Supporting Information

Polystyrene-Based Catalysts with Simultaneous Brønsted and Lewis Acidity for Hydroxymethylfurfural Production from Starch: Molecular Weight and Solvent Effects

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Sulfonation Degree of PSSA Catalysts

The sulfonation degree (SD), or percentage of sulfonated aromatic rings in polystyrene, of PSSA catalysts was calculated using the equation proposed by Bekri-Abbes et al.,[1, 2] assuming that all S atoms were present as sulfonic groups:

$$SD = \frac{10^{-3}(mmol\,S \cdot g_{cat}^{-1}) \times 104}{1 - (81 \times 10^{-3}(mmol\,S \cdot g_{cat}^{-1}))} \cdot 100 = \frac{10^{-3}(mmol\,H^{+} \cdot g_{cat}^{-1}) \times 104}{1 - (81 \times 10^{-3}(mmol\,H^{+} \cdot g_{cat}^{-1}))} \cdot 100$$

Table S1: Sulfonation degree of PSSA catalysts.

Catalyst	Brønsted acid sites (mmol $H^{+} \cdot g_{cat}^{-1}$)	Sulfonation degree (%)
70-PSSA	4.64	77
200-PSSA	4.88	84
1000-PSSA	4.94	86

Particle Size Distribution by Dynamic Light Scattering (DLS)

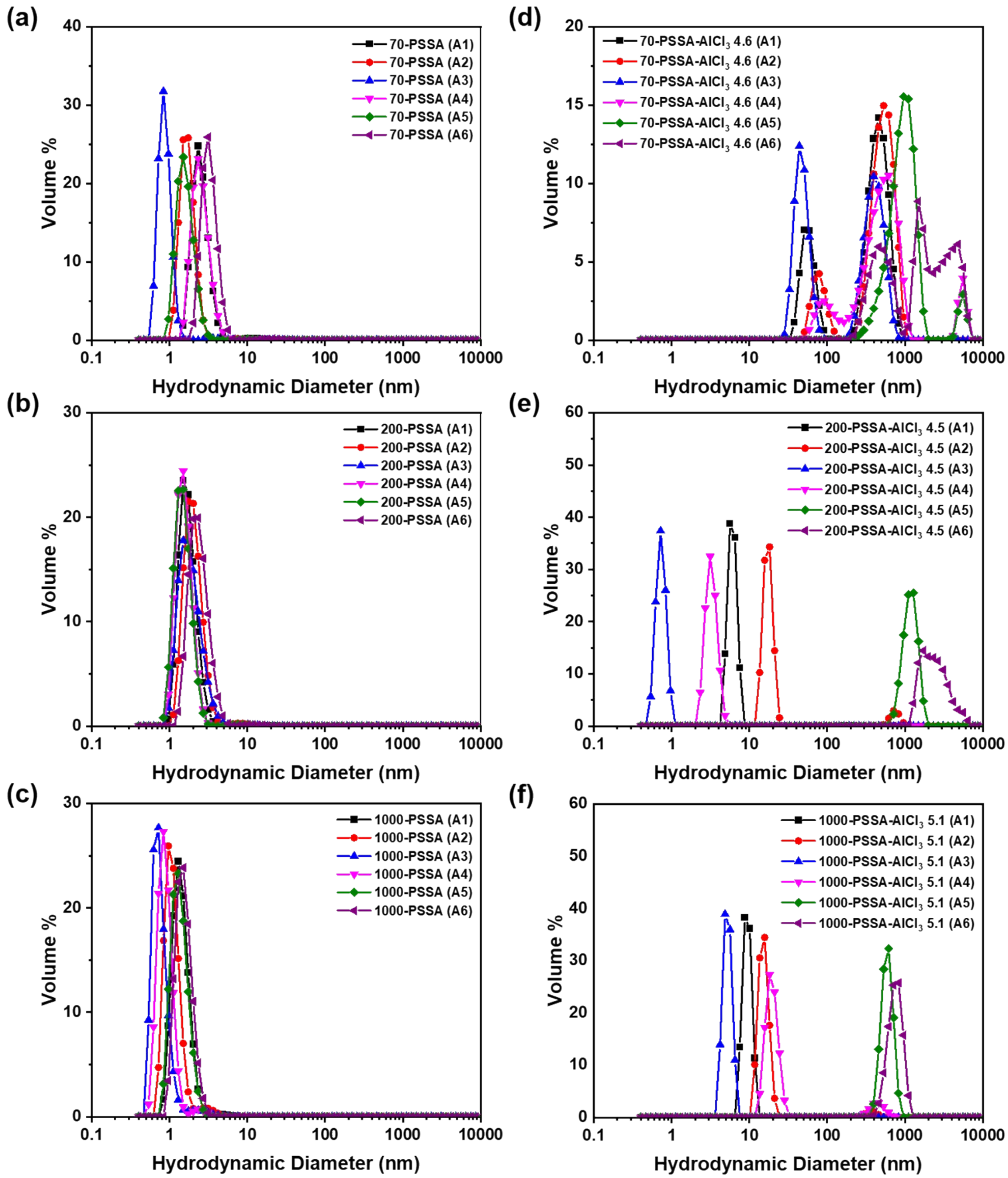

Figure S1: DLS plots obtained with **(a–c)** PSSA and **(d–f)** PSSA-$AlCl_3$ catalysts with different molecular weights.

Fructose and PSSA-$AlCl_3$ Solubility Studies in Water–Acetone Medium

We found that adding 8 mL of acetone to a solution containing 20.5 mg of 200-PSSA and 2 mL of a 25 wt% aqueous solution of fructose resulted in a cloudy solution (**Figure S2**), and even in the absence of a catalyst, fructose precipitated when using a 2:8 (v/v) water–acetone mixture (**Figure S3**).

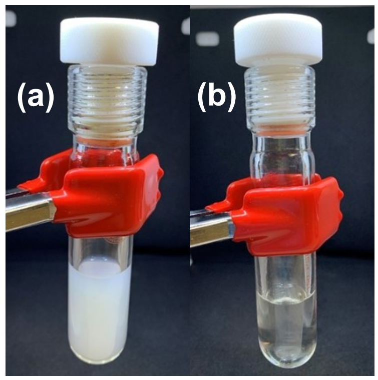

Figure S2: Solubility studies for fructose dehydration with PSSA catalysts: **(a)** 20.5 mg 200-PSSA in 2 mL of a 25 wt% aqueous solution of fructose and 8 mL acetone and **(b)** 20.5 mg 200-PSSA in 2 mL of a 25 wt% aqueous solution of fructose and 5 mL acetone.

Figure S3: Fructose solubility studies in the absence of a catalyst: (a) 2 mL of a 25 wt% aqueous solution of fructose and 8 mL acetone and (b) 2 mL of a 25 wt% aqueous solution of fructose and 5 mL acetone.

Effect of the Solubility on the Catalytic Activity

Production of HMF from Fructose with PSSA Catalysts in a 2:8 v/v Water–Acetone Medium

In order to study the effect of the solubility on the catalytic activity, we also performed the reactions using a 2/8 (v/v) water–acetone reaction medium, in which fructose and PSSA were not fully soluble (**Figure S2** and **Figure S3**). To do so, the total content of Brønsted acid sites was kept constant, and this translated into using different masses of polymer catalysts (21.6 mg of 70-PSSA, 20.5 mg of 200-PSSA, and 20.2 mg of 1000-PSSA). The mixture was then vortexed until dissolution. Then, 8 mL of acetone was added as a cosolvent to increase the reaction rate and minimize the formation of side products.[3, 4] All reactions were performed in ~15 mL Ace pressure tubes (heavy wall borosilicate glass tube, 10.2 cm L × 25.4 mm O.D.) closed with front-seal caps with CAPFE O-rings submerged in a stirred silicone oil bath at 150 ºC (1,000 rpm). As the fructose dehydration reaction proceeds at a fast rate, the reaction time was varied between 10 and 30 min. At the end of the reaction, the catalyst was separated, and the reaction medium was analyzed using the protocol described in the manuscript.

Figure S4 shows the fructose conversion, HMF yield, and levulinic acid yield obtained with 70-PSSA, 200-PSSA, and 1000-PSSA in the production of HMF from a 25 wt% aqueous fructose solution using a 2:8 (v/v) water–acetone medium at 150 ºC. As shown in **Figure S4**, the reaction was very fast, leading to high fructose conversion, as was previously reported in the literature when using water–acetone mixtures.[3, 4] Additionally, the catalytic activity was not affected by the molecular weight of the PSSA catalyst. A maximum fructose conversion of 98 mol% was obtained with an HMF yield of 80 mol% after 30 min of reaction. However, the levulinic acid yield (**Figure S4(c)**) was surprisingly high, as one should expect the hydration of HMF to be hindered at low water–acetone ratios. As an example, Motagamwala et al.[3] reported a

95 mol% fructose conversion and 95 mol% HMF yield when using 50 mM HCl for the dehydration of 25 wt% fructose in a 2:8 (v/v) water–acetone solvent system at 120 ºC. Although our data show a similar fructose conversion, the HMF yield is lower due to the rehydration of HMF to levulinic and formic acids (**Figure S4(c)**).[5] A possible explanation could be that the higher temperature or insoluble sugars could have contributed to lower HMF yields. To verify this hypothesis, we ran additional experiments with a lower water–acetone ratio (2:5 v/v) as described in the manuscript.

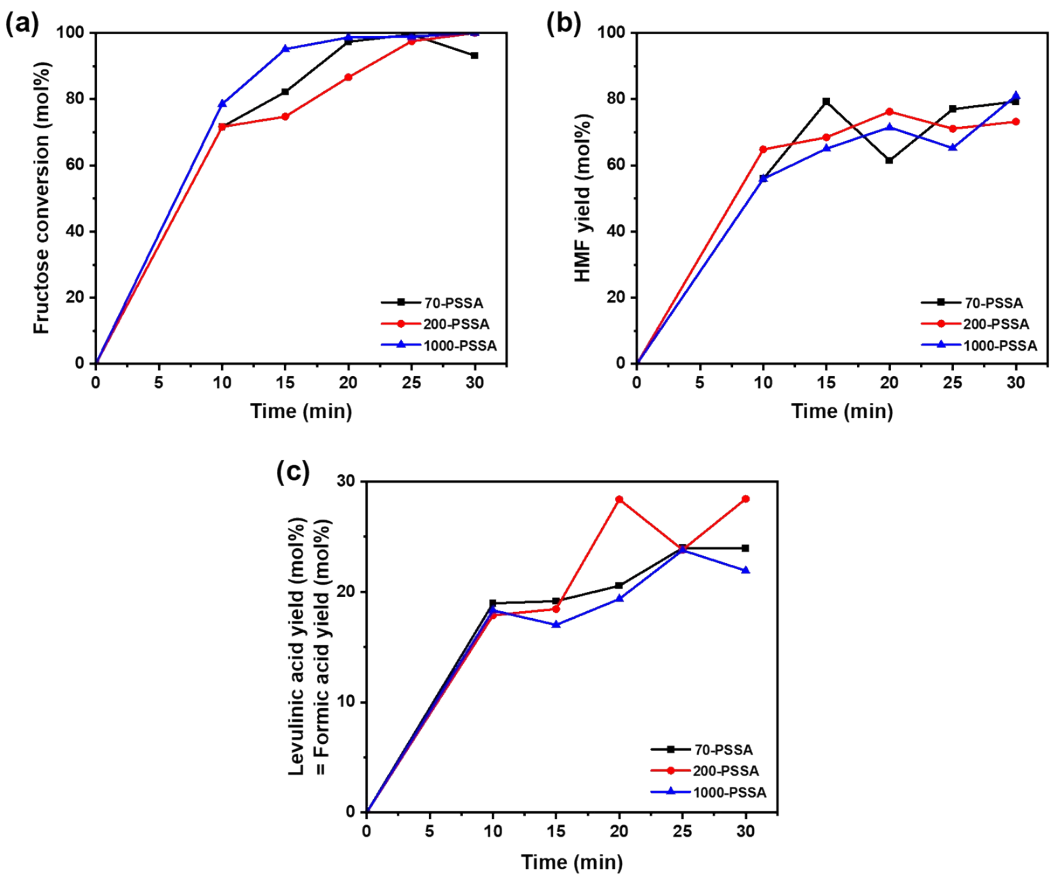

Figure S4: Fructose conversion to HMF in a 2:8 (v/v) water–acetone system. 0.1 mmol H^+ (21.6 mg of 70-PSSA, 20.5 mg of 200-PSSA, and 20.2 mg of 1000-PSSA), 2 mL of a 25 wt% aqueous solution of fructose + 8 mL acetone, 150 ºC, 1,000 rpm: **(a)** Fructose conversion (mol%), **(b)** HMF yield (mol%), and **(c)** Levulinic acid (= Formic acid) yield (mol%).

Effect of the PSSA Catalyst Loading on the Activity and Selectivity in the Dehydration of Fructose to HMF

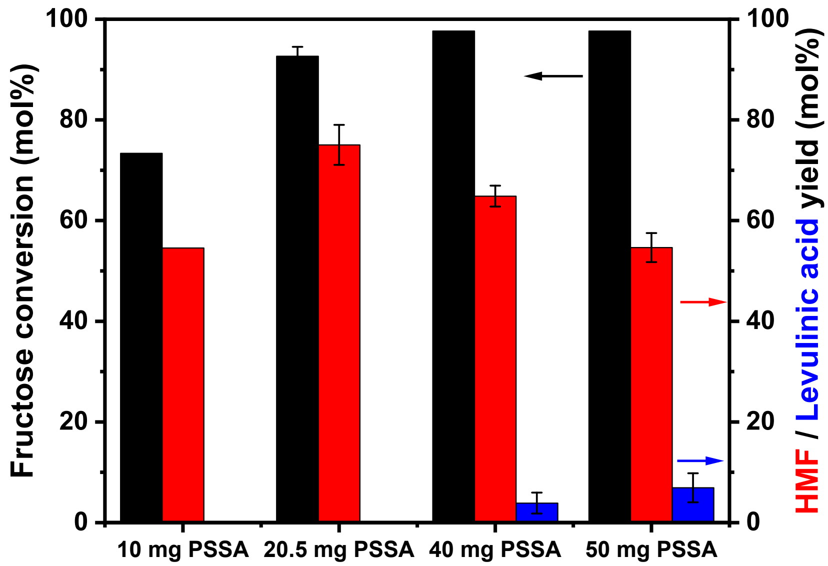

Figure S5: Effect of the 200-PSSA catalyst loading on the activity in the dehydration of fructose to HMF. 10 mg 200-PSSA to 50 mg 200-PSSA, 2 mL of a 25 wt% aqueous solution of fructose + 5 mL acetone (equivalent to 6.5–32.4 mM H^+ reaction medium), 150 ºC, 1,000 rpm. Experiments were repeated at least twice, and the error bars represent the standard deviation from the mean.

Non-Quantified Products on HMF Production from Glucose Using a Water/MIBK–2-Butanol System

We performed a balance to account for the mass of non-quantified products:

Initial mass of glucose – (mass of glucose + fructose + HMF + levulinic acid + formic acid at time *t*).

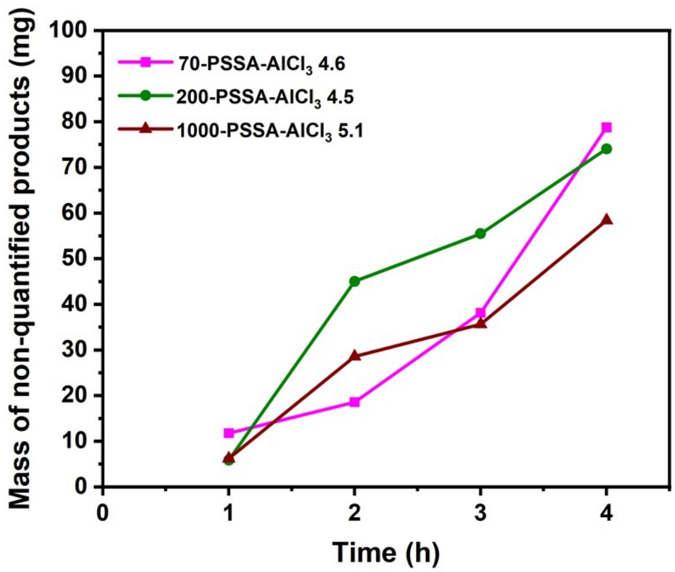

Figure S6: Mass of non-quantified products during the one-pot synthesis of HMF from glucose in a biphasic water/MIBK–2-butanol system. 0.25 mmol H^+ (61 mg of 70-PSSA-$AlCl_3$ 4.6, 55 mg of 200-PSSA-$AlCl_3$ 4.5, and 52 mg of 1000-PSSA-$AlCl_3$ 5.1), 2 mL of a 10 wt% aqueous solution of glucose + 9 mL of a 7:3 (v/v) MIBK–2-butanol mixture, 150 ºC, 1,000 rpm.

Comparing the Activity of the 200-PSSA-$AlCl_3$ 4.5 Catalysts Synthesized Inside and Outside the Glove Box

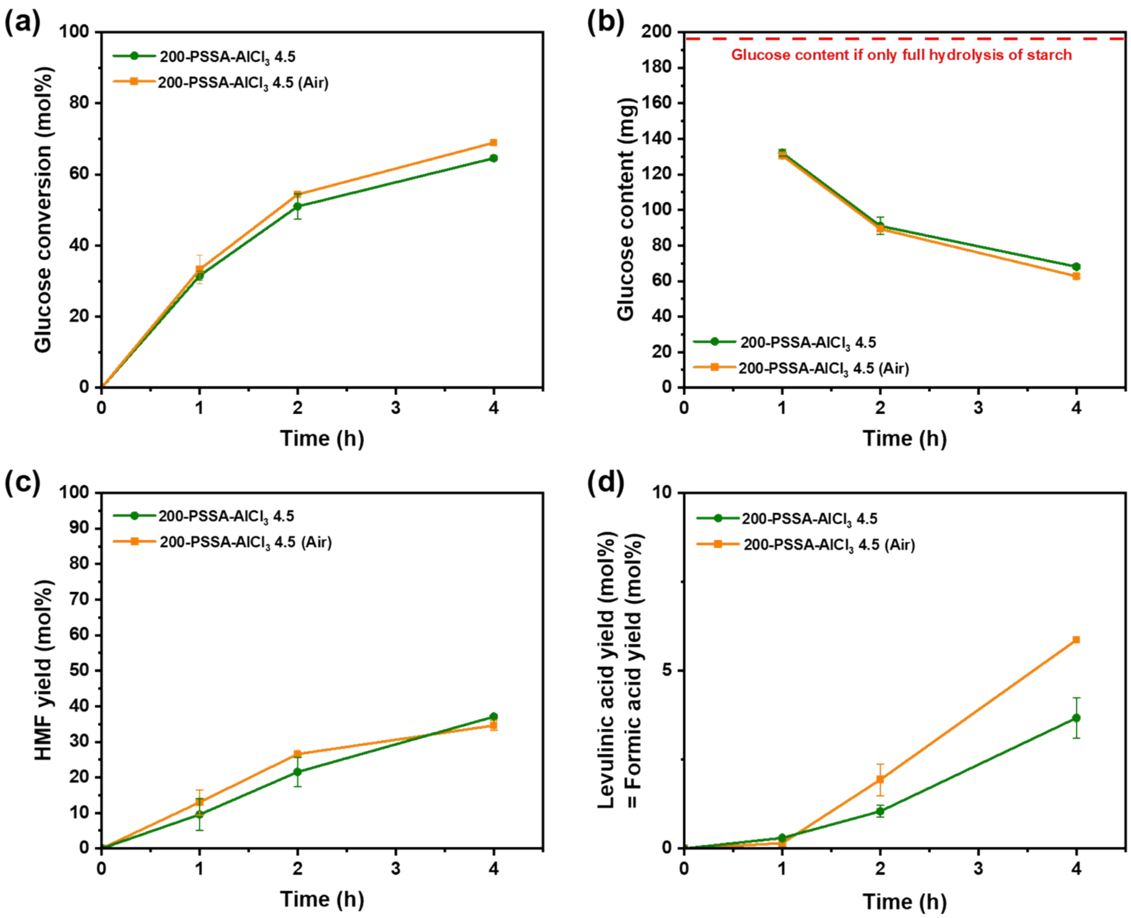

Figure S7: One-pot synthesis of HMF from potato starch in a water/MIBK–2-butanol biphasic system. 0.25 mmol H^+ (55 mg of 200-PSSA-$AlCl_3$ 4.5 and 56 mg of 200-PSSA-$AlCl_3$ 4.5 (Air)) in 2 mL of water + 176 mg starch + 9 mL of a 7:3 (v/v) MIBK–2-butanol mixture, 150 ºC, 1,000 rpm: **(a)** Glucose conversion (mol%), **(b)** Glucose content (mg), **(c)** HMF yield (mol%), and **(d)** Levulinic acid (= Formic acid) yield (mol%). Experiments were repeated at least twice, and the error bars represent the standard deviation from the mean.

Techno-Economic Analysis

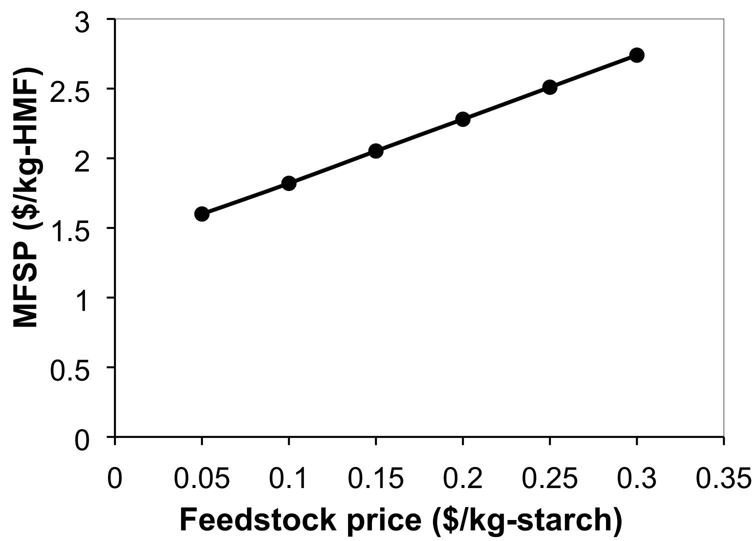

Figure S8: Sensitivity of MFSP to feedstock price.

References

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