

Superacidic porous polymer catalyst and its application in esterification of carboxylic acid

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Received: 27 October 2016 / Accepted: 8 November 2016
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Abstract Two solid acid catalysts, SAC1 and SAC2, with porous structure obtained from mesoporous hard template were synthesized and characterized by Fourier transform infrared spectroscopy, acid-base titration, nitrogen adsorption/desorption, scanning electron microscopy, and their catalytic activity in esterification of carboxylic acid. Acid-base titration showed that these catalysts have acidic concentration of 1.02–1.10 mmol/g. The catalytic test in esterification of 6-bromohexanoic acid with methanol showed that SAC1 with perfluorinated sulfonic acid is catalytically more active than SAC2 with aryl sulfonic acid. In spite of lower acid loading, SAC1 showed a comparable catalytic activity with commercially available solid acid catalyst Amberlyst 15 with higher acid capacity (4.80 mmol/g) due to high acidity and well-defined pore structure. SAC1 could be recycled up to three times without significant loss in activity.

Keywords Superacid · Solid acid catalyst · Esterification · Mesoporous polymer

Introduction

Solid acid catalysts for organic synthesis have received a significant attention over the past decades because of their advantages in environment friendliness and safety compared to

corrosive liquid acids [1]. When a solid acid catalyst is used in organic reactions, it increases general safety compared to its homogeneous counterparts. It can be easily separated from the reaction mixture by filtration, thus allowing rapid recovery of the catalyst while generating less waste. Thus, reusability and recyclability of solid catalyst significantly contribute to sustainable chemical process and green chemistry [2].

Cross-linked polystyrene is one of the most commonly used insoluble supports for catalysts in chemical reactions. These polymers are widely used because of their low cost, readily availability of monomers, good mechanical robustness, inertness, and rigidity [3]. Depending on their preparation methods, a number of factors may affect the polymers' physical properties including internal structure, surface morphology, and accessibility of catalytic functional sites [4]. For polymers prepared using a high level of cross-linkers, the inner pores are permanently porous and are hardly affected by changes in environment such as solvent. While diffusion problems may arise in heterogeneous catalysis compared to homogeneous catalysis based on solution phase, such restriction in accessing active sites of solid phase can be mitigated by creating interconnected mesopores [5, 6]. The interior of permanent mesoporous polymers would be easily accessible by reactants regardless of the solvent used in the reaction, expanding the possible uses of such materials.

Solid acid catalysts are generally prepared by attachment of an acidic moiety to a solid support via surface modification. There are numerous examples of sulfonic acid-functionalized cross-linked porous polystyrenes ($-\text{SO}_3\text{H}$, $\text{pK}_a = -2$), and among them, commercially available Amberlyst® is the most widely used example of solid acid catalyst [7]. Unlike aryl sulfonic acid group, which can be easily attached by electrophilic aromatic substitution using a sulfonating reagent, only a few examples are available for polymer functionalization with perfluoroalkylsulfonic acid

Electronic supplementary material The online version of this article (doi:10.1007/s11224-016-0879-6) contains supplementary material, which is available to authorized users.

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group [8, 9], Perfluoroalkylsulfonic acid ($-\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$), where CF_2 groups strongly withdraw electrons from the sulfonic acid, has a significantly higher acidity (so-called superacid) than aryl sulfonic acid that is found in Amberlyst®: a superacid refers to highly acidic system that is more acidic than 100% sulfuric acid ($H_0 = -12$) [10]. Although it is known to induce excellent catalytic activity in organic reactions due to the increased acid strength, incorporation of a superacidic group into porous polymer system is quite challenging. Commercially available perfluorinated sulfonic acid resins, such as Nafion NR50, typically have a lower ion exchange capacity (IEC) and a smaller surface area compared to porous polystyrene counterparts (e.g., Amberlyst®), which limits the utility of the solid acid in catalysis [1].

To introduce perfluorosulfonate superacid group to porous cross-linked polymer and use as a solid acid catalyst, a versatile surface functionalization method is required. Incorporation of boronic acid or boronate group into aromatic rings of polymers and subsequent metal-catalyzed Suzuki-Miyaura coupling reactions can be an effective approach to prepare various functional aromatic polymers [11, 12]. The Suzuki-Miyaura reaction is well known for its advantages of mild conditions, high conversion, and good functional group tolerance [13]. Herein, we report highly efficient synthetic approach for functionalization of cross-linked porous polystyrene with interconnected pore structures to prepare a new class of superacid solid acid catalysts. Two solid acid catalysts, SAC1 and SAC2, were prepared via functionalization of borylated precursor polymer with different sulfonic acid groups that have differences in acid strength. Physical properties of the solid acid catalysts including chemical structure, acid loading, and pore properties were characterized, and their catalytic activity in esterification was evaluated and compared with commercially available solid acid catalysts.

Experimental details

Materials

Unless otherwise noted, all reagents and solvents were purchased from Sigma-Aldrich, Alfa Aesar, Strem Chemicals Inc., and Acros Organics and were used without further purification. Mesostructured silica was obtained from Sigma-Aldrich and dried at 150 °C for 12 h under vacuum prior to use. 3,5-Dimethylphenyl 2-(4-bromophenoxy)tetrafluoroethanesulfonate ester (S_1) and 3,5-dimethylphenyl 4-bromobenzenesulfonate ester (S_2) were prepared using the reported procedures [11]. Aliquat® 336 is a registered trademark of the BASF Corp.

Catalyst preparation

1. Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styrene

Vinylphenylboronic acid was prepared according to the procedure in literature [14]. A solution of 4-vinylphenylmagnesium chloride (prepared from 0.414 g of magnesium powder and 2.00 g (14.4 mmol) of 4-chlorostyrene) in 20 mL of anhydrous THF was added dropwise to a solution of trimethyl borate (2.54 g, 24.5 mmol) in 40 mL of anhydrous THF at -45 °C. Upon addition, the mixture was slowly warmed to room temperature over 3 h and then quenched with 50 mL of 3 M HCl with stirring. The organic layer was set aside, and the aqueous layer was extracted with diethyl ether (2×20 mL). The combined organic phases were evaporated until dried and 40 mL of water was added. The reaction mixture was heated until it boils and decanted. The residual solid was treated with an additional 40 mL of water, heated until it boils, and decanted again. The supernatants were combined and allowed to cool to room temperature, then stored at 2 °C for 5 h. The mixture was filtered, and the filtered white solid was washed with water and dried under vacuum overnight to give 4-vinylphenylboronic acid (1.10 g, 52%): ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.03 (br s, 2H), 7.76 (d, 2H, $J = 8.2$ Hz), 7.42 (d, 2H, $J = 8.2$ Hz), 6.72 (dd, 1H, $J = 17.6, 11.1$ Hz), 5.87 (d, 1H, $J = 17.6$ Hz), 5.28 (d, 1H, $J = 11.1$ Hz).

Pinacol (3.10 g, 26.2 mmol) and MgSO_4 (1.0 g) were added to a solution of 4-vinylphenylboronic acid (3.50 g, 23.6 mmol) in 60 mL of dichloromethane at room temperature. The mixture was gently stirred for 1 h at room temperature, and MgSO_4 was removed by filtration and washed with dichloromethane. The filtrate was concentrated on a rotary evaporator and the crude product was purified with flash chromatography by eluting hexane:ethyl acetate (4:1) to give colorless oil (5.23 g, 96%): ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.65 (d, 2H, $J = 8.7$ Hz), 7.47 (d, 2H, $J = 8.7$ Hz), 6.72–6.78 (dd, 1H, $J = 18.1, 12.7$ Hz), 5.90 (d, 1H, $J = 18.1$ Hz), 5.32 (d, 1H, $J = 12.7$ Hz), 1.28 (s, 12H).

2. Silylation of mesoporous silica

The porous silica template was silylated using a procedure similar to literature [15]. To a solution of the porous silica template (2.5 g) suspended in toluene (125 mL), triethylamine (2.24 mL, 16.0 mmol) and chlorotrimethylsilane (1.02 mL, 8.0 mmol) were added with stirring. The reaction mixture was refluxed for 3 h, and the solid was filtered and washed thoroughly with toluene, methanol, and acetone and dried under vacuum. The resulting silylated silica template was obtained as a white powder (2.41 g).

3. Synthesis of porous borylated precursor polymer (PS-BA)

The monomers were infiltrated and polymerized using a procedure similar to literature [16]. A solution of divinylbenzene (6.9 mmol, 0.90 mL), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styrene (2.96 mmol, 0.68 g), 2,2'-azobis(2-methylpropionitrile) (AIBN) (3.0 mmol, 48.6 mg), and 1.0 mL of dichloromethane was added to a 50-mL Schlenk flask containing 1.15 g of the silylated silica template, and the reaction mixture was subjected to vacuum freeze-thaw cycles three times. The mixture was heated to 60 °C for 12 h and 80 °C for 12 h. After cooling to room temperature, it was washed extensively with dichloromethane followed by methanol. The resulting powder was filtered and dried under vacuum. The silica template and pinacol were removed by treatment with a mixture of 5 M NaOH and ethanol (1:1) at 60 °C for 12 h. The obtained off-white powder was filtered and dried at 60 °C under vacuum to give PS-BA (1.03 g). FT-IR (cm⁻¹, KBr) 3450 (O–H), 2930 (alkyl C–H), 1600 and 1410 (aromatic C = C), 1362 (B–O). Elemental analysis: C 78.01%, H 7.52%, and B 1.9% (1.73 mmol/g of Boron).

4. General procedure of functionalization of porous polymers

In a nitrogen-filled glove box, porous PS-BA (514 mg, 0.87 mmol –B(OH)₂), Pd(OAc)₂ (9.9 mg, 5 mol%), triphenylphosphine (23 mg, 2 equiv. relative to Pd), anhydrous toluene (10.4 mL), and a stirring bar were added to a glass vial. Sulfonated aryl bromide (S₁ or S₂, 2.62 mmol, 3 equiv.) and tetramethylammonium hydroxide (4.35 mmol, 5 equiv.) as a base, and a drop of Aliquat® 336 were added by a syringe under nitrogen atmosphere. After stirring at 90 °C for 14 h, the reaction was filtered to recover light brown colored powder, which was repeatedly washed with tetrahydrofuran, water, 0.5 M HCl and tetrahydrofuran and dried under vacuum.

5. Deprotection and acidification of sulfonic acid on the porous polymers

The 3,5-dimethylphenol protecting group of above S₁- and S₂-functionalized porous polymers was removed by treatment with a mixture of dioxane and aqueous NaOH at 80 °C for 4 h followed by at 100 °C for 4 h. After cooling to room temperature, the polymer was filtered and washed thoroughly with water until the filtrate becomes neutral and was dried under vacuum at 80 °C for 12 h. Sodium sulfonate form of the polymer was acidified by treatment with 1 M H₂SO₄ for 48 h at room temperature while the solution was replaced every 12 h. Acidified powder (in –SO₃H form) was washed with deionized water to remove any remaining acid and dried under vacuum.

6. Characterization

¹H NMR spectra were collected with a Varian Unity 500 MHz spectrometer at room temperature, and chemical shifts were referenced to the solvent residue peaks of DMSO-*d*₆ (at 2.50 ppm). FT-IR spectra of powder samples were recorded on a Thermo Scientific Nicolet 4700 FT-IR using KBr pellet method. TGA was recorded using a TA Q50 instrument operated under nitrogen atmosphere with a heating rate of 10 °C/min. N₂ physisorption analyses were performed on a Quantachrome Autosorb iQ2 instrument at 77 K to determine the pore properties. Prior to the measurement, samples were outgassed by heating at 100 °C under vacuum for 12 h. Surface area was calculated by Brunauer–Emmett–Teller (BET) method, and pore size and pore volume were calculated by DFT function. SEM analyses were carried out with a field emission SEM (JEOL JSM-6330F), and samples were platinum-sputtered prior to analyses. GC/MS analysis was conducted using a Shimadzu QP2010S equipped with a 30 m × 0.25 mm SHR-XLB GC column and an EI ionization MS detector.

7. Determination of sulfonic acid amount by titration

The loading capacity of sulfonate group (in mmol/g) was determined using an acid-base titration method. Sulfonated porous solid catalyst was gently stirred in 1 M NaCl solution at room temperature for 48 h before titration. The protons released into the aqueous solution were titrated with 0.025 M NaOH solution using phenolphthalein as an indicator. The experimental amount of sulfonate group of functionalized polymers was calculated using the equation below:

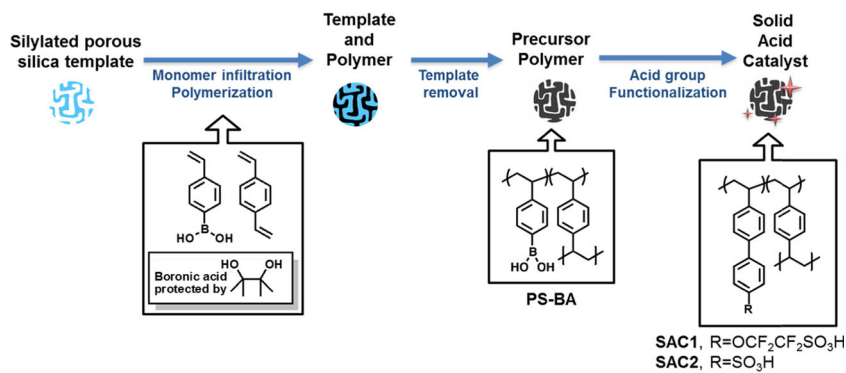
$$\text{Ion exchange capacity (–SO}_3\text{H amount in mmol/g)} \\ = M_{\text{NaOH}} \times V_{\text{NaOH}} / W_{\text{dry}}$$

where M_{NaOH} and V_{NaOH} are molar concentration and volume (mL) of the aqueous NaOH solution used in titration, W_{dry} (g) is the weight of dried polymer.

8. Catalytic activity tests

Catalytic activity of solid acid catalysts was evaluated by performing esterification of 6-bromohexanoic acid (1.0 g, 5.1 mmol) and methanol (10 mL, 0.25 mol) with 0.5 wt% of solid catalyst in a 25-mL two-neck flask. The reaction was conducted at either 45 or 65 °C, and reaction progress was monitored by GC/MS. After the reaction was completed, the reaction mixture was filtered to remove solid catalyst and the filtrate was concentrated using a rotary evaporator and dried under vacuum to afford methyl 6-bromohexanoate product. ¹H NMR (500 MHz, CDCl₃) δ 3.67 (s, 3H), 3.39–3.42 (d,

Fig. 1 Synthetic route of porous solid acid catalysts



2H), 2.32–2.34 (d, 2H), 1.86–1.90 (m, 2H), 1.65–1.67 (m, 2H), 1.46–1.49 (m, 2H). GC-MS: 211, 209 (M^+), 177, 129, 97, 87, 74.

Recycling experiment was performed using filtered SAC1 from the esterification reaction. Filtered solid catalyst was washed thoroughly with methanol and dried under vacuum. Recovered catalyst was directly used for the next reaction cycle without any further treatment.

Results and discussion

Preparation of precursor polymer PS-BA

Well-defined porous polymer containing boronic acid as a reactive functional group was prepared by free radical polymerization of boronate ester-functionalized styrene monomer and divinyl cross-linker inside commercially available mesostructured silica that has a cellular foam pore structure (Fig. 1). A silica template with interconnected pore structures was chosen to replicate the pore structures because common porous silica used for chromatography has less ordered pore structures and is not suitable for infiltration of styrenic monomers. The surface of the template was first treated with chlorotrimethylsilane to convert hydrophilic silanol groups to hydrophobic trimethylsilyl ether groups and increase the surface affinity towards hydrophobic organic monomers.

Styrene monomer containing boronic acid precursor was synthesized by two-step reactions (Fig. A1 and A2). The acidic –OH group of 4-vinylphenylboronic acid was protected by

pinacol ester, so the boron-functionalized styrene monomer can be mixed efficiently with nonpolar cross-linkable divinylbenzene monomer.

To replicate the pore structure of template, cross-linked network of polymer was created inside the pores of the template. Monomer ratio between the boron-functionalized styrene monomer and divinylbenzene (i.e. cross-linker) is an important factor to consider in order to form mesoporous polymeric materials replicating the pore structure of silica template. The pinacol boronate-functionalized monomer (30 mol%), divinylbenzene (70 mol%), and a small amount of AIBN radical initiator were infiltrated through the internal wall of the silylated porous silica template. Methylated surface of the silica helps this process to induce efficient solution imbibition [17]. The monomers adsorbed into the pore walls were heated to 60–80 °C to form cross-linked polymer structures. Then, the silica template was selectively removed using a mixture of concentrated alkaline solution and ethanol, leaving the permanent porous polymers. The boronate ester group on the polymer was also deprotected to generate its corresponding boronic acid moiety during the alkaline treatment. Due to the network structure of cross-linked polymer, the obtained powder was not soluble in any organic solvents.

Removal of silica template was confirmed by Fourier-transform infrared spectra (FT-IR) using KBr pellet method (Fig. A3). After removal of the template and deprotection of pinacol boronate group with alkaline treatment, alkyl C–H stretch peak (2979 cm^{-1} , the methyl group on pinacol) and broad, strong absorption peak of silicon-oxygen bond ($900\text{--}1250\text{ cm}^{-1}$, silica template) disappeared, and a new absorption

Fig. 2 Scanning electron micrograph of **a** silica template and **b** PS-BA

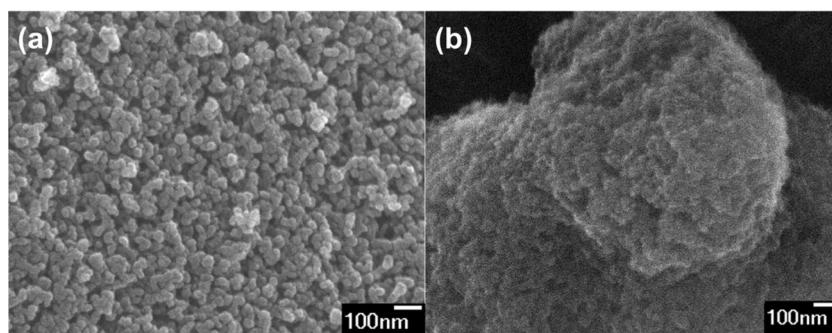


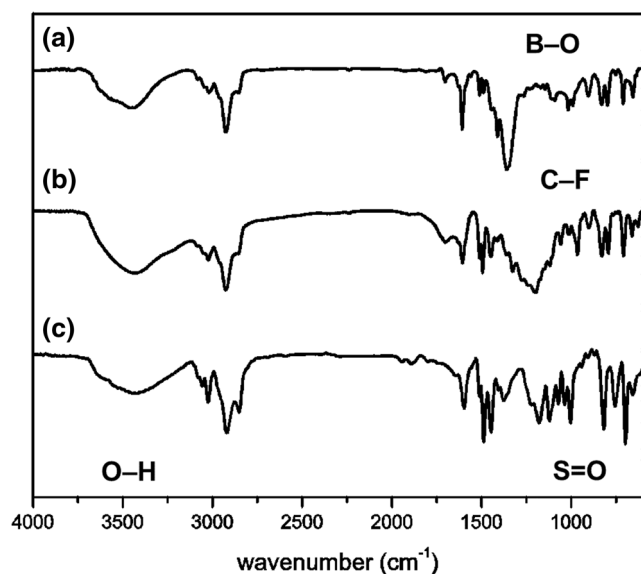
Table 1 Adsorption data calculated from N₂ adsorption isotherms

	-SO ₃ H amount (mmol/g) ^a	Surface area (m ² /g) ^b	Pore volume (mL/g) ^c	Pore size (nm) ^c
Silylated silica template	–	550	2.2	9.0
PS-BA	–	333	0.28	4.8
SAC1 ^d	1.02	113	0.14	3.4
SAC2 ^d	1.10	150	0.27	4.9

^a Determined using an acid-base titration method^b BET surface area calculated from nitrogen adsorption isotherms at 77 K using BET equation. ^c Pore volume and pore size calculated from Density Functional Theory model at 77 K^d Solid acid catalysts after deprotection

peak for O–H stretch (3400 cm⁻¹) from boronic acid appeared. There was no change in the intensity of B–O absorption (1362 cm⁻¹), which remained in the polymer structure. These changes in FT-IR absorption of the polymers confirmed successful removal of the silica template and conversion to boronic acid-containing precursor polymer. Thermogravimetric analysis (TGA) also confirmed that silica template was completely removed; the most weight loss was seen below 500 °C where hydrocarbon polymer backbone degradation occurs (Fig. A3c).

The porous structure of PS-BA derived from the silica template was visualized by field emission scanning electron microscopy (FESEM) (Fig. 2). Quantitative pore properties including surface area, pore volume, and average pore size were determined by gas adsorption analysis using N₂ isotherm (Table 1). Boronic acid functionalized PS-BA has surface area of 333 m²/g with pore size of 4.8 nm, which is within the range of mesoporosity (i.e., 2–50 nm). The pore properties of polymer can be controlled using different amounts of monomers to fill the pores of the template since the pores were replicated from the silica template.

**Fig. 3** FT-IR spectra of porous functional polymers: (a) PS-BA, (b) SAC1 after deprotection, and (c) SAC2 after deprotection

Elemental analysis of boron using inductively coupled plasma optical emission spectrometry indicated that quantity of boron present in PS-BA is 1.73 mmol/g. The presence and accessibility of boronic acid group was tested by oxidation with a solution of NaOH and H₂O₂. The FT-IR spectra in Fig. A4 illustrate complete conversion of –B(OH)₂ to –OH; the intensity of B–O stretch band (1362 cm⁻¹) was significantly reduced while a new peak at 1258 cm⁻¹ from C–O stretch appears.

Preparation of solid acid catalysts

PS-BA were converted to two different solid acid catalysts, SAC1 and SAC2, using Suzuki-Miyaura coupling reaction with S₁ and S₂, respectively. Fig. A5 shows functionalized aryl bromides that contain sulfonic acids with different acidity; S₁ contains a perfluoroalkylsulfonic acid group, which has a higher acidity than S₂ of aryl sulfonic acid. S₁ and S₂ were protected with 3,5-dimethylphenol group to prevent interference in basic condition of the Suzuki-Miyaura coupling reaction. The protecting group was removed after the coupling reaction to generate their acidic form (–SO₃H), affording SAC1 and SAC2, respectively. Immobilization of the sulfonate groups was confirmed by FT-IR spectra (Fig. 3). After the coupling reaction, the strong B–O stretch peak (1362 cm⁻¹) disappeared and a new peak at 1210 cm⁻¹ appeared for S = O absorption of SAC2 (Fig. 3c). This peak is not clearly visible for SAC1 due to overlap with C–F stretch which broadly

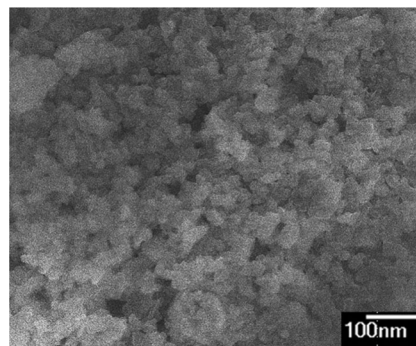
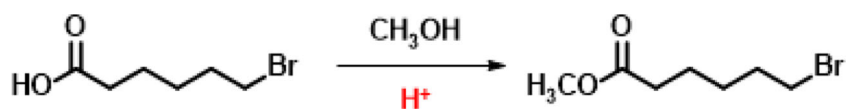
**Fig. 4** Scanning electron micrograph of the SAC1

Fig. 5 Esterification of 6-bromohexanoic acid with methanol



appears in region of 1000–1300 cm^{-1} (Fig. 3b). The sulfonic acid amount of solid acid catalysts was determined by acid-base titration. SAC2 showed slightly higher acid loading capacity of 1.10 mmol/g compared to 1.02 mmol/g of SAC1, possibly due to smaller size of the acid group in SAC2. PS-BA did not show the presence of acidic group in titration.

Maintaining porous structure after acidic functionalization is important for application in acid catalysis. As shown in the SEM image of SAC1 after deprotection (Fig. 4), no significant change was observed in the pore structure compared to that of PS-BA (Fig. 2b). Table 1 shows quantitative data of pore properties; surface area, pore volume, and pore size decreased to some extent after Suzuki-Miyaura coupling reaction to generate solid acid catalysts. Introduction of additional functional group that contains an aromatic ring and acid group caused further decrease in surface area and pore size. Between two solid acids, pore volume and pore size were less affected for SAC2 because of a smaller acid group. To incorporate a sizable functional group, the use of a hard template with mesopores (2–50 nm) is important. Although not all pore properties were completely replicated from the silylated silica template, the resulting solid catalysts still feature mesoporosity with desired acid functional groups.

Solid acid catalyzed esterification

To investigate catalytic activity of these solid catalysts, SAC1 and SAC2 were evaluated for esterification of 6-bromohexanoic acid with methanol (Fig. 5). The product, methyl

6-bromohexanoate, is a useful intermediate for synthesis of drug carriers [18–20] and adsorbents for dye-sensitized solar cells [21]. The experiments were carried out using a catalytic amount (0.5 wt%) of heterogeneous acid and the reaction progress was monitored by GC-MS. Catalytic activities of SAC1 and SAC2 were compared to see how difference in acid strength affects the conversion rate of esterification (Fig. 6). At 65 °C, superacidic SAC1 achieved complete conversion within 4 h while less acidic SAC2 needed 6 h. Since SAC1 has a lower acid capacity (1.02 and 1.10 mmol/g for SAC1 and SAC2, respectively) and less favorable pore properties (see Table 1), the enhanced catalytic activity of SAC1 can be attributed to the stronger acidity of the functional group. The difference in catalytic activity between SAC1 and SAC2 widens when the esterification reaction was carried out at a lower temperature 45 °C. Only a slight decrease in conversion was observed for SAC1 when temperature decreased from 65 to 45 °C, still achieving almost 100% after 4 h. In contrast, the catalytic activity of SAC2 was more temperature dependent; the conversion rate was significantly reduced when temperature decreased to 45 °C and only 80% conversion was obtained even after 6 h. Despite having a smaller BET surface area and pore volume and a lower acid loading capacity, SAC1 showed better catalytic activity than SAC2 especially at lower temperature which would be ascribed to its higher acid strength [1]. The greater activity of SAC1 with superacidic –CF₂CF₂SO₃H group at lower temperature may help saving energy in a large scale synthesis.

The catalytic activity of SAC1 in esterification was also compared with commercially available solid acid catalysts Amberlyst 15 (A15) and Nafion (NR50) at 45 °C under

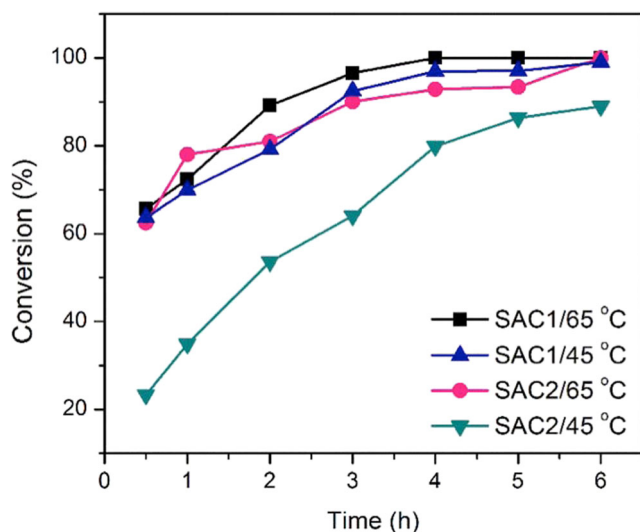


Fig. 6 Comparison of catalytic activity of SAC1 and SAC2. All reactions were carried out with 0.5 wt% catalyst loading

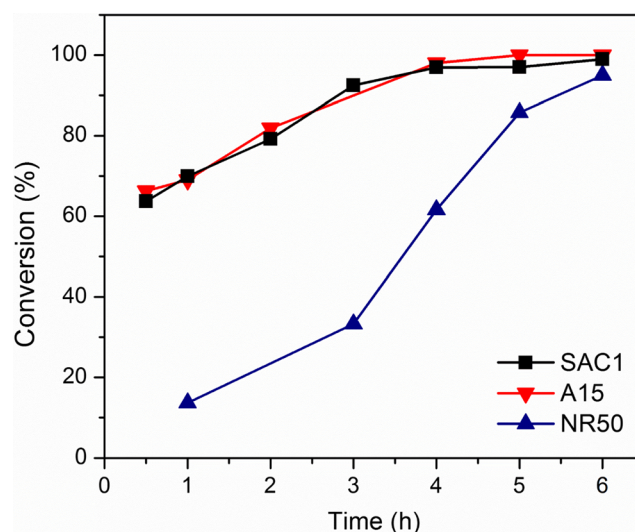


Fig. 7 Comparison of different acid catalysts. All reactions were carried out with 0.5 wt% catalyst loading at 45 °C

0.5 wt% loading of catalyst (Fig. 7). Although the same weight percent of catalysts was employed, A15 has a much more acidic groups per gram because of its higher loading capacity (4.8 mmol/g). This value is almost five times higher than that of SAC1 (1.02 mmol/g). Nafion has a similar molar loading capacity of 0.90 mmol/g but it does not have a porous structure. Due to the high acid loading capacity, A15 showed good conversion throughout the reaction, achieving complete conversion in 4 h. With the same 0.5 wt% of catalyst loading, the activity of SAC1 was comparable to that of A15 under the entire reaction period. This is possibly due to the mesoporous structure of SAC1 which allows easy access of reactants into the pores of the catalyst and facilitates mass diffusion of reactants and product. Additionally, the hydrophobic surface of pores made of polystyrene with a high degree of cross-linking density would be helpful to achieve good catalytic performance by repelling water that is formed as a byproduct, otherwise it may push the reaction back to an equilibrium [22]. In spite of having a similar acidity strength of SAC1, NR50 showed much lower conversion because of its non-porous structure and low surface area [23].

Reusability of solid acid catalysts to reduce environmental impact is an important criteria for practical application. In reusability study, after first run of esterification with 0.5 wt% of SAC1, the solid catalyst was filtered, washed and dried, and used for the next cycle of reaction without any additional treatment. The recycled catalyst showed almost the same level of catalytic activity and achieved full conversion within 6 h up to 3 cycles, demonstrating reusability of the catalyst in acid-catalyzed organic reaction. After the third cycle, the catalyst showed a slight decrease in activity.

Conclusion

Two solid acid catalysts with well-defined porosity and different acid strength were synthesized, and their catalytic activities in esterification were compared with commercially available solid acid catalysts. The use of borylated precursor polymer allowed convenient preparation of solid acid catalysts with different acid strength. The solid acid catalyst with perfluoroalkyl sulfonate (SAC1) showed a greater activity compared to the solid acid catalyst with less acidic aryl sulfonate (SAC2) and the difference in activity becomes wider as decreasing temperature. Despite high degree of cross-linking and lower acid loading, the mesoporosity and superacidity of SAC1 afforded good conversion rate of esterification which is comparable to that of commercially available Amberlyst 15 with higher acid loading. After the reaction, catalyst was easily recovered and recycled up to three times without additional treatment, demonstrating a potential for use as a recyclable solid acid catalyst in organic reactions.

The methodology of pre-formed porous polymers using a porous silica template can offer a convenient synthetic platform for creation of solid catalysts with a variety of micro- and meso-porous structures that will be used in broader catalysis applications.

Acknowledgments The authors appreciate the generous support of the Rensselaer Polytechnic Institute (Bae startup) for this work.

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