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3D printed palladium/activated carbon-based catalysts for the dehydrogenation of formic acid as hydrogen carrier

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Table S1. Characterization of AC powders including specific surface area (S_{BET}), external area (A_{EXT}), pore volume (V_{PORE}), pore diameter (D_{PORE}) and elemental analysis.

S_{BET} ($m^2 \cdot g^{-1}$)	A_{EXT} ($m^2 \cdot g^{-1}$)	V_{PORE} ($cm^3 \cdot g^{-1}$)	D_{PORE} (nm)	Carbon (wt.%)	Oxygen (wt.%)	Nitrogen (wt.%)	Sulphur (wt.%)
738	514	0.098	3.53	87.6 ± 0.5	7.3 ± 0.3	< 0.16	0.34 ± 0.05

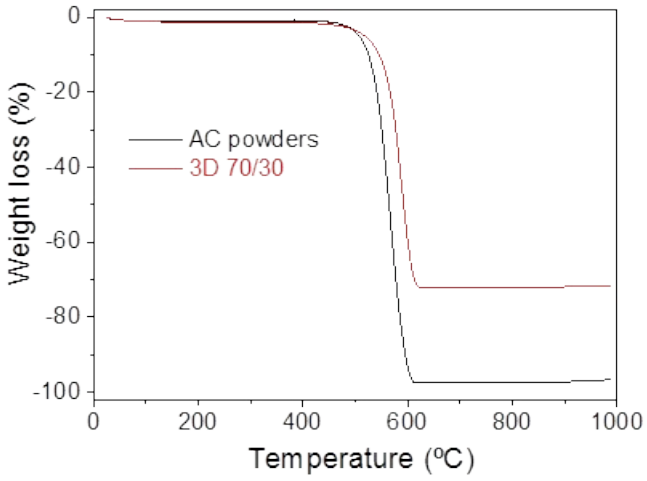

Figure S1. Weight loss (TGA) as a function of the temperature for the pristine AC powders and the as-printed 3D AC/B (70/30) structure.

Calculation of the gas produced upon reaction:

$$Q_{GAS}(mL\ min^{-1}) = Q_{He}(mL\ min^{-1}) \cdot dilution\ factor$$

$$dilution\ factor = \frac{D}{1 - D}$$

$$D = \frac{\%H_{2GC} + \%CO_{2GC} + \%CO_{GC}}{100}$$

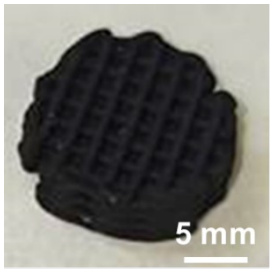

Figure S2. 3D AC/Al_2O_3 structure after placing the monolith into a beaker containing FA at 55 ºC for 1 h and using mechanical stirring.

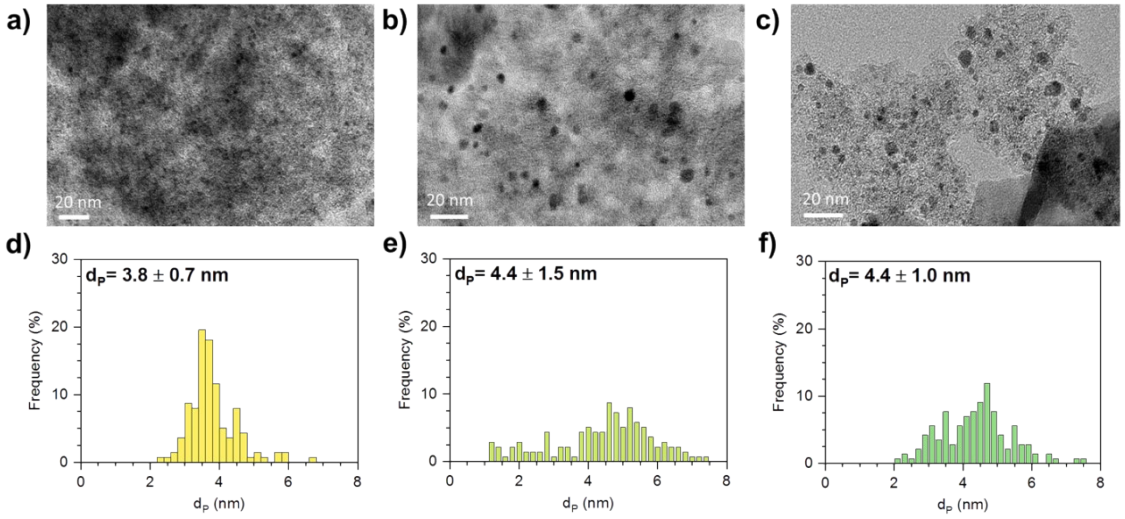

Figure S3. TEM images and particle size distribution (d_P) histograms of the 3D Pd/AC catalysts at T = 55 ºC after the following uses: a,d) 1st use, b,e) 3rd use and c,f) 5th use.

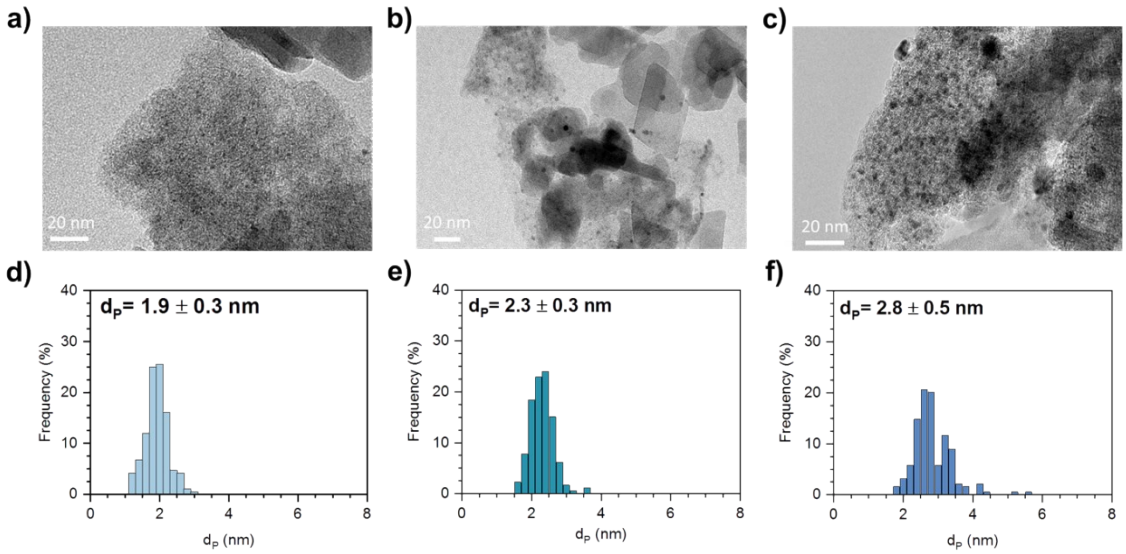

Figure S4. TEM images and particle size distribution histograms (d_P) of the use 3D Pd/AC catalysts at T = 25 ºC after the following uses: a,d) 1st use, b,e) 3rd use and c,f) 5th use.

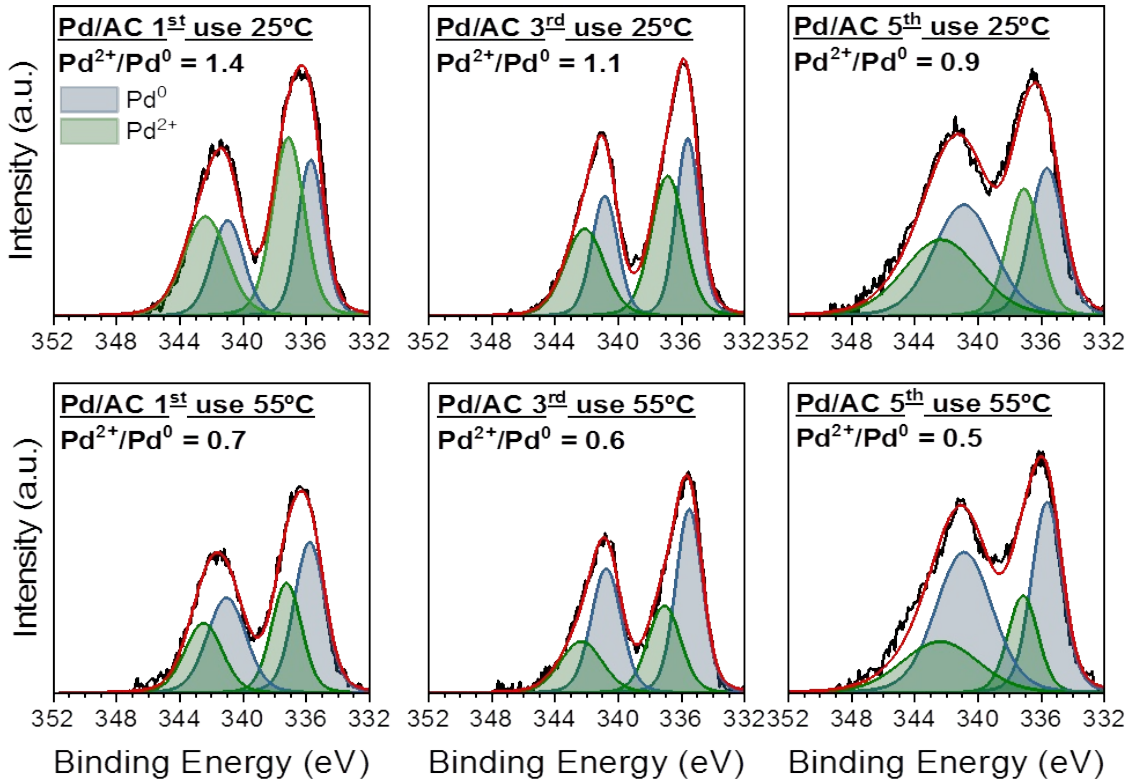

Figure S5. XPS spectra of Pd 3d core level after different uses (1st, 3rd, 5th) of the 3D Pd/AC catalysts tested at 25 and 55 ºC.

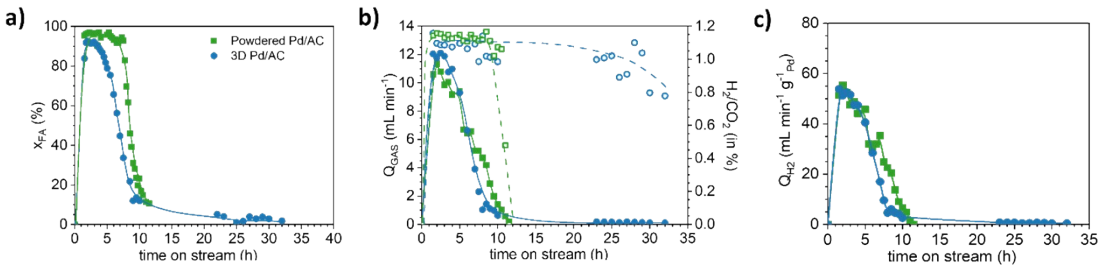

Figure S6. Performance of powdered and 3D Pd/AC catalyst in terms of: (a) X_{FA}, (b) Q_{GAS} produced and H_2/CO_2 ratio and (c) H_2 production per gram of Pd upon time-on-stream at $C_{FA,0}$ = 1 M, τ = 160 $g_{CAT}\cdot h\cdot L^{-1}$ and T = 55 ºC.

The powdered 5 wt.% Pd/AC catalyst was prepared according to the following method: 3D AC monoliths were crushed and ground in an agate mortar and, then, 3 g of AC monolith powder (previously hydrated with 30 mL of Milli-Q water) were added to the $PdCl_2$ precursor solution at 65 ºC. After 1 h of magnetic stirring, the temperature was increased to 95 ºC and maintained until complete evaporation of water. The Pd impregnated powders were washed with Milli-Q water and oven dried at 60 ºC overnight. Finally, they were reduced to remove the residual chlorides in a quartz tube under a H_2/N_2 stream (50/100 $NmL\cdot min^{-1}$) at 250 ºC for 2 h at a heating rate of 10 $ºC\cdot min^{-1}$.

Table S2. Main chemical characteristics of the 3D and powdered Pd/AC catalysts.

Fresh catalysts	Pd (wt.%)	Pd^{2+}/Pd^0 (at.%)	d_p (nm)

3D Pd/AC	4.9	1.4	1.9 ± 0.4
Powdered Pd/AC	4.5	1.4	2.2 ± 0.8