Electronic Supplementary Material

Direct biogas reforming to turquoise H_2 and carbon material in a catalytic fluidised-bed reactor

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Table S1: Conditions of the experimental runs and equipment setup.

Equations for WHSV

$$WHSV\ (cm^3 g^{-1} h^{-1}) = \frac{total\ mass\ flow\ of\ the\ reactants\ per\ time\ (cm^3\ h^{-1})}{total\ mass\ of\ the\ catalyst\ (g)}$$

$$Q_{TP}\left(\frac{cm^3}{min}\right) = Q_{STP}\frac{101.3kPa}{P}\frac{T}{273K}$$

$$\tau(s) = \frac{60(V_0 - V_{cat})}{Q_{TP}}$$

In this context, V_0 represents the volume of the empty reactor (cm^3), V_{cat} stands for the overall catalyst volume in cm^3, and Q_{TP} denotes the total gas flow rate at the specific reforming temperature and pressure and Q_{STP} the total flow at 273K and 101.3kPa. τ represents the residence times estimated at 950°C

Experimental conditions	
Reaction system	Dry reforming of biogas
System configuration	Catalytic fluidized bed operation
Pressure (kPa)	101.325
Temperature (°C)	750–950
Total gas flow rate ($cm^3\ min^{-1}$) at STP*	300
Gas flow rate ratio	$CH_4/CO_2/N_2$ = 2/1/1
Weight Hourly Space Velocity (WHSV, $cm^3\ g^{-1}\ h^{-1}$)	1637
Catalyst weight (g)	11
Volume of void (cm^3) = V_0–V_{cat}	89.1 = 101.8–12.7
Q_{TP} ($cm^3\ min^{-1}$)	1344
Residence time at 950 °C (s)	3.98
Reynolds number	<40 (laminar)
*Standard Temperature and Pressure	
Electric furnace configuration	
Frequency (Hz)	50
Power (kVA)	3.6
Current (A)	16
Summary of bed characteristics	
Static bed height (cm)	5
Diameter (mm)	16
Average bed mass (g)	11
Bulk density ($g\ cm^{-3}$)	1.22

Table S2: N_2 physisorption (77K) of the fresh and spent Fe/C catalyst after biogas reforming

Materials	**SSA (m^2 g^{-1})**	**V_p (cm^3 g^{-1})** (p/p0=0.98)
Fresh Fe/C catalyst	2	6.8
Spent Fe/C catalyst	11	26.6

Table S3: H_2O physisorption (293K) of the fresh and spent Fe/C catalyst (before and after biogas cracking)

Materials	**Amount of adsorbed water (mg/g) at 20°C** (p/p0=0.95)
Fresh Fe/C catalyst	0.7-1.7
Spent Fe/C catalyst	3.0-6.0

at 293K.

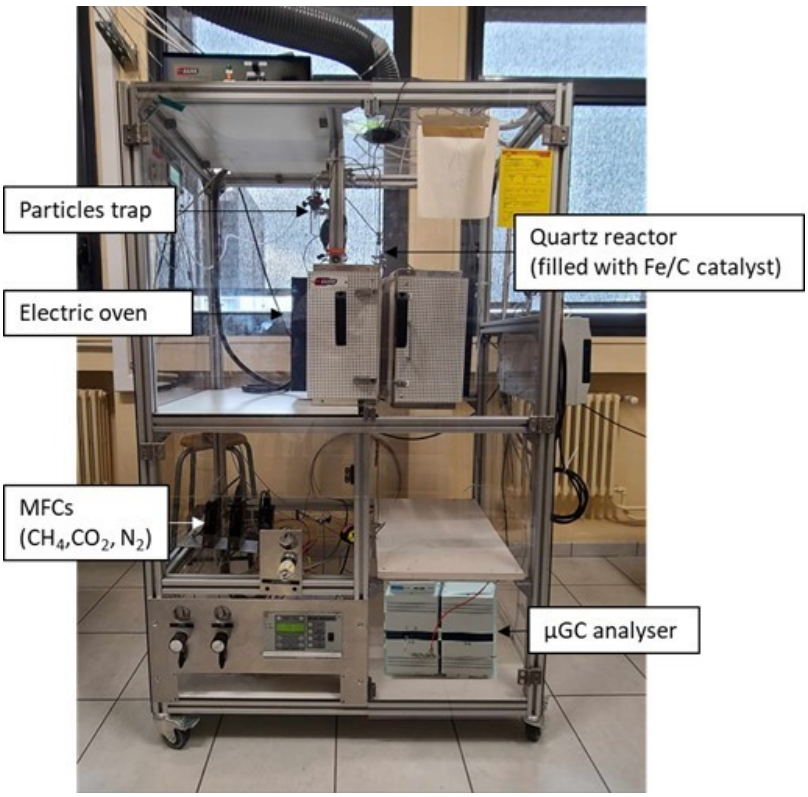

Figure S1: Scheme of the experimental set-up for biogas reforming.

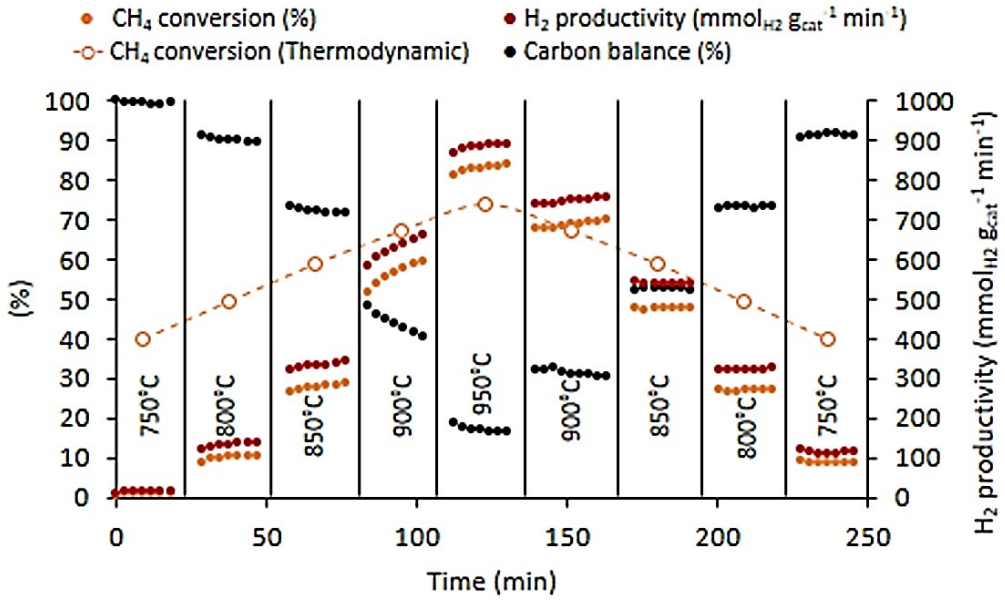

Figure S2: Methane conversion as function of the temperature, Carbon balance estimated from gas phase reactants and products. Inlet flow: CH_4/N_2 1/1, 300 mL min^{-1}, 1 bar.

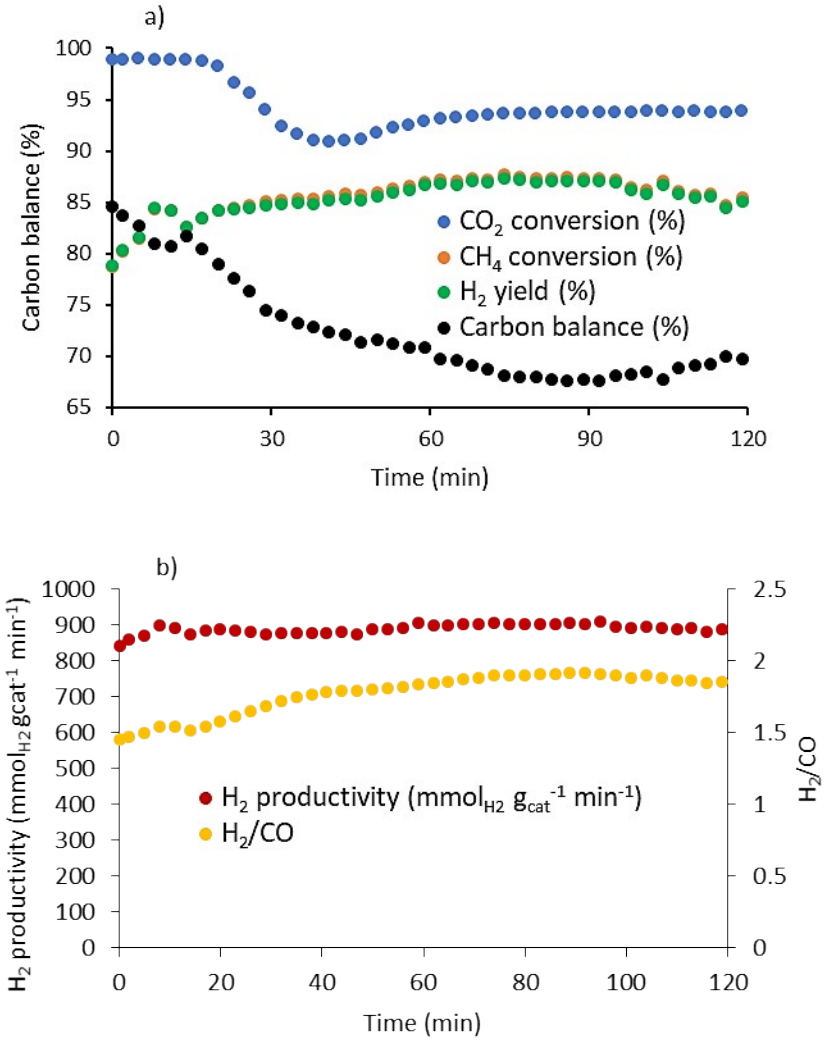

Figure S3: a) CH_4 and CO_2 conversion, H_2 yield and carbon balance (%) as function of time, Carbon balance estimated from gas phase reactants and products, b) H_2 productivity and H_2/CO ratio as function of time for biogas reforming, T=950°C, 1 bar, CH_4:CO_2:N_2 2:1:1, 300 mL min^{-1}.

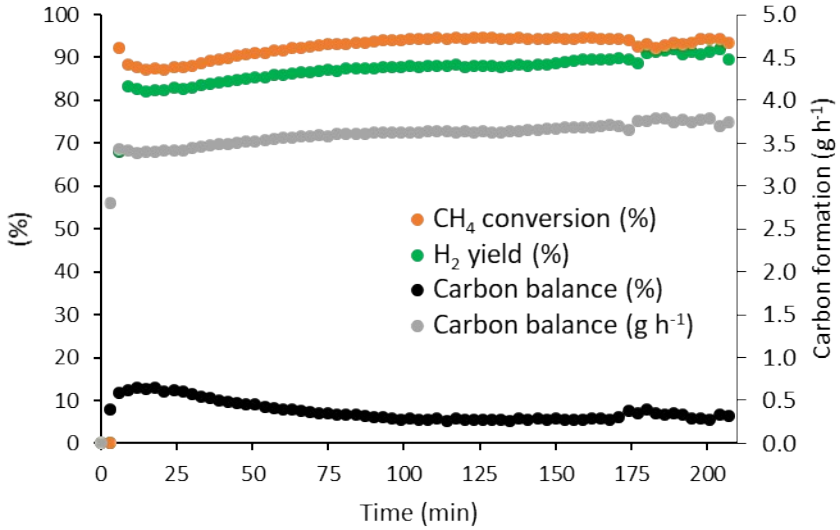

Figure S4: Methane conversion, H_2 yield, carbon balance (%) and carbon formation (g h^{-1}) as function of time for methane cracking, T=950°C, 1 bar, CH_4:N_2 (1:1), 300 mL min^{-1}. Carbon balance estimated from gas phase reactants and products.

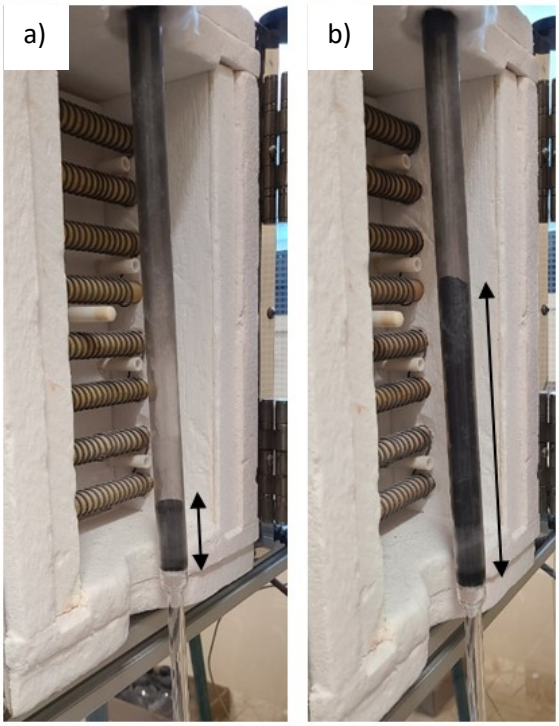

Figure S5: Quartz reactor filled with a) fresh and b) spent Fe/C catalyst. Black arrow is for catalyst bed height: 5 cm before cracking, 18 cm after biogas reforming, T=950°C, 1 bar, CH_4:CO_2:N_2 2:1:1, 300 mL min^{-1}.

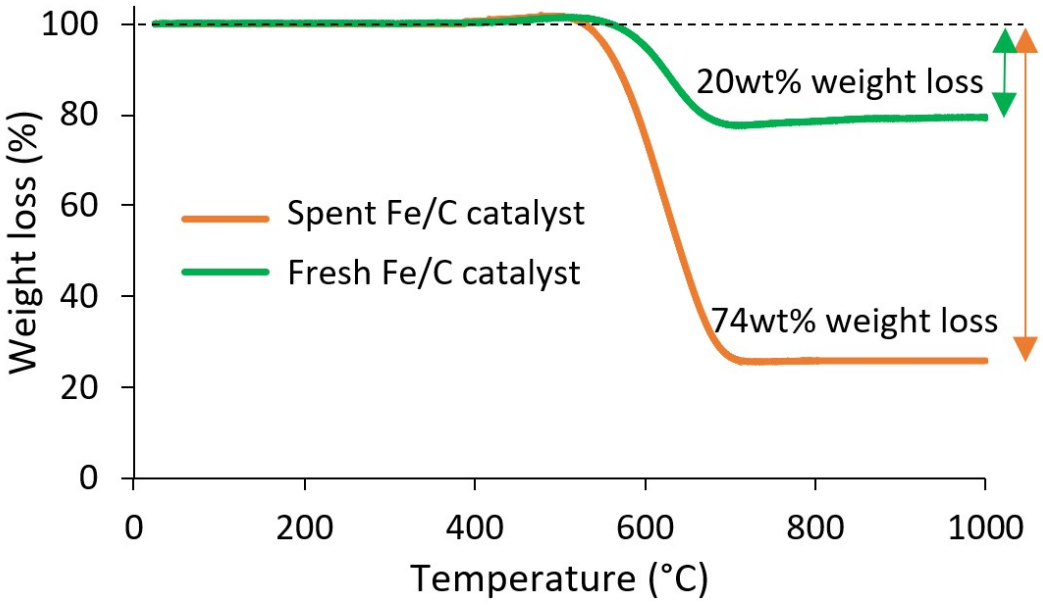

Figure S6: TGA of the fresh and spent Fe/C catalyst, under air, from 20 to 1000°C, heating rate 5°C min^{-1}.

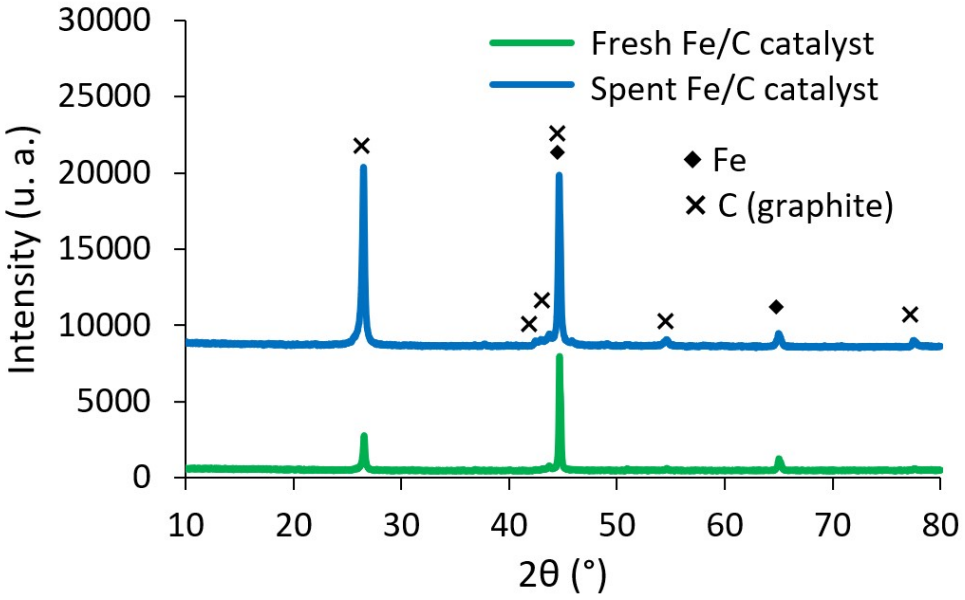

Figure S7: XRD analysis of the fresh and spent Fe/C catalyst after biogas reforming.

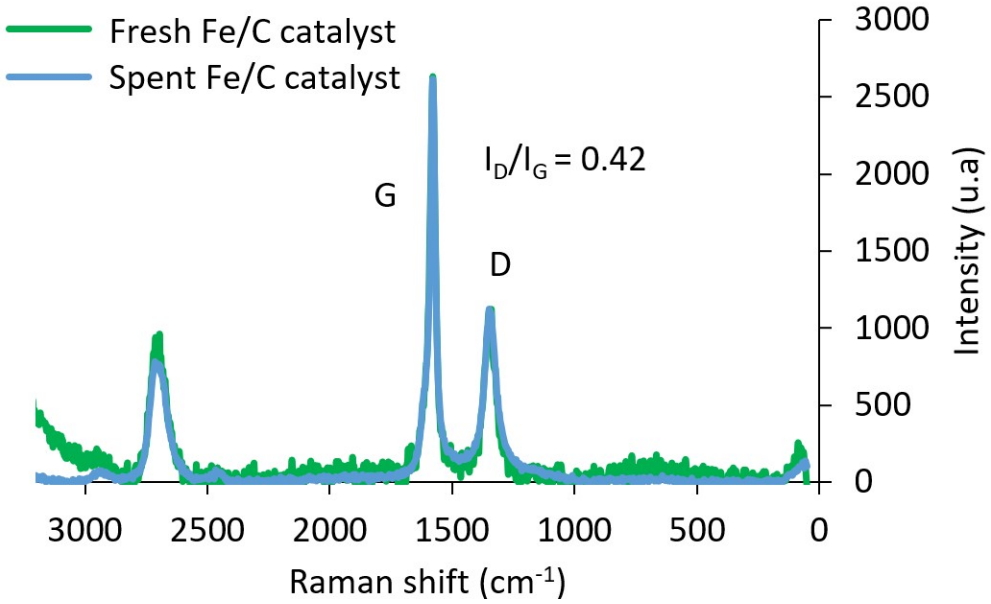

Figure S8: Raman spectroscopy of the fresh and spent Fe/C catalyst after biogas reforming.

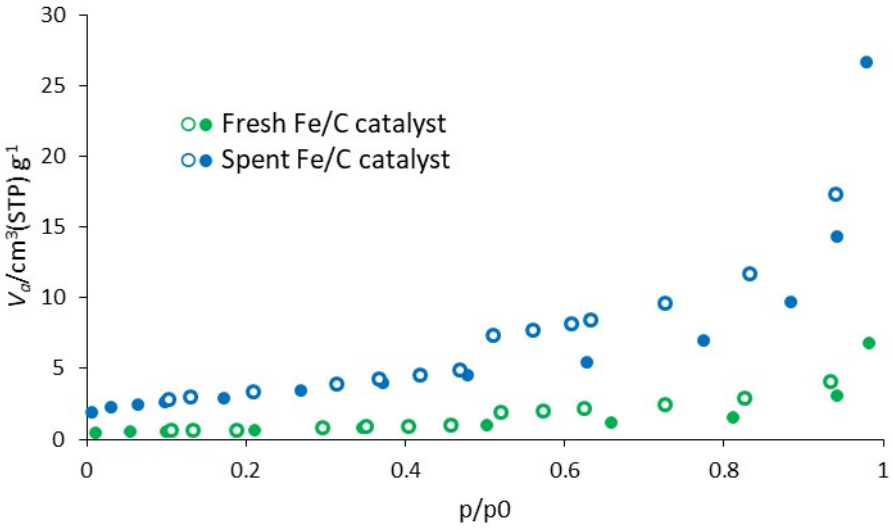

Figure S9: N_2 physisorption (77K) of the fresh and spent Fe/C catalyst (before and after biogas cracking).

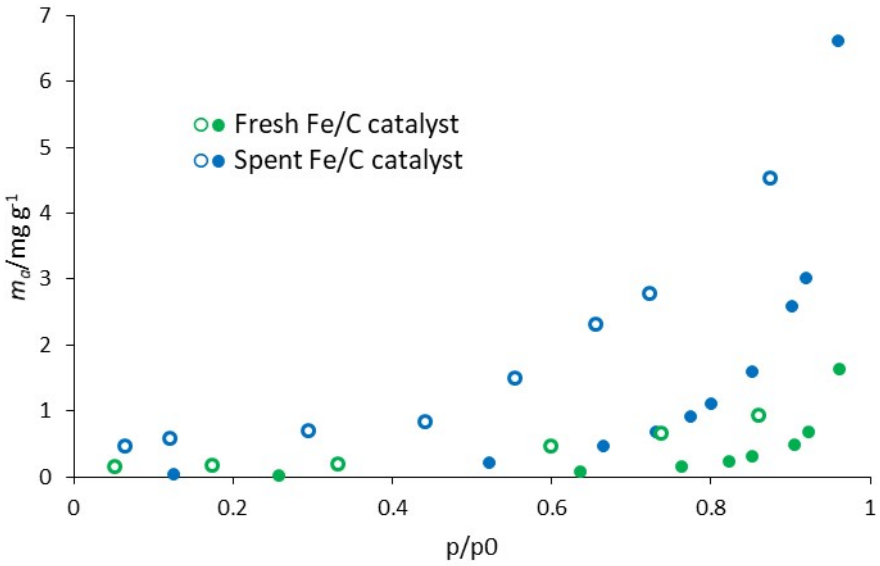

Figure S10: H_2O physisorption (293K) of the fresh and spent Fe/C catalyst after biogas reforming.