

Sulfonated Hypercrosslinked Polystyrene: Synthesis, Characteristics and Use in the Process of Conversion of Fructose to Levulinic Acid

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Levulinic acid is a precursor to a large number of industrially important chemicals and is widely used in the production of lubricants, chiral reagents, resins, biologically active substances, adsorbents, electronics, and batteries. Levulinic acid is a product of the dehydration of fructose, and acids play an important role in this reaction. High yields of levulinic acid were obtained using sulfuric acid. However, the use of inorganic acids is becoming less attractive, and solid acids may become a viable alternative. A very promising direction in this area is the use of hypercrosslinked polymers, which have many unique properties: large specific surface area, controlled porosity, possibility of modification, exceptional adsorption, chemical and thermal stability, and low cost. This study proposes a method for the synthesis of sulfonated hypercrosslinked polystyrene – SMN270. The synthesized samples were characterized by various methods and tested in the conversion reaction of fructose to levulinic acid. When using SMN270, LA yields of up to 39.5 % were obtained at 180 °C in 1 h with 100 % conversion of the fructose. SMN270 can be an effective replacement for environmentally hazardous mineral acids. The results of the study can become the basis for the creation of stable and efficient solid acid catalysts for the conversion of plant biomass into valuable chemicals.

1. Introduction

Levulinic acid (LA) is one of the most valuable chemical compounds that can be obtained from biomass (Kohli et al., 2019). In 2004, the US Department of Energy (DOE) compiled a list of biomass-derived chemicals with the highest added value: 1,4-diacids (succinic, fumaric, malic acids), 2,5-furandicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, 3-hydroxybutyrolactone, glycerol, sugar alcohols (sorbitol, xylitol, etc.), and levulinic acid (Werpy et al., 2004). Due to the presence of two highly active functional groups (carbonyl and carboxyl), LA easily undergoes oxidation, reduction, esterification, substitution, and condensation reactions, which makes it a very valuable raw material (“platform compound”) (Yan et al., 2015). LA is a precursor to a large number of reagents necessary for the chemical industry and is widely used in the production of lubricants, fuel additives, solvents (Demolis et al., 2014), chiral reagents, resins, pharmaceuticals, and biologically active substances (Bozell et al., 2000), adsorbents, electronics, and batteries (Lopes et al., 2020).

In a simplified form, the process of formation of LA from fructose is presented in Figure 1. In the first stage, in the presence of an acid catalyst, fructose loses three molecules of water and is converted into 5-hydroxymethylfurfural (5-HMF) (Liu et al., 2020). As a result of subsequent reactions of keto-enol isomerization, dehydration, and rehydration, 5-HMF forms molecules of formic and levulinic acids (Badgujar et al., 2019).

Mineral acids are very effective catalysts for these processes. The most commonly used are H₂SO₄ and HCl (Liu et al., 2020), of which H₂SO₄ has the maximum efficiency in the process of converting fructose into LA since its activation energy for fructose dehydration is lower than that of HCl (Fachri et al., 2015). With the

introduction of increasingly stringent environmental standards, the use of inorganic acids is becoming less attractive, and solid acids may become a viable alternative. To date, a fairly large number of solid acid catalysts have been proposed for the process of converting carbohydrates into LA. For example, based on modified zeolites such as ZSM-5 (Kislitsa et al., 2021), ETS-10 (Xiang et al., 2017), and Fe/HY (Ramli and Amin, 2015). Zr-containing catalysts are distinguished by good activity, with the use of which, in particular, a 53.9 % yield of LC from cellulose was obtained (Joshi et al., 2014). High yields of LA from various substrates (more than 50 %) are demonstrated by acid catalysts based on polymers, such as Amberlyst 70 (Alonso et al., 2013), Amberlyst 15 (Ma et al., 2021), Nafion SAC 13 (Hegner et al., 2010) and others.

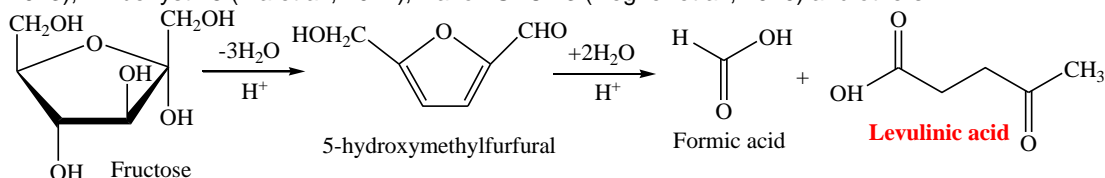


Figure 1: Scheme of conversion of fructose into levulinic and formic acids in the presence of acid catalysts

From this point of view, the possibility of using sulfonated hypercrosslinked polystyrene (HPS) as an acid catalyst is of interest. HPS are rigid polymer networks, the nature of porosity and specific surface area of which strongly depend on the nature of the starting reagents and the method of synthesis and average 600-2000 m²/g or even more (Ahn et al., 2006). Due to its properties, HPS has gained great popularity in the commercial market. Many companies produce it for use in large-scale sorption processes in the chemical, food, and water treatment industries, for example, Purolite (Hypersol-Macronet, MN series), Dow Chemical (Optipore), Lanxess (Lewatit VP OC 1163 and S 7768), etc. (Huang and Turner, 2017). Thanks to the possibility of functionalization, the field of application of hypercrosslinked polymers is significantly expanding. For example, a series of methylamine-modified hypercrosslinked resins have been proposed for the selective sorption of citric acid (Peng et al., 2020), and the sulfonated polymer has been successfully used in redox flow batteries (Branchi et al., 2018). To date, extensive practical experience has been accumulated in the use of HPS for the synthesis of highly efficient heterogeneous catalytic systems for various purposes (Manaenkov et al., 2023).

Given the good efficiency in the process of fructose dehydration, solid acid catalysts based on HPS can become an excellent alternative to mineral acids and existing analogs due to their low cost, simple sulfonation procedure, and stability under hydrothermal conditions. In this study, a method for sulfonation of commercial hypercrosslinked polystyrene MN270 (Purolite, UK) was proposed, the results of its physicochemical studies were presented, and the possibility of its use as an acid catalyst in the dehydration reaction of fructose with the formation of levulinic acid was shown.

2. Experimental

2.1 Materials and methods

The starting material was commercial non-functionalized hypercrosslinked polystyrene MN270 (Purolite, UK), which is a sorbent whose porosity is micro-mesoporous with a predominance of micropores. Also used in the study were concentrated sulfuric acid (99.999 %, Sigma-Aldrich, USA), 1,2-dichloroethane (99.8 %, Sigma-Aldrich, USA), ethanol (95 %, Acros Organics, USA), D-fructose (≥ 99 %, Sigma-Aldrich, USA), distilled water.

2.2 Synthesis of sulfonated HPS

Mix 0.5 g of ground HPS ($< 45 \mu\text{m}$) with 5 mL of 1,2-dichloroethane in a round bottom flask. The mixture is stirred on a magnetic stirrer for 1 h at 25 °C. Then 25 mL of concentrated H₂SO₄ is added to the mixture in small portions and heated to 80 °C. The mixture is kept at a given temperature for a given time with vigorous stirring (≈ 1000 rpm).

The suspension is then very carefully poured into a heat-resistant glass filled with crushed ice (~ 300 mL distilled water). The sulfonated polymer is separated on a paper filter in a Buchner funnel, washed with a large amount of distilled water (≈ 1 L), ethanol and dried for 24 h at a temperature of 65 °C.

2.3 Characterisation of catalysts

The specific surface area and porosity of the magnetic materials and the initial sorbents were determined by low-temperature nitrogen adsorption using a Beckman Coulter SA 3100 surface analyzer (Coulter Corporation, USA). The texture characteristics of the samples were calculated by mathematical processing of nitrogen adsorption isotherms in accordance with the Brunauer-Emmett-Teller (BET), Langmuir, and de Boer-

Lipens (t-plot) models. The study of samples by NH_3 chemisorption was carried out using a Chemosorb 4580 gas chemisorption analyzer (Micrometrics, Norcross, GA, USA). Thermogravimetric analysis of the samples was done using thermogravimetric analyzer TG 209 IRIS, equipped with differential scanning calorimeter DSC 204 PHOENIX (Netzsch, Selb, Germany). All measurements were carried out in accordance with operating procedures on the appropriate equipment recommended by the manufacturer. To reduce the influence of random errors on the final result, experiments, and related measurements were carried out in at least two repetitions.

2.4 Catalyst testing procedure and product analysis

Our tests were conducted in a 50-cm³ high-pressure steel reactor (Parr Instruments, Moline, USA) equipped with a PARR 4843 controller and a propeller stirrer. In a typical test, the fructose, the catalyst, and 30 mL of distilled water were placed into the reactor. The reactor was triply purged with nitrogen at a pressure of 10 bars; heating and stirring (≈ 100 rpm). After reaching the operating temperature, the stirrer speed was increased to 600 rpm to transfer the reaction to the kinetic region. This moment served as the beginning of the countdown of the experiment. At the end of the experiment, the reactor was quickly cooled, the catalyst was separated by filtration through a paper filter, and the catalysate was diluted to 100 cm³ in a volumetric flask. The analysis of the liquid phase of the catalysate was carried out by the method of capillary zone electrophoresis under the following conditions: the background electrolyte is an aqueous solution of benzoic acid (10 mM), cetyltrimethylammonium bromide (0.25 mM) and 2.5 % KOH for pH correction (7.0); analysis temperature 20 °C; detector wavelength 254 nm (indirect detection); voltage -25 kV; inner diameter of the capillary is 75 μm ; capillary length up to the detector 50 cm; hydrodynamic sample injection for 5 s at a pressure of 30 mbar. Analyzes were carried out using the Kapel-105M capillary electrophoresis system (Lumex, St. Petersburg, Russia).

3. Results and discussions

As a result of varying the sulfonation conditions of the initial HPS, five samples of acid catalysts were synthesized: SMN270-1H, SMN270-2H, SMN270-4H, SMN270-6H (samples were obtained at different sulfonation times - 1, 2, 4, and 6 h) and SMN270-2H-60 (sample obtained by sulfonation in sulfuric acid at 60 °C). The synthesized samples were characterized by low-temperature nitrogen adsorption (Table 1).

Table 1: Characteristics of the porosity of the initial and sulfonated HPS

Sample	S_{BET} , m ² /g	S_{L} , m ² /g	S_{t} , m ² /g	V , cm ³ /g
MN270_initial	1,236	1,380	347 ¹ ; 925 ² ; 1272 ³	0.41
SMN270-1H	687	774	151 ¹ ; 536 ² ; 687 ³	0.24
SMN270-2H	793	894	174 ¹ ; 619 ² ; 793 ³	0.28
SMN270-4H	641	749	124 ¹ ; 539 ² ; 663 ³	0.24
SMN270-6H	715	835	132 ¹ ; 602 ² ; 734 ³	0.27
SMN270-2H-60	690	798	130 ¹ ; 583 ² ; 713 ³	0.26

¹ specific surface area calculated by the t-graph model; ² specific surface area of micropores; ³ total specific surface area; S_{L} - specific surface area (Langmuir model); S_{BET} - specific surface area (BET model); S_{t} - specific surface area (t-graph); V - volume of micropores.

As the results of the study showed, the sulfonation time and reaction temperature do not have a significant effect on the porosity characteristics of sulfonated HPS. In each of the cases presented in Table 1, a decrease in the specific surface area and volume of micropores is observed by approximately 1.5-2 times. However, no clear patterns can be traced. The data obtained from the t-plot model (Table 1) and the appearance of the nitrogen sorption-desorption curves (Figure 2) show that all sulfonated HPS samples retain the same micro-mesoporous character as the original polymer (the curves contain sections characteristic of isotherms of types I and IV according to the Brunauer classification).

It is also obvious that concentrated sulfuric acid in the temperature range of 60-80 °C quickly and easily destroys a certain proportion of the chemical bonds of polymer macromolecules (most likely, some of the methylene "bridges" between aromatic rings are broken), as a result of which the surface area for each sample decreases to close values.

For the effective use of sulfonated HPS as an acid catalyst, an important condition is its thermal stability since the process of conversion of carbohydrates into LA occurs at fairly high temperatures. To assess the thermal stability of SMN270, a thermogravimetric analysis was carried out. The results of the analysis showed that sulfonated polymers are stable up to temperatures of the order of 200-250 °C, while the initial HPS MN270 begins to degrade with intense weight loss only at temperatures above 400 °C. Obviously, this is explained by

the fact that sulfo groups are more thermolabile, and the destruction of the polymer, accompanied by desulfurization (Aleksienko et al., 2004), begins at lower temperatures. The differential curve for sample SMN270-4H clearly shows two peaks. The first peak at a temperature of 100 °C is due to the evaporation of moisture from the pores of the polymer. The second peak at 450 °C appears when intensive destruction of the main polystyrene network begins with the formation of low molecular weight destruction products. Thus, the data obtained indicate the possibility of using sulfonated HPS as an acid catalyst at reaction temperatures up to 200 °C.

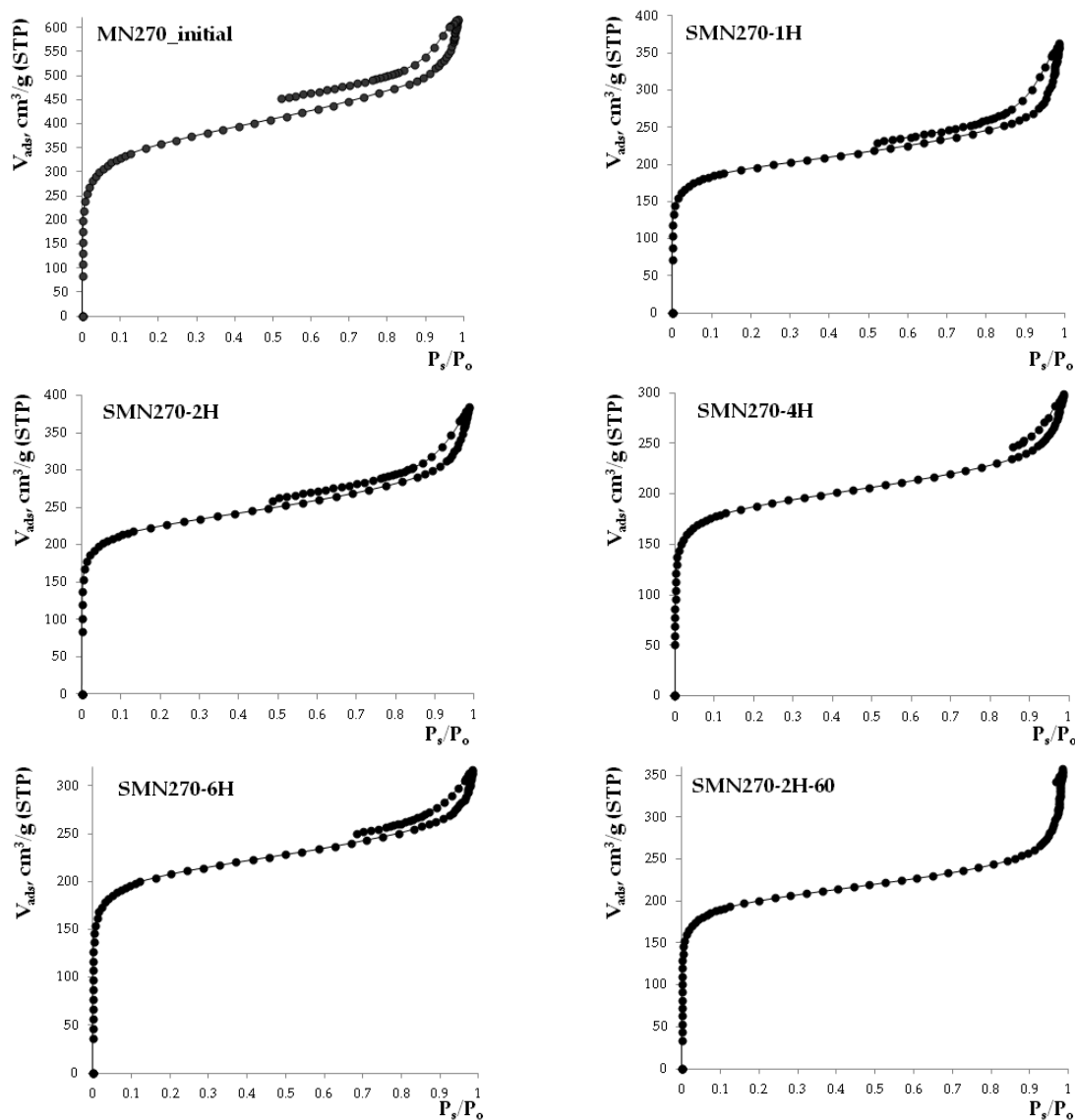


Figure 2: Nitrogen sorption-desorption curves for the original MH270 sample and sulfonated samples based on it, demonstrating that sulfonated polymer samples retain the micro-mesoporous characteristics of the original polymer

The most important characteristic of a solid acid catalyst is the number of active acid sites on its surface. To assess the acidic properties of sulfonated HPS samples, samples were analyzed by NH_3 chemisorption (Table 2). According to the results obtained, with increasing duration of exposure of the initial HPS in sulfuric acid, the number of acid sites on which sorption of ammonia molecules occurs increases significantly. The most dramatic increase is observed in the first two hours of the sulfonation process. Then, gradually, the concentration of acid sites decreases, which may be due to their deactivation as a result of prolonged exposure to concentrated H_2SO_4 .

The synthesized samples of acid catalysts were tested in the conversion reaction of fructose to LA (Table 2).

Table 2: Results of studying samples of original and sulfonated HPS using ammonia chemisorption method, levulinic acid yield and fructose conversion depending on the type of acid catalyst

Sample	Amount of desorbed NH ₃ in the range of 100-250 °C, mM/g	LA Yield (% of theoretical maximum)	Fructose conversion, %
MN270_initial	0.02	4.4	100
SMN270-1H	24.0	38.5	100
SMN270-2H	47.0	34.7	100
SMN270-4H	34.0	33.3	100
SMN270-6H	26.0	34.8	100

180 °C; 3 h; N₂ 10 bar; 0.2 g catalyst; 0.2 g fructose; 30 mL H₂O.

Test results showed that all samples of sulfonated HPS have similar activity, however, when using the SMN270-1H catalyst, the LA yield is several percent higher and approaches 25 %. Fructose conversion in all cases was 100 %. When using unmodified HPS MN270 as a catalyst, yellow-brown solutions with an odor characteristic of sugar caramelization products are formed. When using sulfonated catalysts, clear, uncolored solutions are formed. It is obvious that treatment of the initial HPS with sulfuric acid leads to a sharp, approximately eightfold, increase in the yield of LA, which clearly indicates the key role of acid sites (in this case, sulfo groups) in the reaction of conversion of fructose to LA. At the same time, a clear effect of sulfonation time on the yield of LA was not revealed, which indicates the need for further research and optimization of fructose conversion reaction conditions to increase the yield of levulinic acid. In particular, optimization of the reaction time made it possible to increase the LA yield to 39.5 % (Table 3).

Table 3: Dependence of LA yield and fructose conversion on reaction time

Reaction time, h	LA Yield (% of theoretical maximum)	Fructose conversion, %
0.5	33.4	90.4
1.0	39.5	100
2.0	37.0	100
3.0	38.3	100

180 °C; N₂ 10 bar; 0.2 g catalyst; 0.2 g fructose; 30 mL H₂O.

The obtained result is very promising in comparison with the results obtained, in particular, when using ZSM-5 zeolites (LA yield up to 20 %), sulfonated tetrafluoroethylene Nafion SAC-13 (LA yield up to 32.5 %) (Acharjee and Lee, 2018) or ion exchange resin Amberlyst-15 (LA yield up to 52 %) (Son et al., 2012) as acid catalysts.

4. Conclusions

This study proposes a simple and inexpensive method for the synthesis of solid acid catalysts based on sulfonated commercially available hypercrosslinked polystyrene MN270. The synthesized samples were characterized by various methods and tested in the conversion reaction of fructose to LA. It has been shown that sulfonation of a polymer in concentrated H₂SO₄ leads to at least a thousandfold increase in the concentration of acid sites on its surface. The samples themselves retain their micro-mesoporous character when the specific surface area decreases from 1200 to 650-750 m²/g and are thermally stable up to a temperature of 200 °C. It was shown that the sulfonation time and process temperature do not have a noticeable effect on the catalytic properties of SMN270. When using SMN270 in the fructose dehydration reaction, LA yields of up to 39.5 % were obtained with 100 % conversion of the original sugar. Obviously, further research should be aimed at optimizing reaction conditions to increase the yield of LA, as well as studying the possibility of regeneration and reuse of catalysts. It can be assumed that solid acid catalysts based on HPS can become an effective replacement for mineral acids due to their availability, ease of synthesis, high yields of LA, safety for the environment, and the absence of problems with equipment corrosion. Thus, the results of the study can become the basis for the creation of effective technologies for the catalytic conversion of plant biomass into valuable chemicals.

Acknowledgments

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