Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Controlling Cobalt Fischer-Tropsch Stability and Selectivity through Manganese Titanate formation

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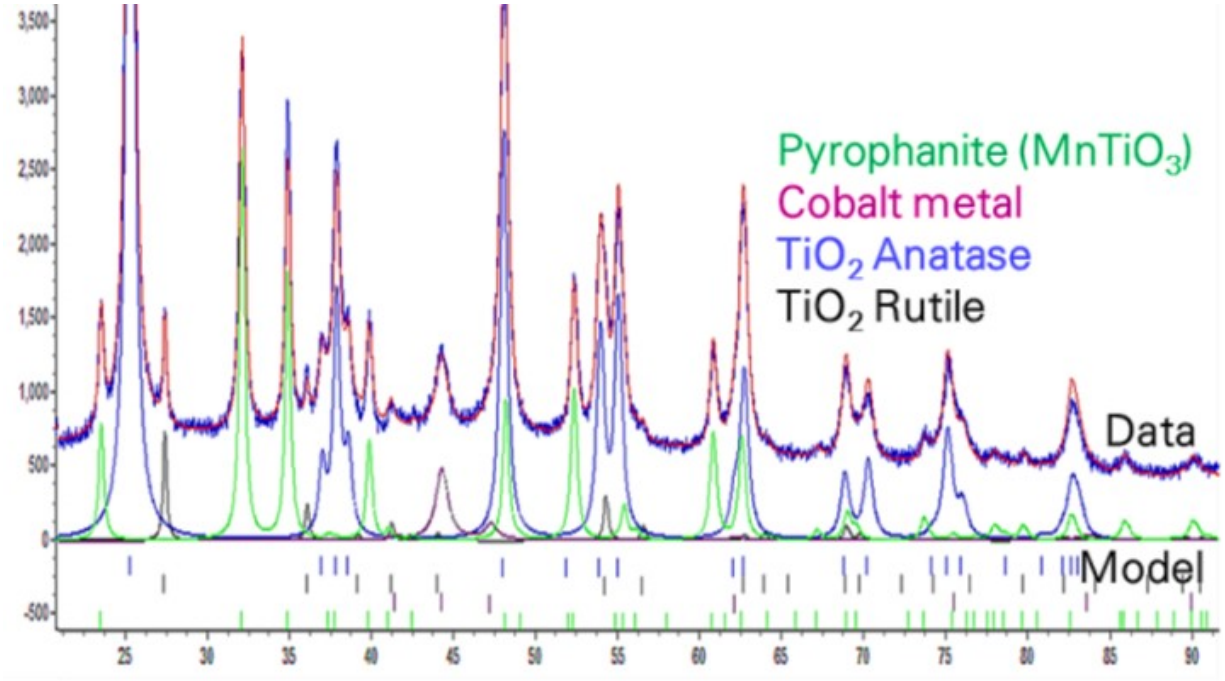


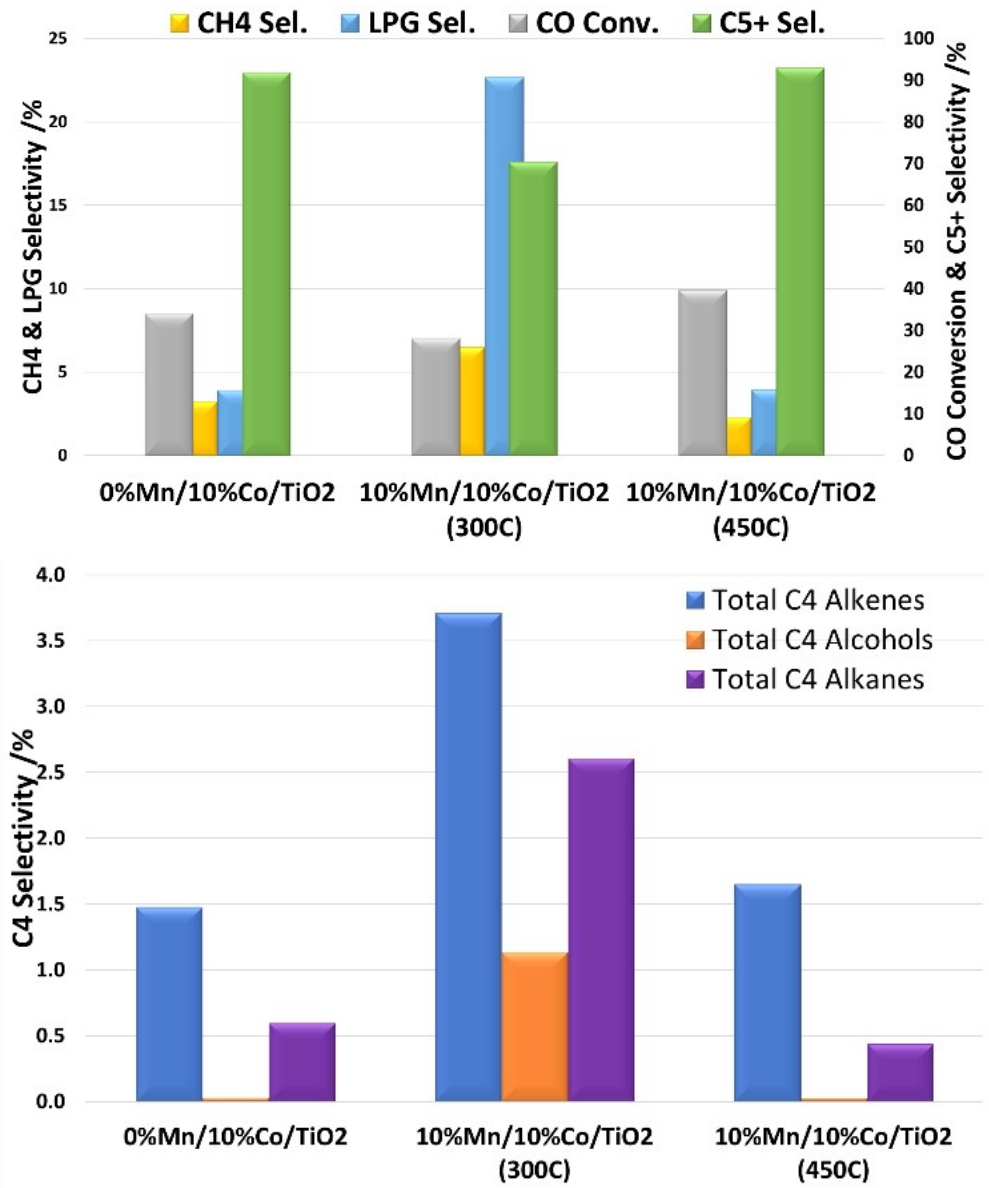
SI 1 – XRD pattern of the high temperature reduced CoMnTiO2 sample, and the XRD modelled pattern for $MnTiO_3$

	Rutile		Co_3O_4		CoO		MnTiO	
e, Å	%, Wt/Wt	Cryst Size, Å	%, Wt/Wt	Cryst Size, Å	%, Wt/Wt	Cryst Size, Å	%, Wt/Wt	Cryst
	12.5	295	16.1	73				
	12.1	300	7.1	82	7.1	48		
	12.1	314			14.3	51		
	12.6	302			8.0	57		
	13.2	314			1.2	92		
	13.2	313						
	8.2	198	20.6	41				
	8.1	209	23.3	39				
	7.5	212	20.2	32	3.9	53		
	7.1	230	6.3	25	17.1	52		

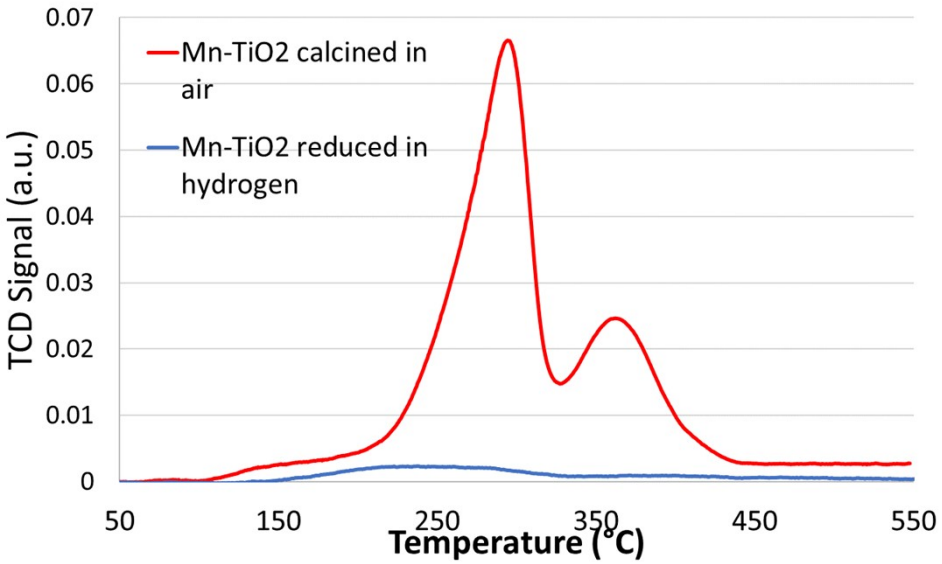
SI 2 – In situ XRD reduction data for the low and high manganese promoted samples. In particular showing the sudden onset of the MnTiO3 phase at 450C (extended data from table in manuscript)

	T-Rx [°C]	GHSV [h-1]	CO Conv [%]	Sel. CH4 [%]	Sel C5+ [%]	Sel. C2-C4 [%]	Sel. CO2 [%]	Total Alkenes [%]	1-Butanol [%]	Total Alkanes [%]
0%Mn	220	8825	34.15	3.24	91.90	3.93	0.01	1.48	0.03	0.59
5%Mn	245	8823	29.60	5.46	71.24	22.86	0.04	4.77	1.01	2.19
10%Mn (300C)	243	8819	28.03	6.50	70.37	22.67	0.04	3.71	1.13	2.60
10%Mn (450C)	214	8821	39.62	2.30	92.92	3.96	0.00	1.65	0.03	0.44

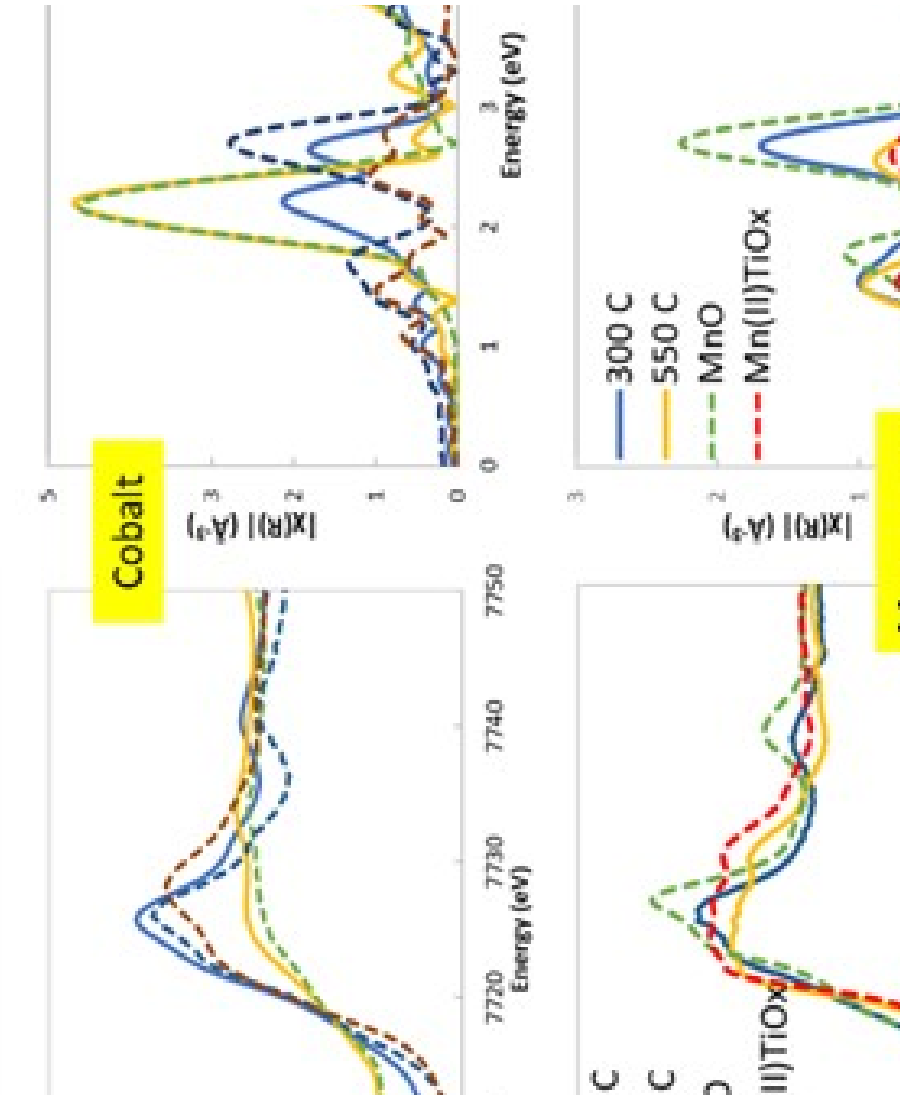
SI 3 – Summary data showing selectivity to C5+ products, alkenes and alcohols for the 10%Mn (450C) returning to a 0%Mn type level rather than matching the 10%Mn(300C) condition



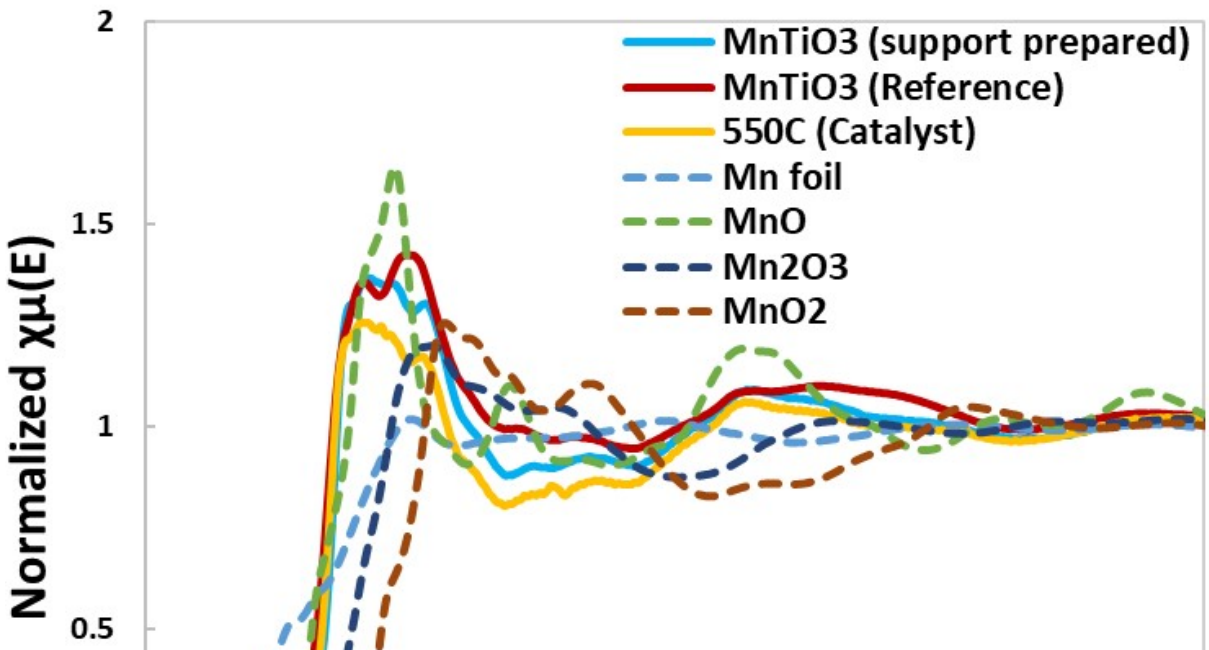
SI 4 – Graphical comparison of the data comparing the mon-manganese and the high manganese samples at 300C and 450C



SI 5 - Temperature programmed reduction of the calcined and reduced manganese-titania ex situ support samples

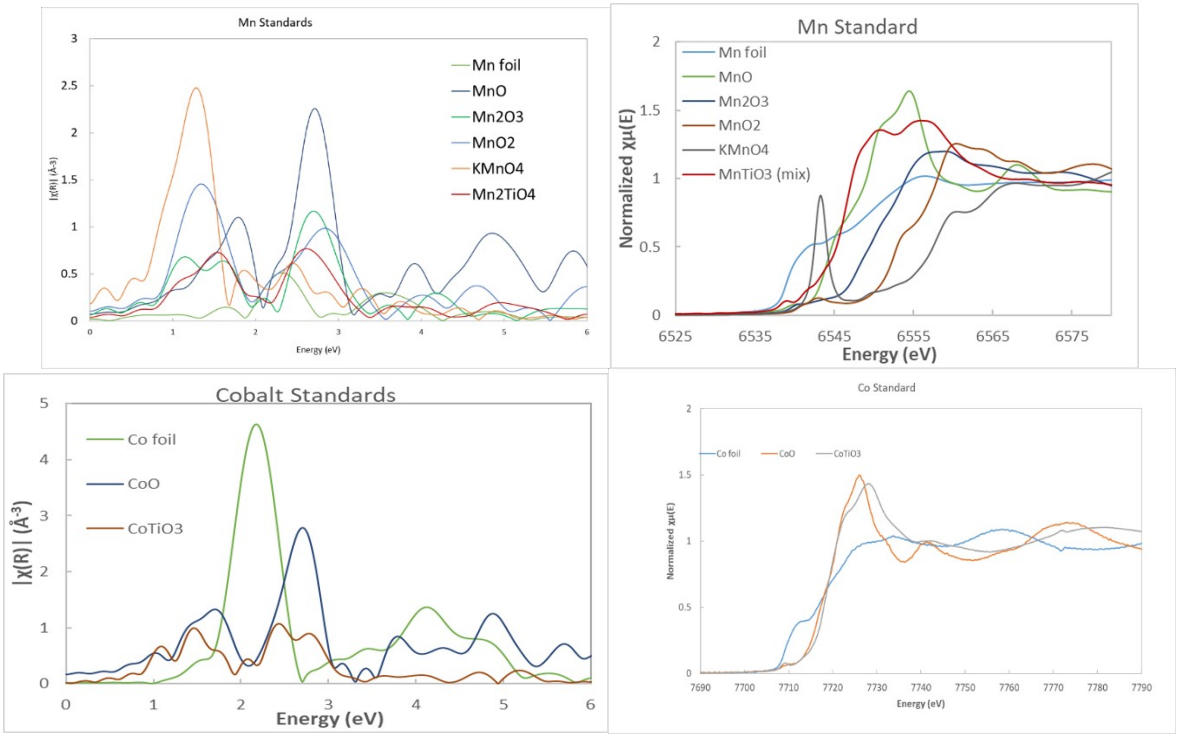


SI 6 - EXAFS and XANES images from manuscripts, expanded for clarity

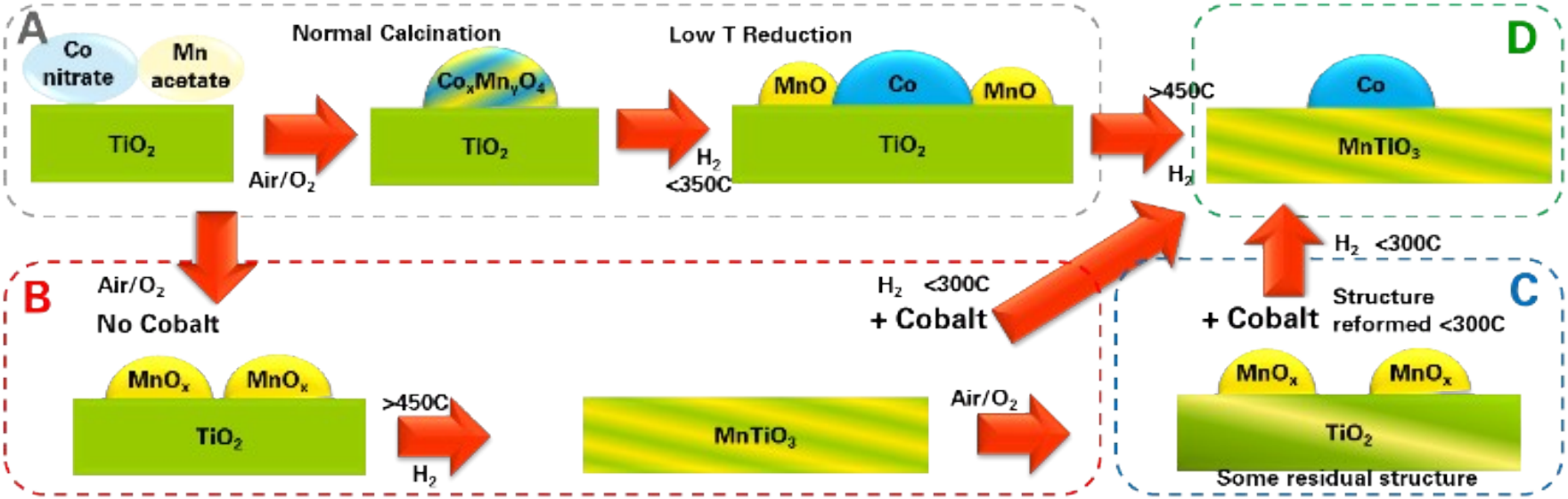


		Mn-O/Å	CN	σ^2	Mn-Mn/ Å	CN	Mn-Ti/ Å	CN	σ^2
10%Co/5%Mn/TiO2	300 ° C	2.10	5.6	0.010	3.12	4.8	-	-	0.009
	550 ° C	2.12	5.1	0.010	3.06	3.9	3.41	2.5	0.007
10%Co/5%Mn/TiO2	300 ° C	2.12	4.6	0.007	3.12	7.3	-	-	0.009
	550 ° C	2.12	5.7	0.011	3.05	4.5	3.43	3.0	0.008
References	MnO	2.22	6	-	3.14	12	-	-	-
	Mn_2O_3	2.012	6	-	3.13	6	-	-	-
	MnO_2	1.883	6	-	3.418	8	-	-	-
	$MnTiO_3$	2.11, 2.28	6	-	3.063	3	3.433	3	-
	$MnTi_2O_4$	2.041	4	-	3.724	4	-	-	-
Ex situ Support	(b) $MnTiO_3$	2.11, 2.29	6	0.009	3.058	4.3	3.474	2.9	0.008

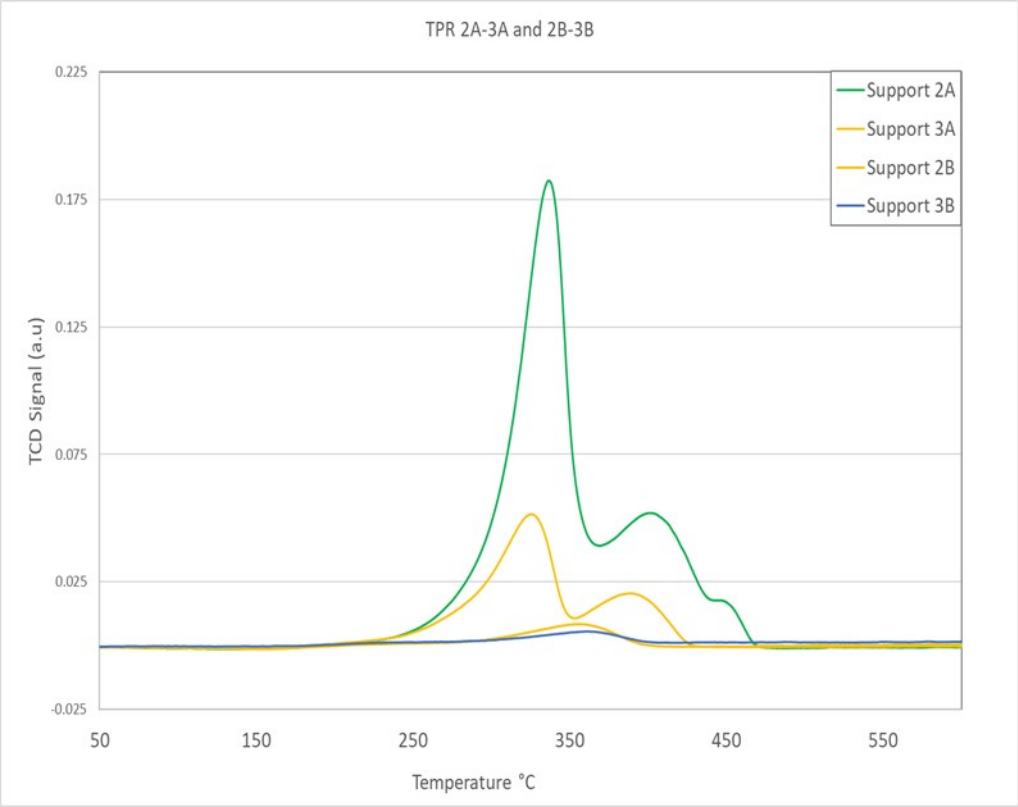
SI 7 – XAS analysis of samples with references, and comparison with the ex situ prepared support



SI 9 - XAS Standards for EXAFS and XANES for manganese and cobalt edge species

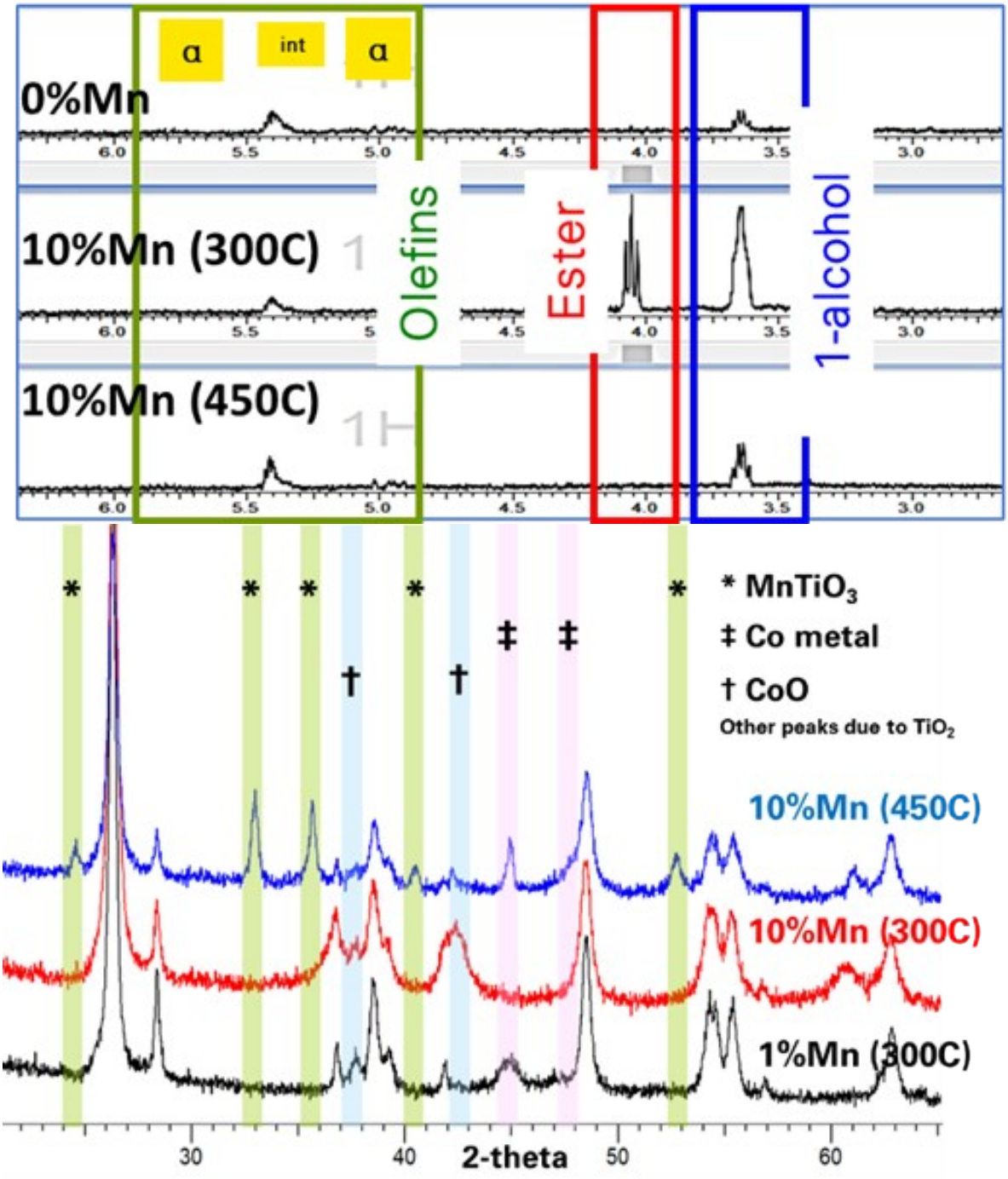

A
Co nitrate
Mn acetate
TiO2
Air/O2
Normal Calcination
CoxMnyO4
TiO2
H2
<350C
Low T Reduction
MnO
Co
MnO
TiO2
>450C
H2
D
Co
MnTiO3
B
Air/O2
No Cobalt
MnOx
MnOx
TiO2
>450C
H2
MnTiO3
Air/O2
H2 <300C
+ Cobalt
H2 <300C
+ Cobalt
Structure reformed <300C
C
MnOx
MnOx
TiO2
Some residual structure

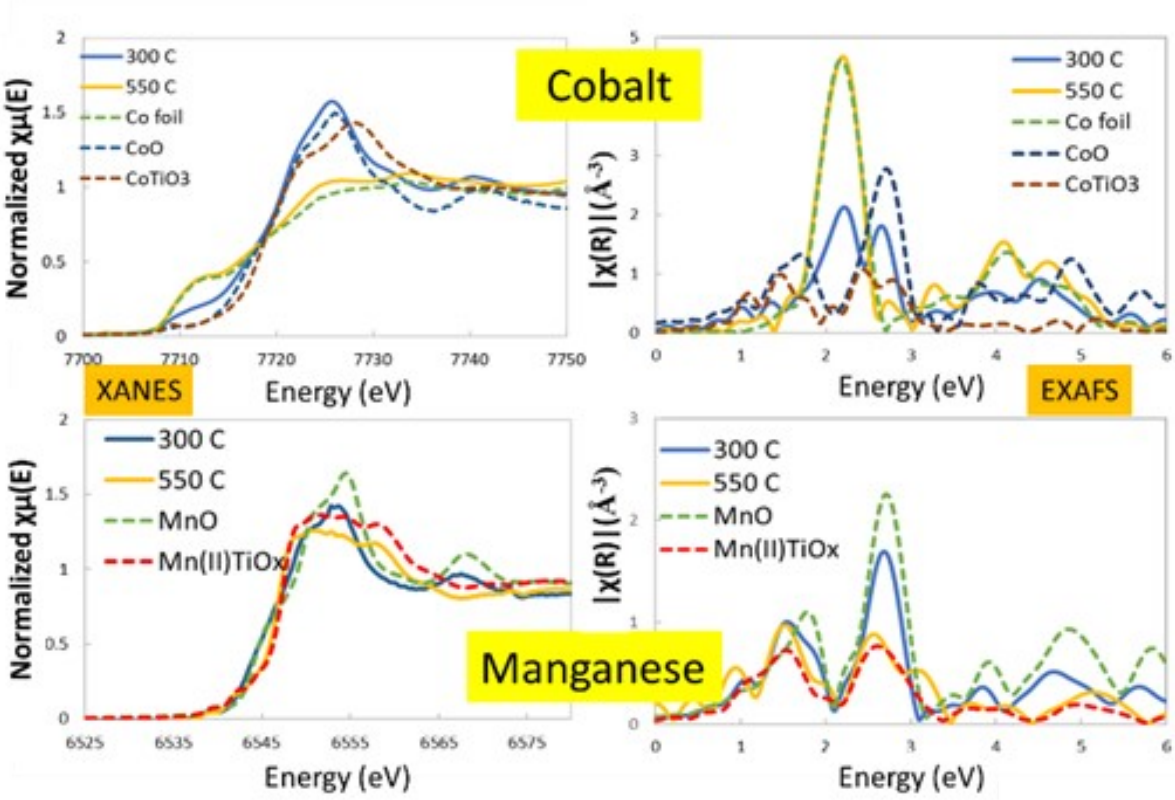
SI 10 – Overview of the catalyst transitions

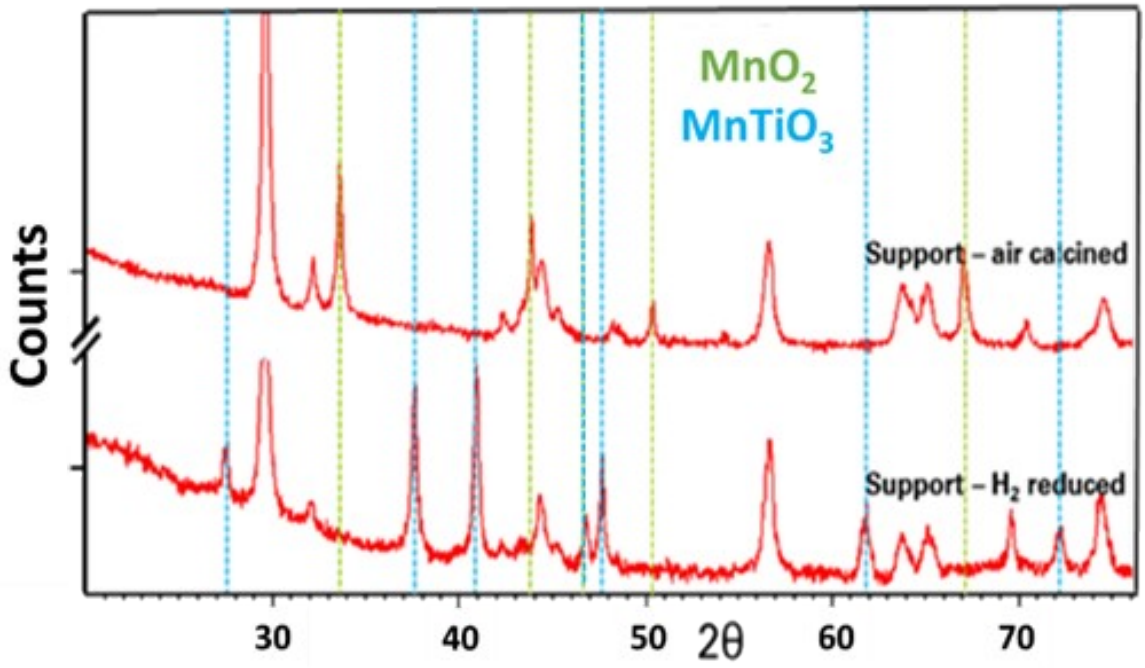


SI-11 Temperature programmed reduction of the oxidised support materials and reduced support materials. Reduced supports show very small amounts of hydrogen uptake (2B and 3B, 30%Mn:70%Ti, and 10%Mn:90%Ti)). Of the oxide forms, some reduction is seen, likely from MnO_2 to MnO initially, but also a small peak at 450°C which is likely to be the $MnTiO_3$ transition. While there is no stoichiometry mass loss between $MnO.TiO_2$ and $MnTiO_3$, there is likely to be some reorganisation which forms this peak at 450°C.

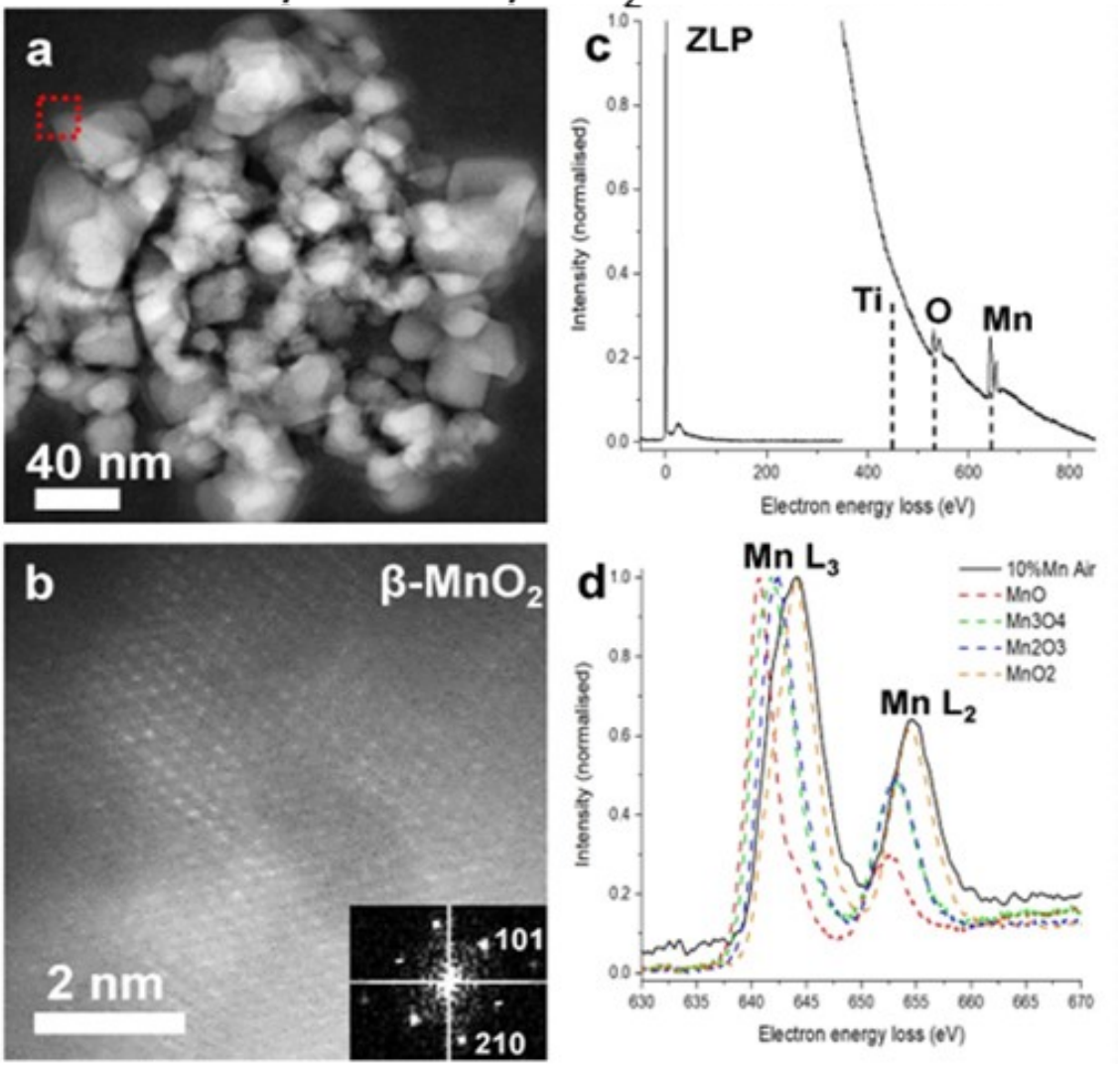
A larger version of the images from the main manuscript:



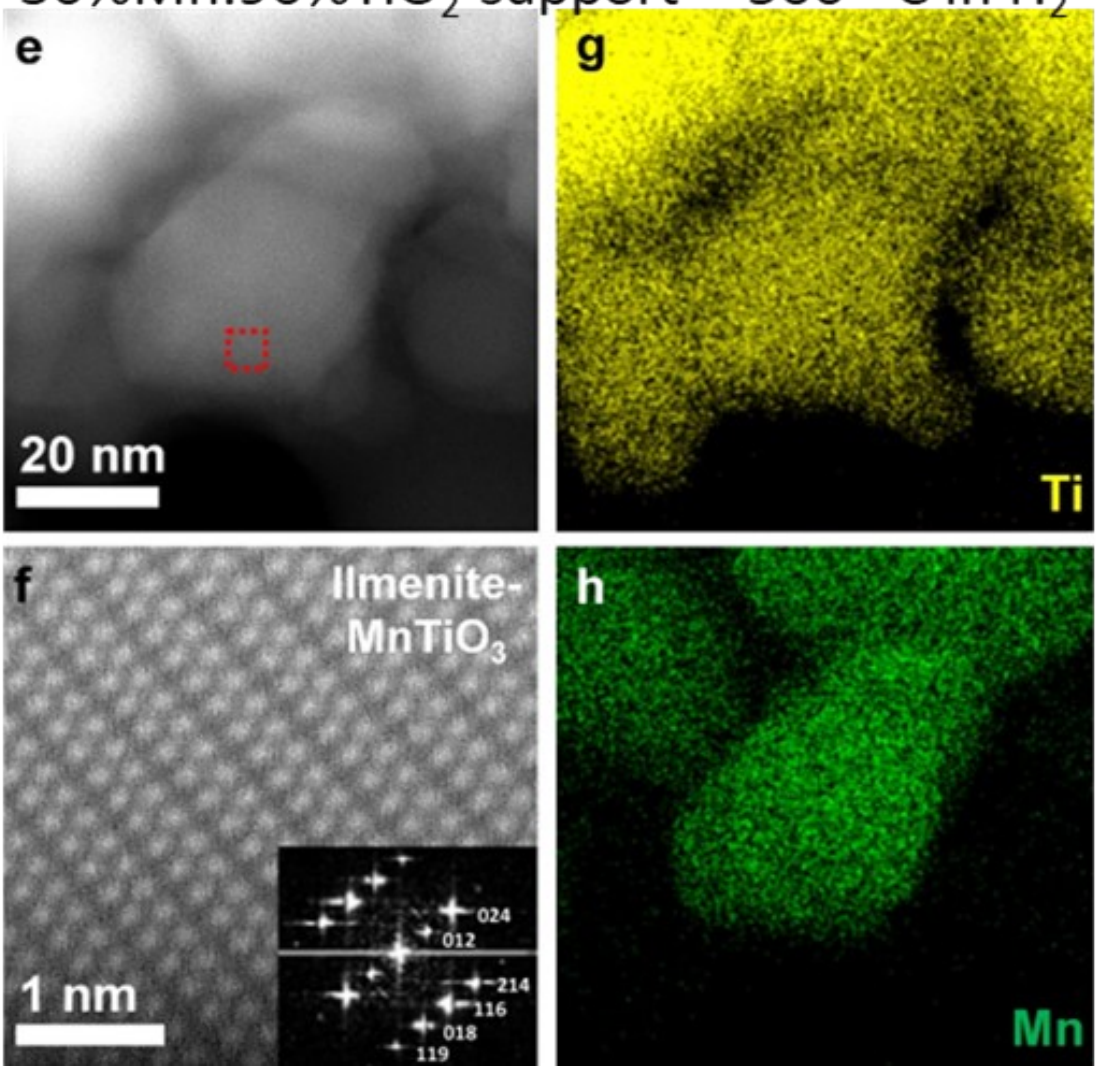

Cobalt
300 C
550 C
Co foil
CoO
CoTiO3
Normalized χμ(E)
Energy (eV)
XANES
|χ(R)| (Å-3)
EXAFS
Manganese
MnO
Mn(II)TiOx

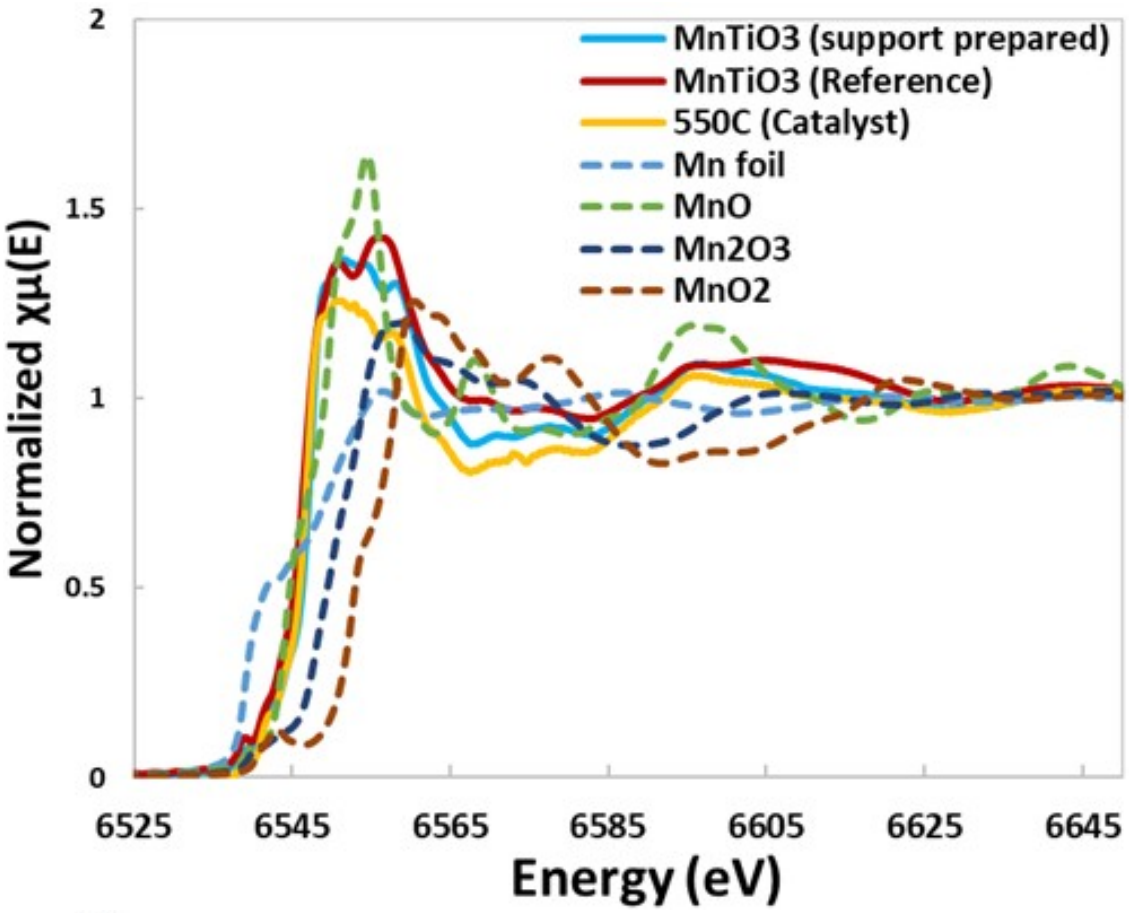

MnO2
MnTiO3
Support – air calcined
Support – H2 reduced
Counts
2θ

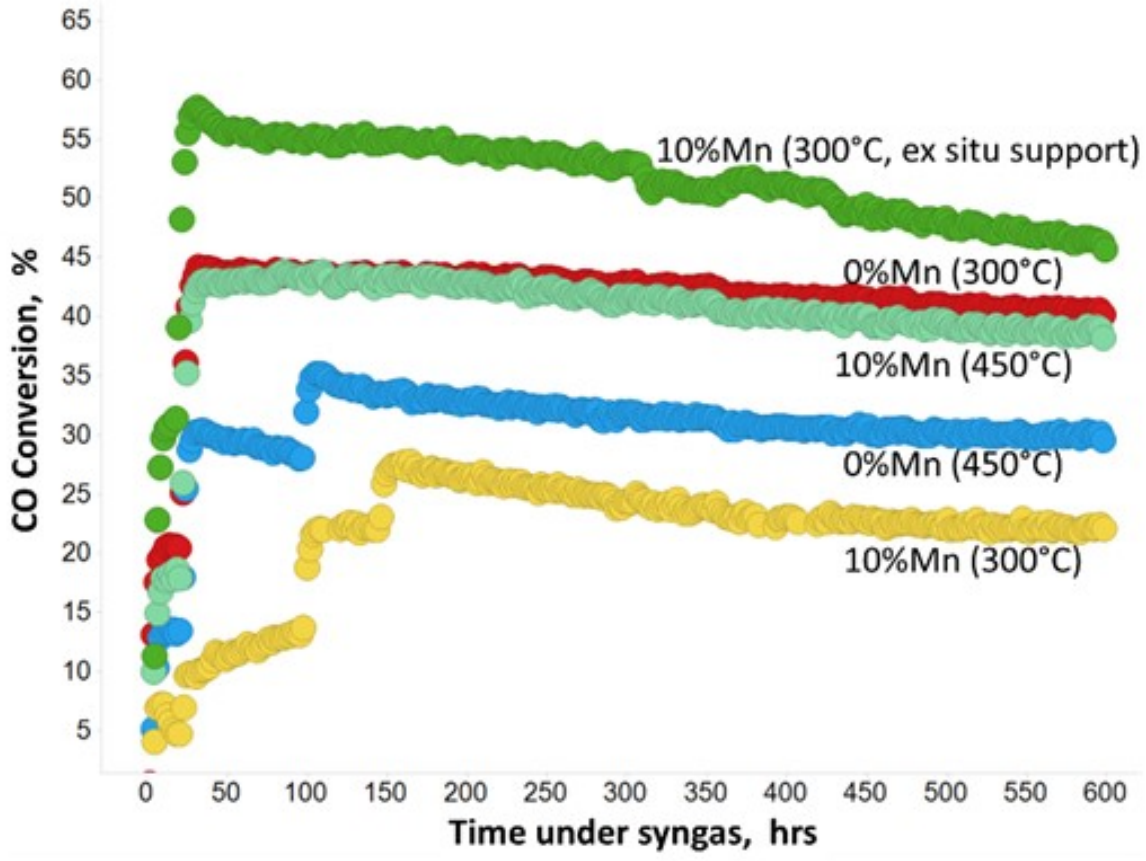
10%Co/10%Mn/TiO_2 – 500°C in air

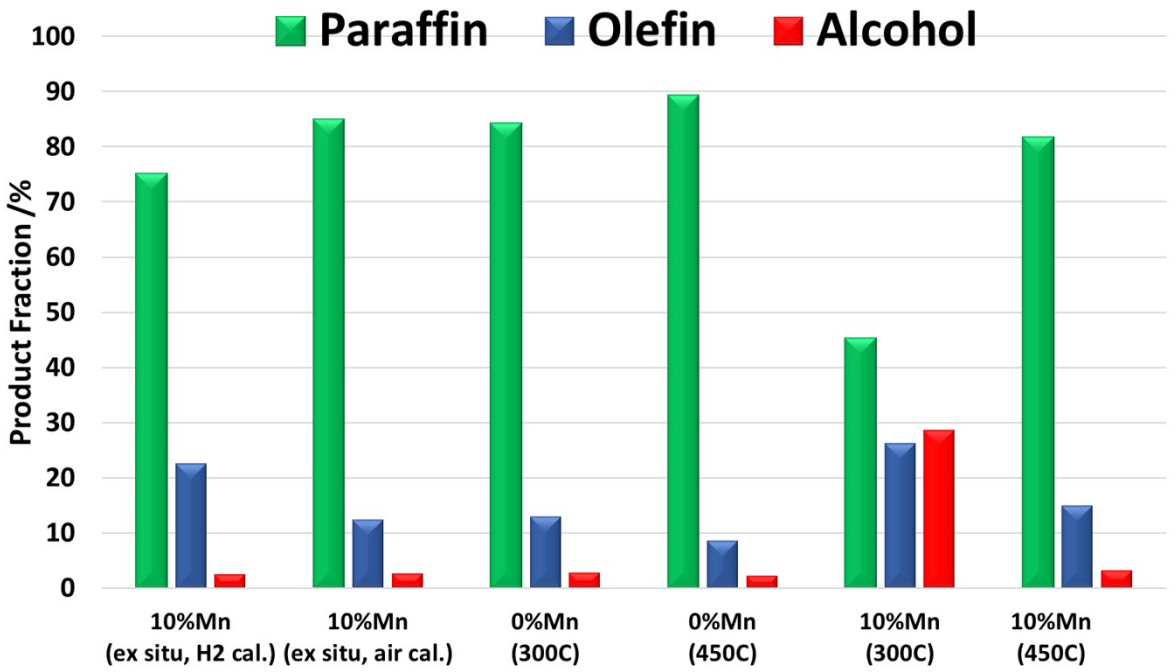


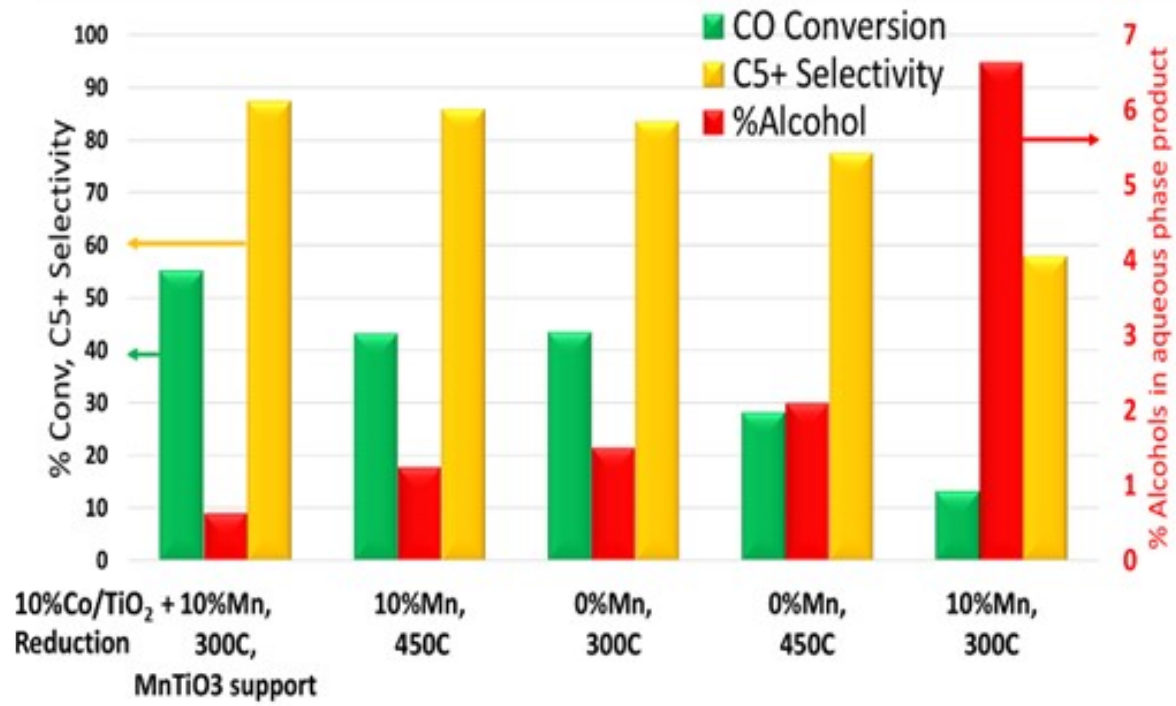
30%Mn:90%TiO_2 support – 500 ° C in H_2

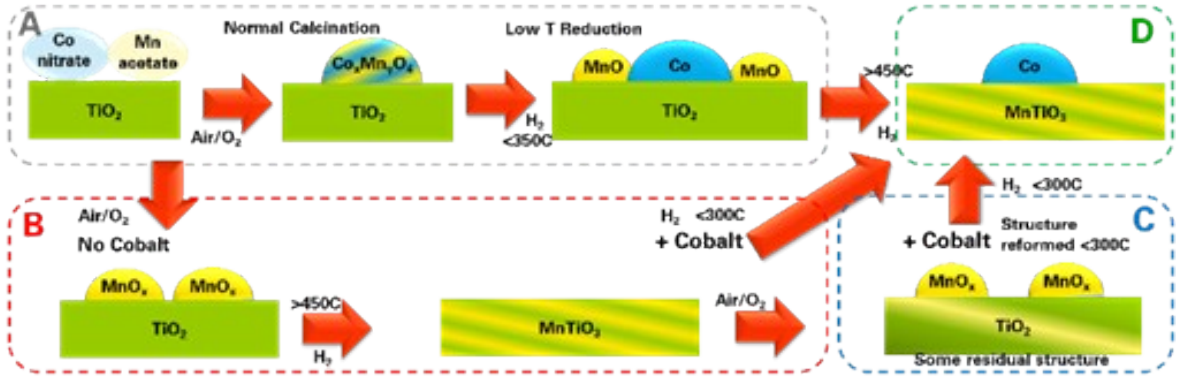



MnTiO3 (support prepared)
MnTiO3 (Reference)
550C (Catalyst)
Mn foil
MnO
Mn2O3
MnO2
Normalized χμ(E)
2
1.5
1
0.5
0
6525
6545
6565
6585
6605
6625
6645
Energy (eV)


10%Mn (300°C, ex situ support)
0%Mn (300°C)
10%Mn (450°C)
0%Mn (450°C)
10%Mn (300°C)
CO Conversion, %
65
60
55
50
45
40
35
30
25
20
15
10
5
0
50
100
150
200
250
300
350
400
450
500
550
600
Time under syngas, hrs







SI-12 – images from the main publication for easier viewing