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Supporting Information

Borohydride Hydrolysis Using a Mechanically and Chemically Stable Aluminium-Stainless Steel Porous Monolith Catalyst Made by 3D Printing

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<u>3D printing parameters</u>

Incorporating aluminium into the printing powder mixture required optimisation of the printers laser parameters. This was to ensure that the Al formed a proper melt and was alloyed to the stainless steel, rather than being left in its powder form where it could not be leached. The contour exposure parameters (laser power and laser speed) remained the same in order to maintain structural integrity of edges. However, the surface area parameters (laser power and laser speed) were explored as these are the most important process parameters to ensure overall structural integrity. The other printer parameters (layer height, spot size, hatch distance) were not changed as the particle sizes within the powder supply were kept the same.

We started by decreasing laser power from 90 W and increasing laser speed from 600 mm/s. Increasing power allowed for a maintained structural integrity. Decreasing laser power to 60 W or lower consistently resulted in structural failure. This was particularly noticeable when removing the print pieces from the stainless steel plate, where the pieces would disintegrate. Increasing the laser speed also showed a loss in structural integrity, as a full melt could not be achieved. Overall, a laser power of 90.25 W and a laser speed of 600 mm/s was found to be the optimum combination for surface area exposure when incorporating aluminium with stainless steel.

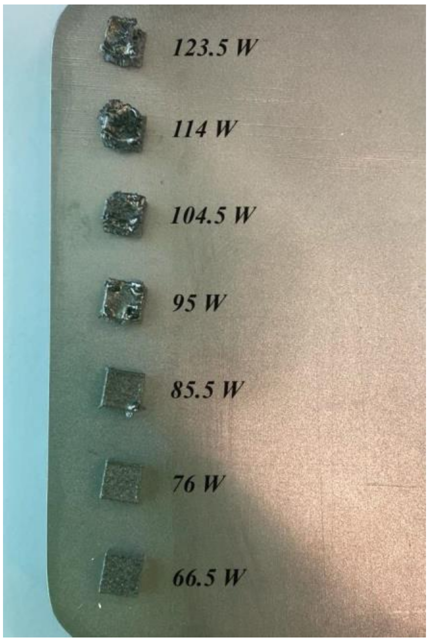

Figure S1. Photo of Al-SS cubes printed on a stainless steel plate at different laser powers. This clearly demonstrates how, even on the printing plate, the laser power influences the structural integrity of a printed piece.

Table S1. Description of printing parameter combinations tested on 20% Al and stainless steel monoliths. This used both contour and surface area exposure in the printing process.

Laser power (W)	Laser scan speed (mm/s)	Structural integrity	Mass loss after leaching (%)
35	600	Failed	-
40	600	Failed	-
45	600	Failed	-
50	600	Failed	-
55	600	Failed	-
60	600	Failed	-
80.75	600	Maintained	5.91
80.75	630	Maintained	5.18
80.75	660	Maintained	8.33
80.75	690	Maintained	7.83
85.5	600	Maintained	5.73
90.25	600	Maintained	3.39

Leaching parameters

Leaching aluminium from the macroscale alloyed monoliths required testing due to the low surface area (in comparison to leaching from powders). Firstly, a range of leaching solutions were made and tested with Al powder to confirm that a reaction (i.e. forming a salt in solution) would occur. Then, this was tested on whole alloy pieces.

Table S2. Description of leaching parameters tested including the solution, temperature and % mass loss. All techniques were obtained from the Literature. These tests were done on 4 g of Al powder to see if Al would leach into the solution to form a salt. Mass loss refers to remaining solid mass after 2 h.

Solution	Concentration (M)	Temperature (°C)	Time (h)	Al powder mass loss (%)	Ref
Oxalic acid	0.5	85	2	–	[1]
Potassium sodium tartrate	0.35	80	2	47	[2]
Sulfuric acid	5.6	100	2	-	[3]
Sodium hydroxide	3	70	2	90	[4]
Sodium hydroxide	7	90	2	99	[4]

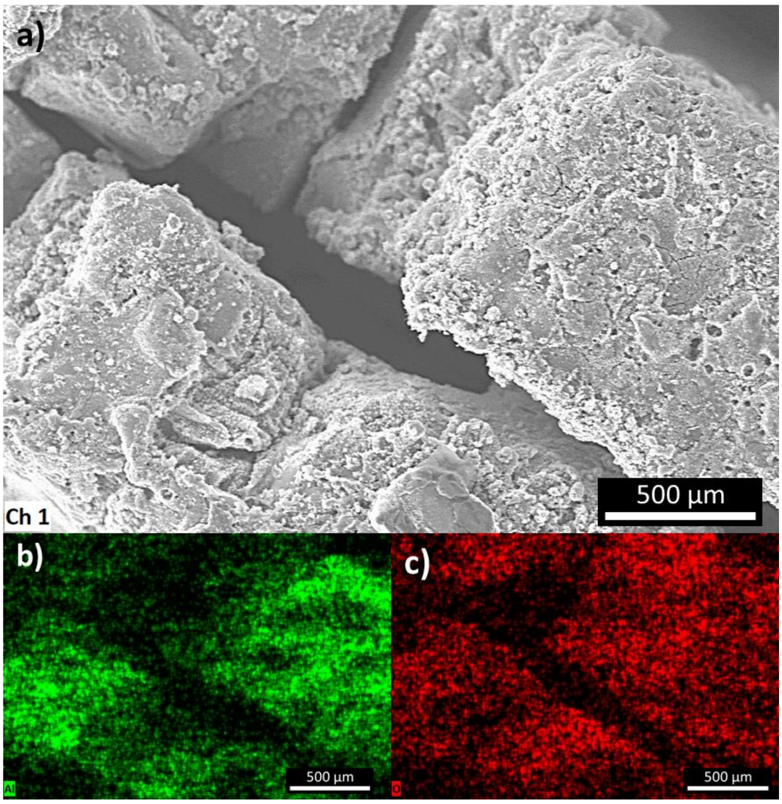

Figure S2. SEM image and corresponding EDX mapping (Al and O) of the Al-SS monolith post-leaching.

Additional N_2 sorption

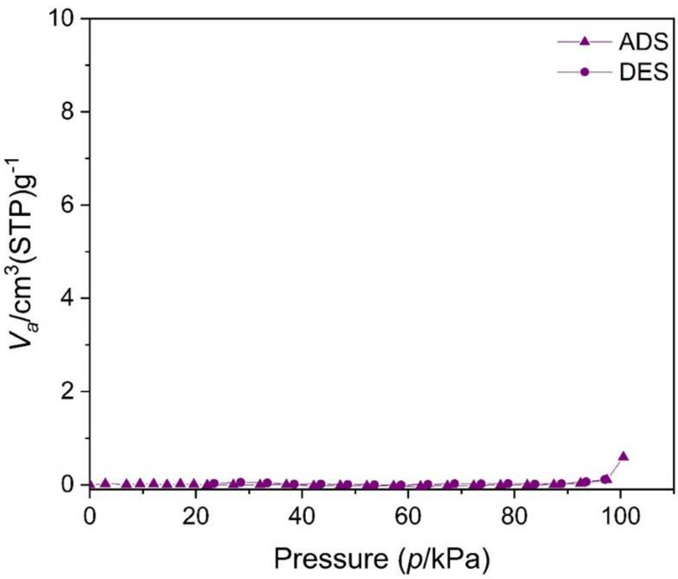

Figure S3. The unleached Al-SS shows no N_2 adsorption.

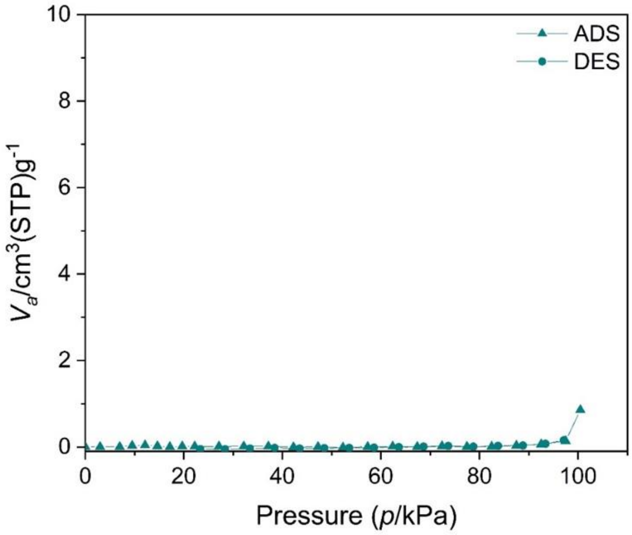

Figure S4. The unleached 1.5% Co-Al-SS shows no N_2 adsorption.

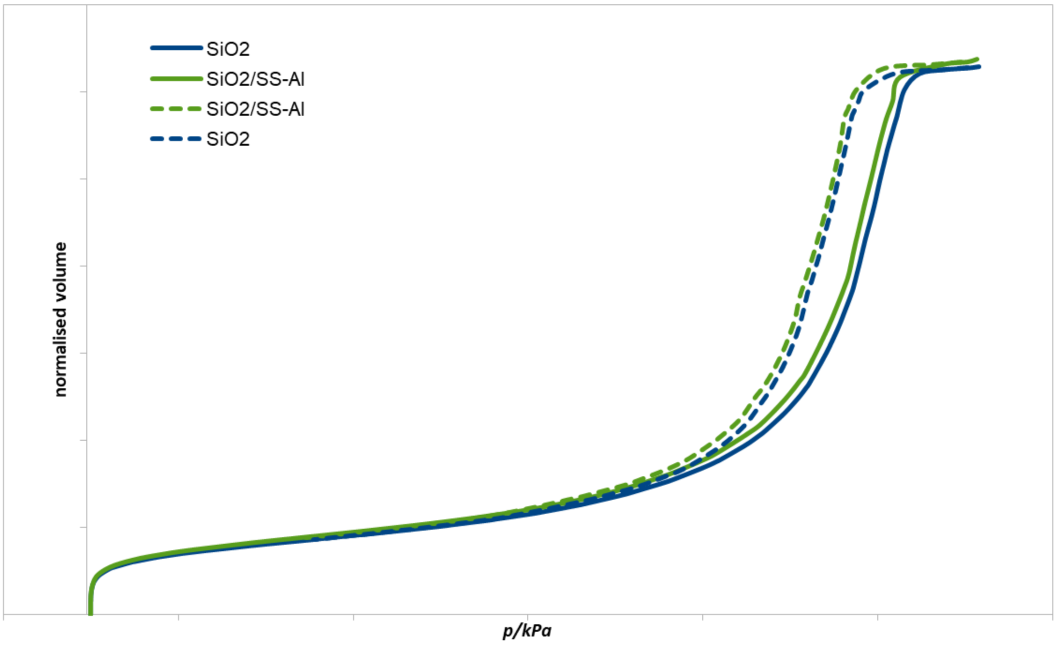

Figure S5. Normalised N_2 adsorption isotherm of SiO_2 vs an SiO_2/leached Al-SS mixture where SiO_2 is used as an internal standard to confirm the BET surface area and porosity of the leached monolith. The difference between the two isotherms (a shift to the left) confirms porosity contributed by leached Al-SS.

Table S3. BET surface area vs actual surface area of SiO_2, leached Al-SS and combination of SiO_2/leached Al-SS where SiO_2 is used as an internal standard.

	SiO2	**SiO2-Al-SS**	**Al-SS**
Surface area (m^2/g)	286.16	147.97	7.0205
Mass (g)	0.0552	0.3693 (0.1842 Al-SS, 0.1851 SiO_2)	0.5022
Surface Area (m^2)	15.796	54.645	3.525

Theoretical calculated area (m^2)		54.261	

Additional catalytic reactions

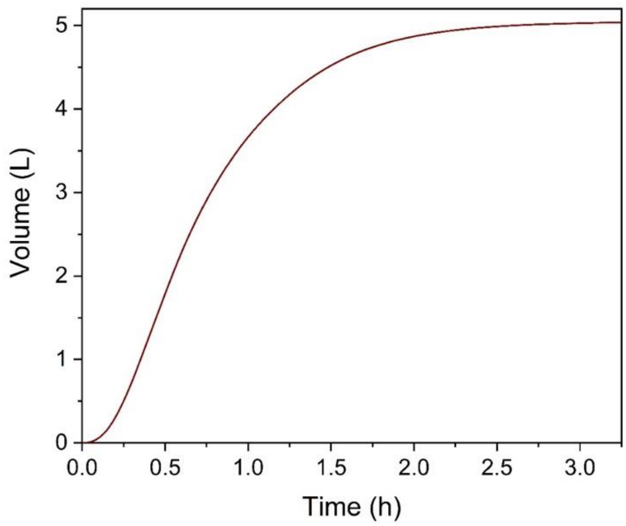

Figure S6. Hydrogen volume generated by leached Al-SS in a batch reaction after 100 h in the continuous reactor. We see that the activity is maintained and can run the reaction to completion after this long exposure time.

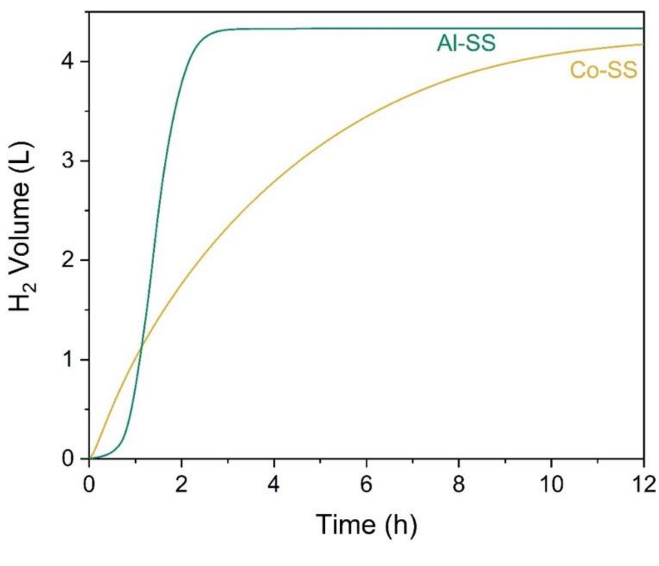

Figure S7. Comparison of H_2 volume generated in a batch reaction between leached Al-SS (this work) with Co-SS (previous work). Although we see an induction period in our porous Al-SS catalyst, the overall activity is significantly higher.

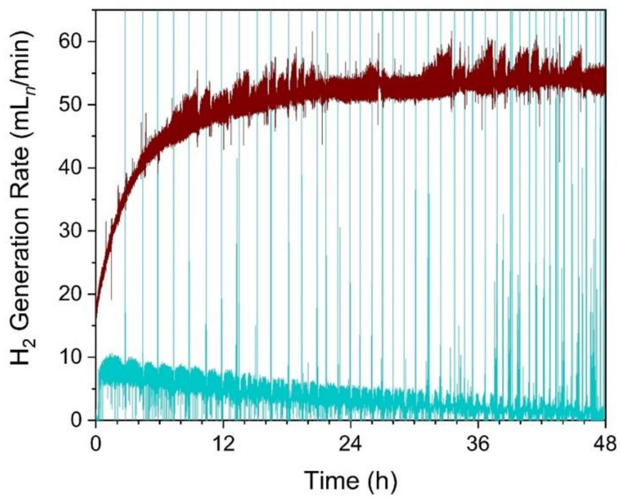

Figure S8. Comparison of H_2 generation rate of previously reported Co-SS and porous Al-SS reported in this work. This is the same data as Figure 6 (main text) but includes the data points previously removed for clarity. Due to the higher activity of Al-SS, and therefore H_2 flow rate, we also see smaller fluctuations in H_2 generation rate as there is no need for gas pressure build up to pass through the water bubbler. To combat this with the non-porous Co-SS, more catalyst would need to be used to achieve both the higher flow rate and smaller gas fluctuation artefacts.

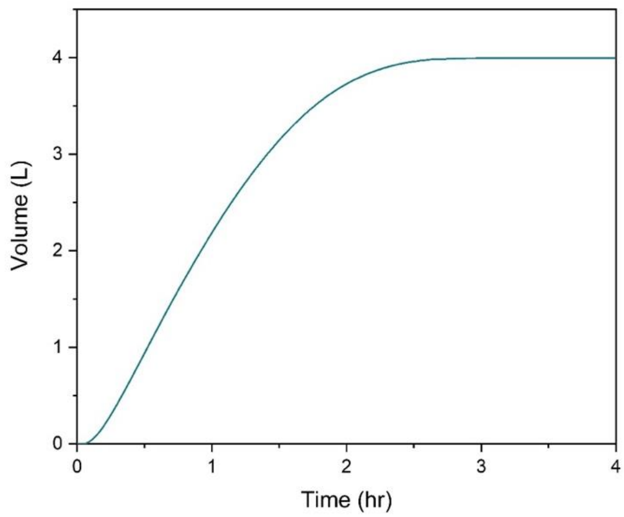

Figure S9. H_2 volume generated in a batch reaction by a leached 1.5% Co-Al-SS monolith. The same conditions were used for the synthesis of the catalyst and reaction conditions.

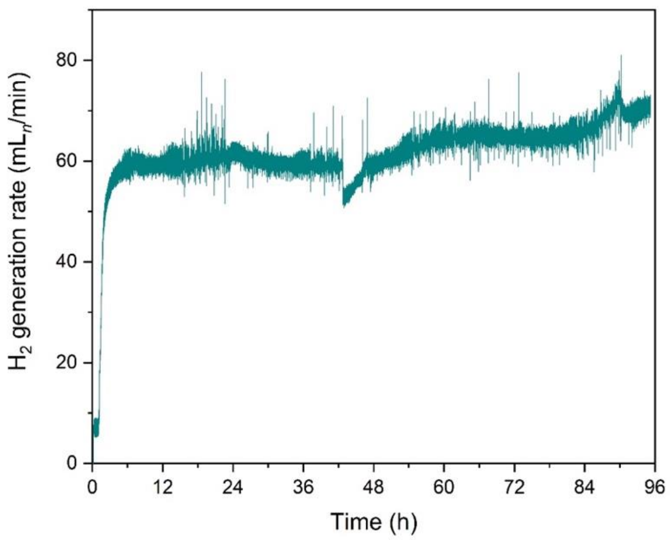

Figure S10. H_2 generation rate of leached 1.5% Co-Al-SS monolith in a continuous system. The hydrogen generation rate was measured every second by two mass flow meters in series. This graph shows over 340,000 data points.

References

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[2] J. Lindsay, *Products Finishing* **2015**, *79*, 14.
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[4] D. A. Ferreira, L. M. Z. Prados, D. Majuste, M. B. Mansur, *J. Power Sources* **2009**, *187*, 238–246.