Operando XAFS investigation on the effect of ash deposition on three-way catalyst used in Gasoline Particulate Filters and the effect of the manufacturing process on the catalytic activity.

Supporting information

EXAFS analysis of the Non-ash containing sample

Table S1 Fitting parameters for the washcoat sample.

Conditions	Abs-Scatterer	E_0 (eV)	CN	R (Å)	σ^2	R_{factor}
20C [a]	Pd-O	-2±3	3.6±0.3	1.97±0.02	0.0029	0.008
	Pd-Pd^0		0.4±0.3	2.67±0.05	0.0019	
	Pd-Pd		-	-	-	
100C [a]	Pd-O	-2±3	2.8±0.2	1.98±0.02	0.0029	0.01
	Pd-Pd^0		0.6±0.3	2.73±0.04	0.0019	
	Pd-Pd		-	-	-	
130C [a]	Pd-O	-5±1	2.4±0.3	1.97±0.02	0.0029	0.018
	Pd-Pd^0		1.3±0.3	2.73±0.03	0.0019	
	Pd-Pd		-	-	-	
230C [a]	Pd-O	-5±3	1.3±0.4	1.96±0.04	0.0042	0.03
	Pd-Pd^0		4.5±0.7	2.76±0.03	0.0078	
	Pd-Pd		-	-	-	
750C[b]	Pd-O	-2±3	1.8±0.3	2.00±0.03	0.0040	0.031
	Pd-Pd^0		2.6±0.7	2.87±0.06	0.0068	
	Pd-Pd		2.3±0.8	2.70±0.07	0.0059	
200C cooling [a]	Pd-O	-5.6 ±0.5				0.003
	Pd-Pd^0		9.6±0.7	2. 733±0.005	0.0078±0.0009	
	Pd-Pd		-	-	-	

Fitting parameters: S_0^2 determined from Pd foil = 0.85, 1 < R < 3.0 Å, [a] k-range 3.0– 10.6, no. of independent points 9.4. [b] k-range 3.0– 10, no. of independent points 8.69.

Table S2 Fitting parameters for the washcoat sample.

Conditions	Abs-Scatterer	E_0 (eV)	CN	R (Å)	σ^2	R_{factor}
53C [a]	Pd-O	3±2	3.5±0.2	1.99±0.02	0.0027	0.009
	Pd-Pd		-	-	-	
	Pd-Pd^0		0.4±0.3	2.68±0.05	0.0026	
120C [a]	Pd-O	3±3	2.7±0.3	1.99±0.02	0.0044	0.020
	Pd-Pd		-	-	-	
	Pd-Pd^0		1.1±0.5	2.77±0.05	0.0089	
156C [a]	Pd-O	-1±2	2.3±0.3	1.97±0.03	0.0032	0.019
	Pd-Pd		-	-	-	
	Pd-Pd^0		2.4±0.5	2.74±0.03	0.0064	
	Pd-O	0±2	2.2±0.3	1.97±0.02	0.0033	0.018

199C [a]	Pd-Pd		-	-	-	
	Pd-Pd^0		3.5±0.5	2.75±0.02	0.0066	
223C [a]	Pd-O	-1±3	1.8±0.4	1.96±0.03	0.0041	0.034
	Pd-Pd		-	-	-	
	Pd-Pd^0		3.9±0.7	2.74±0.03	0.0075	
_265C [a]	Pd-O	-1±2	1.2±0.4	1.95±0.03	0.0053	0.036
	Pd-Pd		-	-	-	
	Pd-Pd^0		5.1±0.7	2.77±0.01	0.0085	
357C [b]	Pd-O	-2±2	0.7±0.4	1.95±0.04	0.0057	0.070
	Pd-Pd		-	-	-	
	Pd-Pd^0		5.4±0.8	2.75±0.02	0.0096	
414C [b]	Pd-O	-0±3	2.0±0.4	2.02±0.03	0.0051	0.065
	Pd-Pd		-	-	-	
	Pd-Pd^0		4.4±0.8	2.77±0.03	0.0110	
437C [b]	Pd-O	1±4	2.3±0.5	2.00±0.04	0.0036	0.105
	Pd-Pd		-	-	-	
	Pd-Pd^0		2.5±0.8	2.72±0.04	0.0078	
471C [b]	Pd-O	-4±4	2.4±0.5	1.95±0.03	0.0051	0.010
	Pd-Pd		-	-	-	
	Pd-Pd^0		2.5±0.7	2.68±0.03	0.0084	
529C [b]	Pd-O	3±2	2.7±0.3	2.01±0.02	0.0054	0.004
	Pd-Pd		-	-	-	
	Pd-Pd^0		2.1±0.6	2.76±0.03	0.0093	
595C [b]	Pd-O	5±2	2.9±0.2	2.01±0.02	0.0050	0.002
	Pd-Pd		-	-	-	
	Pd-Pd^0		1.5±0.4	2.79±0.03	0.0097	
667C [b]	Pd-O	6±3	2.5±0.2	2.02±0.02	0.0032	0.009
	Pd-Pd		1.4±1.0	2.99±0.08	0.0090	
	Pd-Pd^0		1.7±0.7	2.79±0.05	0.0092	
713C [b]	Pd-O	-6±5	2.2±0.4	1.97±0.03	0.0041	0.005
	Pd-Pd		2.6±1.6	2.76±0.09	0.0101	
	Pd-Pd^0		1.6±1.4	2.60±0.11	0.0102	
739C [b]	Pd-O	5±2	2.2±0.2	2.01±0.02	0.0042	0.011
	Pd-Pd		1.4±1.2	2.98±0.09	0.0125	
	Pd-Pd^0		1.9±0.7	2.77±0.05	0.0114	
769C [b]	Pd-O	1±4	1.4±0.3	1.99±0.03	0.0038	0.025
	Pd-Pd		2.8±1.4	2.93±0.07	0.0100	
	Pd-Pd^0		6.0±1.1	2.73±0.06	0.0147	
834C [b]	Pd-O	-3±3	0.8±0.3	1.97±0.03	0.0049	0.026
	Pd-Pd		3.3±1.2	2.81±0.07	0.0097	
	Pd-Pd^0		6.2±1.1	2.65±0.06	0.0146	
891C [b]	Pd-O	-6±1	-	-	-	0.016
	Pd-Pd		-	-	-	
	Pd-Pd^0		10.8±0.4	2.68±0.01	0.0232	
961C [b]	Pd-O	-6±2	-	-	-	0.008
	Pd-Pd		-	-	-	
	Pd-Pd^0		9.5±0.8	2.68±0.02	0.0222	

929C [b]	Pd-O	-3±1	-	-	-	0.016
	Pd-Pd		-	-	-	
	Pd-Pd^0		10.5±0.4	2.73±0.01	0.0195	
463C [b]	Pd-O	-3±0	-	-	-	0.003
	Pd-Pd		-	-	-	
	Pd-Pd^0		10.3±0.2	2.727±0.004	0.0125	
318C [b]	Pd-O	-2±1	-	-	-	0.010
	Pd-Pd		-	-	-	
	Pd-Pd^0		10.3±0.4	2.732±0.006	0.0105	
234C [b]	Pd-O	-2±0	-	-	-	0.005
	Pd-Pd		-	-	-	
	Pd-Pd^0		10.5±0.3	2.737±0.004	0.0088	
80C [b]	Pd-O	-1±0	-	-	-	0.003
	Pd-Pd		-	-	-	
	Pd-Pd^0		10.1±0.3	2.739±0.003	0.0056	

Fitting parameters: S_0^2 determined from Pd foil = 0.85, 1 < R < 3.0 Å. [a] K-range 3.1– 8.8, no. of independent points 7.06. [b] K-range 3.1– 10.0, no. of independent points 8.56.

EXAFS analysis of the 20g ash-GPF sample

Table S3 Fitting parameters for the 20g ash-GPF sample.

Conditions	**Abs-Scatterer**	**E_0 (eV)**	**CN**	**R (Å)**	**σ^2**	**R_{factor}**
20C	Pd-O	0±3	3.8±0.3	2.02±0.02	0.0033	0.03
	Pd-PdO(1)		4±1	3.06±0.02	0.0088	
	Pd-PdO(2)		6±1	3.44±0.02	0.0076	
100C	Pd-O	2±3	3.7±0.3	2.03±0.02	0.0037	0.03
	Pd-PdO(1)		5±1	3.05±0.02	0.0102	
	Pd-PdO(2)		5±1	3.46±0.02	0.0071	
130C	Pd-O	0±2	3.5±0.2	2.01±0.01	0.0031	0.02
	Pd-PdO(1)		3.9±0.9	3.02±0.02	0.0097	
	Pd-PdO(2)		5.5±0.9	3.44±0.02	0.0075	
230C	Pd-O	-1±2	3.0±0.2	2.02±0.02	0.0033	0.01
	Pd-PdO(1)		3.3±0.8	3.06±0.02	0.0074	
	Pd-PdO(2)		4±1	3.45±0.02	0.0091	
	Pd-Pd(m)		2±1	2.81±0.05	0.0183	
750C	Pd-O	-9±3	1.1±0.4	1.94±0.03	0.0041	0.04
	Pd-PdO(1)		3±1	3.30±0.06	0.0088	
	Pd-Pd(m)		3.5±0.6	2.70±0.03	0.0087	
1C_230C cooling	Pd-O	-7±1	-	-	-	0.04
	Pd-PdO(1)		-	-	-	
	Pd-Pd(m)		9±1	2. 74±0.008	0.008±0.0012	

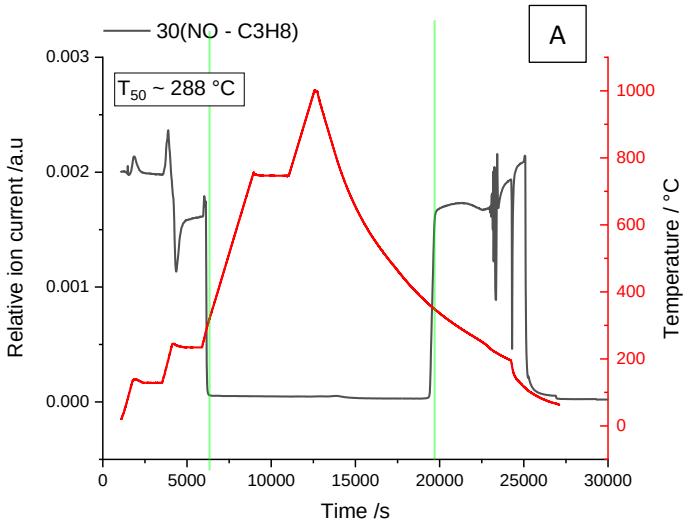
Fitting parameters: S_0^2 determined from Pd foil = 0.85, 1 < R < 3.0 Å, k-range 3.0– 10.6, no. of independent points 11.9.

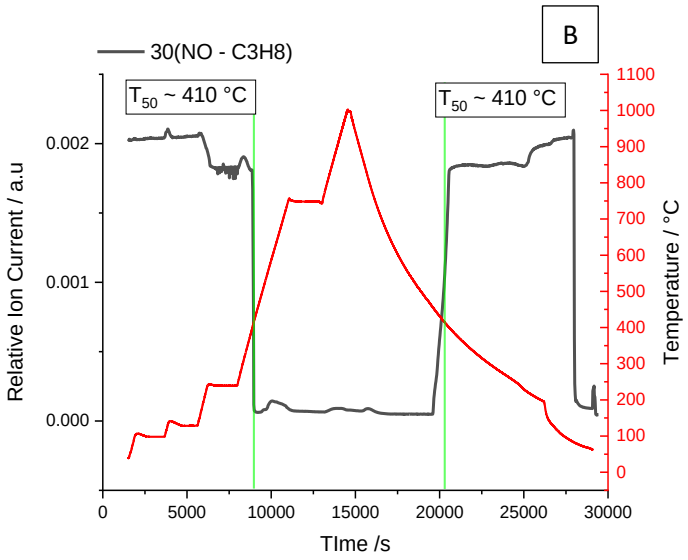
Table S4 Fitting parameters for the 20g ash-GPF sample.

Conditions	Abs-Scatterer	E_0 (eV)	CN	R (Å)	σ^2	R_{factor}
49C [a]	Pd-O	1±3	3.6±0.4	2.02±0.02	0.0013	0.028
	Pd-Pd		3.7±1.2	3.07±0.03	0.0052	
	Pd-Pd^0		-	-	-	
119C [a]	Pd-O	2±3	3.5±0.4	2.03±0.02	0.0022	0.030
	Pd-Pd		3.5±1.1	3.08±0.03	0.0050	
	Pd-Pd^0		-	-	-	
154C [a]	Pd-O	2±3	3.4±0.3	2.03±0.02	0.0020	0.021
	Pd-Pd		3.0±0.8	3.06±0.03	0.0042	
	Pd-Pd^0		-	-	-	
211C [a]	Pd-O	2±2	2.9±0.3	2.03±0.02	0.0012	0.022
	Pd-Pd		2.3±0.7	3.07±0.02	0.0031	
	Pd-Pd^0		-	-	-	
276C [a]	Pd-O	0±4	2.8±0.4	2.02±0.03	0.0026	0.009
	Pd-Pd		3.1±1.9	3.02±0.06	0.0066	
	Pd-Pd^0		2.2±1.6	2.78±0.06	0.0072	
382C [a]	Pd-O	0±4	2.3±0.2	2.02±0.02	0.0025	0.02
	Pd-Pd (PdO)		2.1±0.6	3.02±0.03	0.0042	
	Pd-Pd^0		1.6±0.6	2.78±0.03	0.0050	
472C [a]	Pd-O	-1±2	2.7±0.2	2.02±0.02	0.0026	0.026
	Pd-Pd		1.6±0.8	3.00±0.04	0.0053	
	Pd-Pd^0		1.3±0.8	2.77±0.04	0.0070	
564C [a]	Pd-O	-2±3	2.7±0.3	2.01±0.02	0.0025	0.004
	Pd-Pd		1.3±1.1	2.99±0.07	0.0055	
	Pd-Pd^0		1.3±1.0	2.77±0.07	0.0077	
690C [a]	Pd-O	-2±3	1.9±0.2	2.02±0.02	0.0029	0.003
	Pd-Pd		2.9±1.2	3.03±0.03	0.0062	
	Pd-Pd^0		4.04±0.7	2.79±0.03	0.0079	
775C [a]	Pd-O	-4±2	0.9±0.2	1.98±0.02	0.0039	0.026
	Pd-Pd		3.9±0.9	2.92±0.04	0.0071	
	Pd-Pd^0		5.5±0.7	2.73±0.03	0.0084	
855C [a]	Pd-O	-9±3	-	-	-	0.034
	Pd-Pd		2.6±1.5	2.90±0.05	0.0103	
	Pd-Pd^0		9.2±1.3	2.70±0.03	0.0161	
936C [a]	Pd-O	-10±1	-	-	-	0.037
	Pd-Pd		-	-	-	
	Pd-Pd^0		7.2±0.6	2.70±0.02	0.0153	
988C [a]	Pd-O	-11±1	-	-	-	0.022
	Pd-Pd		-	-	-	
	Pd-Pd^0		11.4±0.7	2.70±0.02	0.0227	
474C [a]	Pd-O	-10±1	-	-	-	0.018
	Pd-Pd		-	-	-	
	Pd-Pd^0		10.2±0.6	2.71±0.01	0.0146	
	Pd-O	-8±1	-	-	-	0.017

351C [a]	Pd-Pd		-	-	-	
	Pd-Pd^0		9.3±0.6	2.73±0.01	0.011	
234C [a]	Pd-O		-	-	-	
	Pd-Pd	-8±1	-	-	-	0.007
	Pd-Pd^0		9.0±0.4	2.73±0.06	0.080	
131C [a]	Pd-O		-	-	-	
	Pd-Pd	-8±1	-	-	-	0.008
	Pd-Pd^0		9.3±0.4	2.73±0.06	0.064	
76C [a]	Pd-O		-	-	-	
	Pd-Pd	-8±1	-	-	-	0.005
	Pd-Pd^0		9.5±0.3	2.73±0.05	0.061	

Fitting parameters: S_0^2 determined from Pd foil = 0.85, 1 < R < 3.0 Å. [a] K-range 3.0– 9.1, no. of independent points 7.56.





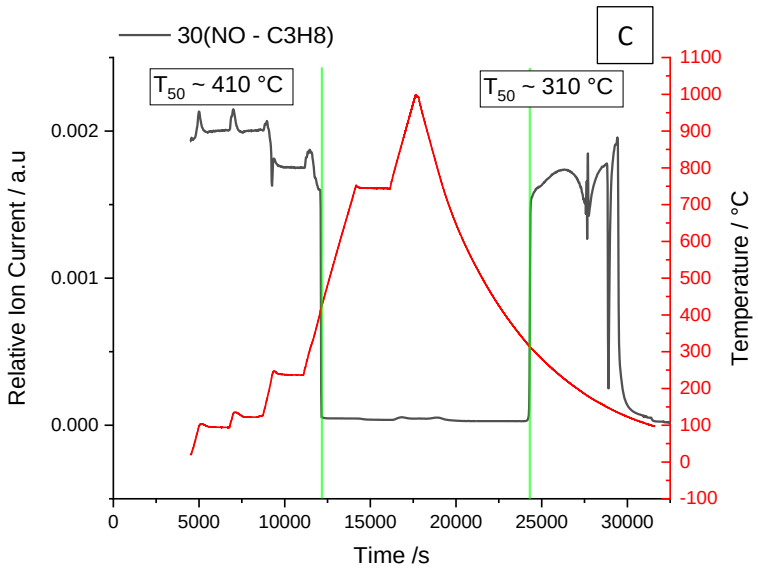


Figure S1: Full NO (m/z 30) profile during reaction of of the Non ash sample (A) and the Ash loaded sample (B) and a separate catalyst extracted from a GPF containing no ash (C)

EXAFS fitting of the 20g ash-GPF sample in the temperature region containing the 2.9Å Pd-Pd scattering contribution.

Table S5 Fitting parameters for the ash-loaded sample at the temperatures where the radial distance ~2.9 Å was observed, using a Pd-Pd scattering path associated with PdH and PdO .

Conditions	Abs-Scatterer	E_0 (eV)	CN	R (Å)	σ^2	R_{factor}
564 °C	Pd-O	-2±3	2.7±0.3	2.01±0.02	0.0027	0.005
	Pd-PdO		1.4±1.2	2.99±0.07	0.0072	
	Pd-Pd^0		1.3±1.1	2.76±0.07	0.0083	
690 °C	Pd-O	-2±2	1.7±0.1	2.02±0.02	0.0033	0.002
	Pd-PdO		2.7±1.0	3.03±0.03	0.0076	
	Pd-Pd^0		3.2±0.5	2.78±0.02	0.0072	
750 °C	Pd-O	-3±3	1.2±0.2	1.99±0.03	0.0062	0.003
	Pd-PdH		3.7±1.2	2.94±0.05	0.0098	
	Pd-Pd^0		4.3±0.6	2.74±0.03	0.0083	
775 °C	Pd-O	-5±2	0.9±0.2	1.98±0.02	0.0040	0.003
	Pd-PdH		3.4±0.8	2.91±0.05	0.0077	
	Pd-Pd^0		4.3±0.5	2.72±0.03	0.0074	

Fitting parameters: *S_0^2 determined from Pd foil = 0.85, 1 < R < 3.0 Å. [a] K-range 3.0– 9.1, no. of independent points 7.56.*

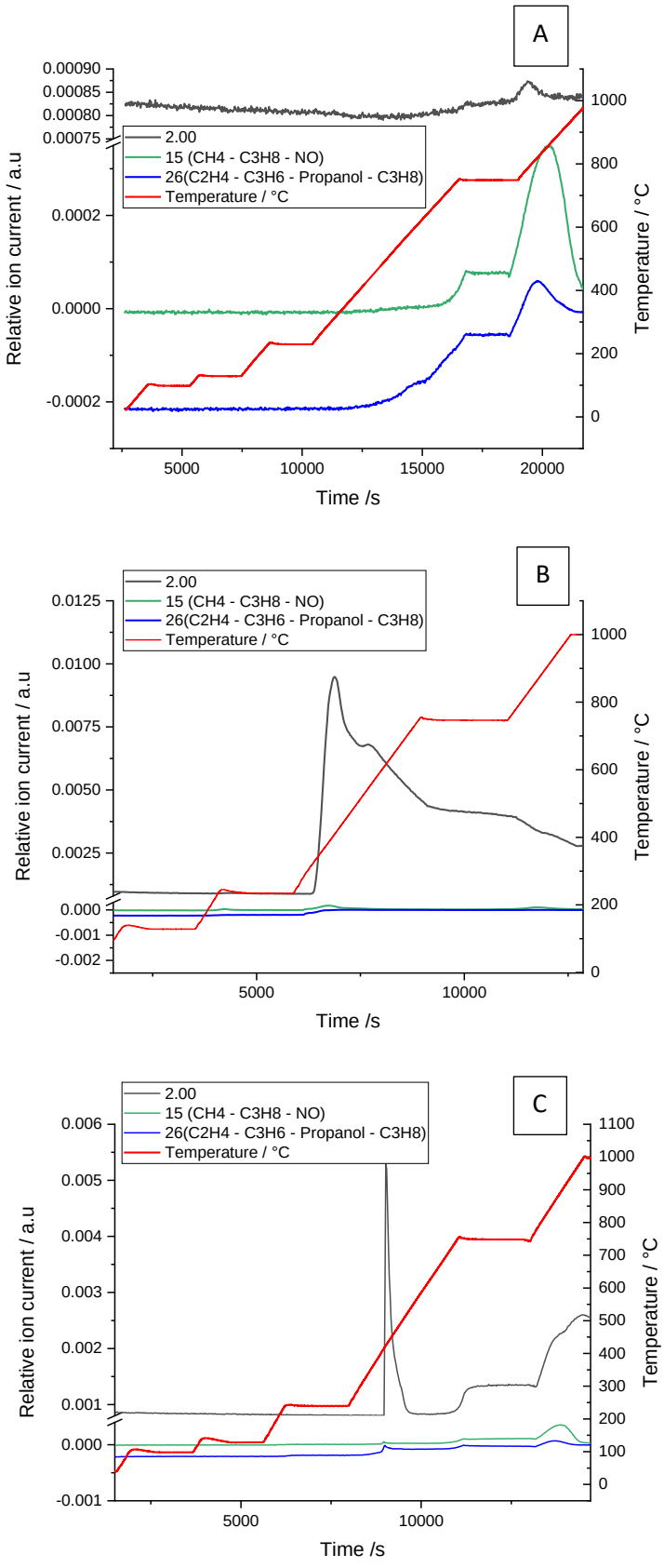


Figure S2: MS Profile of H_2, CH_4 and C_2H_4 during an uncatalyzed reaction (A), and during catalytic reaction with the washcoat (B) and 20g ash GPF (C).

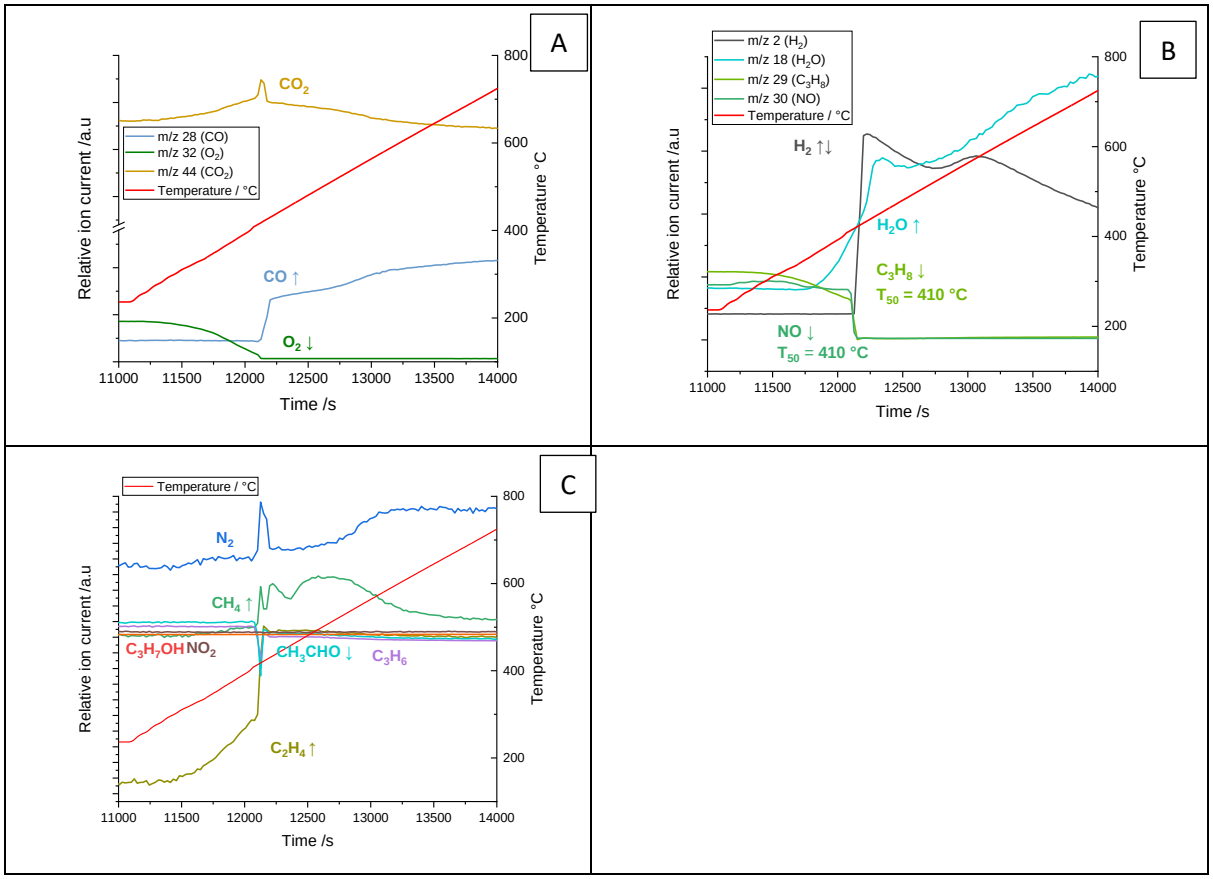
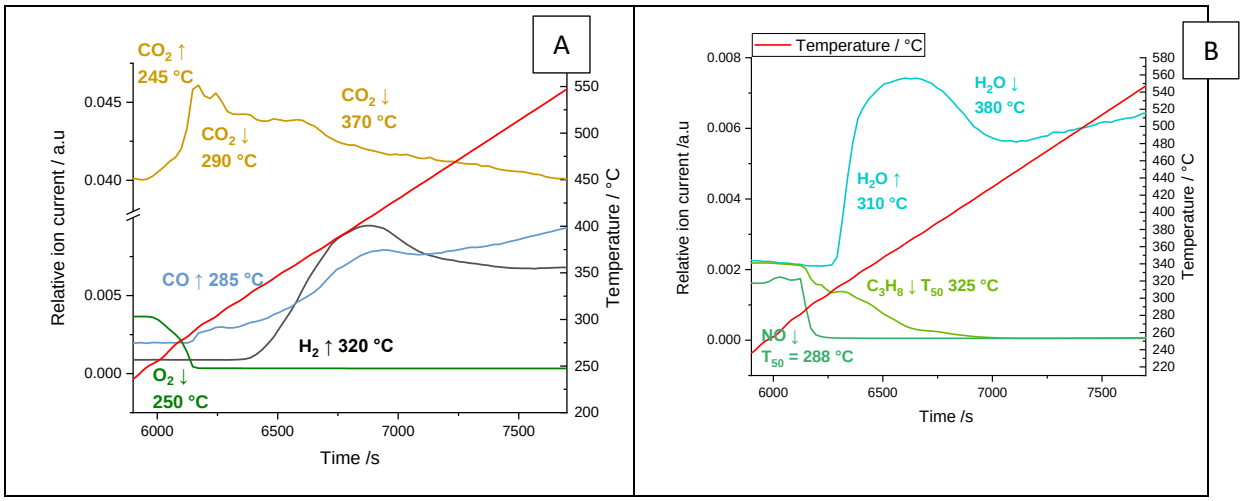


Figure S3: MS profiles between 230 °C to 720 °C of the 0g ash loaded sample, propane consumption.



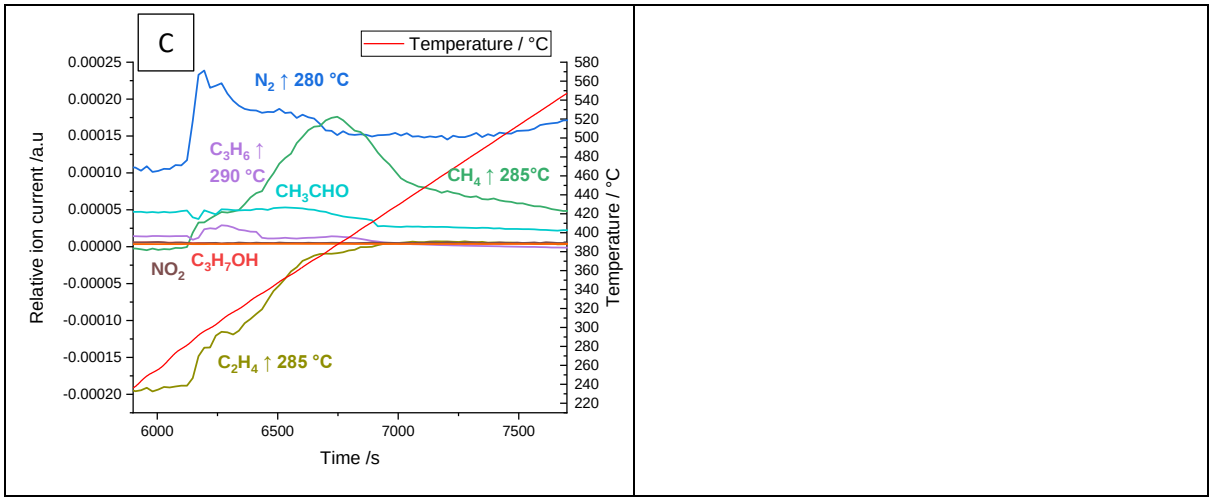


Figure S4: MS profiles between 230 °C to 550 °C of the washcoat sample

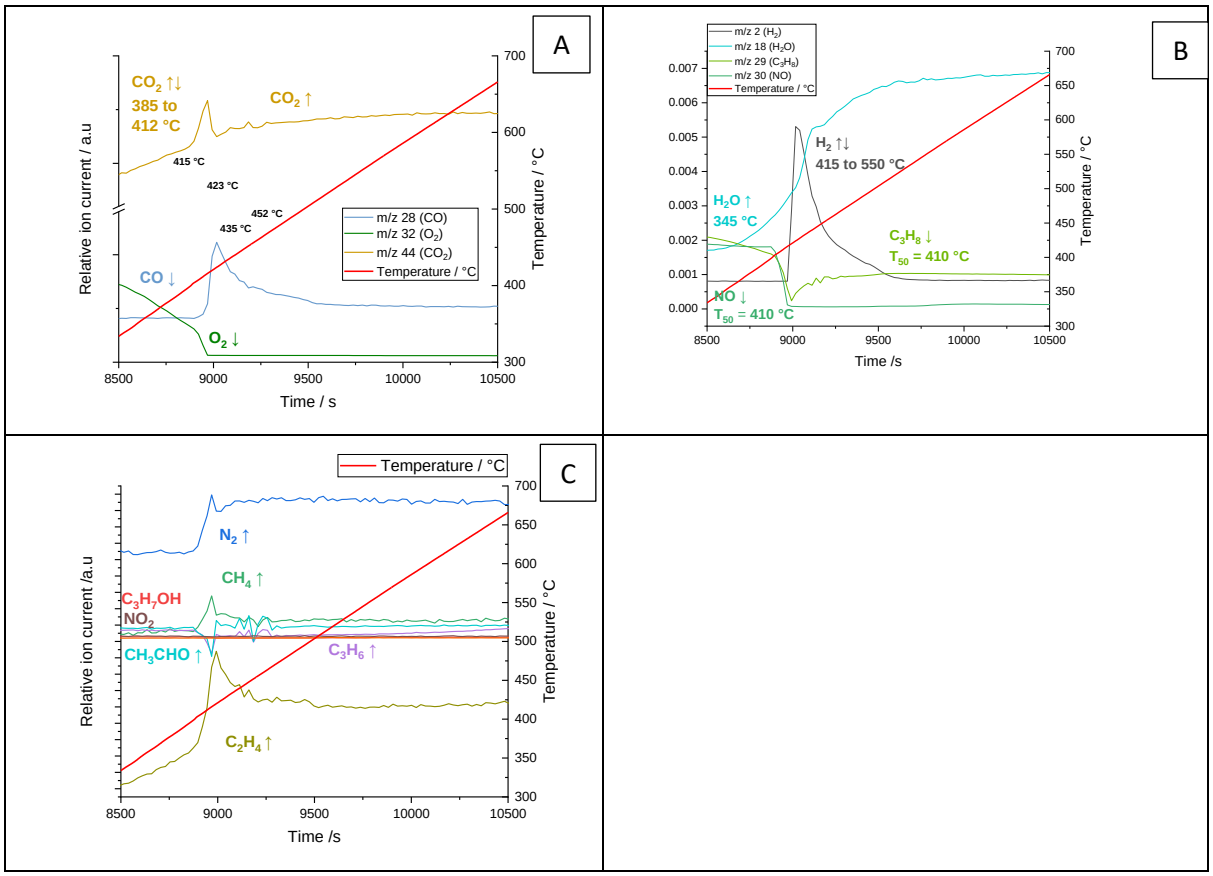


Figure S5: MS profiles between 330 °C to 665 °C of the 20g ash GPF sample