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Polystyrene-based superacidic solid acid catalyst: synthesis and its application in biodiesel production†

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A polystyrene-supported superacidic fluoroalkyl sulfonic acid catalyst (sPS-S) was synthesized using a combination of iridium-catalyzed C–H borylation and Suzuki–Miyaura coupling reactions. Catalytic activity of the new solid acid catalyst was examined for esterification of fatty acids and transesterification of triglyceride with methanol. Significantly higher activity than those of commercial sulfonated ion-exchange resins (Amberlyst 15 and Nafion NR50) was achieved with a catalyst loading as low as 0.5 wt%. The solid catalyst could be easily recovered by filtration and reused. Consistently high activities were obtained from the esterification for up to ten consecutive runs.

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Introduction

Acid catalysts are widely used in a variety of important organic transformations, such as Friedel–Crafts reactions of arenes, dehydration of alcohols, and esterification of carboxylic acids. Although they are commonly used in chemical industries, the use of homogeneous acid catalysts (*e.g.*, sulfuric acid or aqueous hydrochloric acid) in organic reactions requires additional steps to neutralize the remaining acid, generates waste byproducts and sometimes complicates the purification process. They are also highly corrosive, resulting in safety concern in industries.

Due to the environmental and safety issues of mineral acids, the use of solid acid catalysts in organic reactions has gained an increasing interest over the decades. Those heterogeneous catalysts are non-corrosive, easy to separate from products, and often recyclable. Thus, the development of highly efficient solid acid catalysts and their catalysis applications have been a major interest in the field of green chemistry.¹ Depending on the nature of support materials, solid acid catalysts could be categorized into inorganic solid acids and polymer-supported solid acids (also known as cation exchange resins). Inorganic solid acids (*e.g.*, silicas, zeolites, sulfated and/or mixed metal oxides) are known to have high surface areas but they have low acidity and low effective densities of acidic sites, generally requiring

high temperature to achieve good conversions.² In contrast, sulfonic acid bearing ion-exchange resins, such as sulfonated polystyrene-based Amberlyst and perfluorosulfonated resin Nafion, are more acidic and possess higher density of acid sites. Accordingly, they have been widely employed as a solid catalyst for numerous acid-catalyzed organic reactions under mild conditions.³

Recently, ever increasing consumption of fossil fuels and the effect on the global temperature has led to an urgent need to search for sustainable alternative energy sources. Biodiesel is comprised of monoalkyl esters of fatty acids and is a promising renewable bio-energy source with many advantages, such as non-toxicity, biodegradability and low emissions of gaseous pollutants. B20 which contains 20% biodiesel and 80% of petroleum diesel could be directly used in unmodified diesel engines.⁴ The main hurdle for broader use of biodiesel as an alternative “green fuel” stems from its high production cost in comparison to petroleum-based fuels.⁵ Current technology of industrial biodiesel production relies on transesterification of triglycerides with short chain alcohols in the presence of alkaline catalyst (*e.g.*, sodium hydroxide or sodium methoxide).⁶ Unfortunately, the alkaline catalyzed process requires high purity feedstocks (*i.e.*, free fatty acid (FFA) content less than 0.5%) to avoid soap formation, thereby increasing the cost of biodiesel production. Low quality feedstocks (*e.g.*, waste cooking oils and non-edible oils) have a high percentage of FFA which needs to be removed by pre-treatment with homogeneous acid catalysts (*e.g.*, sulfuric acid) and methanol and then esterified to fatty acid methyl esters.

The drawbacks of alkaline-catalyzed process have led to search for alternative approaches for biodiesel production. They include (a) acid catalysis,⁷ (b) enzymatic catalysis,⁸ and (c) catalyst-free supercritical method.⁹ Enzymes are usually expensive and sensitive, and require sophisticated process

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managements to avoid their deactivation. Supercritical method employs high temperature and pressure and requires complicated equipment systems. Acid-catalyzed process is attractive because it allows (a) both esterification of FFA and transesterification of triglycerides simultaneously, simplifying the overall process and (b) the use of low quality feedstocks that contain high levels of FFAs, making biodiesel production more economically viable. However, homogenous acid catalysis still has to overcome the aforementioned problems of corrosiveness, treatment and disposal of remaining acid. Especially, the removal of sulfuric acid from fuel is a must because of its corrosiveness and the restrictions on sulfur content in transportation fuels. These drawbacks can be overcome with the use of solid acid catalysts which have inherent advantages of convenient separation and non-corrosiveness.^{10,11}

Esterification and transesterification are equilibrium-limited chemical processes. Their reaction rates can be increased by facilitating protonations of the carbonyl oxygen and the leaving group oxygen with an acid catalyst. An acid that is stronger than 100% sulfuric acid is called superacid, of which perfluoroalkyl sulfonic acids (e.g., trifluoromethanesulfonic acid) is a well known example.¹² Superacidic solid catalysts, which possess the advantageous properties of both conventional solid acid catalysts and strong acidity, have been a target of research in both academia and industry for a long time.¹³ Unfortunately, other than Nafion only a few examples of superacidic polymer-supported solid catalysts have been reported to date. The primary reason for their scarcity is the synthetic challenge of incorporating a superacidic fluoroalkyl sulfonated moiety into a polymer substrate.¹⁴ Although Nafion has been extensively investigated as a solid superacid catalyst,¹⁵ its low content of acidic sites (0.9 mmol SO₃H per gram) and low surface area are major limitations for its practical use in organic synthesis.¹⁶

In search for such a superacidic solid catalyst, we recently reported a novel synthetic method of polystyrene functionalized with fluoroalkylated sulfonic acid.¹⁷ We chose polystyrene as a support of new solid superacids because textural properties (e.g., surface area and pore volume) of polystyrene can be easily manipulated. Although our effort to develop new polymeric superacid catalyst has not achieved such a favorable textural property yet, we herein report its effectiveness in esterification of long-chain carboxylic acids and transesterification of triglycerides with methanol, the two key reactions of biodiesel production. We also investigated recyclability of our solid acid catalyst and compared its catalytic activity with other commercial polymer-supported solid acid catalysts.

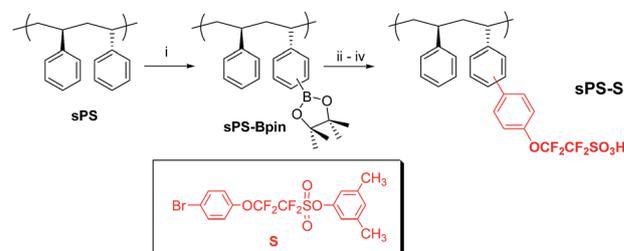
Results and discussion

Catalyst preparation and characterization

Recently, we reported a controlled functionalization of polystyrenes *via* iridium-catalyzed borylation of aromatic C–H bonds.^{17,18} Using this method, the C–H bonds of aromatic rings of polystyrene could be replaced with C–B bonds and incorporate a pinacolboronate ester (Bpin) group in a controllable manner. Because of the high stereo-regularity of aromatic rings along the backbone of syndiotactic polystyrene (sPS),¹⁹ this non-

crosslinked polymer could be recovered in much higher yields than similar amorphous atactic polystyrene when precipitated by adding poor solvent (e.g., methanol).²⁰ The high stereo-regularity of the phenyl rings also gives a well-resolved ¹H NMR spectrum, allowing convenient characterization of the functionalized polymer. Due to the above advantageous properties over atactic polystyrene, sPS was chosen as a polymer support of this study.

By adding appropriate amount of bis(pinacolato)diboron (B₂pin₂) in C–H borylation of sPS, we were able to prepare 40 mol% borylated polymer, sPS-Bpin. The borylation degree was determined by comparing the integrals of CH₃ of Bpin (at 1.16–1.19 ppm) and CH of polymer backbone (2.09 ppm) in ¹H NMR spectrum (Fig. S4†). This borylated polymer was subsequently reacted with fluoroalkylsulfonated phenyl bromide **S** using Suzuki cross-coupling reaction in the presence of Pd(PPh₃)₄ catalyst (Scheme 1, detailed synthetic procedure is given in the ESI†). The structure of the Suzuki coupling reaction product was also confirmed by ¹H NMR spectroscopy: the resonance of the methyl groups of Bpin disappeared completely and was replaced by a new resonance at 1.98 ppm which was assigned to the methyl groups of benzylic position of **S** (Fig. S1†). Comparison of relative ratio of the proton integrals from the attached **S** and CH of polymer backbone indicates 40 mol% of polymer repeating unit contains the protected fluorosulfonate group (Fig. S5†). Deprotection of the sulfonate ester group was performed using sodium hydroxide in a mixture of dioxane and water, and the resulting sodium sulfonate polymer was precipitated during the course of the reaction due to a dramatic solubility change of the polymer. The deprotected sulfonate polymer (in –SO₃Na form) is soluble in polar aprotic solvents such as *N,N*-dimethylformamide, *N*-methylpyrrolidone, dimethylsulfoxide, and *N,N*-dimethylacetamide. The ¹H NMR spectrum of the deprotected polymer showed disappearance of the methyl groups (Fig. S1†) and the difluoromethylene group adjacent to sulfonate (–CF₂SO₃–) shifted from –112.0 to –116.2 ppm in the ¹⁹F NMR spectrum (Fig. S2†). Acidification of the sodium sulfonate polymer by refluxing in 1 M H₂SO₄ solution followed by washing with water and hot methanol afforded 40 mol% sulfonic acid-functionalized polymer, sPS-S, as a dark fine powder. More detailed synthesis and characterization of



Scheme 1 Synthesis of polystyrene-based superacidic sulfonic acid catalyst. ^aReagents and conditions: (i) B₂pin₂, [IrCl(COD)]₂ (1.5 mol%), dtbpy (3 mol%), cyclooctane, 150 °C, 6 h; (ii) **S** (2 equiv.), Pd(PPh₃)₄ (4 mol%), K₃PO₄ (4.5 equiv.), THF/H₂O (10/1), 80 °C, 12 h; (iii) NaOH (8 equiv.), dioxane/H₂O, 100 °C, 4 h; and (iv) 1 M H₂SO₄.

sPS-S could be found in ESI† and in our previous publication.¹⁷ Although the sulfonated polymer (in $-\text{SO}_3\text{H}$ form) is not a chemically crosslinked, it was insoluble in organic solvents presumably due to an extensive hydrogen bonding network formation among sulfonic acid groups on the polymer side chains. Instead, it swells in certain polar solvents such as methanol. The polystyrene-supported superacid was also characterized by FT-IR (Fig. S3†) and its surface area was measured using the BET method.²¹

The properties of sPS-S are summarized in Table 1 and compared with Amberlyst 15 (ref. 22) and Nafion (NR50).²³ Although sPS-S itself is not a porous polymer, unlike Nafion NR-50, it can be easily ground into fine particles to increase surface areas. Thus, the surface area of sPS-S is $0.10 \text{ m}^2 \text{ g}^{-1}$ which is five times higher than that of NR50, but it is much lower than that of Amberlyst 15 ($45 \text{ m}^2 \text{ g}^{-1}$). The latter fact is because Amberlyst 15 is manufactured as a cross-linked macroreticular ion-exchange resin with high inner surface areas, whereas non-porous sPS was used as a starting material to prepare sPS-S.

Due to the presence of strong electron-withdrawing fluoroalkyl group, the acid group of sPS-S is more acidic than that of Amberlyst 15 (although measuring $\text{p}K_{\text{a}}$ values of solid acids is difficult, similar superacid $\text{CF}_3\text{SO}_3\text{H}$ has an estimated $\text{p}K_{\text{a}} = -14$ while $\text{C}_6\text{H}_5-\text{SO}_3\text{H}$ has an estimated $\text{p}K_{\text{a}} = -6.5$).¹² Both NR50 and sPS-S contain similar superacidic fluoroalkylated sulfonic acid side chains, but the acid content of sPS-S is almost two times higher than that of Nafion (1.67 mmol g^{-1} vs. 0.90 mmol g^{-1}).

Esterification of fatty acids

Biodiesel can be synthesized by esterification of fatty acids ($\text{C}_{12}-\text{C}_{22}$). To demonstrate our new solid acid catalyst in green organic synthesis, we decided to explore its catalytic property in esterification reaction of fatty acids. Dodecanoic acid and methanol were chosen as model reagents to optimize the esterification conditions. We first screened effect of various parameters, such as molar ratio, temperature and catalyst loading, on reaction rates to optimize the reaction conditions. Esterification scope of fatty acids with different chain lengths and catalyst recyclability were also investigated.

Molar ratio of alcohol to fatty acid. Because of the nature of equilibrium process in acid-catalyzed esterification reaction (so-called Fisher esterification), molar ratio of alcohol to carboxylic acid is an important factor and an excess of simple alcohol (*e.g.*, methanol) is generally required to achieve high conversion. Effect of molar ratio of methanol relative to dodecanoic acid on

the conversion to the ester product was investigated. As the methanol molar ratio increased from 2 : 1 to 16 : 1, the reaction rate and conversion were increased and complete conversion was achieved in 8 h (Fig. 1). However, no further increase in the product yield was obtained when 25 equivalent of methanol was used. Actually, a slight decrease in yield was observed when 25 equivalent of methanol was used. This is probably due to the dilution effect of the catalyst when more amount of methanol was employed. Therefore, 16 equivalent of methanol was chosen as optimum ratio for esterification.

Effects of temperature and catalyst loading. Effect of reaction temperature on the rate of the esterification was studied by comparing the product yields at 40, 65, and 70 °C (Fig. 2). As expected, the reaction rate was enhanced as temperature was increased from 40 to 65 °C. However, there was no significant additional enhancement as temperature was increased from 65 to 70 °C. Complete conversion to methyl dodecanoate was achieved in 8 h at 65 °C.

An obvious increase in yield was observed when catalyst loading was increased from 0.1 wt% to 0.5 wt%, and 100% yield was obtained after 8 h with a catalyst loading of 0.5 wt% (Fig. 3). Therefore, we chose 0.5 wt% catalyst loading and 65 °C for 8 h as the standard condition of the reaction.

Comparison of catalytic activity with other acid catalysts. A model esterification reaction of dodecanoic acid with methanol was examined to compare the activities of sPS-S, commercially available solid sulfonic acid catalysts (*i.e.*, Amberlyst 15 and

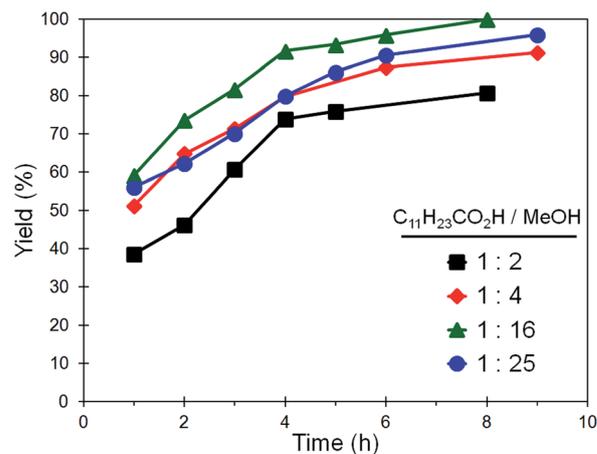


Fig. 1 Effect of molar ratio of methanol to dodecanoic acid. All reactions were performed at temperature 65 °C with 0.5 wt% catalyst loading.

Table 1 Comparison of properties of solid acid catalysts

Catalyst	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Average pore diameter (nm)	$\text{SO}_3\text{H}^{\text{a}}$ (mmol g^{-1})	$\text{p}K_{\text{a}}^{\text{b}}$	Ref.
sPS-S	0.10	8.1	1.67	-14	This work
Amberlyst 15	45	24	4.8	-6.5	22
Nafion (NR50)	0.02	Non-porous	0.9	-14	23

^a Based on titration. ^b Estimated $\text{p}K_{\text{a}}$ values from ref. 12.

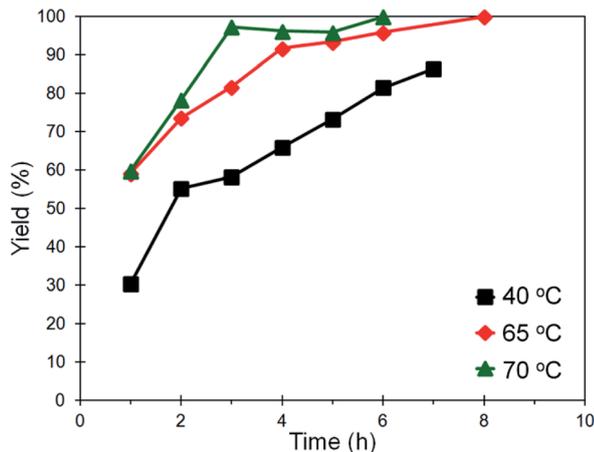


Fig. 2 Effect of temperature on the esterification reaction of dodecanoic acid and methanol. All reactions were carried out with a molar ratio of $C_{11}H_{23}CO_2H/MeOH = 1/16$ and 0.5 wt% catalyst loading.

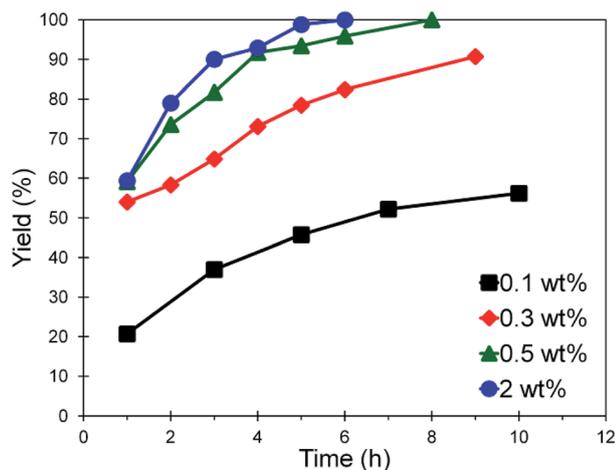


Fig. 3 Effect of sPS-S catalyst loading on the esterification reaction of dodecanoic acid and methanol. All reactions were carried out with a molar ratio of $C_{11}H_{23}CO_2H/MeOH = 1/16$.

NR50), and homogeneous sulfuric acid catalyst (Fig. 4). To validate catalytic effect on the esterification, a blank reaction was also conducted without catalyst. The esterification was found to be very slow in the absence of acid catalyst and less than 10% yield of the product was obtained after 8 h.

At the same weight-based catalyst loading level (*i.e.*, 0.5 wt%), sulfuric acid-catalyzed reaction gave 100% yield of ester product within 1 h. Considering the fact that 1 g of sPS-S contains 1.67 mmol of sulfonic acid group while the same weight of sulfuric acid contains more than 5 times of acid (10.2 mmol g^{-1}), it is not fair to compare the activities of those two catalysts under the same weight percent. For a better comparison, we thus compared catalytic activities of sPS-S and sulfuric acid under the same molar concentration (the molar percentage of acid group in 0.5 wt% of sPS-S is approximately 0.2 mol%). Under the same molar-based loading (*i.e.*, 0.2 mol%), the

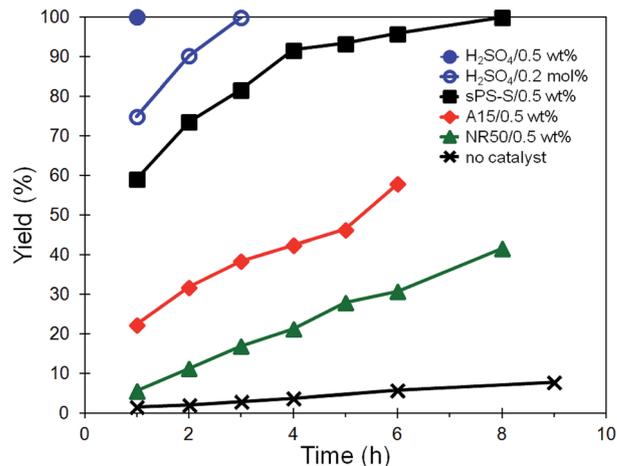


Fig. 4 Comparison of different acid catalysts. All reactions were carried out at 65 °C with a molar ratio of $C_{11}H_{23}CO_2H/MeOH = 1/16$.

reaction catalyzed by sulfuric acid still has faster rate and was completed within 3 h.

Among solid catalysts examined, sPS-S showed the highest activity. At 0.5 wt% loading level, the molar percentage of acid group in Amberlyst 15 is about 0.5 mol%, which is more than two times higher than that of sPS-S. Considering that sPS-S has lower acid concentration (1.67 mmol g^{-1}) and lower surface area ($0.10 \text{ m}^2 \text{ g}^{-1}$) than those of Amberlyst 15 (4.8 mmol g^{-1} , $45 \text{ m}^2 \text{ g}^{-1}$), the higher catalytic activity of sPS-S might be ascribed to its stronger acidity and swelling ability in methanol. The low catalytic activity of NR50 might be due to its low surface area and non-porous nature as documented in literature.^{21,23} Like other solid acids, Nafion is known to have acidic property only at its surface. Therefore, even though Nafion has the advantage of having strong acidity, it could not overcome the disadvantage of having low surface area.

Reaction scope study. To examine the scope of sPS-S catalyst, esterifications of fatty acids bearing different lengths of alkyl chain (C12, C14, C16 and C18) with methanol were examined

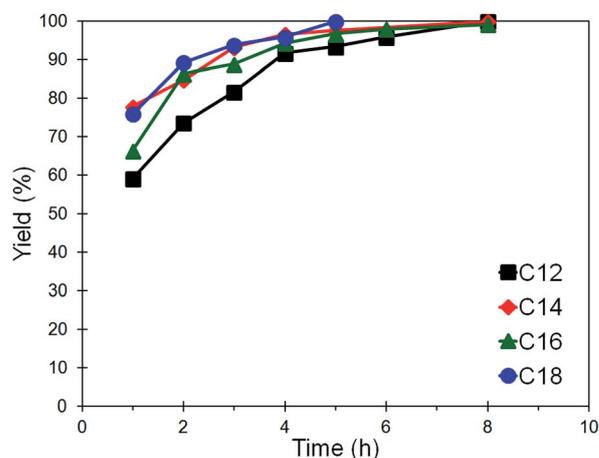


Fig. 5 Esterification of fatty acids with methanol.

(Fig. 5). For all the fatty acids examined, full conversions were achieved within 8 h. Thus, the polymeric superacid can effectively convert FFA of various chain lengths to their methyl esters, which is the key pre-treatment step to remove FFA from low-cost biodiesel feedstock.^{24,25}

Convenient work-up and recycling of catalyst. Besides environmental and safety concerns of handling and disposal of liquid acid catalyst, the advantages of convenient product separation and recyclability of the catalyst give a strong economic drive for adoption of solid acid catalyst. For example, the heterogeneous nature of solid catalyst allows a convenient work-up procedure of biodiesel synthesis. Once esterification is completed, sPS-S was recovered by simple filtration. Evaporation of volatile liquid (*i.e.*, remaining methanol) from the filtered solution gave methyl ester of FFA in high purity. Unlike homogeneous acid catalyzed esterification, no neutralization or extraction is necessary.

To examine recyclability of sPS-S catalyst, ten consecutive runs of esterification of dodecanoic acid with methanol were conducted using recovered sPS-S without any regeneration treatment. Excellent recovery yields of the solid catalyst and consistently high product yields were obtained for all ten consecutive runs (Table 2). There is no significant change in activity of the catalyst. These results clearly demonstrate excellent recyclability of sPS-S. Although the recovery yields during recycling experiments were not 100%, they were all above 95% and the slightly lower yield was ascribed to physical weight loss during filtration. We collected the solid catalyst on filter paper. Since the catalyst is hygroscopic, it tends to stick to surface of filter paper and a minor weight loss (1–5 wt% in each cycle; 1–5 mg of 100 mg sPS-S catalyst) was unavoidable. After recovering the solid catalyst by filtration, we analyzed the ester product in the filtrate with ¹H and ¹³C NMR spectroscopies after evaporation of methanol without any additional workup (Fig. S7–S14 in ESI†). If there was leaching of the solid catalyst to filtrate, it should have been detected on the NMR spectra but we did not observe any sign of leached catalyst.

Table 2 Recycling experiments of sPS-S catalyst in biodiesel synthesis^a

Cycle	Yield ^b (%)	Catalyst recovery yield ^c (%)
1	100	99
2	96	97
3	92	99
4	83	98
5	89	95
6	88	95
7	85	97
8	81	97
9	87	97
10	88	99

^a C₁₁H₂₃CO₂H (20.0 g), C₁₁H₂₃CO₂H/CH₃OH = 1/16 (molar ratio), sPS-S (0.5 wt%), 65 °C. ^b Yield based on GC-MS. ^c Mass based recovered yield (%) of sPS-S after filtered, washed with hot methanol, and dried in each run.

Transesterification of triglycerides

Compared to esterification, transesterification is known to be kinetically slower.²⁶ Therefore, a higher ratio of alcohol and a higher catalyst loading than those of acid-catalyzed esterification are needed to achieve acceptable reaction rates. To test the catalytic activity of sPS-S in biodiesel synthesis *via* transesterification of triglycerides, trilaurin was chosen to react with methanol. When the transesterification was tested with 100 equivalent of methanol and 1 wt% of the catalyst, only the starting was recovered. With 200 equivalent of methanol and 5 wt% (5 mol%) catalyst loading, 98% yield of methyl laurate was achieved in 22 h (entry 1, Table 3). In comparison, the reaction catalyzed with 5 wt% (33 mol%) of concentrated sulfuric acid was completed within 8 h (entry 2). The slower reactivity of sPS-S compared to sulfuric acid is mainly due to the limited available acidic sites in the heterogeneous catalyst and the higher molar percent of acid of the sulfuric acid under the same weight percent loading.

Experimental

Reagents

Dodecanoic acid (99.5%), tetradecanoic acid (98%), Nafion (NR50) and Amberlyst 15 were purchased from Alfa Aesar. Hexadecanoic acid and trilaurin (98%) were purchased from TCI. Octadecanoic acid (97%) was purchased from Acros. Methanol (99.8%) was purchased from VWR.

Synthetic procedures of 3,5-dimethylphenyl-2-(4-bromophenoxy)-tetrafluoroethanesulfonate ester (S) and sPS-S are given in the ESI.†

Esterification of fatty acids

Dodecanoic acid (1.55 g, 7.78 mmol), sPS-S (7.8 mg, 0.5 wt%) and methanol (5 mL, 124 mmol) were added to a 25 mL two-neck flask. The reaction mixture was heated to 65 °C with a stirring speed of 700 rpm. Reaction progress was monitored by GC-MS equipped with a 30 m × 0.25 mm SHR-XLB GC column and an EI ionization MS detector. After the reaction was completed, the reaction mixture was filtered to remove sPS-S and the filtrate was concentrated using a rotary evaporator and dried under vacuum to afford the methyl ester product.

Transesterification

Trilaurin (300 mg, 0.470 mmol), sPS-S (15 mg, 5 wt%) and methanol (3.01 g, 94.0 mmol) were added to a 25 mL two-neck

Table 3 Biodiesel synthesis by transesterifications of trilaurin with methanol^a

Alcohol	Temp. (°C)	Time (h)	Yield ^b (%)
MeOH	65	22	98
MeOH ^c	65	8	100

^a Trilaurin (300 mg, 0.47 mmol), methanol (3.01 g, 94 mmol), sPS-S (15 mg, 5 wt%). ^b GC yield calibrated with internal reference. ^c Catalyzed by 5 wt% of concentrated (96%) H₂SO₄.

flask. The reaction mixture was stirred at 65 °C with a stirring speed of 700 rpm. Samples taken at regular time interval were analyzed using a GC (conditions: injector temp. 270 °C, detector temp. 270 °C, initial temp. 150 °C, hold 1 min, then heated at 20 °C min⁻¹, final temp. 300 °C).

Recycling experiment of sPS-S catalyst in Table 2

Dodecanoic acid (20.0 g, 100 mmol), sPS-S (0.1 g, 0.5 wt%) and methanol (65 mL, 16 equiv.) were added to a 250 mL two-neck flask. The reaction mixture was stirred at 65 °C with a stirring speed of 700 rpm and reaction progress was monitored using GC-MS. After filtration, the filtered solid catalyst was washed with hot methanol (60 mL) and dried at 75 °C under vacuum for 12 h. The weight of recovered solid catalyst was measured and the percentage of recovered yield in each cycle is included in Table 2. The recovered catalyst was directly used for the next reaction cycle without any further treatment.

Conclusions

In summary, we have developed a polystyrene-supported fluoroalkyl sulfonic acid catalyst *via* C–H borylation and Suzuki coupling reactions. This new superacidic solid catalyst showed high catalytic activity in esterification of fatty acids and transesterification of triglycerides, which are the key synthetic processes of biodiesel production. Despite a lower sulfonic acid content and a lower surface area, the superacidic sPS-S catalyst showed a significantly higher activity than that of Amberlyst 15. sPS-S catalyst also showed excellent recyclability with quantitative recovery yields and maintained high activity even after ten cycles of consecutive runs. Development of highly porous resins containing this type of superacidic group is now undergoing in our laboratory and will be reported elsewhere in due course.

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