319 °C), associated with the destruction of polymeric network. The results show that the fluorinated PS-Cl-
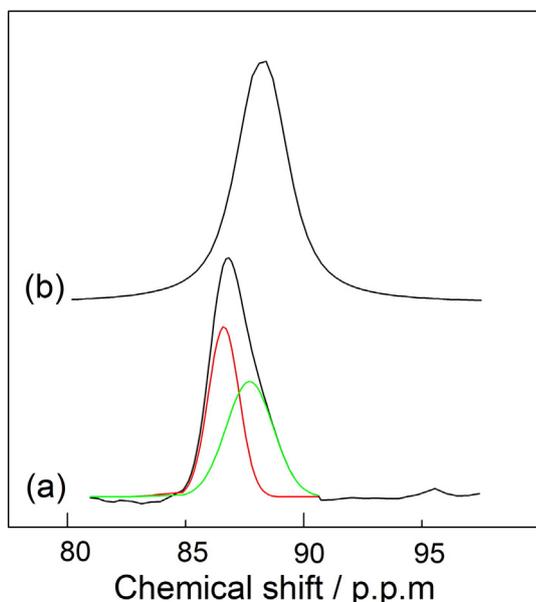


**Fig. 4.** $^{31}$P MAS NMR spectra: (a) parent resin and (b) fluorinated resin.

| Sample | Acid exchange capacity (mmol/g) | Conversion of benzyl alcohol (%) | Products distribution (%) | | Yield (%) |
| --- | --- | --- | --- | --- | --- |
| | | | Benzyltoluene | Ether & others | |
| Amberlyst 15 | 4.6 | 9.6 | 29.06 | 70.94 | 2.79 |
| Parent resin | 3.2 | 10.2 | 37.57 | 64.43 | 3.83 |
| CF$_3$SO$_2$-resin | 2.8 | 9.8 | 46.29 | 53.71 | 4.54 |

CF$_3$SO$_2$-SO$_3$H resin remarkably has a better thermal stability than parent resin, attributing to the presence of electron-withdrawing group and highly cross-linked polymeric network resin [19].

Moreover, other commercial resins fluoridated by CF$_3$SO$_3$H under the same conditions had also been studied in this work (Fig. S5). As seen in Fig. S5, the ordinary macro-porous resin and gel resin were used to prepare fluorinated resin, but the results show that there is the dramatic decline in acid exchange capacity. For macro-porous chlorinated resin, the reduction of the acid exchange capacity is comparatively less. Conclusively, the chlorinated resin as the potential candidate was investigated in detail.

The Friedel–Crafts alkylation of toluene with benzyl alcohol was used as a probe reaction for the investigation of acid strength of the fluorinated resin. It was reported by literature [31] that the reaction selectivity is related to high acid strength. Amberlyst 15, PS-Cl-SO$_3$H and PS-Cl-CF$_3$SO$_2$-SO$_3$H resin were tested in this reaction, and the results at relatively low conversion were listed in Table 1. Comparatively, PS-Cl-CF$_3$SO$_2$-SO$_3$H resin shows the highest selectivity to benzyltoluene (up to 46.29%), which is attributed to the most strong acid sites [4].

The resin was also used in another reaction with relatively high temperature in order to test its recyclability. The esterification of 1, 6-hexanedioic acid with 2-ethylhexanol to produce dioctyl adipate was employed. As seen from Fig. 5(A), all acidic catalysts could reach initially the high conversion around 98%. In comparison of the range from 2nd to 5th run, the conversion fell down only 0.1% for PS-Cl-CF$_3$SO$_2$-SO$_3$H resin catalyst, while there was an obvious decrease (decreasing by 2%) over commercial Amberlyst 15 and PS-Cl-SO$_3$H resin. Moreover, PS-Cl-CF$_3$SO$_2$-SO$_3$H resin had high activity (96%) even after seven recycles, but low conversion of 94% and 89% for PS-Cl-SO$_3$H resin and Amberlyst 15, respectively. Correspondingly, the leaching of acids was determined by measuring acid exchange capacity of resin after the seventh recycle, Amberlyst 15 experienced sharp drop from 4.6 mmol g$^{-1}$ to 1.9 mmol g$^{-1}$, and the same trend existed in PS-Cl-SO$_3$H resin, dropping off nearly 1.2 mmol g$^{-1}$, which may lead to the sudden decrease in catalytic activity. Comparatively, PS-Cl-CF$_3$SO$_2$-SO$_3$H resin exhibited relatively stable acid exchange capacity with slight drop about 0.3 mmol g$^{-1}$ even after the seventh recycle. These results suggest that the –SO$_2$CF$_3$ group could efficiently reinforce the stability of –SO$_3$H, conducive to improve its recyclability. This is because the electron withdrawing group –SO$_2$CF$_3$ can strengthen the bond between phenyl ring and –SO$_3$H, which prevent –SO$_3$H from leaching and decomposition effectively. In addition, some researchers found that after fluorinating the resin exhibits better hydrophobicity than before [19,32]. Water usually acts as a typical byproduct in many acid-catalyzed reactions, further resulting in the loss of active sites. Therefore the enhanced hydrophobicity is also beneficial to protecting –SO$_3$H.

## 4. Conclusion

In summary, a facile one-pot synthetic strategy was demonstrated to introduce the CF$_3$SO$_2$ group onto the phenyl ring of PS-Cl-SO$_3$H resin by the fluorination of CF$_3$SO$_3$H. Tested by the Friedel–Crafts alkylation of toluene with benzyl alcohol and esterification of 1, 6-hexanedioic acid with 2-ethylhexanol, the results indicated that the PS-Cl-CF$_3$SO$_2$-SO$_3$H resin shows higher activity as well as better recyclability than
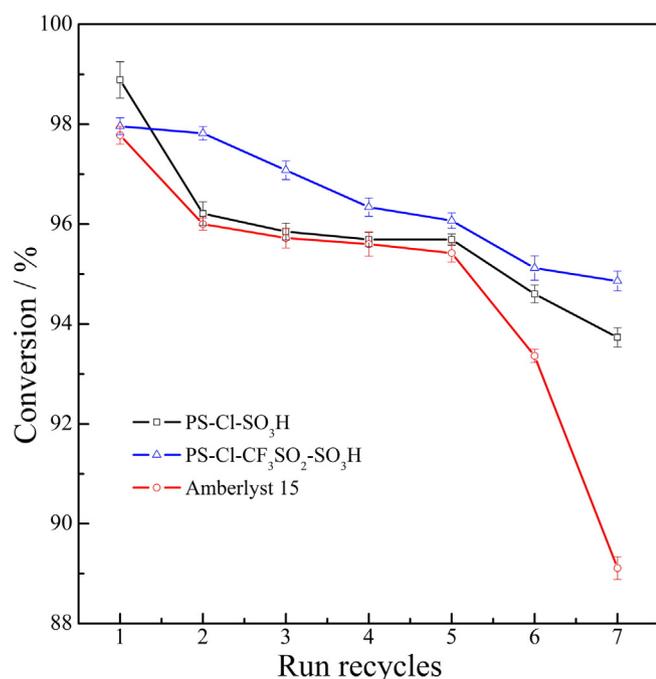
**Fig. 5.** Catalytic recycle stability of Amberlyst 15, ordinary resin and $CF_3SO_2$-resin in the esterification of 1, 6-hexanedioic acid with 2-ethylhexanol.

unfluorinated resin. Prospectively, the new fluorinated resin (PS-Cl-$CF_3SO_2$-$SO_3H$) used as an efficient solid acid will have a wide application in heterogeneous catalysis. Furthermore, a novel fluorination method using the friendly $CF_3SO_3H$ can be used for the development of new and high catalytic fluorinated resin, such as poly (2,6-dimethyl-1,4-phenylene oxide), polyaniline, and polythiophene.

## Acknowledgments

## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.07.017.

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