

# Set of Acidic Resin Catalysts To Correlate Structure and Reactivity in Fructose Conversion to 5-Hydroxymethylfurfural

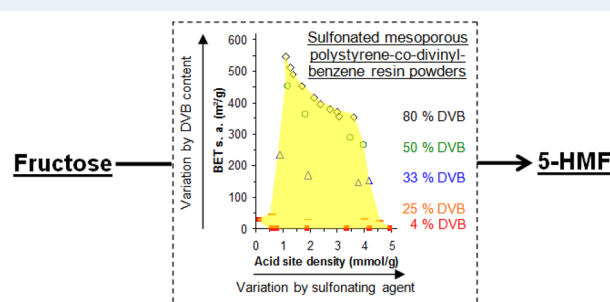
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**ABSTRACT:** A new synthetic route to acidic polystyrene-*co*-divinylbenzene resin catalysts allows systematic variation of cross-linker content, porosity, and acid site density. These resins are prepared in the form of powders by nanocasting, and the acid site density and the distribution of the acid sites in the prepared catalysts is controlled by liquid phase sulfonation with adjusted mixtures of sulfuric acid and oleum. This method allows identical synthesis conditions for the entire range of cross-linker content. With this set of model catalysts, the cross-linker content of the resin was found to be the most influential factor for the liquid phase dehydration of fructose to 5-hydroxymethylfurfural.

**KEYWORDS:** polymer resin, acid catalyst, biomass conversion, dehydration, cross-linker content



The transformation from fossil to renewable hydrocarbon sources for fuels<sup>1</sup> and chemicals<sup>2,3</sup> has been gaining increased attention because the consequences of climate change and limited fossil reserves are becoming more evident.<sup>4</sup> In this context, biomass is of special interest as a renewable carbon resource for sustainable chemical production.<sup>5,6</sup> The development of new catalysts and processes is required because the boundary conditions for the conversion of biomass are so different from those typical of the refining of fossil carbon sources.<sup>7</sup> Biomass processing is often carried out in liquid phase at comparatively lower temperatures, and the starting material is mainly made up of oxygen-rich carbohydrates. A key method of reducing the oxygen content is mild and selective dehydration in an environmentally benign solvent, ideally water.<sup>6,7</sup>

Materials containing either Brønsted<sup>8–10</sup> or Lewis acid sites<sup>11</sup> were proven to be suitable catalysts for the selective dehydration of carbohydrate feedstocks into 5-hydroxymethylfurfural (HMF), a versatile platform molecule.<sup>12</sup> The dehydration of fructose is easier than that of the other feedstocks,<sup>3</sup> and it is therefore an ideal model substrate for the analysis of structure–reactivity relationships of solid acid catalysts for biomass conversion. The solvent strongly influences this reaction, ranging from a HMF yield of up to 100% in DMSO<sup>13</sup> down to 30% in pure water<sup>3</sup> using acidic ion exchange resins. The yield in water can be increased to 72% using an aqueous–organic two-phase system with continuous extraction of the product, as was simulated by Dumesic and co-workers. The organic phase extracts HMF from the aqueous phase that contains the catalyst and fructose, thereby reducing side reactions, such as the rehydration to levulinic and formic acids and the formation of condensation products.<sup>8</sup>

To find a rational approach to the development of improved dehydration catalysts, it is necessary to gain a deeper understanding of the underlying catalytic principles. Studies investigating structure–reactivity relationships of polymer-based solid acid catalysts have focused on gel-type and macroreticular resins in the form of commercially available millimeter-sized beads. Gel-type catalysts typically have cross-linker contents below 12% and no porosity in the dry state. They depend on being swollen by the solvent, thus enabling diffusion of reactants through the polymer matrix. Macroreticular resins additionally contain stable pores in the dry state and have higher cross-linker content.<sup>14</sup> Some studies have revealed an activity dependency on the porosity of the catalyst with other sugars, such as xylose,<sup>15</sup> or sugar polymers, such as inulin.<sup>16</sup> Others indicate a dependency of activity on the cross-linker content of the polymer resins, especially for liquid phase reactions in solvents that are able to swell the resin.<sup>17</sup> Probably the most commonly used commercial ion-exchange resin catalysts are of the Amberlyst or Nafion type. Comparing the two, Nafion catalysts are perfluorinated resin-sulfonic materials and typically have higher stability but lower acid site density than the Amberlyst catalysts that are based on cross-linked sulfonated polystyrene.<sup>18</sup> Both types have been studied in the dehydration of xylose<sup>19</sup> and fructose.<sup>10</sup>

To identify the factors governing reactions catalyzed by acidic resins, we synthesized a systematic series of model catalysts. These are based on sulfonated mesoporous polystyrene-*co*-divinylbenzene (sP-STY-DVB) resin powders.

Received: November 16, 2012

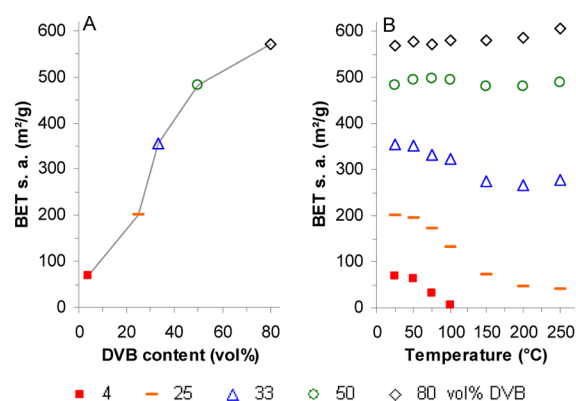
Revised: December 22, 2012

Published: December 24, 2012

They feature tunable acidity of up to 5 mmol/g, specific surface area of up to 500 m<sup>2</sup>/g and a total specific pore volume of up to 1 cm<sup>3</sup>/g. They cover a wide range of cross-linker content up to 80% DVB content. These resins are active, recyclable catalysts suitable for the selective dehydration of fructose to HMF. Furthermore, we analyzed the correlation between cross-linker content, porosity, density of acid sites, and activity of the catalysts.

Porous polymer-based catalysts with a high concentration of sulfonic acid sites are synthesized in two steps: the porous copolymers are made via nanocasting<sup>20</sup> and are subsequently sulfonated to form the active catalyst. In brief, a 2.8 wt % solution of radical initiator 2,2'-azodi(2-methylbutyronitrile) in the desired ratio of monomers STY and DVB<sup>21</sup> is impregnated into dry silica gel<sup>22</sup> calculated to a filling of 80% of the pore volume. Polymerization occurs inside the pore system at 75 °C in a closed stainless steel reactor over a course of 48 h. Selective removal of the silica template<sup>23</sup> produces resin powders of different porosities and specific surface areas dependent on the original STY-to-DVB ratio.

The porosity of the materials increases with the cross-linker content during polymerization, but there is no direct proportionality between the two (Figure 1A). The stability of

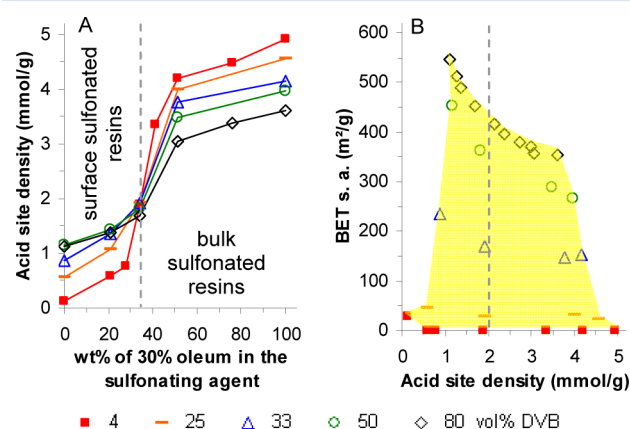


**Figure 1.** Un sulfonated resins. (A) Dependence of the BET surface area of un sulfonated resin on the content of the cross-linker. (B) Temperature stability of the pore system of the different resins as analyzed by nitrogen sorption.

the resins at elevated temperature was analyzed by thermogravimetric analysis (TGA) and nitrogen sorption measurements (Brunauer–Emmet–Teller specific surface area (BET s.a.), total specific pore volume). According to TGA, all resins are chemically stable in air up to 220 °C, above which non-cross-linked parts disintegrate first. Less than 3% residual weight after TGA incidentally also proved that silica had been removed successfully in the preceding leaching step. The temperature stability of the pore system against pore collapse is dependent on the content of DVB and was determined by nitrogen sorption. This is evident from Figure 1B, which plots the BET surface area against the temperature of activation prior to the measurement.<sup>24</sup> For resins with less than 33% content of cross-linker, capillary forces lead to collapse of the pores at temperatures close to the glass transition temperature.<sup>25</sup> This is in contrast to resins that contain more than 50% DVB, which remain unchanged upon heating to the decomposition temperature. No weight loss was observed during heating. Therefore, all changes in BET s.a. are due to restructuring of the polymer.

The polymers were sulfonated<sup>26</sup> by suspension during 1 h at ambient temperature under relatively mild or harsh conditions either in concentrated sulfuric acid (conc H<sub>2</sub>SO<sub>4</sub>, 95–97%) or in 30% oleum,<sup>27</sup> respectively. Intermediate degrees of sulfonation were achieved using mixtures of 30% oleum with conc H<sub>2</sub>SO<sub>4</sub>.

In all reactions, 10 mL of sulfonating agent was used per gram of resin. Dilution in water, filtration, extensive washing, and drying at 50 °C in vacuum made the catalysts ready for use. The acid site density of the resins was determined by titration. It matches with the values calculated from the sulfur content (Schöninger method), and the weight increase of the resin by sulfonation. This indicates that sulfur is present predominantly in the form of SO<sub>3</sub>H acidic sites. There is, surprisingly, no linear correlation between the used fraction of oleum in the sulfonating agent and the resulting acid site density for any of the resins (Figure 2A). Removal of excess SO<sub>3</sub> by residual water



**Figure 2.** Sulfonated resins. (A) Sulfonation diagram of the resins. Acid site density determined by titration with NaOH (aq). (B) Properties of synthesized model catalysts. The colored area indicates the theoretically accessible properties using this synthesis method.

from conc H<sub>2</sub>SO<sub>4</sub> is probably responsible for the slow increase in the acid site density in the left part of the diagram where exclusively the surface of the porous resins is sulfonated.<sup>28</sup> This explains why resins with higher cross-linker content and surface area reach higher acid site densities with sulfonating agents of low oleum content. Above approximately one-third of oleum content in the sulfonating agent, it contains an excess of SO<sub>3</sub>, which is able to permeate the polymer matrix. Hence, the entire bulk of the resin is sulfonated, which explains the sudden increase in the acid site density in Figure 2A for all resins. Saturation to the right of the diagram is explained by the limited number of available sites in the resin. Here, an increasing DVB content reduces the maximum acid site density of the resins, as demonstrated in the right part of the diagram, which is in line with the report by Toro et al.<sup>29</sup>

Pore collapse of the resins during sulfonation is less pronounced at higher cross-linker content. At 80% DVB content, the reduction in BET s.a. can be attributed almost exclusively (95%) to the weight increase by addition of the sulfonic acid groups. A DVB content of 4% results in a total pore collapse on sulfonation. Combining the variability of the BET specific surface area and the acid site density, discussed individually above, gives access to materials within the entire colored area in the BET s.a. vs acid site density diagram of

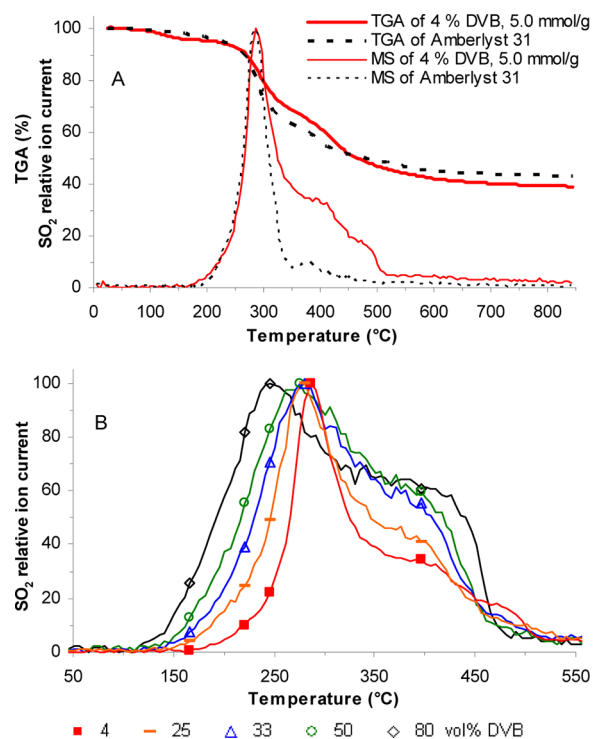
Figure 2B. A wide range of catalysts is thereby prepared in just two steps each.

All of the prepared acidic resins are active catalysts for the dehydration of fructose in water. Their stability is in the same range as that of commercial sP-STY-DVB-based Amberlyst resins (Table 1, Figure 3A). TG/MS analysis in argon (Figure

**Table 1. Characterization of Tested Commercial Catalysts Determined by Titration and Nitrogen Physisorption<sup>a</sup>**

catalyst/DVB content (%)	acid site density (mmol/g)	BET s.a. (m <sup>2</sup> /g)	thermal stability (°C)
Amberlyst 121, 2%	5.1	0	130
Amberlyst 31, 4%	4.9	0	130
Amberlyst 70, 8%	2.6	0	190
Amberlyst 15, 20%	4.5	34	120
Amberlyst 35, 20%	5.0	34	150
Amberlyst 36, 12%	5.2	18	150

<sup>a</sup>The thermal stability is specified by the producer.

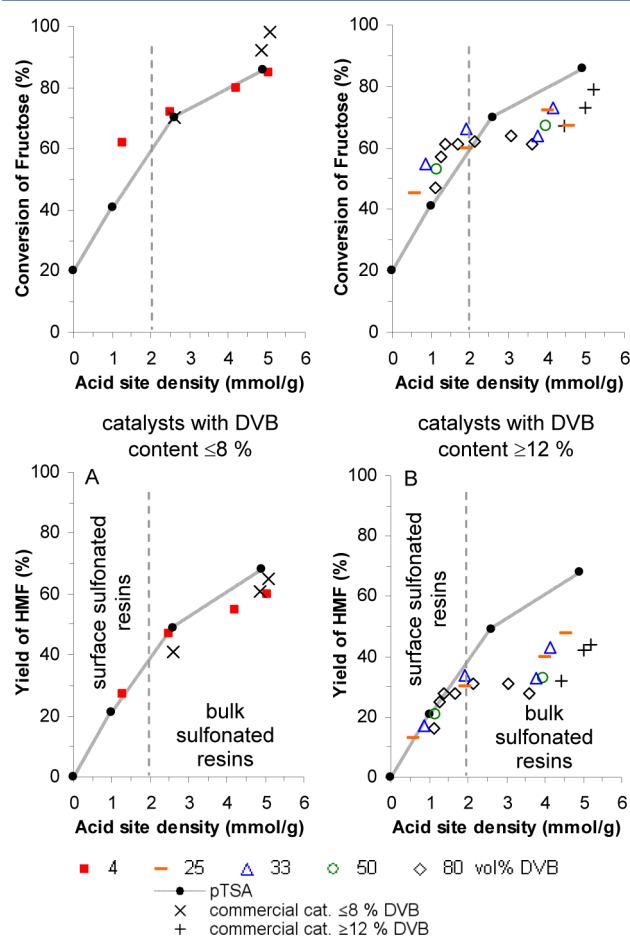


**Figure 3.** TG/MS analysis in argon of sulfonated polymers. The relative ion current is calculated from the absolute ion current of SO<sub>2</sub><sup>+</sup> at  $m/z = 64$  by setting the minimum value of the ion current to 0 and the maximum value of the ion current of the respective measurement to 100. (A) Comparison of commercial Amberlyst 35 with the prepared catalyst having identical DVB content and acid site density. (B) Comparison of prepared catalysts with different DVB contents that were sulfonated with 30% oleum.

3B) shows that the stability of the prepared catalysts increases with decreasing cross-linker content. Although partial leaching of acid sites is observed under the following reaction conditions, the catalyst's stability is sufficient to draw clear conclusions. The sulfur content of the catalyst synthesized with 4% DVB content and 5.0 mmol/g acid site density decreases from 11.9 wt % to 9.1 wt % after four reactions. Accordingly, the yield of HMF decreases from 61% to 34%, which is a somewhat bigger loss than with Amberlyst 31, which shows a

HMF yield drop from 63% to 48% after four runs. Porous catalysts also undergo a reduction in BET s.a. during the reaction. The changes in the material during catalysis are due to partial leaching of sulfonic acid sites and the deposition of humins on the catalyst.

To compare the performance of different catalysts, identical fructose dehydration reactions were performed using the well-established two-phase system.<sup>8</sup> A 50 mL stainless steel batch reactor containing water (3 mL)/catalyst (50 mg)/fructose (300 mg) and 2-methyltetrahydrofuran (20 mL) was heated at a temperature of 130 °C for 1 h. After cooling in an ice bath and removal of the catalyst by centrifugation, the products were quantified by high pressure liquid chromatography. These reaction conditions were chosen to ensure incomplete reaction, since a proper comparison of catalysts is not possible at full conversion. Kinetic analysis demonstrated first-order behavior up to full conversion of fructose. For reaction times longer than necessary to reach full conversion, the HMF yield passes a maximum and decreases slowly with time. Figure 4 shows the conversion of fructose and yield of HMF after 1 h of reaction time plotted against the respective acid site densities for different catalysts. The solid catalysts are benchmarked against



**Figure 4.** Comparison of catalysts in the dehydration of fructose to HMF. The additional symbols are pTSA, (—●—); commercial resin catalysts Amberlyst 70, Amberlyst 31, Amberlyst 121, ≤8% DVB (x); commercial resin catalysts Amberlyst 15, Amberlyst 35, Amberlyst 36, ≥12% DVB (+). In each case, 50 mg of solid catalyst and corresponding molar amounts of pTSA are used. The catalysts were washed and dried before use.



the performance of the molecular catalyst *para*-toluenesulfonic acid (pTSA).

The following correlations between the structure and activity of the catalysts were observed. The prepared catalysts follow the same principles as the commercial catalysts. The dry state porosity of the resins plays a minor role in this reaction, which indicates excellent pore diffusion of reagents in all materials. The conversion of fructose and the yield of HMF generally increase with increasing density of acid sites in the catalyst. A preliminary experiment with Nafion-NR50 suggests that it has a high activity per acid site. However, Nafion catalysts typically have a lower acid site density, and thus, absolute activity was lower than that of the best resins reported here.

The expected direct correlation between the density of acid sites and the yield of HMF is observed for two groups of catalysts:

First, the correlation is observed for all surface sulfonated resins, independent of their DVB content (Figure 4A and B). As explained above with Figure 2A, the surface of the catalysts is sulfonated predominantly by using low oleum content in the sulfonating agent, affording resins of <2 mmol/g acid site density. As a consequence, all the acid sites are accessible to fructose because of the excellent pore diffusion of the substrate. Thus, the yield of HMF correlates directly with the acid site density for all surface sulfonated catalysts, independent of the DVB content.

Second, the correlation is observed for bulk sulfonated resins with  $\leq 8\%$  cross-linker content, independent of their acid site density (Figure 4A). Bulk sulfonated resins are prepared using high oleum content in the sulfonating agent, affording resins of more than 2 mmol/g acid site density (Figure 2A). All tested commercial catalysts are bulk-sulfonated. Swellability in water and diffusion through the polymer matrix becomes an additional factor for the accessibility of the acid sites located inside the pore walls. This influences the apparent rate of dehydration. The diffusion coefficient through the polymer matrix is dependent on the cross-linker content and decreases strongly above 8%.<sup>30</sup> The tested resins that have a cross-linker content of <8% are highly swellable in water. Therefore, most acid sites are accessible to fructose, which allows for the same correlation of HMF yield and acid site density as for the molecular catalyst pTSA over the entire range of sulfonation degrees (Figure 4A). As a consequence, all acid sites are considered to be equal in terms of catalytic performance and are to be distinguished only by accessibility to the substrate. The resin catalysts can be described as an immobilized form of pTSA.

In summary, we present the synthesis and characterization of a systematic set of acidic polymer resin catalysts with tunable porosity, specific surface area, and density of acid sites. Linking the performance of these catalysts in the dehydration of fructose with their individual properties makes it possible to rationalize the best resin catalyst for this reaction. The dehydration of fructose in the aqueous phase is ideally catalyzed by highly acidic resins with low cross-linker content (<8%), which therefore contain a high density of accessible sulfonic acid sites. In the aqueous phase, the porosity of the catalysts in the dry state has little influence on the conversion of small substrates; however, this may be different for the conversion of large substrates, reactions in hydrophobic solvents, or gas-phase reactions. The presented series of catalysts establishes an ideal set in the search for the best resin catalyst for a desired reaction.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was funded by the European Research Council (Grant No. 247081) and by the Excellence Initiative of the German federal and state governments as part of the Cluster of Excellence "Tailor-Made Fuels from Biomass". We are also very grateful to the HPLC department of the institute for the analysis of the samples.

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- (21) Technical DVB of a purity of 80% is distilled and used. The remaining 20% are mostly ethylstyrene. This is taken into account when calculating the content of the cross-linker.
- (22) Silica gel was acquired from Sigma-Aldrich as TLC high purity grade. The particle diameter is 5–25  $\mu\text{m}$ . The total pore volume was determined at 0.74  $\text{cm}^3/\text{g}$ ; the BET s.a., at 268  $\text{m}^2/\text{g}$ ; and the BJH average pore diameter, from the desorption branch at 8 nm by nitrogen physisorption.
- (23) Leaching of silica with either NaOH solution (1 M;  $\text{H}_2\text{O}/\text{EtOH}$ , 1:1) during 48 h ( $\geq 25\%$  DVB) or 10% hydrofluoric acid solution during 2 h (<25% DVB) at ambient temperature. The pure

polymer is filtered, washed extensively with water and ethanol, and dried.

(24) The sample was activated at the specified temperature for 1 h in vacuum previous to the measurement.

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(27) The term  $x\%$  oleum is equivalent to an excess of  $x$  wt %  $\text{SO}_3$  dissolved in conc  $\text{H}_2\text{SO}_4$ , forming a solution of oligosulfuric acids ( $\text{H}_2\text{S}_n\text{O}_{3n+4}$ ), free  $\text{SO}_3$ , and  $(\text{SO}_3)_3$ .

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