Electronic Supplementary Information

Soluble and Reusable Polymer-Based Catalysts with Brønsted and Lewis Acidity for the One-Pot Synthesis of Hydroxymethylfurfural from Glucose

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Volume of Anhydrous Solvents Used for the Synthesis of 200-PSSA-AlCl₃

Catalysts and Phase Diagram Obtained from Solubility Studies

Table S1. Volume of anhydrous solvents (at a constant methanol volume fraction of 0.6) and masses of PSSA and AlCl₃ used to synthesize 200-PSSA-AlCl₃ X catalysts under an inert atmosphere.

200-PSSA-AlCl ₃ X	17.2	7.4	5.0	4.0	3.6	3.0	2.7	1.7	1.2
200-PSSA (g)	1	1	1	1	1	1	1	1	1
AlCl ₃ (mg)	36	72	108	144	180	192	252	288	324
Anh. methanol (mL)	48	96	144	192	240	288	336	384	432
Anh. ethanol (mL)	32	64	96	128	160	192	224	256	288



Fig. S1. Phase diagram used to identify the optimum MeOH/(MeOH+EtOH) volume ratio for the effective synthesis of PSSA-AlCl₃ catalysts.

Analysis of the Aqueous and Organic Phases

An aliquot of the aqueous phase was added to a Vivaspin® 500 centrifugal concentrator to recover the catalyst. Then, aqueous and organic phases were analyzed using a Shimadzu Prominence UFLC equipped with a diode array detector (DAD) and a refractive index detector (RID). Fructose, glucose, and levulinic acid present in the aqueous phase were analyzed using a BIORAD Amine HPX-87H ion column (300 \times 7.8 mm, 9 μ m particle size) at 65 °C, with a 5 mM H₂SO₄ aqueous solution as the mobile phase in isocratic flow mode (0.6 mL/min), using an injection volume of 5 µL. The HMF content in the aqueous and organic phases was determined using an Agilent Zorbax SB-C18 column (4.6 \times 150 mm, 5 μ m particle size) at 35 °C, with the PDA detector at 284 nm, and 2.5 mM H₂SO₄ aqueous solution and 70% acetonitrile in water as the mobile phase in a lowpressure gradient flow mode (0.6 mL/min), with an injection volume of 5 µL. Additionally, the organic phase was also analyzed using a Shimadzu GC-2010 Plus equipped with a flame ionization detector (FID) and a Phenomenex Zebron ZB-WAXplus column (30 m length, 0.25 mm I.D., and $0.25 \,\mu\text{m}$ film thickness) to determine the content of levulinic acid in that phase. Both the injector and the detector were kept at 250 °C, and 1 μ L of the sample was injected. Helium was used as the carrier gas with a constant flow rate of 1.9 mL/min and a split ratio of 1:15. The temperature in the column was initially set at 50 °C for 3 min and subsequently heated to 250 °C with a ramp of 15 °C/min. Then, the final temperature was maintained for 2 min to complete the analysis.

Glucose conversion, HMF yield, and levulinic acid yield were calculated as follows:

 $Glucose \ conversion \ (\%) = \frac{Initial \ moles \ of \ glucose - Final \ moles \ of \ glucose}{Initial \ moles \ of \ glucose} \cdot 100$

$$HMF \ yield \ (\%) = \frac{Moles \ of \ HMF \ produced}{Initial \ moles \ of \ glucose} \cdot 100$$
(2)

Levulinic acid yield (%) =
$$\frac{Moles \ of \ levulinic \ acid \ produced}{Initial \ moles \ of \ glucose} \cdot 100$$
 (3)

For formic acid, another side product from HMF hydration, we assumed the same yield as levulinic acid based on the stoichiometry of the reaction (**Fig. 1**).

Thermogravimetric Analysis of Fresh and Used 200-PSSA-AlCl₃ 4.8 Catalyst



Fig. S2. (a) Weight loss and **(b)** derivative weight loss curves for fresh and used 200-PSSA-AlCl₃ 4.8 catalyst. The curve of the fresh catalyst is slightly different from that in Fig. 6 for 200-PSSA-AlCl₃ 4.0 because this catalyst was prepared in a different batch.

Calculations to Determine the Extent of the Deactivation of the 200-PSSA-AlCl₃ 4.8 Catalyst in the One-Pot Synthesis of HMF from Glucose

As stated in the manuscript, it would be necessary to consider the real mass (without humins) of the used catalyst to properly assess the potential contribution of leaching, and the same consideration would apply to the Al content determined by ICP–OES. However, it is difficult to determine the exact mass of the catalyst at the end due to losses from handling, leaching, and the catalyst gaining mass from the formation of humins. If we focus on the C content in **Table 5**:

200-PSSA-AlCl₃ 4.8 fresh: 42.42 wt% C

200-PSSA-AlCl₃ 4.8 used (after 5 cycles): 53.23 wt% C

it can be concluded that the catalyst gained 10.81 wt% C, which means that 1 g of catalyst would have gained 0.1081 g of C = 9.01 mmol C. Considering $C_{17}H_6O_5$ as a general formula for humins,¹ that would result in 0.159 g humins. As a result, the mass would increase to 1 + 0.159 = 1.159 g, from which (1/1.159) × 100 = 86.3 wt% would be real catalyst. This should be taken into account to recalculate the values in **Table 5** for the used catalyst. To do that, all values were divided by 0.863, which is the real mass of catalyst without humins. Those values are also shown in **Table 5**.

The reutilization started with 330 mg of 200-PSSA-AlCl₃ 4.8, which contained 4.7 mmol H⁺· g_{cat}^{-1} ; therefore, the first cycle was performed with 1.551 mmol H⁺ (**Table 4**). After 5 cycles, the total amount of H⁺ lost was 0.479 mmol H⁺ (**Table 4**); therefore, in the end, the catalyst should have 1.551 - 0.479 = 1.072 mmol H⁺. Assuming that the total mass of the catalyst is ~constant

(not true because some catalyst is lost due to handling, there might be some deactivation, and there is mass gain due to the formation of humins), 1.072 mmol H⁺/0.33 $g_{cat} = 3.25$ mmol H⁺· g_{cat} ⁻¹ (after 5 cycles), which is not too far from the 3.7 mmol H⁺· g_{cat} ⁻¹ value in **Table 5**.

If we look at the S content and assume that mmol H⁺ = mmol S, 4.7 mmol H⁺·g_{cat}⁻¹ = 4.7 mmol S \cdot g_{cat}⁻¹ = 150.7 mg S \cdot g_{cat}⁻¹ = 15.04 wt% S, which is very close to the 14.95 wt% value obtained by elemental analysis (**Table 5**). However, this is not true because AlCl₃ is being incorporated into the PSSA structure. Based on the ICP results (**Table 3** and **Table 5**), when converting 200-PSSA into 200-PSSA-AlCl₃ 4.8, the catalyst loses 5.4 mmol H⁺·g_{cat}⁻¹ – 4.7 mmol H⁺·g_{cat}⁻¹ (value obtained with the second batch used for reutilization) = 0.7 mmol H⁺·g_{cat}⁻¹, but it should not lose any S. Therefore, 1 g of 200-PSSA would contain 5.4 mmol H⁺ = 5.4 mmol S, but 1 g of 200-PSSA-AlCl₃ 4.8 would contain 4.7 mmol H⁺ and 5.4 mmol S. If we take this into account in the previous calculation, 4.7 mmol H⁺·g_{cat}⁻¹ = 5.4 mmol S · g_{cat}⁻¹ = 172.8 mg S · g_{cat}⁻¹ = 17.28 wt% S, which is still not too far from the 14.95 wt% value obtained by elemental analysis (**Table 5**).

As 0.479 mmol H⁺ (30.9% of the initial number of moles of H⁺) was lost after 5 cycles (**Table 4**), if we assume that all is due to leaching of the sulfonic groups, we should expect the S content to be reduced at the same rate (0.479 mmol S after 5 cycles). Taking into account that the fresh catalyst contained 14.95 mg S/100 mg catalyst × 330 mg catalyst = 49.3 mg S = 1.54 mmol S, and that it should have lost 0.479 mmol S after 5 cycles, it should contain 1.54 - 0.479 = 1.06 mmol S = 34 mg S at the end. Assuming that the total mass of the catalyst is ~constant (not true because some catalyst is lost due to handling, there might be some deactivation, and there is mass gain due to the formation of humins), 34 mg S/330 mg catalyst × 100 = 10.3 wt% S, which is close to the

11.02 wt% value in **Table 5**. Therefore, it is likely that some leaching of the entire sulfonic groups is happening. However, it cannot be discarded that some loss of H⁺ might derive from the solvation and hydrolysis of coordinated aluminum chloride.

Additionally, it can be concluded that the loss of Al after 5 cycles is not due to the gain of catalyst mass, as that would be 0.66 wt% in contrast to the 0.57 wt% value obtained by ICP–OES (**Table 5**). As a result, the possibility of some Al leaching can neither be discarded.

Reference

 T. M. C. Hoang, E. R. H. van Eck, W. P. Bula, J. G. E. Gardeniers, L. Lefferts and K. Seshan, *Green Chemistry*, 2015, 17, 959-972.