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Catalytic Performance of SBA-15-Supported Poly (Styrenesulfonic Acid) in the Esterification of Acetic Acid with *n*-Heptanol

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Received: 29 July 2020; Accepted: 21 August 2020; Published: 23 August 2020



Abstract: A polystyrene sulfonic acid-functionalized mesoporous silica (SBA-15-PSSA) catalyst was synthesized via an established multistep route, employing 2-bromo-2-methylpropionyl bromide as initiator of atom transfer radical polymerization. Fourier-transform infrared spectroscopy, thermogravimetric/differential thermal, Brunauer–Emmett–Teller, and transmission electron microscopy analyses revealed outstanding structural characteristics of the catalyst, including highly ordered mesopores, high surface area (726 m²/g), and adequate estimated concentrations of active sites (0.70 mmol H⁺/g). SBA-15-PSSA's catalytic performance was evaluated in the esterification of acetic acid and *n*-heptanol as a model system at various temperatures (50–110 °C), catalyst loads (0.1–0.3 g), and reaction times (0–160 min). The conversion percentage of acetic acid was found to increase with the temperature, catalyst load, and reaction time. Furthermore, results indicated a fast conversion in the first 20 min of the reaction, with remarkable conversion values at 110 °C, reaching 86%, 94%, and 97% when the catalyst load was 0.1, 0.2, and 0.3 g, respectively; notably, at this temperature, 100% conversion was achieved after 60 min. At 110 °C, the reaction conducted in the presence of 0.3 g of catalyst displayed more than 6.4 times the efficiency of the uncatalyzed reaction. Such activity is explained by the concomitant presence in the polymer of strong sulfonic acid moieties and a relatively high hydrophobic surface, with adequate numbers of active sites for ester production.

Keywords: heterogeneous catalyst; mesoporous silica; SBA-15; polystyrene sulfonic acid; esterification; acetic acid

1. Introduction

Solid acid catalysts have emerged as green alternatives to their liquid acid counterparts, such as sulfuric, hydrofluoric, hydrochloric, and nitric acids, which constitute a major source of harmful industrial waste and cannot be easily recycled. In fact, the demand for high-efficiency, environmentally friendly, recoverable, and reusable catalytic systems is quite high. A substantial class of these catalysts consists of silica-supported sulfonic acids. These species have demonstrated an outstanding catalytic performance in a wide range of chemical transformations, including substrate alkylation, etherification, esterification, retro-esterification, and gas-phase glycerol dehydration [1–7]. Among silica-supported sulfonic hybrid solid catalysts, (poly)styrene sulfonic acid-modified Santa Barbara Amorphous-15 (SBA-15) materials are very attractive, particularly in the catalysis of esterification reactions, with activities comparable to the commercially available sulfonic-based catalysts Nafion

and Amberlyst resins [8,9]. SBA-15-supported polystyrene sulfonic acids (henceforward referred to as SBA-15-PSSA) are also actively used in the catalysis of reactions like, for example, transesterifications and retro-esterifications [1,2,10,11].

Notably, although esterification is a reversible reaction, with low yields achieved at equilibrium, this reaction's yield may be improved with the use of suitable catalysts. In conventional catalytic processes, mineral acids such as sulfuric acid or nitric acid are used as liquid homogenous catalysts for ester synthesis. However, use of these species in industrial applications is associated with many disadvantages, including corrosion effects and the need for costly post-processing procedures dictated by safety and environmental considerations. On the other hand, heterogeneous organic–inorganic hybrid catalysts have recently replaced such hazardous and corrosive mineral acids in industrial processes. In particular, silica-supported polystyrene sulfonic acids are an attractive class of solid catalysts, as they combine the desirable traits of having acid catalytic functionalities and polymer–silica-associated hydrophobicity. Furthermore, they are 'green', generally efficient, reusable, and cost-effective [2].

A convenient approach to immobilizing the intended polymers comprising acid functionalities on the inorganic silica-based support consists of the well-known surface-initiated atom transfer radical polymerization (ATRP) method; in it, the key elementary reaction responsible for the uniform growth of the polymeric chain is the transfer step. Various pathways have been used to implement ATRP to realize the synthesis of SBA-15-PSSA. However, each protocol for the production of SBA-15-PSSA has its own benefits and disadvantages. According to literature, the catalytic performance of sulfonic acid-functionalized SBA-15 varied depending on several factors, including the surface texture of the silica, the type of grafted intermediates, the ATRP initiator, the degree of polymerization, the type of active site ($-\text{SO}_3\text{H}$) isomer, the catalytic reaction system type and its precursors, and the applied synthetic method [1–4,7,10–13].

For example, Li et al. [2] prepared a series of PSS/SBA-15(xx) species using 4-(chloromethyl)-phenyltrimethoxysilane (CTS) as ATRP initiator. Notably, in the mentioned formula xx represents the polystyrene/SBA-15-CTS (wt/wt) ratio (i.e., 0.3, 1.2, and 1.8). Experimentally, CTS was immobilized on SBA-15, and sodium 4-styrenesulfonate (SSNa) was polymerized successfully; remarkably, these species were reported to display a higher catalytic performance than commercial Nafion resin in the esterification of lauric acid with ethanol. Other catalyst series were prepared by Martín et al. [10]; in particular, multi-intermediates were generated under various conditions employing 3-(chlorodimethylsilyl) propyl bromoisobutyrate as the immobilized ATRP initiator. These catalysts were employed in the esterification of oleic acid and *n*-butanol. In each case, the catalytic activity of the obtained species depended on several factors, such as preparation conditions, type and amount of ATRP initiator intermediate, degree of polymerization, type of active site isomer (ortho-, meta-, or para-isomer), and the product's hydrophilicity–hydrophobicity character [2,7,9,10]. Moreover, the surface area and porosity of the silica-based support and, as a consequence, of the catalyst, are highly important characteristics that significantly influence catalytic performance.

The synthesis of solid acids with excellent catalytic properties remains a challenge; however, with many trials already made, whereby the type of silica precursor, the type of organo-silanes, and the fabricating methods used for support modification were made to vary [5,6,14]. Mesoporous materials are generally characterized by high surface areas and uniformly sized pores (2–30 nm). The generation of pores with specific target shapes and sizes close to 30 nm can be facilitated employing micelle expanders and structure-directing agents during the synthetic step [10,15]. Thus far, evidence indicates the ATRP method to be the most powerful to generate uniform layers, control polymeric film thicknesses, and avoid pore blockage by polymers [10,16,17]. Importantly, the sulfonic acid active sites supported on mesoporous organosilica displayed the advantage of being effective even in water-sensitive reactions [10,18]. These advantages were attributed to an increased hydrophobicity near the active sites (i.e., the sulfonic acid moieties) and the promotion of the diffusion of reactants within the hydrophobic environment of mesopores. Notably, balancing between the requirement of a

high organic surface area and the risk of pore saturation is one important concern in the design and synthesis of such catalysts.

Taking into consideration the demand for efficient catalysts and the reported advantage of using solid acid catalysts based on poly (styrenesulfonic acid)-functionalized SBA-15 in, for instance, the acceleration of the esterification reaction, a novel SBA-15-PSSA species has hereby been prepared implementing a newly developed pathway. The catalyst thus obtained was characterized by Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and differential thermal analysis (DTA), transmission electron microscopy (TEM), and nitrogen adsorption isotherms; subsequently, its catalytic performance was evaluated using acetic acid and *n*-heptanol as reactants in a model reaction system whereby fairly long-chain esters were expected to be generated. The effects of various factors on catalyst activity, including temperature, catalyst dose, and reaction time were examined, as well as catalyst reusability after two catalytic runs.

2. Materials and Methods

2.1. Materials

Tetraethyl orthosilicate (TEOS) (99%), triblock copolymer Pluronic 123 (P123, $M_n \approx 5800$), ammonium fluoride (NH_4F) (99.99%), 1,3,5-triisopropylbenzene (TIPB) (95%), (3-aminopropyl)triethoxysilane (APTES) (99%), 2-bromo-2-methylpropionyl bromide (BMPB) (98%), 2,2'-bipyridine (BiPy) ($\geq 99\%$), copper (I) chloride (CuCl) (97%), styrene-4-sulfonic acid sodium salt (SSNa) ($\geq 90\%$), *n*-dodecane (nDD) (99%), acetic acid (AA) ($\geq 99.85\%$), *n*-heptanol (nHTL) (98%), trimethylamine (TMA) ($\geq 99\%$), dichloromethane (DCM) ($\geq 99.8\%$), and toluene (99.6%) were purchased from Sigma Aldrich (Taufkirchen, Bavaria, Germany). Methanol (MeOH) (99.5%) and ethanol (EtOH) (96%) were obtained from Fisher Scientific (Loughborough, England, UK). All chemicals were used as received unless otherwise stated in the text.

2.2. Synthesis of the Catalyst

The solid acid catalyst, poly (styrenesulfonic acid)-graft-silica (SBA-15-PSSA), was synthesized following a four-step protocol (Figure 1).

Step (i)—preparation of SBA-15. Pore-expanded mesoporous silica (SBA-15) was prepared implementing a modification of the method described in several reports [10,16,19]. In a 250-mL round-bottom flask, a solution of P123 (3.6 g)/ NH_4F (0.041 g)/1.3 M HCl (126 mL) was stirred at 17 °C for 1 h, in a water bath whose temperature was controlled by a chiller device (Recirculating Chiller F-105, Buchi, Flawil, Switzerland). To this solution, was added dropwise a mixture of TEOS (8.25 mL) and TIPB (1.8 mL); the obtained mixture was stirred at 17 °C for 24 h and, subsequently, refluxed at 130 °C overnight. The white precipitate produced was washed several times, sequentially, with distilled water and EtOH (5×15 mL) employing a repeated suspension–centrifugation process; it was then dried in a vacuum oven at 40 °C until a constant weight was achieved. Finally, the obtained silica was calcined at 550 °C, reached at a ramp rate of 2 °C/min, for 5 h in a nitrogen gas environment.

Step (ii)—synthesis of amino-functionalized silica (SBA-15- NH_2). Attachment of amine functionalities onto the surface of SBA-15 was performed following a standard method described in the literature [10,20,21]. Here, 1.5 g of SBA-15 was suspended in 50 mL of APTS/toluene (1:100 by volume), and the resulting mixture was refluxed with stirring in an oil bath at 110 °C for 24 h. The resultant SBA-15- NH_2 was collected by centrifugation, washed with EtOH (3×15 mL), and dried as in step (i).

Step (iii)—synthesis of the initiator-modified intermediate (SBA-15-Br). The synthesis of the SBA-15-supported ATRP initiator was carried out through the Yamamoto method [19]. To a stirred mixture of SBA-15- NH_2 (0.5 g)/TMA (0.75 mL, 9.5 mmol)/DCM (25 mL) was added dropwise a solution of BMPB (1.2 mL) in DCM (5 mL) over 10 min. After 48 h of stirring, about 20 mL DCM was added to the mixture, which was then sonicated for 5 min; the solvent was subsequently evaporated with a

rotary evaporator (Buchi, R-210, Boston LabCo, Boston, MA, USA) at 40 °C. The final solid product was washed with EtOH (3 × 15 mL) and dried as described above.

Step (iv)—polymerization of SBA-15-Br with sodium 4-styrenesulfonate to produce SBA-15-PSSNa. The surface-initiated ATRP reaction of SBA-15-Br with SSNa was carried out under a nitrogen gas inert atmosphere in a 100-mL three-necked flask equipped with a magnetic stir bar and a reflux condenser. Initially, a solution containing SBA-15-Br (100 mg) and SSNa (412 mg, 2 mmol) in 6 mL of MeOH was bubbled with nitrogen gas at 40 °C while stirring. After 15 min, a mixture of BiPy (31.23 mg, 0.2 mmol) and CuCl (0.197 mg, 0.002 mmol) was added to the solution, and the polymerization was allowed to proceed overnight at room temperature under nitrogen atmosphere. The product was filtered off, washed with water and EtOH, and dried under vacuum. Finally, the obtained SBA-15-PSSNa was acidified with an excess of 0.2 M HCl for 1 h; it was then naturalized with water and dried as above.

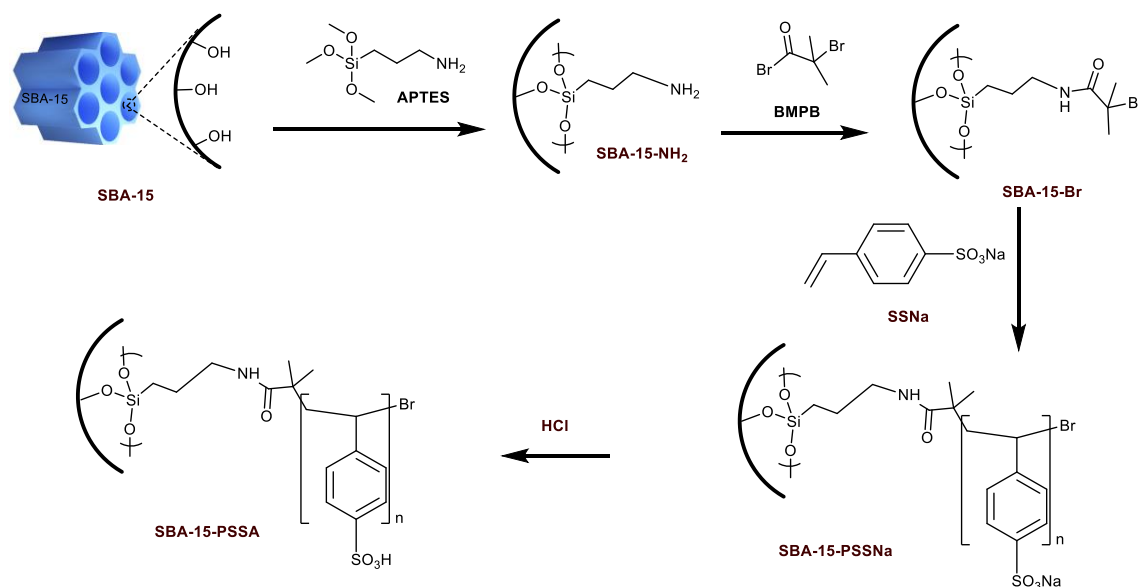


Figure 1. Preparation of SBA-15-supported polystyrene sulfonic acids (SBA-15-PSSA) solid catalyst. APTES: (3-aminopropyl) triethoxysilane; BMPB: 2-bromo-2-methylpropionyl bromide; SBA-15: pore-expanded mesoporous silica; SSNa: sodium 4-styrenesulfonate.

2.3. Characterization Techniques

FTIR spectra were recorded employing the KBr disk method in an FTIR spectrometer (Nicolet iS10, Thermo scientific, Madison, WI, USA), in the 4000–500 cm^{−1} wavenumber range with a resolution of 4 cm^{−1} and a total number of scans per spectrum of 16. The surface morphology of SBA-15-PSSA was analyzed by TEM (using a JEM-1011 instrument, JEOL, Tokyo, Japan). TGA experiments were performed using a Mettler Toledo TGA/DSC 1 Star system (Columbus, OH, USA). Specimens were heated from 25 to 1000 °C at a rate of 10 °C/min under an N₂ gas flowrate of 20 mL/min. The surface area and porosity of SBA-15 was assessed via N₂ adsorption–desorption isotherms using a Gemini VII 2390 V1.03 (V1.03 t) instrument from Micromeritics (Norcross, GA, USA). The samples were outgassed at 350 °C for 3 h before the measurements were performed. The samples' surface area was calculated using the Brunauer–Emmett–Teller (BET) equation over the P/P₀ value range between 0.051 and 0.252, whereby a linear relationship is maintained. The pore size distribution in mesoporous silica were calculated using the Barrett–Joyner–Halenda (BJH) model based on the adsorption branch of the isotherm. The progression of the esterification reaction was assessed through quantification of the residual reactant (AA) in reference to the internal standard (nDD) by gas chromatography (GC) using a GC-7890 instrument from Agilent technologies Inc. (Santa Clara, CA, USA) equipped with a flame ionization detector and a 19019S-001 HP-PONA GC column.

2.4. Catalyst Performance Test

2.4.1. Esterification of AA

The catalytic performance of the produced SBA-15-PSSA was assessed in the esterification of AA with nHTL, as a model reaction system (Figure 2). The described reaction was carried out in a 50-mL two-necked round-bottom flask equipped with refluxing and magnetic stirring systems, and one neck sealed with a rubber septum. The reaction was performed in an oil bath over a dual digitally controlled magnetic stirrer and heater. The reactants, nHTL (9.064 g, 0.0775 mol) and AA (0.936 g, 0.0156 mol), and the catalyst, SBA-15-PSSA, were loaded into the reactor alongside the GC internal standard, nDD (0.2 g, 0.0012 mol). The mixture was stirred at a fixed rate of 400 rpm under atmospheric pressure at a specific temperature and for a predefined period of time. The effect on the yield of the reaction of the reaction time (0–160 min), catalyst dose (0.02–0.3 g), and reaction temperature (50–110 °C) were evaluated, and the overall results were compared with those obtained for the uncatalyzed reaction. In each experiment, 0.5-mL aliquots of the reaction mixtures were carefully collected every 20 min using a glass syringe with a stainless steel needle, centrifuged, and the reactants' concentrations in them was determined by GC.

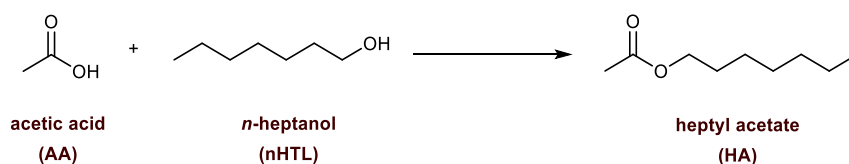


Figure 2. Esterification of acetic acid and *n*-heptanol to produce heptyl acetate.

2.4.2. Calculations

A standard curve was generated by varying the AA amount (0.02–0.27 g, 0.333–0.4496 mmol) while maintaining the amount of the internal standard (nDD) fixed (0.04 g, 0.235 mmol), as well as an excess amount of nHTL (1.8 g, 15.400 mmol). The tests were performed in triplicate by injection of 1 µL of the mixture to be analyzed by GC and, from the chromatogram obtained, the areas of the peaks due to AA (*S*) and nDD (*S*₀) were calculated, with the data averaged. Thus, the AA conversion percentage can be calculated via Equations (1)–(4).

$$K = \frac{\frac{M}{M_0}}{\frac{S}{S_0}} \quad (1)$$

$$X_{AA} = \frac{KM_0S}{S_0} \quad (2)$$

$$Y_{AA} = M - X_{AA} \quad (3)$$

$$C(\%) = \frac{Y_{AA}}{M} \times 100 \quad (4)$$

where M/M_0 and S/S_0 are the AA/nDD feedstock (by mole) and the peak area ratios, respectively, K is the conversion factor, X_{AA} and Y_{AA} are the number of moles of AA unreacted and converted, respectively, and $C\%$ is the conversion percentage of AA under the experimental conditions.

2.5. Catalyst Reusability

The reusability of SBA-15-PSSA was tested under the moderate reaction conditions whereby 0.1 g of catalyst was used at 80 °C for two catalytic runs. The exhausted catalyst from the first cycle was recovered by filtration, washed several times with water, and dried overnight under vacuum at room temperature, before being reused under reaction conditions similar to those described above. The test was performed in duplicate and data were averaged.

3. Results

3.1. Characterization

3.1.1. TEM Analysis

The TEM micrographs of SBA-15 and SBA-15-PSSA are reported in Figure 3. These images are indicative of the presence of well-ordered hexagonal pores in a 2D array with 1D channels and typical $p6mm$ honeycomb space group, confirming that the intended target structure had been obtained [2,22]. As can be inferred from Figure 3B, the hexagonal structure is almost perfectly conserved after polymerization.

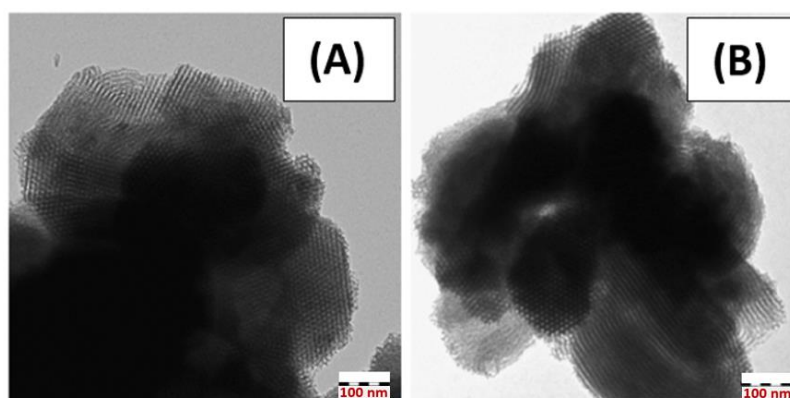


Figure 3. Transmission electron microscopy micrographs of (A) SBA-15 and (B) SBA-15-supported polystyrene sulfonic acids. SBA-15: pore-expanded mesoporous silica. Scale bars, 100 nm.

3.1.2. FTIR Analysis

In Figure 4 are reported the FTIR spectra of SBA-15, SBA-15-NH₂, SBA-15-Br, and SBA-15-PSSA. The spectrum of SBA-15 is similar to that reported in the literature [10,23,24]. Typically, the stretching bands of silanol groups appear at 3600–3200 cm^{−1}. Several types of silanols on the surface of silica, including hydrogen-bonded, isolated, and geminal, were reported to be observable at 3738 cm^{−1}, in the case of the first two silanol types, and at 3630–3180 cm^{−1} in the case of geminal silanols [25]. Thus, the silanols in the as-prepared SBA-15 are mainly of the hydrogen-bonded type (the highest peak was at 3440 cm^{−1}), combined with water hydroxyls [26]. The asymmetric and symmetric stretching bands of the siloxane framework, Si–O–Si, were observed at about 1086 and 803 cm^{−1}, respectively. The weak band at 970 cm^{−1} is ascribed to the asymmetric stretching of the Si–OH bond [25,27]. After functionalization, the intensity of this peak decreased simultaneously with those of the peaks at 1632 and 3440 cm^{−1}, as a result of the consumption of OH groups, indicating the success of the reaction [28]. The peak around 1632 cm^{−1} is due to the bending mode of OH, including water H–O–H [29]; however, some authors assigned this band to an overtone of the Si–O stretching [30]. The spectrum of amino-functionalized SBA-15 (SBA-15-NH₂) was characterized by an additional band at 1541 cm^{−1}, corresponding to N–H bending; however, this band is one characterize C–N of amide II [31] as well. In addition, the absorption pattern in the area of the spectrum where the CH, NH, and OH bands appear (2850–3400 cm^{−1}) is obviously different from that of silica, due to peak overlapping. After initiator functionalization, and the resulting formation of SBA-15-Br, no substantial spectral differences with SBA-15-NH₂ were observed, due to the amount of anchored initiator being too small [32]. The vibrational peak centered at 1639 cm^{−1} is assigned to the amidic C = O moieties, which overlapped with the peak due to the OH bending mode of silanol. After polymerization, the spectrum of the thus produced SBA-15-PSSA included new bands that can be attributed to PSSA, such as those at 1408 cm^{−1}, due to C–N and aromatic rings, at 846 cm^{−1}, due to C–H out-of-plane bending vibrations of para-disubstituted benzene [33,34], and at 684 cm^{−1}, due to skeletal alkyl groups in the polymeric

chain [10]. The presence of separated bands at 3440 and 3355 cm^{-1} may indicate a trivial effect of hydrogen bonding, a conclusion supported by the low OH and NH mole percentage with respect to the entire molecule [31,35].

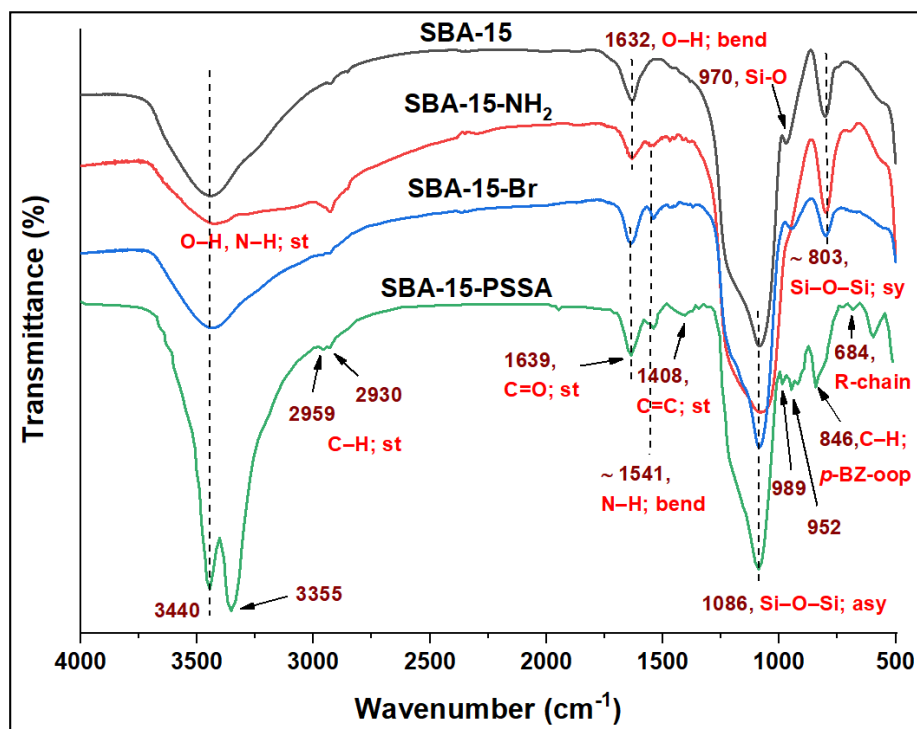


Figure 4. Fourier-transform infrared spectra of SBA-15, SBA-15-NH₂, SBA-15-Br, and SBA-15-PSSA. SBA-15: pore-expanded mesoporous silica; SBA-15-PSSA: SBA-15-supported polystyrene sulfonic acids.

3.1.3. Thermal Analysis

Thermal analyses were conducted to determine the amount of anchored styrenesulfonic acid in the catalyst as well as to assess the catalyst's thermal stability under an inert atmosphere of nitrogen gas. In Figure 5 are reported the superimposed TGA, DTA, and derivative-TGA (DTG) curves of SBA-15-Br and SBA-15-PSSA; relevant data are listed in Table 1. SBA-15-Br decomposition occurs basically in three temperature intervals. The first step (25–157 °C, mass loss of 0.81%) is generally due to a drying process; in other words, volatile compounds such as adsorbed water and gaseous molecules are released in the mentioned temperature range. However, as no clear peaks in this temperature range are present in the DTA curve. The second decrease in weight occurs at 157–319 °C, with an estimated weight loss of 6.24% and an exothermic peak at 249 °C in the DTA curve ascribed to the attached initiator. The appearance of the TGA/DTG thermogram in the third temperature interval (up to 700 °C) was indicative of the stepwise volatilization of small molecules (total mass loss of 3.40%) with an endothermic peak at 395 °C and an exothermic peak at 494 °C corresponding to the thermal degradation of the remaining organic components, including APTES fragments. Thermal degradation of the catalysts can also be inferred to occur in three stages, as can be evinced from Figure 5 and Table 1. The first stage corresponds to the loss of adsorbed volatile compounds (mass loss of 2.87%, DTG 66 °C, and DTA-endothermic ~71 °C). The second stage corresponds to the multistep degradation of intermediates such as amines, alkyls, carbon-oxides, organo-halides, and water (total mass loss of 8.69%). The third stage, above 458 °C, clearly indicates one exothermic heat transition at 556 °C (DTG at 545 °C), with the major weight loss belonging to the polymer. An endothermic heat transformation was observed to occur at temperatures above 700 °C, which is due to phase changes in the residual materials.

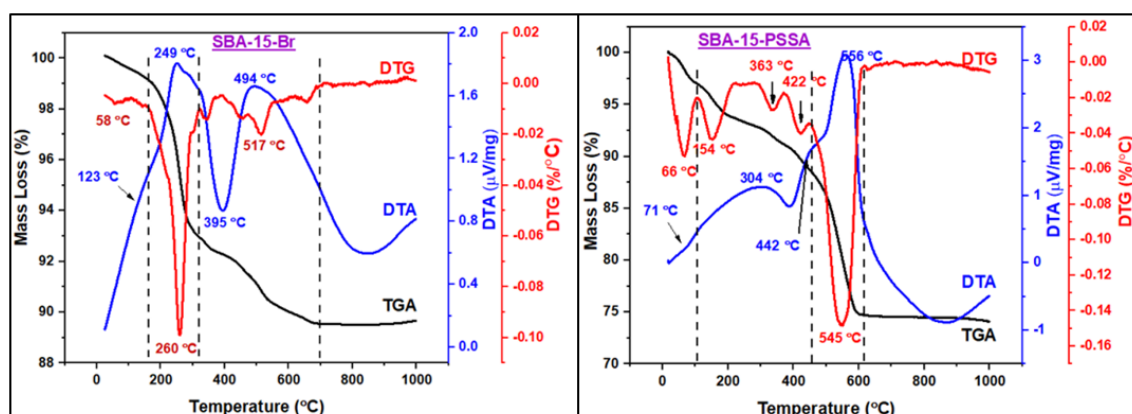


Figure 5. Thermogravimetric analysis (TGA; black line, left y -axis), derivative-TGA (DTG; red line, the rightmost y -axis), and differential thermal analysis (DTA; blue line, right y -axis) curves of SBA-15-Br and SBA-15-PSSA. SBA-15: pore-expanded mesoporous silica; SBA-15-PSSA: SBA-15-supported polystyrene sulfonic acids.

Table 1. Thermal properties of SBA-15-PSSA.

Sample	TGA		DTG (°C)	DTA (°C)	Assignment	Residue (%)
	Temperature (°C)	Mass Loss (%)				
SBA-15-Br	25–157	0.81	58	-	Volatiles	99.19
	157–319	6.24	260	(+) 249	Initiator	92.95
	319–700	3.4	517	(+) 494	Amine	89.55
SBA-15-PSSA	25–100	2.87	66	-	Volatiles	97.12
	100–212	3.33	154	-	Initiator-amine-based	93.80
	212–365	2.53	363	(+) 304		91.27
	365–457	2.83	422	(+) 442		88.44
	458–617	13.81	545	(+) 556	Polymer-based	74.63

(+): exothermic process; DTA: differential thermal analysis; DTG: derivative thermogravimetric analysis; SBA-15: pore-expanded mesoporous silica; SBA-15-PSSA: SBA-15-supported polystyrene sulfonic acids; TGA: thermogravimetric analysis.

The results of TGA data analysis were used to estimate the catalyst's polymer contents. The estimated organic-based contents were 9.64 wt% in SBA-15-Br and 22.50 wt% in SBA-15-PSSA. The 12.86 wt% difference is an approximation of the polymer contents of SBA-15-PSSA; therefore, 0.70 mmol of styrenesulfonic moieties were present per gram of catalyst which, by assuming complete conversion of sulfonates into sulfonic acids, equals the number of active sites ($-\text{SO}_3\text{H}$ or H^+) as well (Table 2).

Table 2. Surface area, pore diameter, and pore volume of SBA-15-PSSA.

Surface Area BET (m ² /g)	Pore Size BJH _{ads} (Å)	Pore Volume BJH _{ads} (cm ³ /g)	Acidity by TGA (mmol H ⁺ /g)
726	107.61	1.52	0.70

BET: Brunauer–Emmett–Teller; BJH_{ads}: Barrett–Joyner–Halenda; SBA-15: pore-expanded mesoporous silica; SBA-15-PSSA: SBA-15-supported polystyrene sulfonic acids; TGA: thermogravimetric analysis.

3.1.4. Nitrogen Adsorption Isotherms

The physical characteristics (surface area, pore size, and pore volume) of SBA-15-PSSA are reflected by the data listed in Table 2. In Figure 6 are reported the N₂ adsorption–desorption isotherm

of SBA-15-PSSA and this catalyst's pore size distribution; the isotherm has the typical features of a type IV, with clear H1-type hysteresis loops, indicating the presence of cylindrical mesopores of fairly uniform sizes and shapes. The obtained values for surface area ($726 \text{ m}^2/\text{g}$) and average pore diameter ($107.6 \text{ \AA}$) are consistent with literature reports, whereby researchers also claimed increased surface area of silica-supports when prepared at low initial temperature [3,10]. However, the texture properties of functionalized silica (e.g., SBA-15-PSSA) are not much affected after modification. According to Martin et al. [10], the surface area of functionalized silica is slightly reduced compared to SBA-15; however, the average pore size and distribution are not much influenced by functionalization, which is a promising observation from the standpoint of catalytic applications.

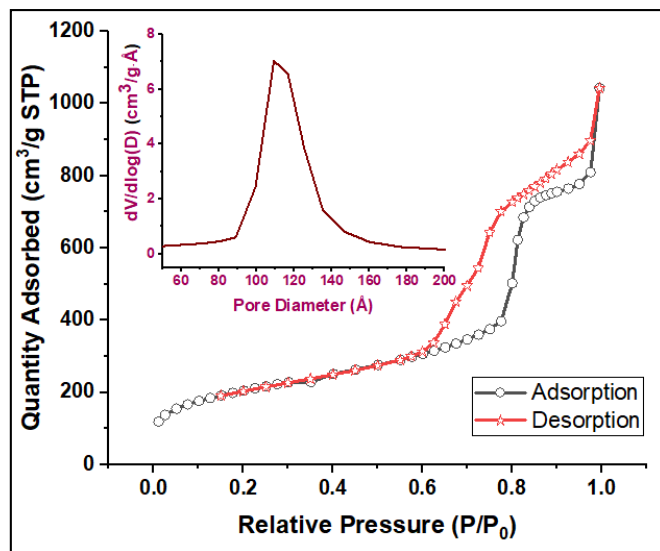


Figure 6. N_2 adsorption–desorption isotherms of SBA-15-PSSA. In the inset is the pore size distribution of SBA-15-PSSA. SBA-15: pore-expanded mesoporous silica; SBA-15-PSSA: SBA-15-supported polystyrene sulfonic acids; STP: standard temperature and pressure.

3.2. Catalytic Performance Studies

The catalytic performance of the prepared sulfonic acid-functionalized silica, SBA-15-PSSA, was evaluated in the esterification of AA with nHTL. This reaction was chosen to produce an appropriate ester with moderate molecular weight and hydrophobicity. To prevent the evaporation of materials, including reactants, internal standard, and product, a refluxing system was used, and the reaction temperature was kept below the lowest component's boiling point (b.p. = 117, 175, 227, and 216°C for AA, nHTL, nDD, and HA, respectively). The reaction kinetic (0–160 min) and substrate conversion at different temperatures (50, 80, and 110°C) and catalyst doses (0.1, 0.2, and 0.3 g) were monitored by GC. The esterification was conducted employing fixed amounts of alcohol (nHTL, 9.06 g) and internal standard (nDD, 0.2 g), and at a stirring rate of 400 rpm. In Figure 7 are reported reaction data obtained in the presence and absence of catalyst SBA-15-PSSA at 110°C . Evidence indicates the uncatalyzed reaction to be very slow, with calculated conversion of 33% after 160 min. However, results of experiments on the catalyzed reactions indicate catalyst-dose-dependent conversion. Moreover, the high AA conversion values and the speed of the reaction prove that the prepared SBA-15-PSSA is an excellent solid acid catalyst, with $>90\%$ AA conversion observed after 40 min. The esterification activities at 80 and 50°C as a function of the catalyst amount are reported in Figures 8 and 9, respectively. Generally, results indicated that AA conversion increased with the temperature, catalyst amount, and reaction time. Moreover, the majority of the AA was converted to ester during the first 20 min; at 110°C and in the presence of 0.3 g of catalyst, AA conversion was 97% (Figure 7). Regardless of the catalyst amount, the esterification activity at 110°C was the highest, with conversion values of 100% after 140, 100, and 60 min, when the catalyst amount was 0.1, 0.2, and 0.3 g, respectively. After 160 min,

the obtained maximum conversion values at 80 °C were 94, 97, and 98%, and at 50 °C they were 52, 69, and 79%, with catalyst doses of 0.1, 0.2, and 0.3 g, respectively (Figures 7–9). The high performance of the SBA-15-PSSA in terms of AA conversion into the corresponding ester can be attributed to an adequate combination of both SBA-15 and PSSA properties represented by the large mean pore size and the hydrophobic polymeric chain, respectively, resulting in an improved diffusion of hydrophobic reactants and products [6,10], the nHTL and HA respectively. The higher hydrophobicity of the sulfonic acid site microenvironment reduces the poisoning effect by water by-product of the esterification reaction. Moreover, the structure of the synthesized SBA-15-PSSA facilitates the exposure of the acid sites, resulting in an elevated performance even at lower acid contents [10].

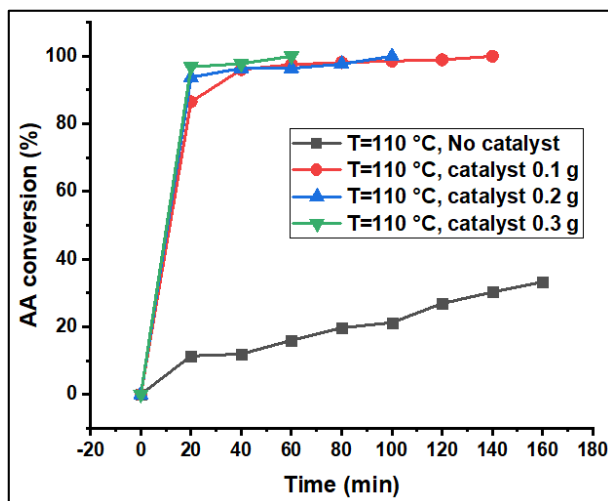


Figure 7. Acetic acid (AA) conversion in the catalyzed (with 0.1, 0.2, or 0.3 g of catalyst) and uncatalyzed esterification reaction conducted at 110 °C as a function of time.

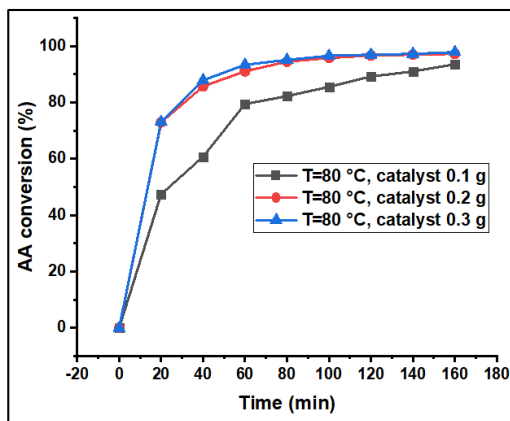


Figure 8. Acetic acid (AA) conversion in the catalyzed esterification reaction (with 0.1, 0.2, or 0.3 g of catalyst) at 80 °C as a function of time.

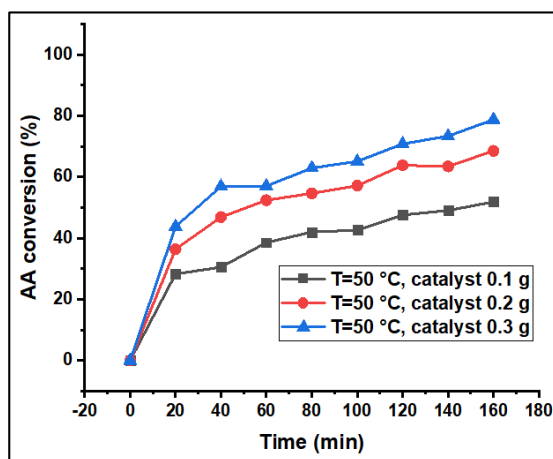


Figure 9. Acetic acid (AA) conversion in the catalyzed esterification reaction (with 0.1, 0.2, or 0.3 g of catalyst) at 50 °C as a function of time.

Catalyst stability and reusability in the esterification of AA was evaluated over at least two cycles, and the results of these experiments are reported in Figure 10. As can be evinced from this figure, by the end of the second run, more than one third of the activity was lost with respect to the first cycle; after 160 min, the AA conversion into the corresponding ester decreased from 94% in the first cycle down to 55% in the second cycle. A comparable behavior has been reported by Aboelhassan et al. [12] in the esterification of linoleic acid with ethanol. The cause of such deactivation was unclear but, it could be the result of incomplete regeneration of the H^+ active sites of the sulfonic groups those are apparently the most important parameter for the catalytic activity [10,12], or of the detachment of the polymer chains from the silica support [1]. This phenomenon necessitates further future investigation. However, the regeneration protocols of alike solid catalysts reported in the literature suggest either the use of diluted acids such as HCl [2] or the sequential wash using polar and non-polar solvents such as methanol and *n*-hexane [12], respectively followed by water, to assure the removal of embedded residues of both reactants and products. Accordingly, the regeneration protocol of SBA-15-PSSA as well as its reusability conditions have to be optimized further in the future.

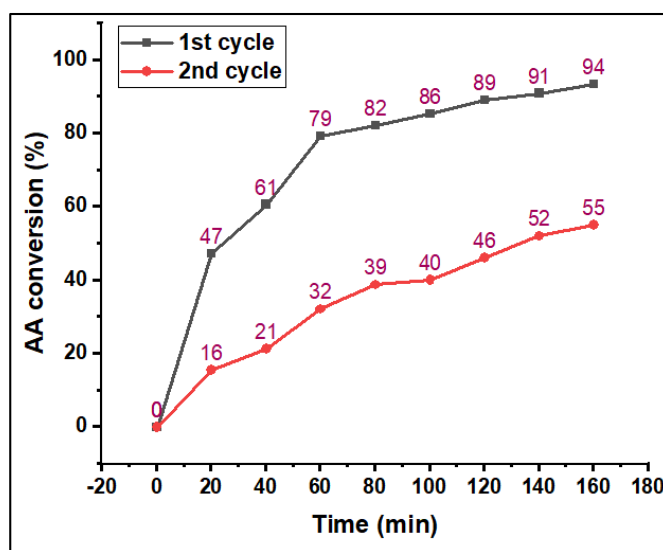


Figure 10. Reusability of catalyst SBA-15-PSSA after two catalytic cycles. Reaction conditions: 0.1 g of catalyst, 80 °C reaction temperature, 160 min reaction time. SBA-15-PSSA/acetic acid (AA) = 10.7 wt%, *n*-heptanol/AA = 4.97 mol ratio. SBA-15: pore-expanded mesoporous silica; SBA-15-PSSA: SBA-15-supported polystyrene sulfonic acids.

4. Conclusions

Catalyst SBA-15-PSSA was successfully prepared implementing a four-step protocol: production of mesoporous and high surface area SBA-15, grafting of APTS as a source of the amine functionality used for the subsequent immobilization of BMPB acting as the ATRP initiator intermediate, and 4-styrenesulfonate polymerization to produce the target catalyst. The catalyst's structural properties, determined by FTIR, TGA/DTA, BET, and TEM, confirmed its potential as an effective catalyst. The catalytic performance was assessed performing the esterification of acetic acid and *n*-heptanol as a model reaction. Results indicated the catalytic activity to steadily increase with increasing temperature, catalyst dose, and reaction time. The esterification kinetic was initially fast with curvature behavior steadily progressed afterward. At high temperature (110 °C), almost 100% of acetic acid underwent conversion within the first 20 min of the reaction. The acetic acid conversion percentage observed for the catalyzed reaction was 6.4 times larger than that observed for the uncatalyzed counterpart. Reusability experiments indicated the catalyst to display low stability; however, regeneration conditions have to be optimized further. In summary, SBA-15-PSSA, as prepared in this work, is an esterification catalyst with high application potentials. Furthermore, it could be exploited as a green and highly efficient solid acid catalyst in, for example, the production of biodiesels from the inexpensive and widely available waste biomass; therefore, additional efforts should be dedicated to fully understand its properties.

Author Contributions: Conceptualization, A.A.A. and F.A.A.; Data curation, A.A.A.; Formal analysis, Y.M.M. and A.-B.A.-O. Funding acquisition, A.A.A. and F.A.A.; Investigation, Y.M.M. and A.-B.A.-O.; Methodology, Y.M.M.; Project administration, A.A.A.; Software, A.-B.A.-O.; Supervision, A.A.A.; Visualization, A.-B.A.-O.; Writing—original draft, A.-B.A.-O.; Writing—review & editing, A.-B.A.-O. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to acknowledge the Researchers Supporting Project (RSP-2020/155), King Saud University, Riyadh, Saudi Arabia.

Conflicts of Interest: The authors declare no conflict of interest.

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