

## Supporting Documents

### 1) Temperature Programmed Decomposition (TPD) of the Dried Cake of FC67 Oxygen Carriers

The cake obtained after drying the filtered precipitates (in co-precipitation method) was subjected to a temperature ramp from 100 – 1000 °C (at a rate of 20 °C/min, in air) in TGA. The derivatives of mass change as a function of temperature are shown below.

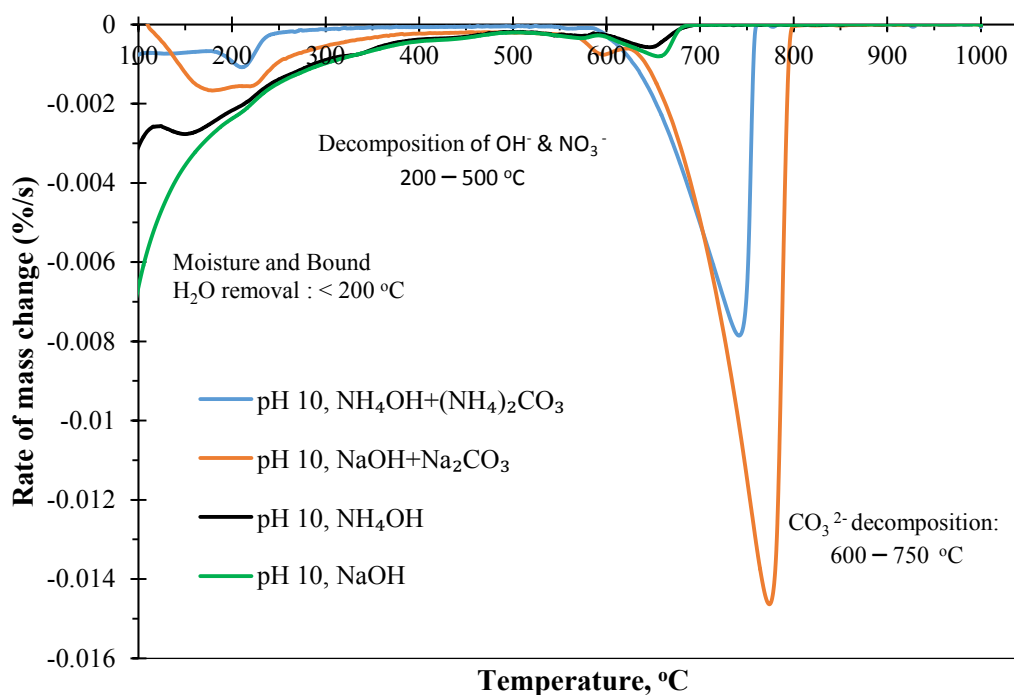


Figure S11: Rate of mass change (i.e. DTG) of the TPD at various temperatures during calcination of co-precipitated dried FC67 cake for four of the precipitants, (a) NH<sub>4</sub>OH + (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, (b) NaOH + Na<sub>2</sub>CO<sub>3</sub> (c) NH<sub>4</sub>OH and (d) NaOH.

## 2) XRD Patterns of Co-precipitated Fresh FC67 after Calcination at 1000 °C, 6 h

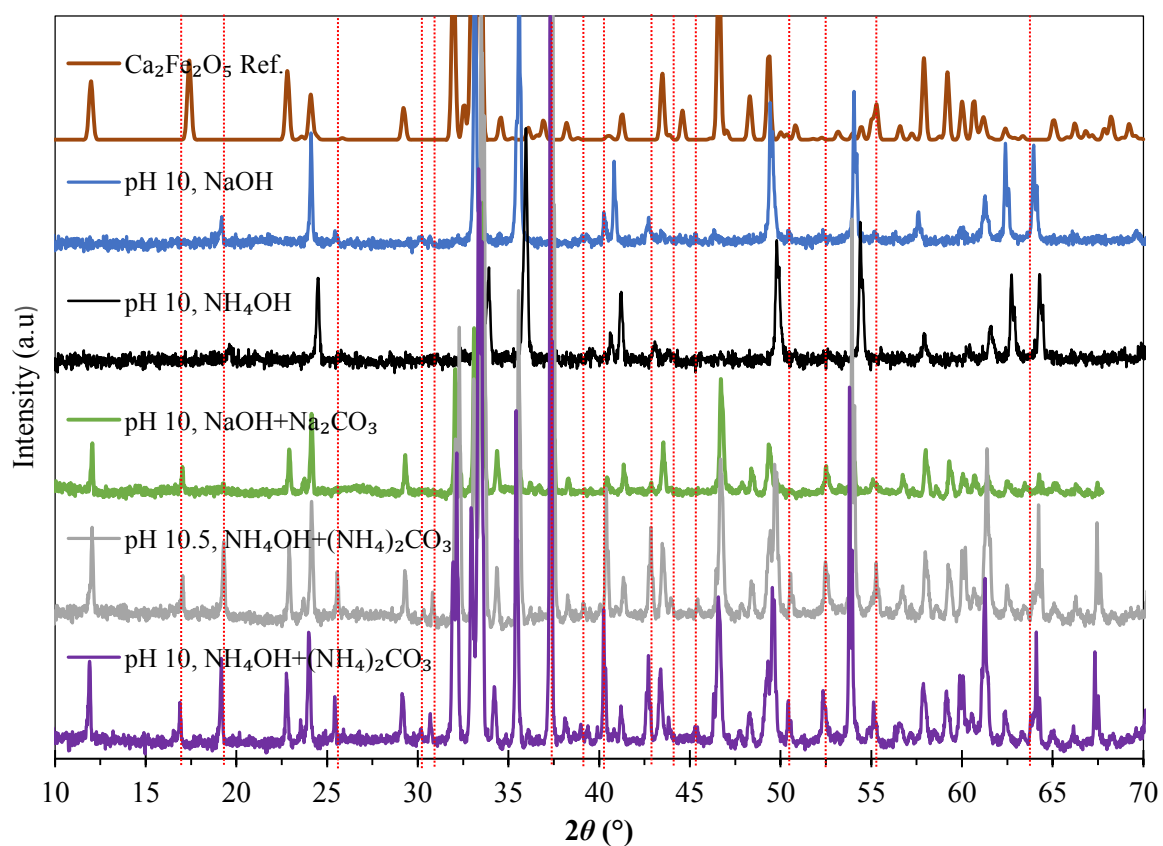


Figure S12: XRD patterns of co-precipitated FC67 particles after calcination at 1000 °C for 6 h. Unique (non-overlapping) peaks of  $\text{CaFe}_2\text{O}_4$  are indicated by dotted vertical lines (orange colour).

### 3) TPR (in H<sub>2</sub>) of fresh FC67 particles prepared by co-precipitation Method

Figure SI3 shows the TPR (in 5 vol.% H<sub>2</sub>) and DTG of fresh FC67 particles (calcined at 1000 °C, 6 h) prepared by co-precipitation using different precipitants. The experiments were carried out in TGA. Theoretically, FC67 is expected to lose 17.6% of its mass if it is reduced completely.

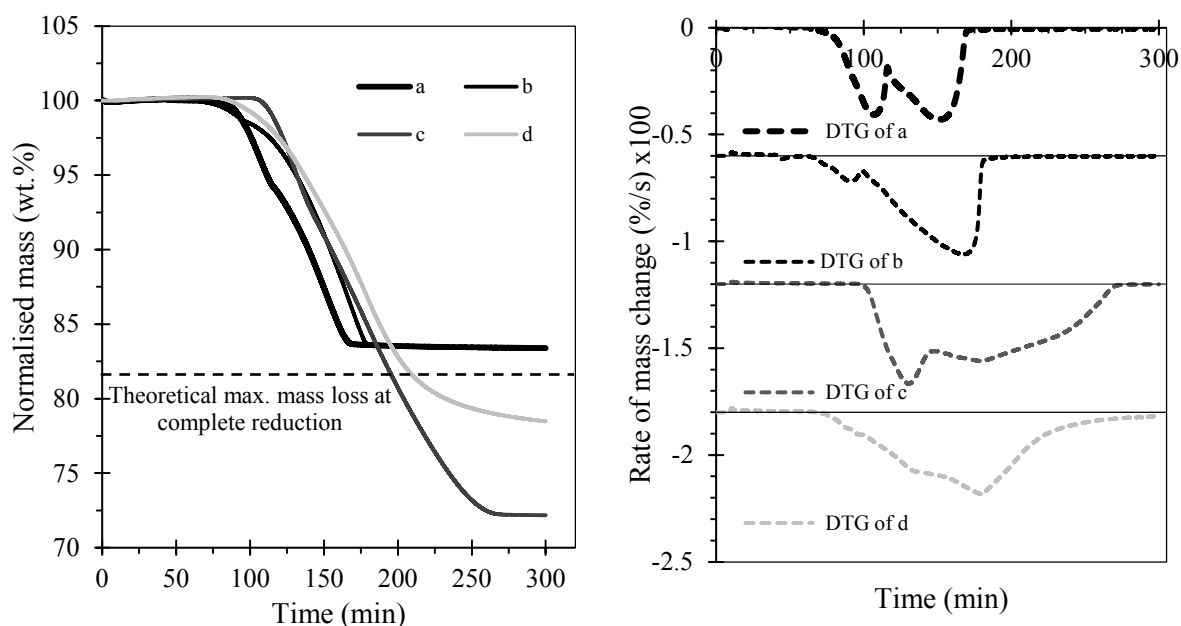


Figure SI3: Normalised mass during 5 vol.% H<sub>2</sub> TPR (Left figure) and DTG (Right figure) of TPR of co-precipitated fresh FC67 particles (calcined at 1000 °C for 6 h. Here: a) OCs prepared by using NH<sub>4</sub>OH + (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> with pH-10, b) OCs prepared by using NaOH + Na<sub>2</sub>CO<sub>3</sub> with pH-10, c) OCs prepared by using NH<sub>4</sub>OH with pH-10 and d) OCs prepared by using NaOH with pH-12.5.

#### 4) XRD of the Particles prepared by MCS method

Figure SI4 shows the XRD pattern of the fresh FC67 prepared by MCS method after calcination at 1000 °C in air for various durations. At thermodynamic equilibrium, only  $C_2F$  should be present after calcination at 1000 °C in air. Here, both CF and  $C_2F$  were observed even after a 36 h calcination. The characteristic peaks of CaO were also found in the XRD patterns for materials prepared with shorter calcination periods. Unique peaks of CF and CaO are marked by ‘O’ and ‘×’, respectively. The unmarked peaks are of  $C_2F$ ; it is hard to identify the unique peaks of  $Fe_2O_3$  as those are overlapped with either CF or  $C_2F$ .

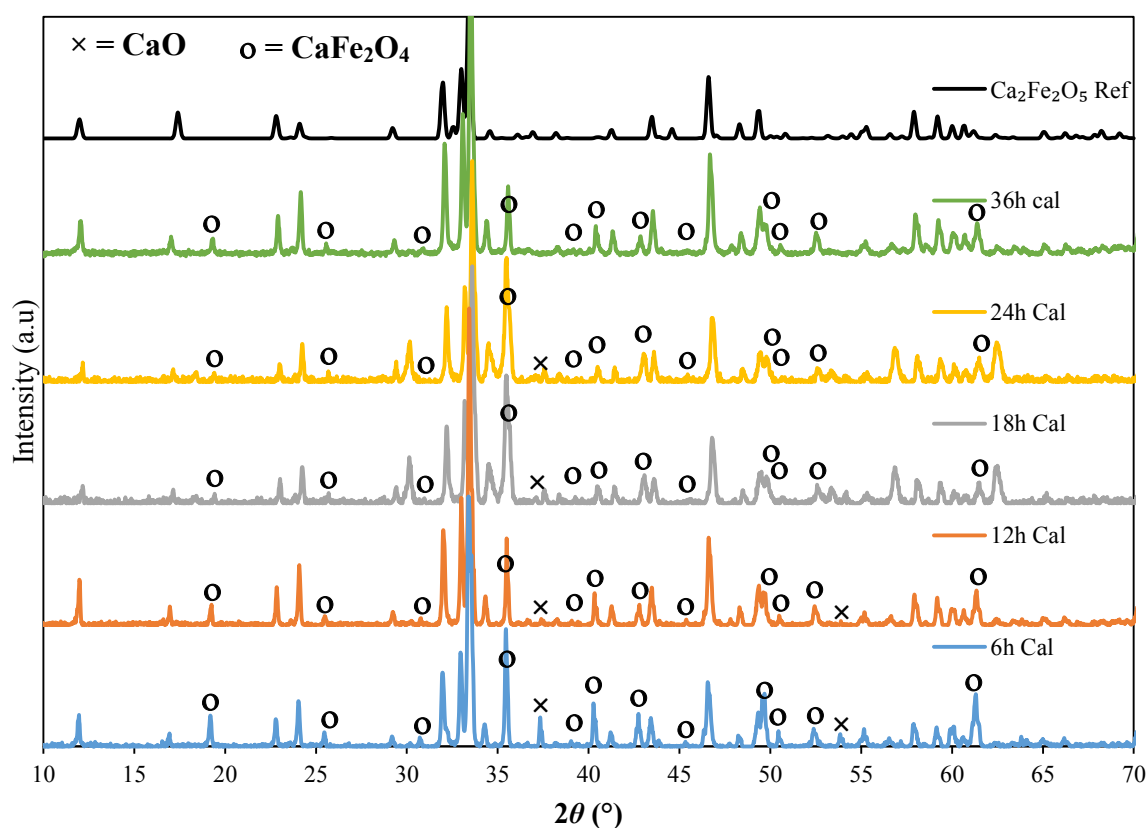


Figure SI4: XRD patterns of fresh FC67 (prepared by MCS method) calcined at 1000 °C, maintaining different calcination durations. Selected peaks labelled by: O ( $CaFe_2O_4$ ), × (CaO). The reference XRD patterns used for comparison are:  $CaFe_2O_5$  (ICSD- 14296, PCMN),  $CaFe_2O_4$  (ICSD- 16695, PNMA) and CaO (ICSD- 51409, FM3-M).

## 5) TPR (in H<sub>2</sub>) of fresh FC67 particles prepared by MCS Method

Figure SI5 shows the TPR (in 5 vol.% H<sub>2</sub>) and DTG of fresh FC67 materials prepared by the MCS method in which the particles were calcined at 1000 °C for different time periods. There is a small difference between the amount of CF in the sample calculated from the first mass loss and the amount determined from XRD (shown in Table SI1), possibly owing to reduction of free Fe<sub>2</sub>O<sub>3</sub> in the particles.

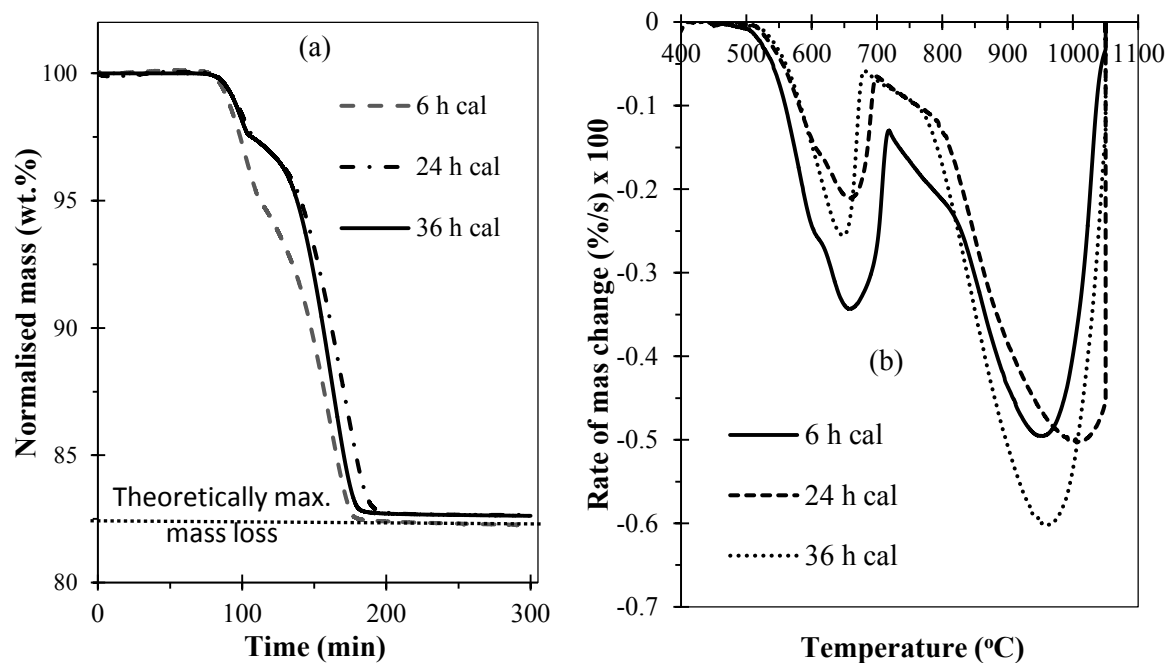


Figure SI5: (a) Normalised mass change during TPR in 5 vol% H<sub>2</sub> and (b) Normalised rate of mass change (with temperature) during TPR of FC67 oxygen carriers prepared by the MCS method in which the particles were calcined at 1000 °C for different time periods.

## 6) Composition of Phases:

Table SII: Composition of phases in the freshly prepared oxygen carriers, quantified by Rietveld refinements of the XRD patterns, and inferred indirectly from the TPR measurements

Preparation Method	Calcination temperature	Phase fractions calculated from Rietveld Refinement					Results from TPR			
		CaFe <sub>2</sub> O <sub>4</sub> (wt. fr.)	Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub> (wt. fr.)	CaO (wt. fr.)	Fe <sub>2</sub> O <sub>3</sub> (wt. fr.)	Total amount of Fe (mol. fr. in OCs)	CaFe <sub>2</sub> O <sub>4</sub> (wt. fr.) based on 1 <sup>st</sup> mass loss during TPR <sup>1</sup>	Temp. (° C) at which 1 <sup>st</sup> mass loss completed	Total amount of Fe (mol. fr. in OCs)	
Mechanochemical Synthesis	1000°C, 6h	0.397	0.555	0.047		0.53	0.46	711° C	0.53	
Mechanochemical Synthesis	1150°C, 6h	0.294	0.704	0.008		0.54	0.33	811° C	0.54	
Mechanochemical Synthesis	1250°C, 6h	Particles melted								
Mechanochemical Synthesis	1150°C, 12h	0.272	0.737			0.54	0.29	819° C	0.54	
Mechanochemical Synthesis	1000°C, 6h + 1150°C, 6h	0.285	0.714			0.54	0.29	803° C	0.54	
Mechanochemical synthesis	1000°C, 36h	0.14	0.86			0.52	0.19	656° C	0.49	
Mechanochemical Synthesis	1000°C, 36h + 1150°C, 6h	0.137	0.87			0.52	0.16	678° C	0.49	
Co-ppt., pH-10, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> + NH <sub>4</sub> OH	1000°C, 6h	0.22	0.672	0.11	-	0.47	0.28	722° C	0.47	
(Co-ppt., pH-10, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> + NH <sub>4</sub> OH	1150°C, 6h	0.009	0.919	0.063	0.001	0.47	0.14	705° C	0.53	
Co-ppt., pH-10, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> + NH <sub>4</sub> OH	1000°C, 6h + 1150°C, 6h	0.021	0.896	0.06	0.023	0.48	0.04	697° C	0.53	
Co-ppt., pH-10, Na <sub>2</sub> CO <sub>3</sub> + NaOH	1000°C, 6h	0.022	0.893	0.06	0.024	0.48	0.14	650° C	0.48	
Co-ppt., pH-10, Na <sub>2</sub> CO <sub>3</sub> + NaOH	1150°C, 6h	0.003	0.924	0.057	0.016	0.48	0.03	601° C	0.48	
Co-ppt., pH-10, Na <sub>2</sub> CO <sub>3</sub> + NaOH	1000°C, 6h + 1150°C, 6h	-	0.97	0.03	-	0.48	0.02	623° C	0.48	

<sup>1</sup>Calculated assuming that only CF and C<sub>2</sub>F is present in the particles

## 7) BET surface area, BJH volume and pore size measurements

Table SI2 shows the surface area, BJH volume and average pore size of the fresh and cycled materials.

*Table SI2: Summary of specific surface area, BJH volume and pore width<sup>1</sup> of the freshly prepared particles and particles cycled in the fluidized bed reactor*

<b>Particles</b>	<b>BET specific surface area (m<sup>2</sup>/g)</b>	<b>BJH volume (cm<sup>3</sup>/g)</b>	<b>'d' pore (nm)</b>
FC0 fresh	0.9	0.0016	8.01
FC67MCS	1.34	0.0024	7.03
FC67(MCS,36h)	1.0	0.0022	2.4
FC67(COP,12h)	0.5	0.0049	6.7
FC0 after 10 cycles	0.26	0.0007	9.76
FC67MCS after 10 cycles	1.36	0.0023	6.62
FC67MCS after 37 cy	1.2	0.002	6.8
FC67MCS after 50 cy	0.95	0.0019	5.74
FC67(MCS,36h) after 20 cycles	1.2	0.0025	2.97
FC67(COP,12h) after 20 cycles	1.4	0.0476	11.68

<sup>1</sup>Adsorption average pore width (4V/A by BET)

## 8) Temperature Programmed Reduction and Oxidation of Particles

Temperature programmed oxidation (TPO) of FC67(MCS,36h) of the completely reduced sample (*i.e.* after the TPR) was carried out using 20 vol.% CO<sub>2</sub>. Figure SI6a shows the normalised mass and its derivative as a function of temperature during TPR in H<sub>2</sub> and TPO in CO<sub>2</sub>.

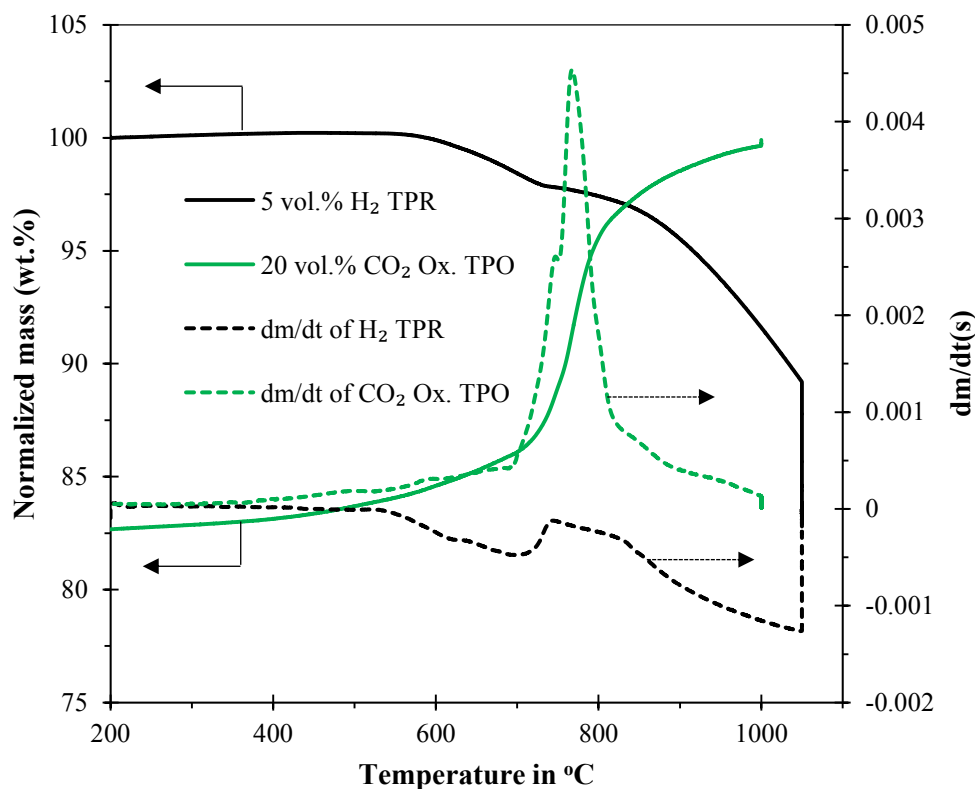
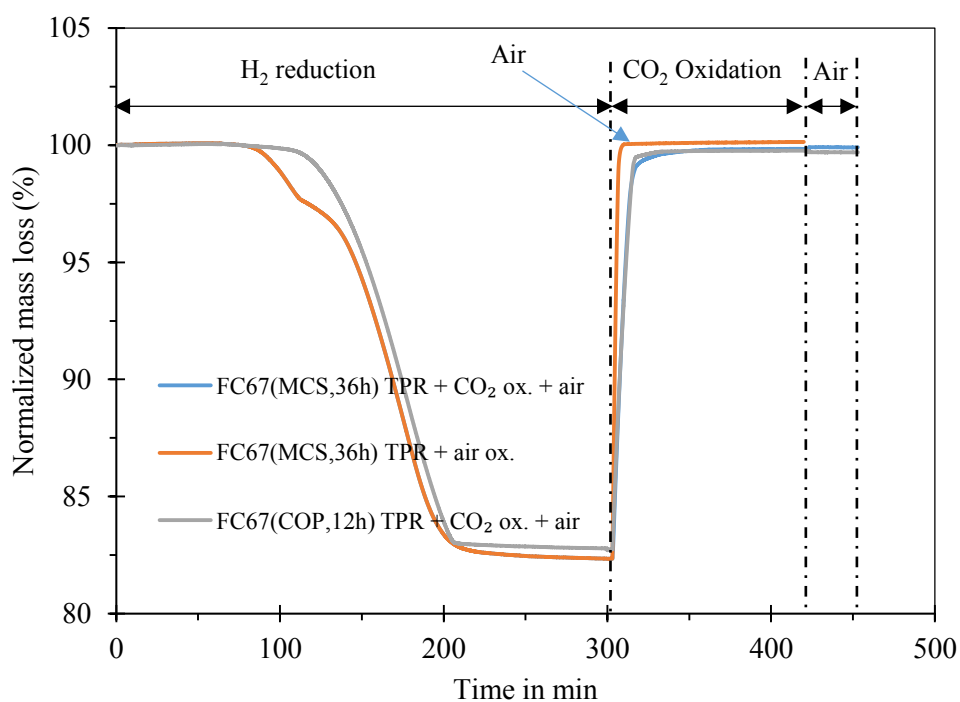


Figure SI6a: Mass of sample, and its derivative, during H<sub>2</sub> TPR followed by CO<sub>2</sub> TPO (heating from 50 -1000 °C at a rate of 5 °C/min and then 30 mins at 1000 °C) for fresh FC67(MCS,36h).

It can be seen that during TPR all the ferrites reduced to Fe and CaO (the mass loss during TPR is consistent with the expected mass loss of 17.7 wt.%). The oxidation (TPO) of the reduced particles by CO<sub>2</sub> led to the formation of CaCO<sub>3</sub> until ~ 650 °C is reached, when the gradual decomposition of carbonate occurred simultaneously with the oxidation of the iron phases. At temperatures below 650 °C, the oxidation of Fe to FeO or Fe<sub>3</sub>O<sub>4</sub> or CF or C<sub>2</sub>F is kinetically slow [61],[62] and if the oxidation is done by CO<sub>2</sub>, it may be competitively inhibited by carbonation in the particles. Furthermore, according to **Figure -2**, any free CaO would have been carbonated below 650 °C at  $P_{CO_2} = 1$  bar, preventing the formation of Fe-Ca-O phases. During CO<sub>2</sub> oxidation of the reduced OCS, ~ 99.7% of the mass lost during TPR was recovered indicating that oxidation of the reduced particles by CO<sub>2</sub> could re-generate the C<sub>2</sub>F without any need for air oxidation. Additional evidence for this regeneration was also observed during the isothermal CO<sub>2</sub> oxidation (at 900 °C) of the reduced (by TPR) particles shown in Figure SI6b. A small fraction (0.3 wt.%) of the lost mass (during reduction) did not fully re-oxidised to a



state equivalent to oxidation of Fe to Fe<sub>2</sub>O<sub>3</sub> during re-oxidation) during CO<sub>2</sub> oxidation at 900 °C (in Figure SI6b) suggests the presence of minor amounts of CF or other iron-containing phases.



Figures SI6b: Air oxidation and the CO<sub>2</sub> oxidation behaviour at 900 °C of TPR reduced particles of FC67(MCS,36h) and FC67(COP,12h).

## 9) XRD Patterns of the FC67 Particles (Fresh and Reduced) Oxidised by CO<sub>2</sub>

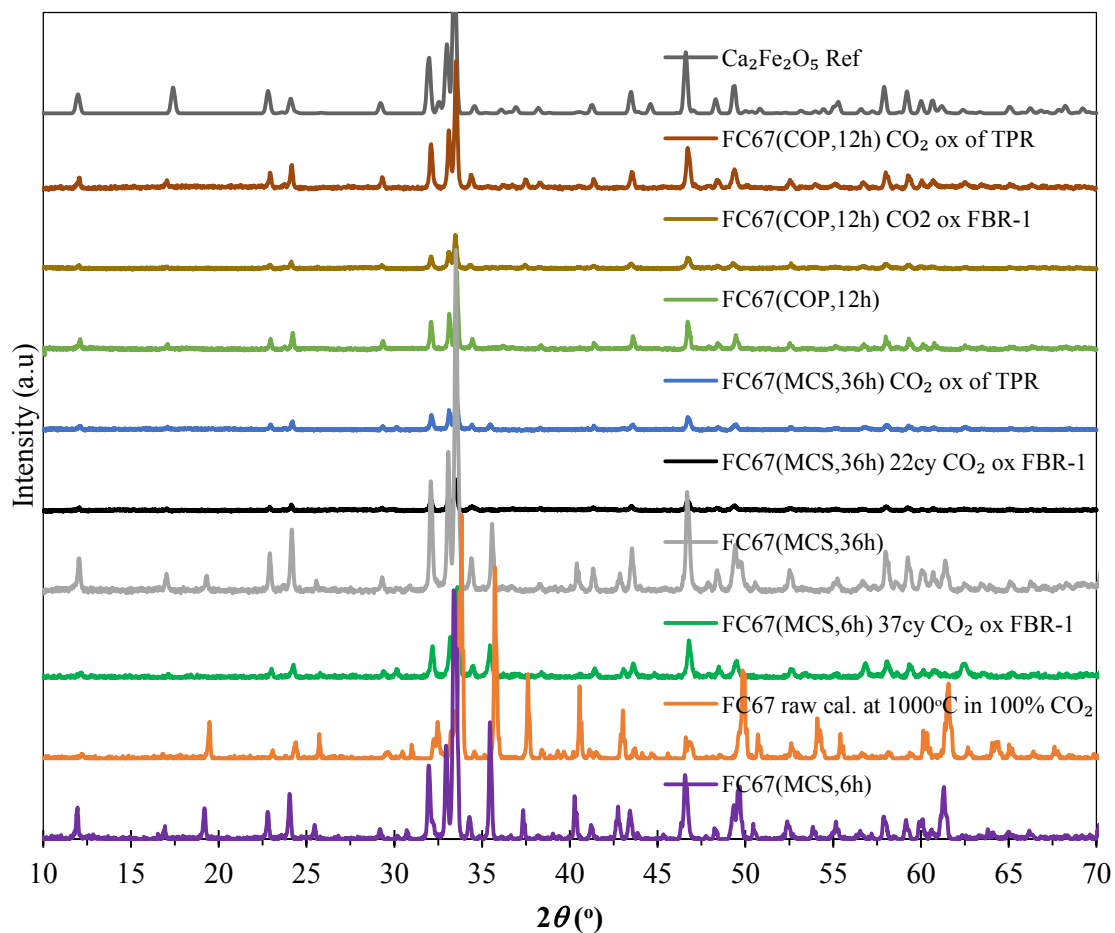


Figure SI7: XRD of a selection of fresh and CO<sub>2</sub> oxidized samples (obtained from FBR-1 and after TPR in TGA). Here, 'FC67 raw Cal. at 1000 °C in 100 % CO<sub>2</sub>' means the dried (not calcined) particles were calcined at 1000 °C in 100 vol.% CO<sub>2</sub> and then XRD of the particle was carried out.