Electronic Supporting Information

Direct conversion of calcium carbonate to C_1 – C_3 hydrocarbons

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Table S1: Temperature variation studies of the reaction.

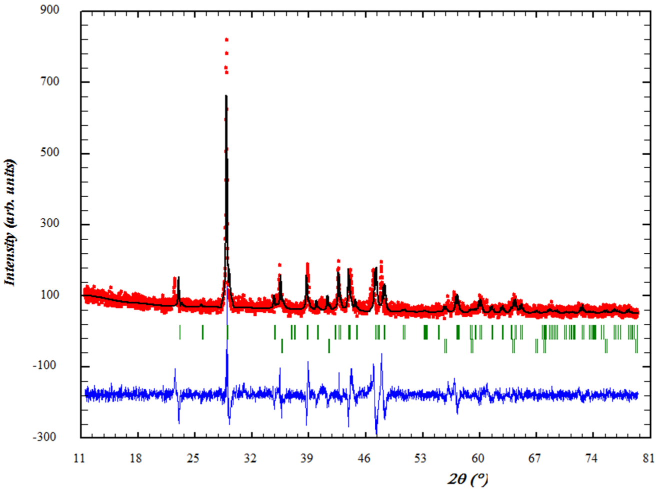
Table S1 presents the decomposition, specific mole conversion, HC TON and yield of the products for FeCaCO (x = 2) heated in H_2 at different temperature for a period of 2 h.

T (K)	Total mole conversion of CO_3 (%)	Specific HC mole conversion (%)	HC TON (S^{-1})	Yield (%)					
				CH_4	C_2H_4	C_2H_6	C_3H_8	CO	CO_2
573	13	12	7.1×10^{-9}	1	1	-	0	2	9
673	34	20	1.6×10^{-8}	2	3	2	1	9	17
773	30	10	1.8×10^{-8}	2	3	4	1	6	14
873	25	8	1.5×10^{-8}	2	2	3	1	5	12

Table S2: X-ray diffraction data

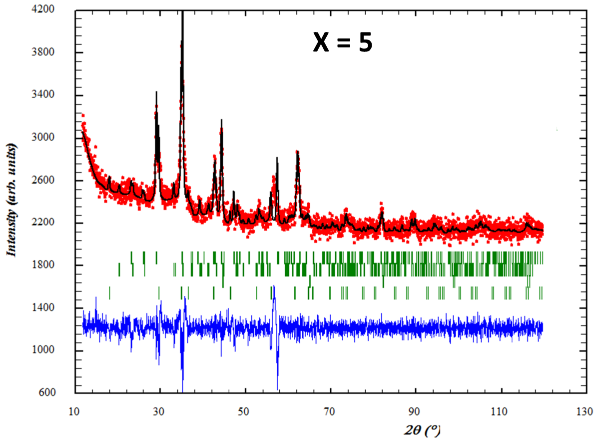
Red colour represents the observed diffraction pattern, black represents the calculated pattern, green colour represents the Bragg position, blue colour represents pattern obtained by subtracting the calculated from observed pattern.

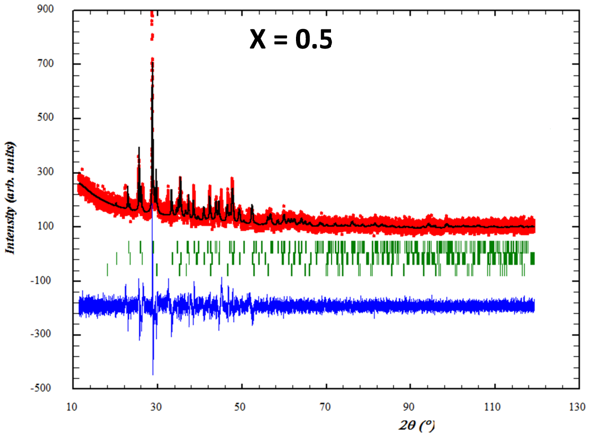
xFeCaCO (x = 0.5)



x	Phase	Space group	Lattice parameters	α, β, γ
0.5	γ -Fe_2O_3 (Tetrahedral)	$P4_32_12$	8.47	90.0
			8.47	90.0
			25.23	90.0
	$CaCO_3$ (Monoclinic)	C2	8.68	90.0
			4.66	94.4
			8.28	90.0
	$CaFeO_2$ (Cubic)	Fm-3m	4.79	90.0
			4.79	90.0
			4.79	90.0

xFeCaD (x = 5 and 0.5)



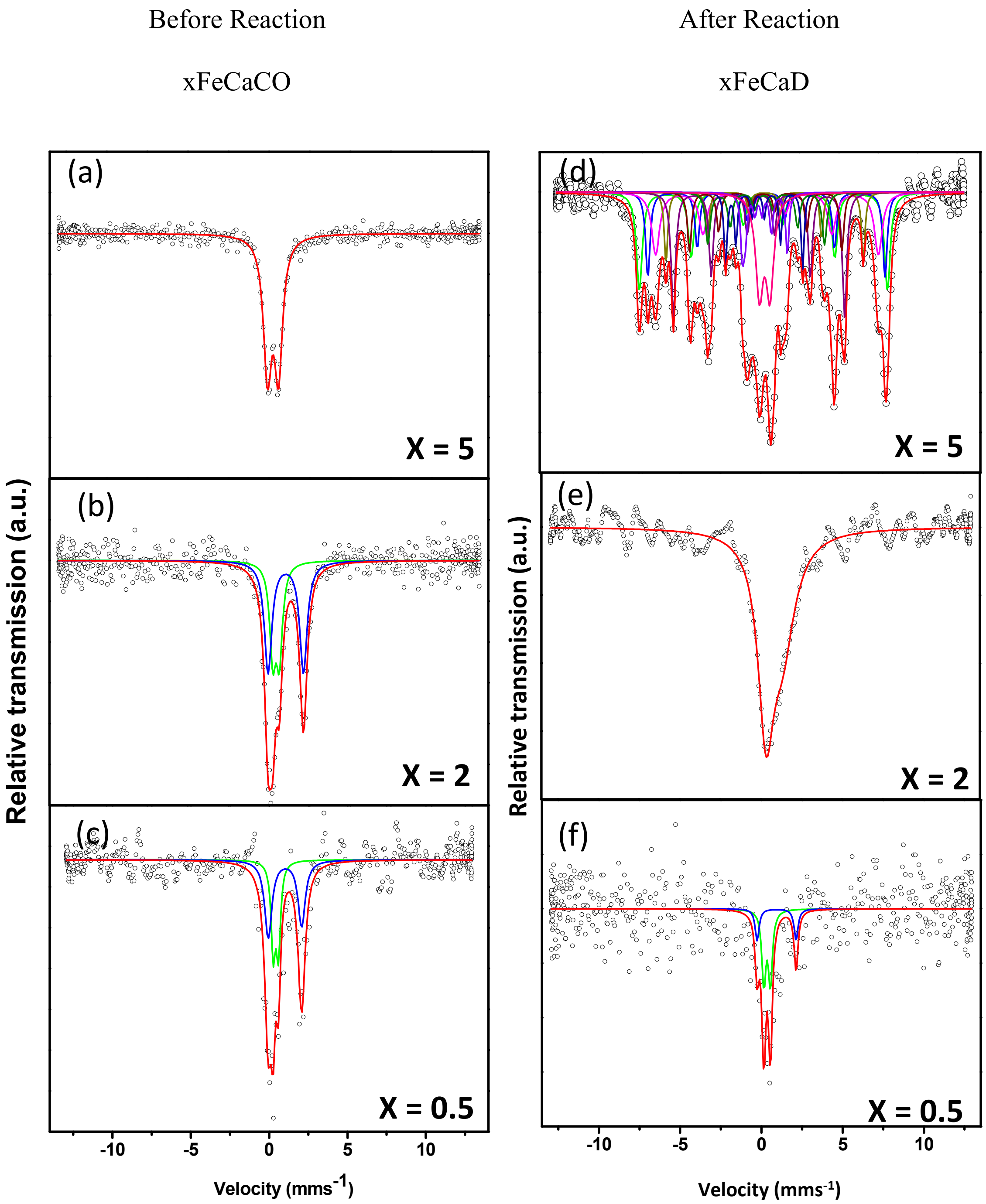


x	Phase	Space group	Lattice parameters	α, β, γ
5	Fe_3C (Orthorhombic)	Pnma	5.12 6.81 4.65	90.0 90.0 90.0
	$CaFe_2O_4$ (Orthorhombic)	Pnma	9.22 10.7 3.02	90.0 90.0 90.0
	α-Fe (bcc cubic)	Im-3m	2.87 2.87 2.87	90.0 90.0 90.0
	Fe_3O_4 (cubic)	Fd-3m	8.53 8.53 8.53	90.0 90.0 90.0
	γ-Fe_2O_3	$P4_32_12$	8.37 8.37 24.1	90.0 90.0 90.0
	Fe_5C_2 (Monoclinic)	C2/c	11.56 4.57 5.06	90.0 97.6 90.0
	α-FeOOH	Pbnm	4.58 9.93 3.01	90.0 90.0 90.0

0.5	γ -Fe_2O_3	$P4_32_12$	8.37 8.37 24.85	90.0 90.0 90.0
	Fe_3O_4 (Cubic)	Fd-3m	8.47 8.47 8.47	90.0 90.0 90.0

Table S3: Mössbauer spectra of carbonate samples with x = 5, 2 and 0.5 before reaction (Figures a, b and c) and after reaction (Figures d, e and f).

In all the Mössbauer figures, the black open circles show the observed data and the red colour solid line is the fit to the observed data. The width of the baseline in the Mössbauer spectra depends on the Fe-content in the samples. Fe-rich samples will result in relative smooth base line of the spectra. The spectrum in Figure (a) shows the presence of Fe^{3+} in paramagnetic state. The subspectra denoted by blue and green doublets in figures (b and c) correspond to paramagnetic Fe^{2+} and Fe^{3+} respectively in the samples. Each of the subspectra from left to right of figure (d) of xFeCaD are identified as γ -Fe_2O_3 (489 kOe), Fe_3O_4 (A-site)/γ-Fe_2O_3 (467 kOe), Fe_3O_4 (B-site) (437 kOe), α-FeOOH (390 kOe), α-Fe (335 kOe), θ-Fe_3C (302 kOe), θ-Fe_3C (230 kOe), χ-Fe_5C_2 (152 kOe), χ-Fe_5C_2 (90 kOe) and superparamagnetic Fe^{3+} (narrow doublet), respectively. The numbers in the brackets represent the corresponding hyperfine field values. The spectrum in figure (e) shows the presence of Fe^{3+} in relaxed-paramagnetic state. The subspectra denoted by blue and green doublets in figure (f) corresponds to superparamgnetic nature (due to very small particle size) Fe^{2+} and Fe^{3+} respectively in the sample.


Before Reaction
xFeCaCO
After Reaction
xFeCaD
(a)
X = 5
(b)
X = 2
(c)
X = 0.5
(d)
X = 5
(e)
X = 2
(f)
X = 0.5
Relative transmission (a.u.)
Relative transmission (a.u.)
-10
-5
0
5
10
Velocity (mms^{-1})
-10
-5
0
5
10
Velocity (mms^{-1})

Mössbauer parameters for xFeCaCO (x = 0.5, 2 and 5).

x	Isomer shift δ (mm/s)	Quadrupole splitting Δ(mm/s)	Line width Γ(mm/s)	Relative absorption area A (%)	Inference
5	0.34 (2)	0.67 (3)	0.61 (4)	100	Paramagnetic Fe^{3+}
2	0.44 (1)	0.41 (2)	0.46 (3)	35.2	Paramagnetic Fe^{3+}
	1.14 (1)	2.18 (1)	0.56 (1)	64.8	Paramagnetic Fe^{2+}
0.5	0.43 (5)	0.33 (8)	0.32 (6)	31.1	Paramagnetic Fe^{3+}
	1.11 (3)	2.13 (3)	0.56 (7)	68.9	Paramagnetic Fe^{2+}

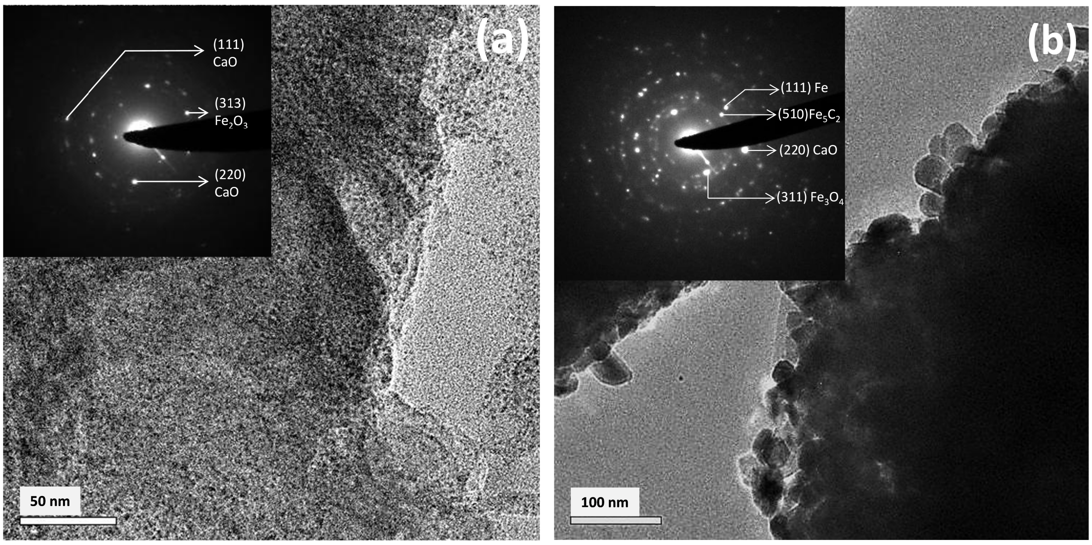
Mössbauer parameters for xFeCaD (x = 0.5, 2 and 5).

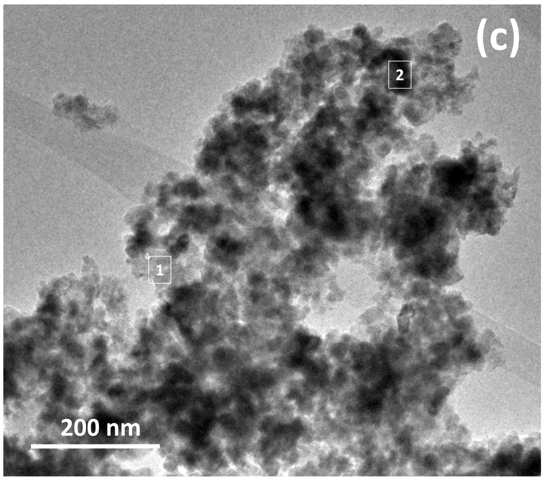
x	Isomer shift δ (mm/s)	Quadrupole Shift (mm/s)	Line width Γ(mm/s)	Hyperfine Field B_{hf} (kOe)	Relative absorption area A (%)	Inference
5	0.31 (3)	0.02 (5)	0.35 (1)	489 (2)	17	γ-Fe_2O_3
	0.38 (3)	0.04 (6)	0.34 (2)	467 (2)	12.9	Fe_3O_4 (A-site)/ γ-Fe_2O_3
	0.46 (3)	-0.05 (4)	0.51 (2)	437 (3)	20.2	Fe_3O_4 (B-site)
	0.28 (5)	-0.10 (1)	0.26 (3)	390 (3)	5.4	α-FeOOH
	0.00 (3)	-0.01 (5)	0.33 (2)	335 (3)	14.7	α-Fe
	0.37 (6)	0.16 (8)	0.31 (3)	302 (4)	5.9	θ-Fe_3C
	0.43 (6)	0.15 (6)	0.35 (2)	230 (4)	7.3	θ-Fe_3C
	0.28 (6)	0.07 (8)	0.23 (5)	152 (4)	3.8	χ-Fe_5C_2
	0.20 (7)	0.40 (8)	0.25 (6)	90 (5)	4.1	χ-Fe_5C_2
	0.31 (4)	0.67 (6)	0.58 (5)	–	8.7	Superparamagnetic

						Fe^{3+}
2	1.0 (1)	1.2 (1)	0.9 (1)	-	100	Relaxed paramagnetic Fe^{+3}
0.5	0.35 (5)	0.41 (2)	0.31 (6)	-	69.9	Superaramagnetic Fe^{3+}
	1.03 (4)	2.40 (5)	0.30 (5)	-	30.1	Superparamagnetic Fe^{2+}

Fig. S4: TEM image of xFeCaD a) x = 0.5 and b) x = 5. Inset shows the corresponding electron diffraction (ED) pattern.

Sample x = 5 which has densely crowded regions of dark contrast showed a number of symmetrical bright spots which could be indexed to different phases of Fe and CaO based on the dominant d spacing of the respective phases. ED pattern for the sample x = 0.5 showed only fewer spots which could be indexed to CaO and Fe_2O_3. Figure c shows the spot elemental X-ray analysis on different regions. The table shows the Fe/Ca ratio of the selected regions.

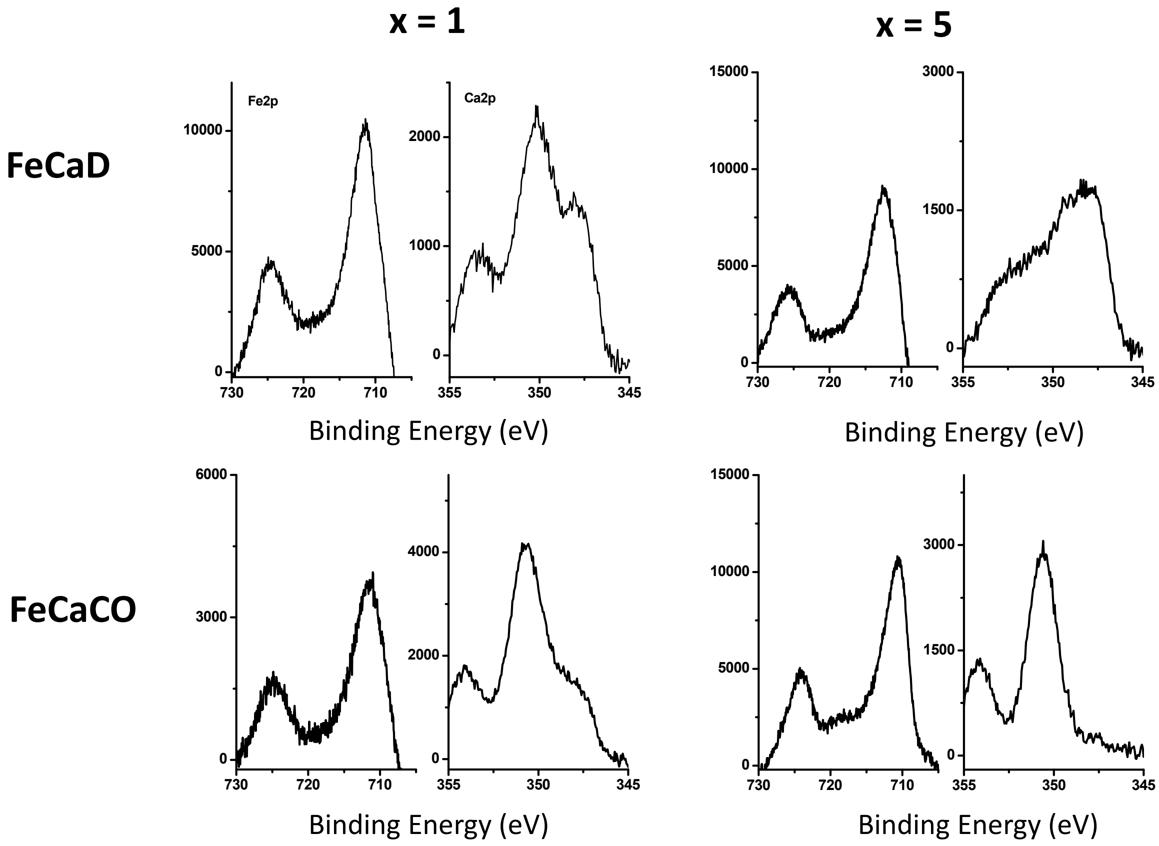




Region	**Fe/Ca Atomic ratio**
1	**0.99**
2	**5.32**

Fig. S5 XPS spectra of FeCaCO and FeCaD for x = 1 and 5. The table below shows surface Fe/Ca ratio on all the samples recorded by calculating the ratio of area of the Fe2p and Ca3p spectra.

Surface Fe/Ca ratio as calculated from this method agrees very well with the bulk ratio for x = 1 and x = 5 for the samples FeCaCO (before reaction). However, the surface Fe/Ca ratio seems to be equal for both the samples after the reaction in FeCaD samples.



x	Fe/Ca (no unit)	
	FeCaCO	FeCaD
1	0.9	4.6
5	5.2	4.2

Fig. S6: Temperature dependent product formation for $CaCO_3$ (open circles) and xFeCaCO (x = 5) (Red circles).

In this Figure, we have shown onset of the formation of products such as CO_2, CO and HCs that are formed when $CaCO_3$ and 5FeCaCO are decomposed in H_2 as a function of temperature (from 350 – 650 K). The onset of decomposition of the carbonates is recognized by the formation of CO_2 at 430 K. This temperature does not shift with the presence of Fe. However, the rate of decomposition is significantly higher in the presence of Fe. The formation of CO occurs at 500 K. There is no formation of HC in case of $CaCO_3$.

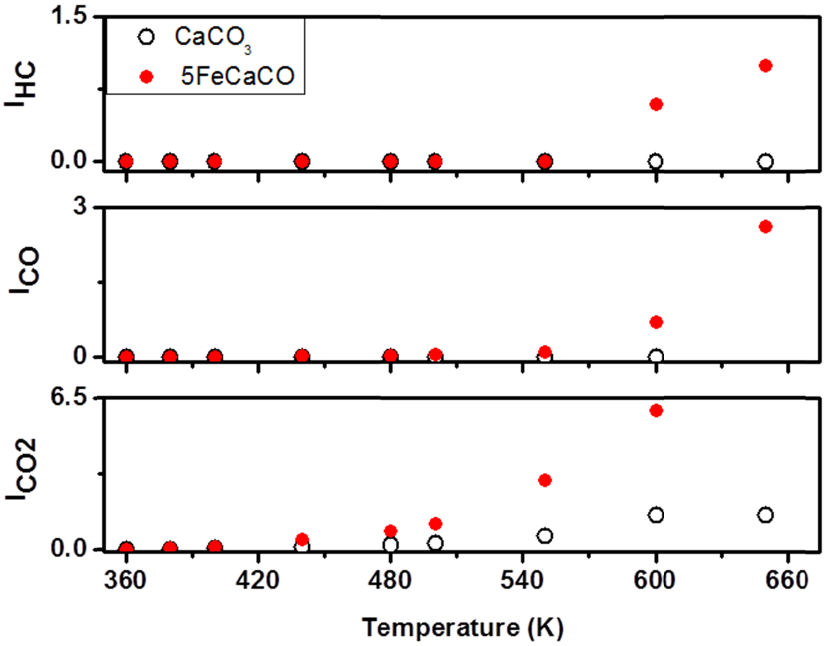


Fig. S7: Time on stream data for 5FeCaD sample heated at 673 K. The figure shows the formation of various products such as CO_2 (●), CO (○), C_2 HCs (Δ and ■) as a function of time.

The sample was heated to 673 K and maintained with a steady flow of H_2 and the time on stream (TOS) data was obtained for 1 h and 30 min. It is possible to observe the change in the concentration of CO_2 and CO throughout the experiment.