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

Supporting Information

In situ generated catalyst: Copper (II) oxide and Copper (I) supported on $Ca_2Fe_2O_5$ for CO oxidation

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Contents

CO oxidation curves of reference samples

Fig. SI1 shows the CO oxidation curves of pure CuO prepared the same manner as the supported CuO samples and CuO deposited on ɣ-Al_2O_3. For comparison, the best impregnated and one-pot catalysts are added (40Cu_CFO_OP_H_2 and 40Cu_CFO_IP). The graphs shows that the CuO supported on CFO converts CO at lower temperatures than unsupported CuO (SSA: 1m^2/g) or ɣ-Al_2O_3 (156 m^2/g) as support.

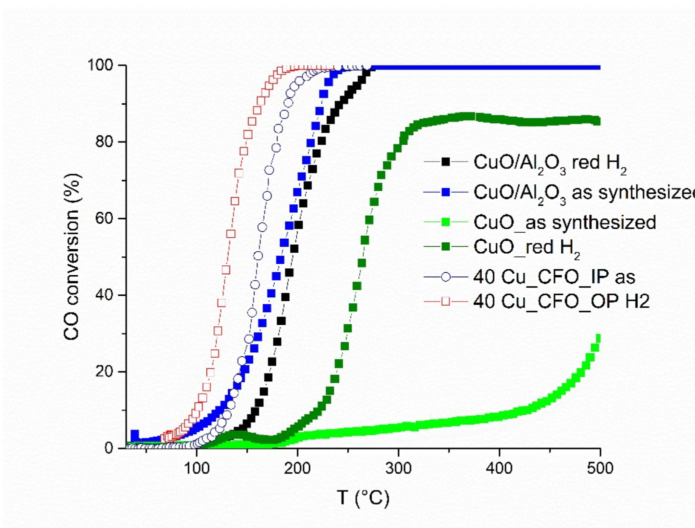


Fig. SI 1: CO oxidation light-off curves of CuO supported on Al_2O_3 and $Ca_2Fe_2O_5$.

Stability test of impregnated and one pot sample

Fig. SI 2 shows the CO conversion for 40Cu_CFO_IP and 40Cu_CFO_OP after hydrogen pretreatment and one light-off curve at 200°C for 24h. The test conditions were 20 mg of sample diluted in SiC,

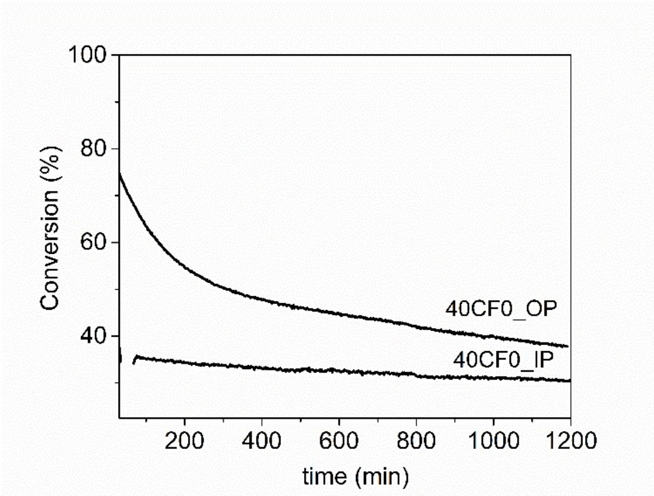


Fig. SI 2: Stability test of 40CFO_0P and 40CFO_IP. Test conditions: 20 mg of sample diluted in 300 mg of SiC, pretreatment at 300°C for 2h under 40%H_2/He, one light-off curve (2000ppm, 10000ppm 0_2) and isotherm at 200°C, 2000 ppm of CO and 10000 ppm of O_2.

Surface properties derived from XPS

Table SI 1

Catalyst	Cu2$p_{3/2}$	surface composition (at% Cu)[a]	I_{ss}/I_{pp}
40_CFO_IP	933.5	24	0.45
40_CFO_IP after CO ox	933.3	23	0.33
40_CFO_OP	933.3	19	0.33
40_CFO_OP_after CO ox	933.5	16	0.41

[a]The surface compositions of Cu was calculating omitting C and O contributions, as the surface is polluted with carbonates. These values have thus a mere comparative purpose and are not absolute values.

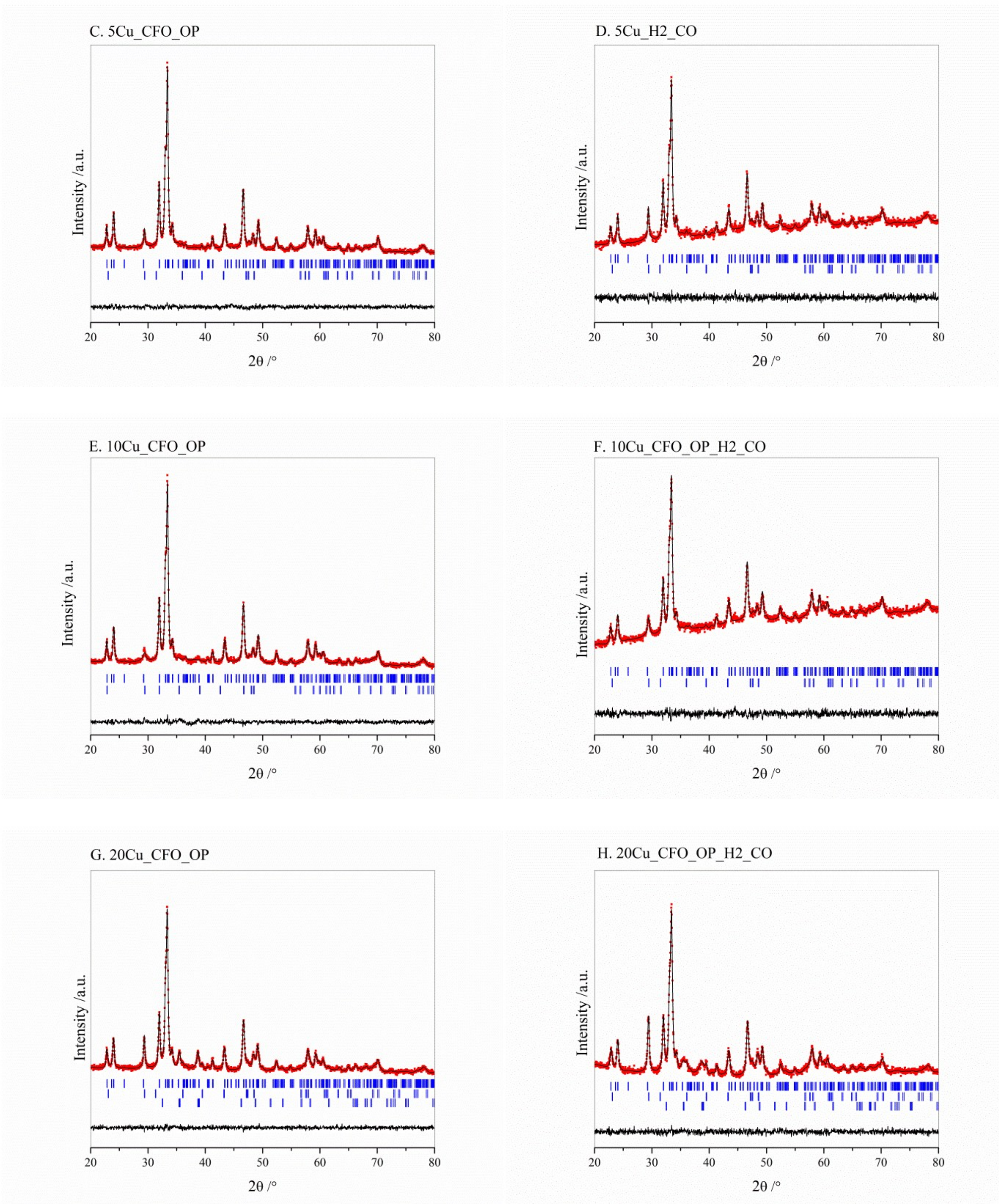
Lattice Parameter of one pot samples

Table SI 2 Refined parameters corresponding to the XRD data presented in **Fig. 4** for xCu-CFO_OP, (where 5<x<50) catalysts as synthetized and after CO oxidation.

Phase	Space Group	a [Å]	b [Å]	c [Å]	vol [Å^3]	Phase fraction[%]	χ^2
CFO							
$Ca_2Fe_2O_5$	P n m a	5.4330(5)	14.7800(20)	5.6049(5)	450.090(75)	100(0)	1.22
5 Cu-CFO_OP							
$Ca_2Fe_2O_5$	P n m a	5.4205(8)	14.7898(20)	5.5971(7)	448.714(107)	97.96(80)	1.34
$CaCO_3$	R -3 c	4.9816 (9)	4.9816 (9)	17.1023(41)	368.101(134)	2.04(31)	
5 Cu-CFO_OP H2_CO							

$Ca_2Fe_2O_5$	P n m a	5.4231(15)	14.7830(30)	5.5972(14)	448.758(198)	97.19 (90)	1.21
$CaCO_3$	R -3 c	4.9897(9)	4.9897(9)	17.0947(35)	368.583(117)	2.81 (39)	
10 Cu-CFO_OP							
$Ca_2Fe_2O_5$	P n m a	5.4167(8)	14.7955(23)	5.5921(9)	448.166(119)	98.21(89)	1.46
$CaCO_3$	R -3 c	4.9854(7)	4.9854(7)	17.0894(32	368.431(134)	1.79(85)	
10 Cu-CFO_OP H2_CO							
$Ca_2Fe_2O_5$	P n m a	5.42634(4)	14.8002(15)	5.6018(9)	449.893(61)	96.98(80)	1.19
$CaCO_3$	R -3 c	4.9889(5)	4.9889(5)	17.0960(21	368.431(134)	3.02(19)	
20 Cu-CFO_OP							
$Ca_2Fe_2O_5$	P n m a	5.4154(3)	14.8248(8)	5.5938(3)	449.085(41)	82.46(68)	
$CaCO_3$	R -3 c	4.9809(9)	4.9809(9)	17.1352(35)	368.165(117)	10.54(39)	1.16
CuO	C 2/c	4.6912(14)	3.4248(8)	5.1367(16)	81.397(41)	6.99(25)	
20 Cu-CFO_OP H2_CO							
$Ca_2Fe_2O_5$	P n m a	5.4135(2)	14.7939(53)	5.5912(20)	447.786(280)	73.80(1.23)	
$CaCO_3$	R -3 c	4.9795 (10)	4.9795(10)	17.0791(38)	366.753(133)	17.57(65)	1.16
CuO	C 2/c	4.6867(74)	3.4285(45)	5.1285(83)	81.269(211)	3.95(25)	
30 Cu-CFO_OP							
$Ca_2Fe_2O_5$	P n m a	5.4141 (5)	14.8022(14)	5.5900(5)	447.986(75)	52.02(9)	
$CaCO_3$	R -3 c	4.9862(5)	4.9862(5)	17.1147(21)	368.514(71)	35.54(48)	2.70
CuO	C 2/c	4.6932 (15)	3.4277(8)	5.1225(13)	81.200(37)	12.44(22)	
30 Cu-CFO_OP H2_CO							
$Ca_2Fe_2O_5$	P n m a	5.4344(19)	14.82448(535)	5.6091(20)	451.884(280)	63.24(1.23)	
$CaCO_3$	R -3 c	4.9833(10)	4.9833(10)	17.1079(38)	367.645(133)	30.44(65)	1.36
CuO	C 2/c	4.6913(74)	3.4290(46)	5.1310 (83)	81.817(211)	6.32(25)	
40 Cu-CFO_OP							
$Ca_2Fe_2O_5$	P n m a	5.4143(8)	14.8247(22)	5.5922(8)	448.865(114)	50.95(32)	
$CaCO_3$	R -3 c	4.9872(6)	4.9872(6)	17.1230 (22)	368.830(78)	31.90(32)	1.92
CuO	C 2/c	4.68828 (101)	3.42443(73)	5.14093(104)	81.412(30)	17.15(19)	
40 Cu-CFO_OP H2_CO							
$Ca_2Fe_2O_5$	P n m a	5.4251(4)	14.8102(11)	5.6035(4)	450.113(60)	46.64(90)	
$CaCO_3$	R -3 c	4.9887(3)	4.9887(3)	17.1107(15)	368.536(50)	40.12(90)	1.72
CuO	C 2/c	4.6839(72)	3.4237(39)	5.1405(82)	81.501(158)	13.2490)	
50 Cu-CFO_OP							
$Ca_2Fe_2O_5$	P n m a	5.4165(3)	14.8386(10)	5.5927(4)	449.506(52)	48.54(42)	
$CaCO_3$	R -3 c	4.9877(4)	4.9877(3)	17.1182(15)	368.797(49)	30.13(31)	1.92
CuO	C 2/c	4.6901(7)	3.4221(5)	5.1345(7)	81.281(20)	21.33(27)	

XRD pattern of one pot samples as-synthesized and after reaction


C. 5Cu_CFO_OP
D. 5Cu_H2_CO
E. 10Cu_CFO_OP
F. 10Cu_CFO_OP_H2_CO
G. 20Cu_CFO_OP
H. 20Cu_CFO_OP_H2_CO
Intensity /a.u.
2θ /°
20
30
40
50
60
70
80

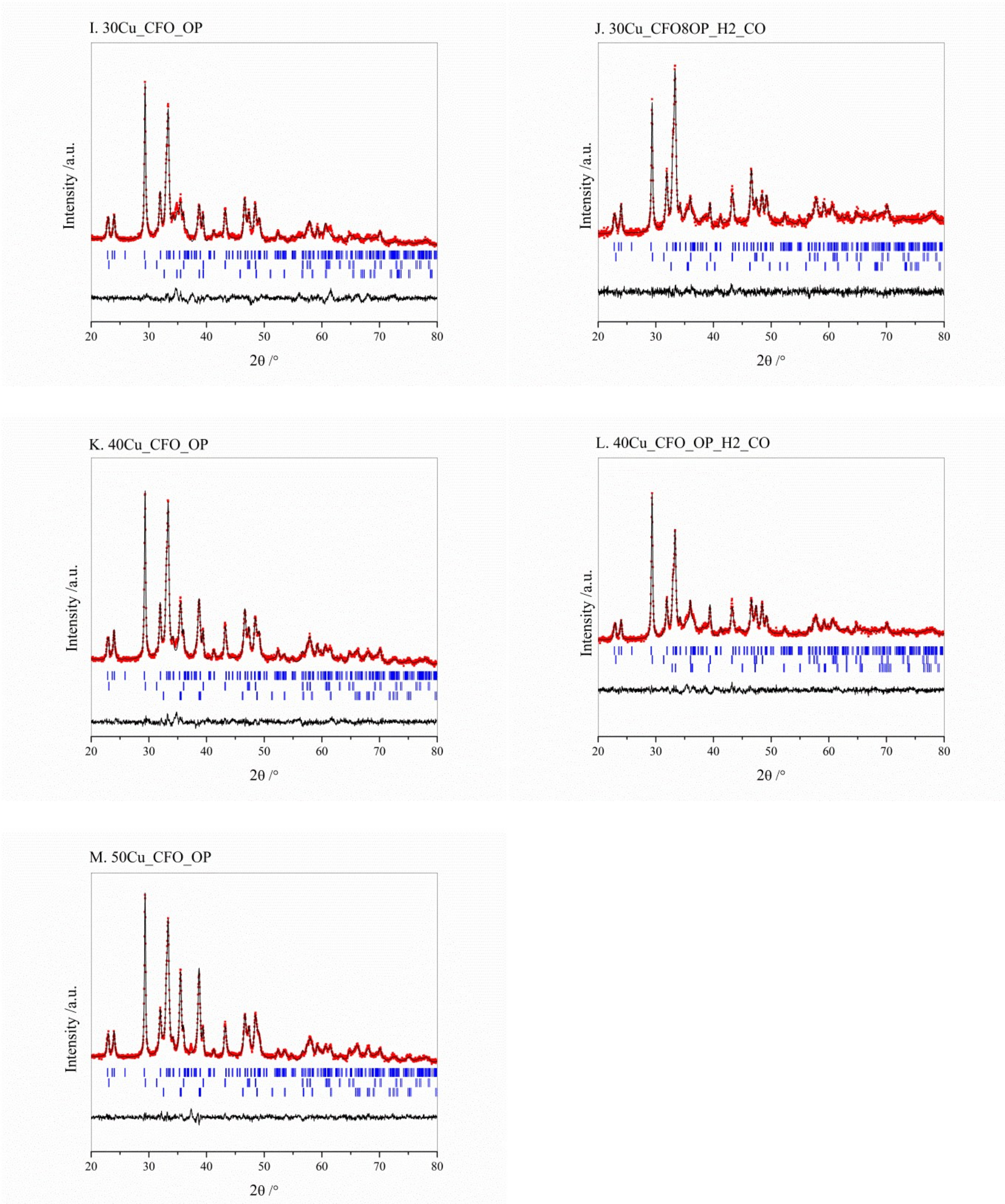


Figure SI 3 Observed, calculated and difference XRD patterns of: **A.** 1Cu-CFO_OP; **B.** 1Cu-CFO_OP after H_2 treatment and CO oxidation; **C.** 5Cu-CFO_OP; **D.** 5Cu-CFO_OP after H_2 treatment and CO oxidation; **E.** 10Cu-CFO_OP; **F.** 10Cu-CFO_OP after H_2 treatment and CO oxidation; **G.** 20Cu-CFO_OP; **H.** 20Cu-CFO_OP after H_2 treatment and CO oxidation, **I.** 30Cu-CFO_OP; **J.** 30Cu-CFO_OP after H_2 treatment and CO oxidation; **K.** 40Cu-CFO_OP; **L.** 40Cu-CFO_OP after H_2 treatment and CO oxidation; **M.** 50Cu-CFO_OP; results were refined in the *Pnma* space group in profile matching mode together with appropriate space group describing secondary phase. Vertical bars are related to the calculated Bragg reflection position. Refined parameters are given in the Table S1.

X-Ray analysis of as-synthesized 40Cu-CFO_OP and after reaction, compared to reference compounds

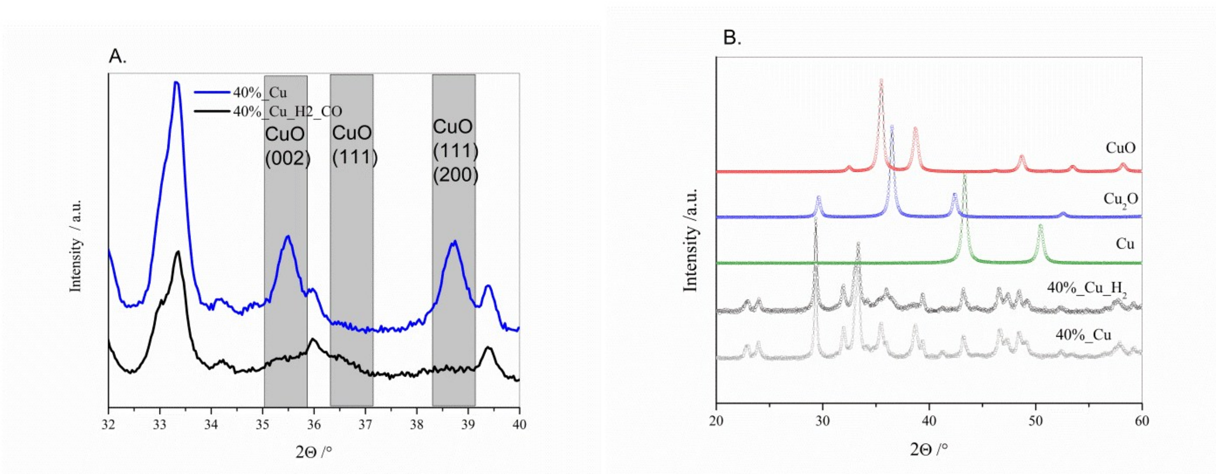


Figure SI 4A. X-Ray diffraction data in the 2θ region between 32° and 40° for as synthetized 40Cu-CFO_OP (blue line) and 40Cu-CFO_OP after H_2 treatment at 300°C followed by catalytic test at 400°C (black line). Grey boxes highlight the most intensive reflections belonging to the CuO phase (002) and (111)/(200) together with (111) reflection belonging to the Cu_2O phase; **B.** Observed XRD patterns for as synthetized 40Cu-CFO_OP (light grey) and 40Cu-CFO_OP after H_2 treatment at 300°C followed by catalytic test at 400°C (dark grey), stacked together with simulated XRD profile for Cu (green line), Cu_2O (blue line) and CuO (red line) phases. Simulations were performed in the Full Prof Package using profile broadening function determined for CuO phase in as-synthetized sample;

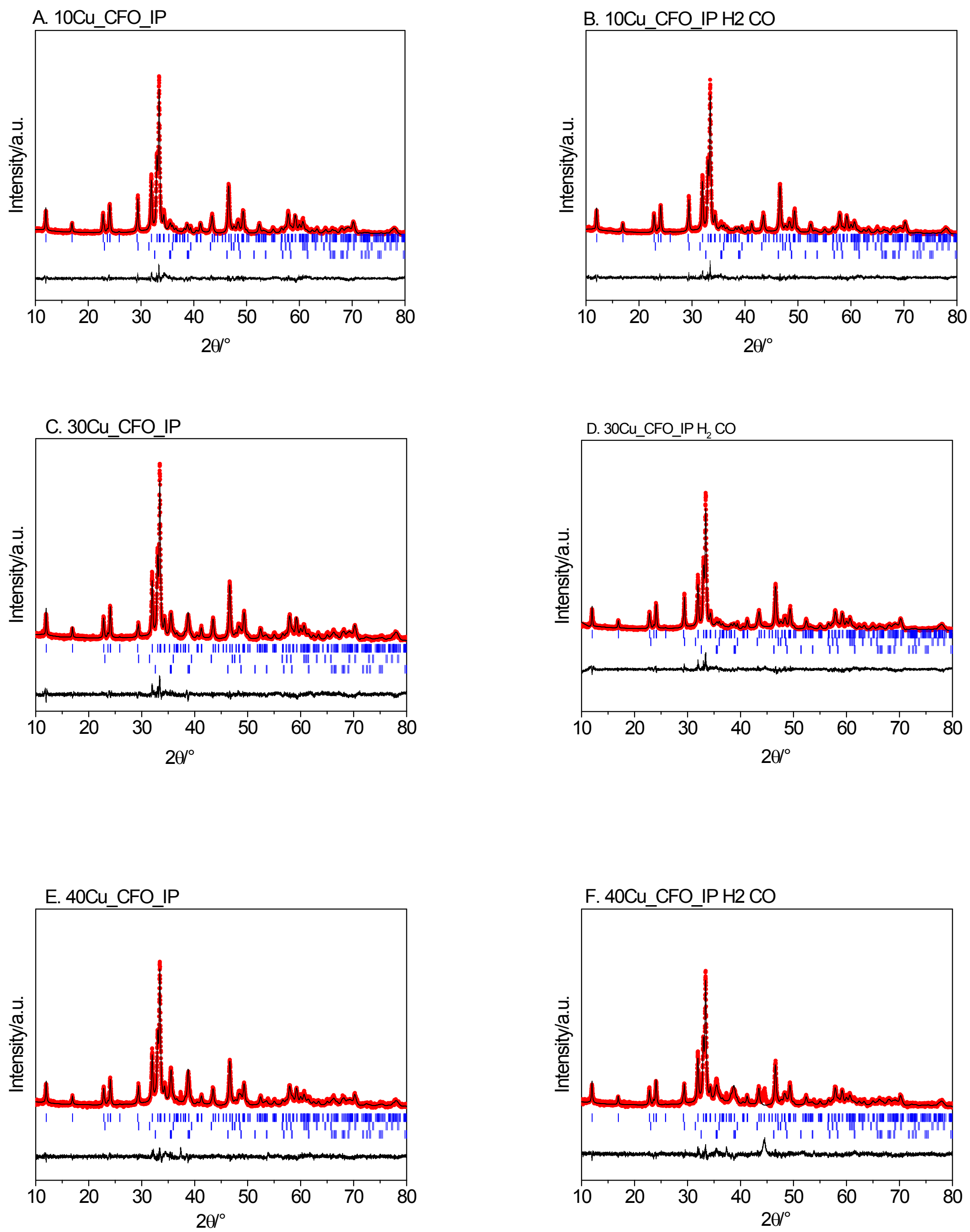
Lattice Parameter of impregnated samples

Table SI 3. Refined parameters corresponding to the XRD data presented in **Fig. 2** for xCu-CFO_IP (where 10<x<40), catalysts as synthetized and after CO oxidation.

Phase	Space Group	a [Å]	b [Å]	c [Å]	vol [Å3]	Phase fraction[%]
10 Cu-CFO_IP						
$Ca_2Fe_2O_5$	P n m a	5.42695(8)	14.7714(20)	5.6016(7)	449.037(107)	86.43(3.41)
$CaCO_3$	R -3 c	4.9978 (9)	4.9978 (9)	17.0583(41)	368.998(134)	9.41(66)
CuO	C 2/c	4.6853(14)	3.4219(8)	5.1122(16)	81.307(41)	4.17(39)

10 Cu-CFO_IP _CO							
$Ca_2Fe_2O_5$	P n m a	5.4261(15)	14.7723(30)	5.6017 (14)	448.758(198)	86.24 (3.90)	
$CaCO_3$	R -3 c	4.9978 (9)	4.9978 (9)	17.0583(41)	368.998(134)	9.63(66)	
CuO	C 2/c	4.6853(14)	3.4219(8)	5.1122(16)	81.307(41)	4.13(39)	
10 Cu-CFO_IP_H2_CO							
$Ca_2Fe_2O_5$	P n m a	5.4281 (8)	14.7722(23)	5.6021(9)	449.202(119)	87.65(3.71)	
$CaCO_3$	R -3 c	4.9978 (9)	4.9978 (9)	17.0583(41)	368.431(134)	9.77(0.72)	
CuO	C 2/c	4.6853(14)	3.4219(8)	5.1122(16)	81.307(41)	2.58(0.39)	
30 Cu-CF_IP							
$Ca_2Fe_2O_5$	P n m a	5.4260 (5)	14.7704(8)	5.5954(3)	448.436(0.080)	85.16(3.53)	
$CaCO_3$	R -3 c	4.9978 (9)	4.9978 (9)	17.0583(41)	368.431(134)	3.03(0.55)	
CuO	C 2/c	4.6853(14)	3.4219(8)	5.1122(16)	81.307(41)	11.81(0.60))	
30 Cu-CFO_IP_CO							
$Ca_2Fe_2O_5$	P n m a	5.4250(2)	14.7726(53)	5.5958(20)	447.786(280)	86.49(3.69)	
$CaCO_3$	R -3 c	4.9978 (9)	4.9978 (9)	17.0583(41)	368.431(134)	1.46(0.54)	
CuO	C 2/c	4.6853(14)	3.4219(8)	5.1122(16)	81.307(41)	12.05(25)	
30 Cu-CFO_IP_H2_CO							
$Ca_2Fe_2O_5$	P n m a	5.4278 (5)	14.7704(14)	5.6017(5)	449.095(75)	86.49(3.74)	
$CaCO_3$	R -3 c	4.9978 (9)	4.9978 (9)	17.0583(41)	368.431(134)	10.79(0.78)	
CuO	C 2/c	4.6853(14)	3.4219(8)	5.1122(16)	81.307(41)	2.72(0.40)	
40 Cu-CFO_IP							
$Ca_2Fe_2O_5$	P n m a	5.4242 (19)	14.7755(19)	5.5957(20)	448.470(0.095)	78.83(1.29)	
$CaCO_3$	R -3 c	4.9978 (9)	4.9978 (9)	17.0583(41)	368.431(134)	4.51(0.05)	
CuO	C 2/c	4.6853(14)	3.4219(8)	5.1122(16)	81.307(41)	16.66(0.17)	
40 Cu-CFO_IP_CO							
$Ca_2Fe_2O_5$	P n m a	5.4276 (8)	14.7746(22)	5.5992(8)	449.009114)	76.20(2.01)	
$CaCO_3$	R -3 c	4.9978 (9)	4.9978 (9)	17.0583(41)	368.431(134)	5.61(0.72)	
CuO	C 2/c	4.6853(14)	3.4219(8)	5.1122(16)	81.307(41)	18.19(1.24)	
40 Cu-CFO_IP_H2_CO							
$Ca_2Fe_2O_5$	P n m a	5.4285(4)	14.7711(11)	5.6005(4)	449.078(0.111)	78.71(1.56)	
$CaCO_3$	R -3 c	4.9978 (9)	4.9978 (9)	17.0583(41)	368.431(134)	5.33(0.60)	
CuO	C 2/c	4.6853(14)	3.4219(8)	5.1122(16)	81.307(41)	15.96(0.82)	
CuO							
CuO	C 2/c	4.69151(31)	3.43179(26)	5.13881(32)	81.609(10)	100(0)	6.04
CFO							
$Ca_2Fe_2O_5$	P n m a	5.43302(52)	14.78038(144)	5.60496(54)	450.090(75)	100(0)	1.22

Figure SI 5 XRD pattern of impregnated samples as-synthesized and after reaction



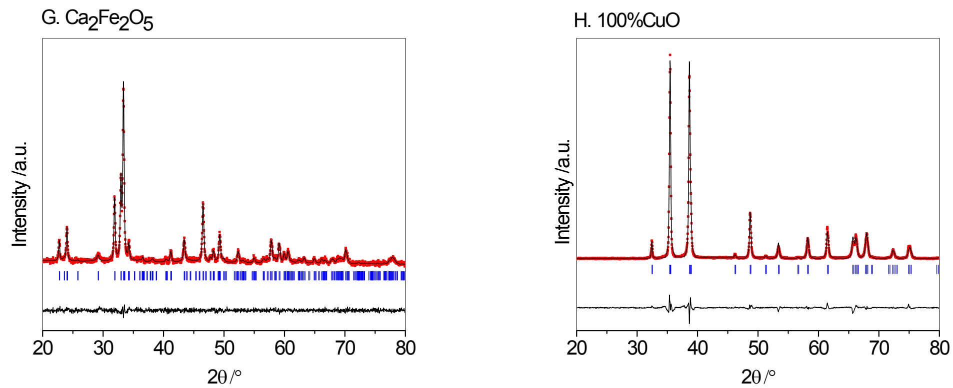


Figure SI 5 Observed, calculated and difference XRD patterns of: **A.** 10Cu-CFO_IP; **B.** 10Cu-CFO_IP after H_2 treatment and CO oxidation; **C.** 30Cu-CFO_IP; **D.** 30Cu-CFO_IP after H_2 treatment and CO oxidation; **E.** 40Cu-CFO_IP; **F.** 40Cu-CFO_IP after H_2 treatment and CO oxidation; treatment and CO oxidation; **G.** as-synthesized pure $Ca_2Fe_2O_5$ **H.** pure CuO. Results were refined in the *Pnma* space group in profile matching mode together with appropriate space group describing secondary phase. Vertical bars are related to the calculated Bragg reflection position. Refined parameters are given in the Table SI 3.

EXAFS fit parameters

Table SI 4 EXAFS fit parameters with S_0^2-passive electron reduction factor, ΔE_0-energy shift, R-internuclear distance, σ^2-mean squared displacement.

T (°C)	30Cu-CFO_OP	Bond	Site	S_0^2	ΔE_0 (eV)	R (Å)	σ^2(Å²)	R_{Factor}
RT/Air	CuO	Cu-O	(1)	1.24±0.13	-0.10±1.96	1.977± 0.002	0.011± 0.002	0.010
	$Ca_2Fe_2O_5$	$Fe-O_1$	O_{h1}	0.45±0.11	-4.25± 3.96	1.968±0.017	0.004±0.002	0.010
		$Fe-O_2$	O_{h2}	0.45±0.11	-4.25±3.96	2.115±0.017	0.005±0.002	0.010
		$Fe-O_2$	T_{d1}	0.45±0.11	-4.25±3.96	1.863±0.013	0.004±0.002	0.010
		$Fe-O_3$	T_{d2}	0.45±0.11	-4.25±3.96	1.904±0.013	0.004±0.002	0.010
300°C/H_2	Cu	Cu-Cu	(1)	0.83±0.09	3.63±0.73	2.534±0.003	0.015±0.001	0.011
	$Ca_2Fe_2O_5$	$Fe-O_1$	O_{h1}	0.47±0.14	-5.01±4.44	1.968±0.017	0.006±0.003	0.014
		$Fe-O_2$	O_{h2}	0.47±0.14	-5.01±4.44	2.115±0.017	0.008±0.007	0.014
		$Fe-O_2$	T_{d1}	0.47±0.14	-5.01±4.44	1.863±0.024	0.006±0.003	0.014
		$Fe-O_3$	T_{d2}	0.47±0.14	-5.01±4.44	1.904±0.024	0.006±0.003	0.014
200°C/ CO/O_2	Cu_2O	Cu-O	(1)	0.27±0.05	-0.63±2.01	1.864±0.013	0.001±0.002	0.008
	$Ca_2Fe_2O_5$	$Fe-O_1$	O_{h1}	0.45±0.13	-3.09±4.31	1.968±0.021	0.005±0.003	0.002
		$Fe-O_2$	O_{h2}	0.45±0.13	-3.09±4.31	2.115±0.021	0.004±0.005	0.002
		$Fe-O_2$	T_{d1}	0.45±0.13	-3.09±4.31	1.863±0.013	0.018±0.003	0.002
		$Fe-O_3$	T_{d2}	0.45±0.13	-3.09±4.31	1.904±0.013	0.018±0.003	0.002
T (°C)	40Cu-CFO_OP	Bond	Site	S_0^2	ΔE_0 (eV)	R (Å)	σ^2(Å²)	R_{Factor}
RT/Air	CuO	Cu-O	(1)	1.27±0.11	-1.12±0.57	1.961±0.009	0.010±0.002	0.007
	$Ca_2Fe_2O_5$	$Fe-O_1$	O_{h1}	0.45±0.12	-1.98±4.68	1.968±0.018	0.005±0.002	0.002
		$Fe-O_2$	O_{h2}	0.45±0.12	-1.98±4.68	2.115±0.018	0.005±0.008	0.002
		$Fe-O_2$	T_{d1}	0.45±0.12	-1.98±4.68	1.863±0.017	0.005±0.002	0.002
		$Fe-O_3$	T_{d2}	0.45±0.12	-1.98±4.68	1.904±0.017	0.005±0.002	0.002

$300^oC/H_2$	Cu	Cu-Cu	(1)	0.83±0.09	3.63±0.73	2.534±0.002	0.014±0.001	0.011
	$Ca_2Fe_2O_5$	$Fe-O_1$	O_{h1}	0.47±0.17	-4.29±5.27	1.968±0.021	0.006±0.003	0.001
		$Fe-O_2$	O_{h2}	0.47±0.17	-4.29±5.27	2.115±0.021	0.010±0.009	0.001
		$Fe-O_2$	T_{d1}	0.47±0.17	-4.29±5.27	1.863±0.026	0.006±0.003	0.001
		$Fe-O_3$	T_{d2}	0.47±0.17	-4.29±5.27	1.904±0.026	0.006±0.003	0.001
$200^oC/CO/O_2$	Cu_2O	Cu-O	(1)	0.27±0.05	-0.02±1.81	1.851±0.004	0.001±0.002	0.068
	$Ca_2Fe_2O_5$	$Fe-O_1$	O_{h1}	0.46±0.13	-3.80±4.23	1.968±0.015	0.004±0.002	0.001
		$Fe-O_2$	O_{h2}	0.46±0.13	-3.80±4.23	2.115±0.015	0.004±0.005	0.001
		$Fe-O_2$	T_{d1}	0.46±0.13	-3.80±4.23	1.863±0.021	0.004±0.002	0.001
		$Fe-O_3$	T_{d2}	0.46±0.13	-3.80±4.23	1.904±0.021	0.004±0.002	0.001

Fourier Transformation of the EXAFS signal of 30Cu-CFO_OP at the Cu edge

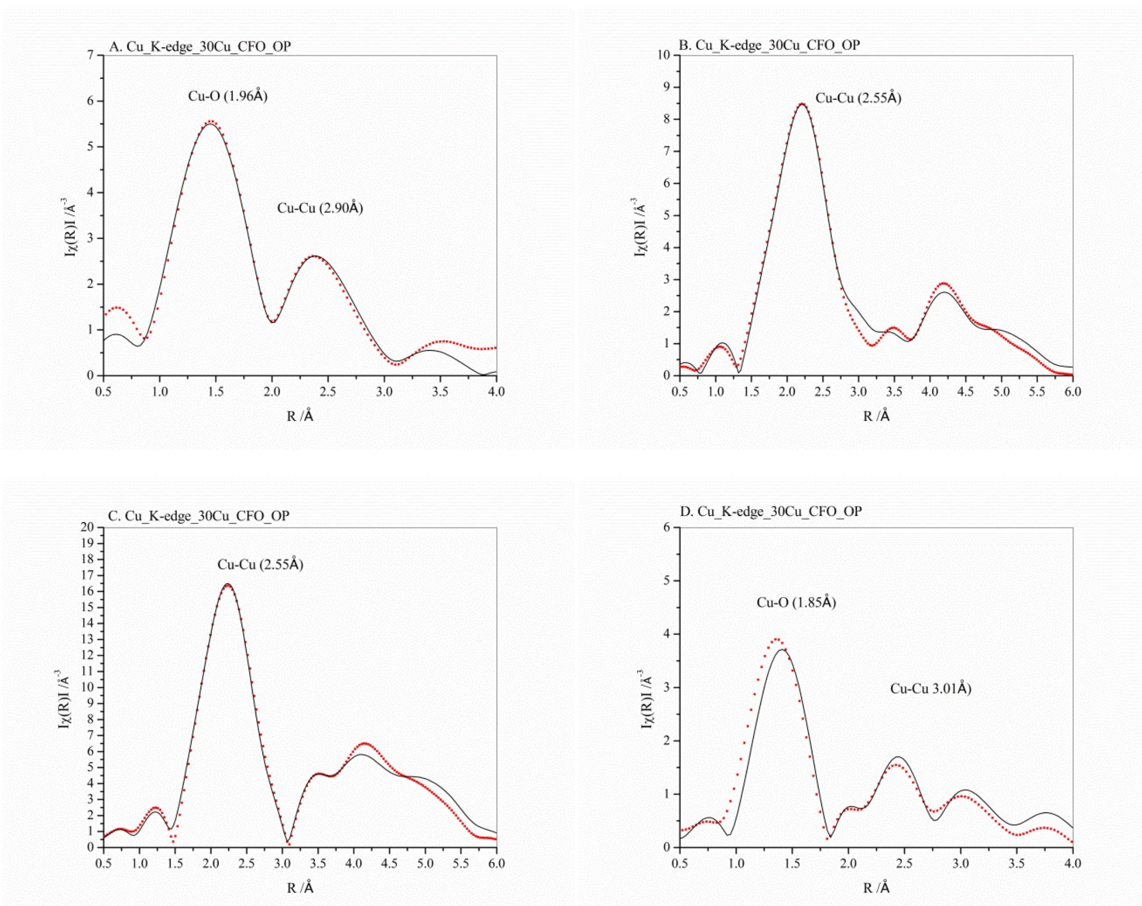


Figure SI 6 Experimental k^3-weighted FT of the $\xi(k)$ function together with the best fit for 30Cu-CFO_OP measured at the Cu K-edge under **A.** Air at RT, **B.** H_2 at 300^oC, **C.** He at RT and **D.** CO/O_2 at 200^oC.

Fourier Transformation of the EXAFS signal of 30Cu-CFO_OP at the Fe-edge

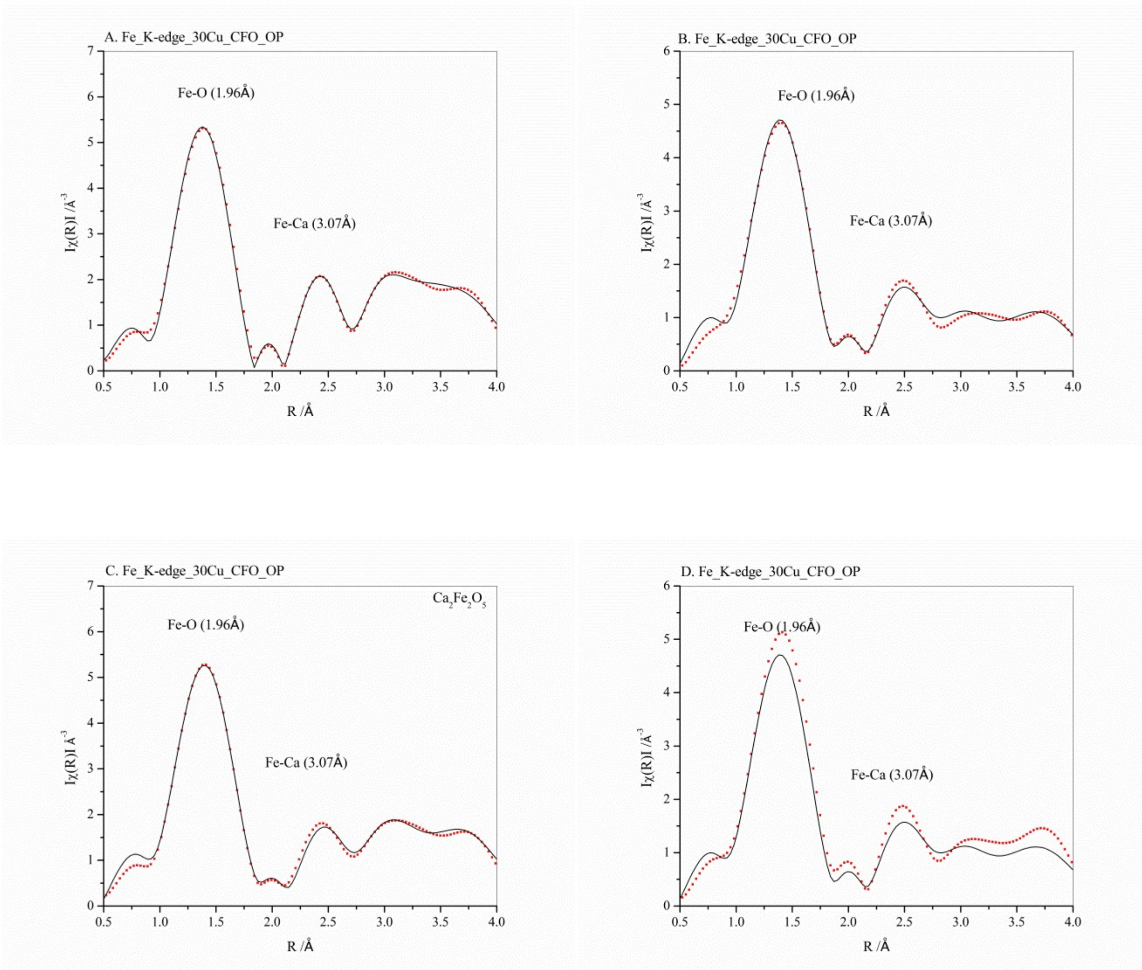


Figure SI 7 Experimental k^3-weighted FT of the $\xi(k)$ function together with the best fit for 30Cu-CFO_OP measured at the Fe K-edge under **A.** Air at RT, **B.** H_2 at 300^{o}C, **C.** He at RT and **D.** CO/O_2 at 200^{o}C.

Fourier Transformation of the EXAFS signal of 40Cu-CFO_OP at the Cu-edge

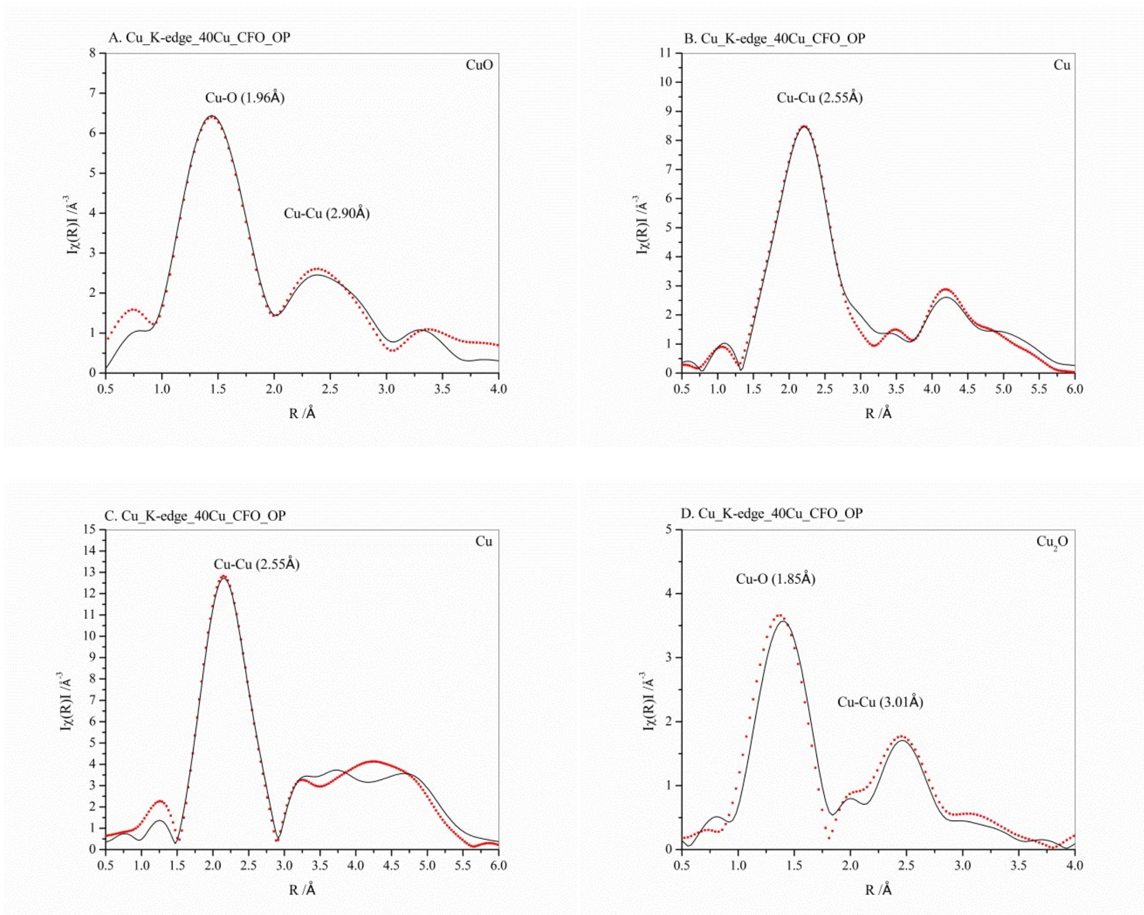
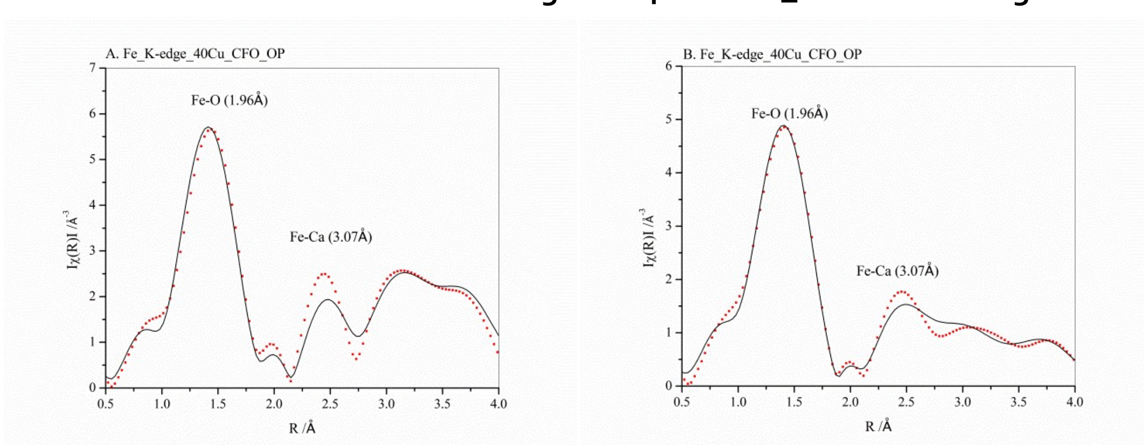


Figure SI 8 Experimental k^3-weighted FT of the $\xi(k)$ function together with the best fit for 40Cu-CFO_OP measured at the Cu K-edge under **A.** Air at RT, **B.** H_2 at 300^{o}C, **C.** He at RT and **D.** CO/O_2 at 200^{o}C.

Fourier Transformation of the EXAFS signal of 40Cu-CFO_OP at the Fe-edge



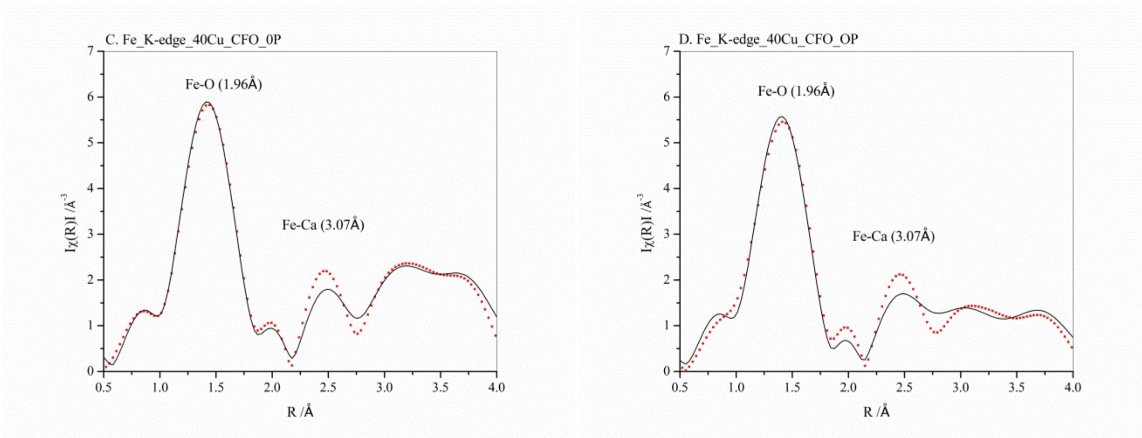


Figure SI 9 Experimental k^3-weighted FT of the $\xi(k)$ function together with the best fit for 40Cu-CFO_OP measured at the Fe K-edge under **A.** Air at RT, **B.** H_2 at 300°C, **C.** He at RT and **D.** CO/O_2 at 200°C.

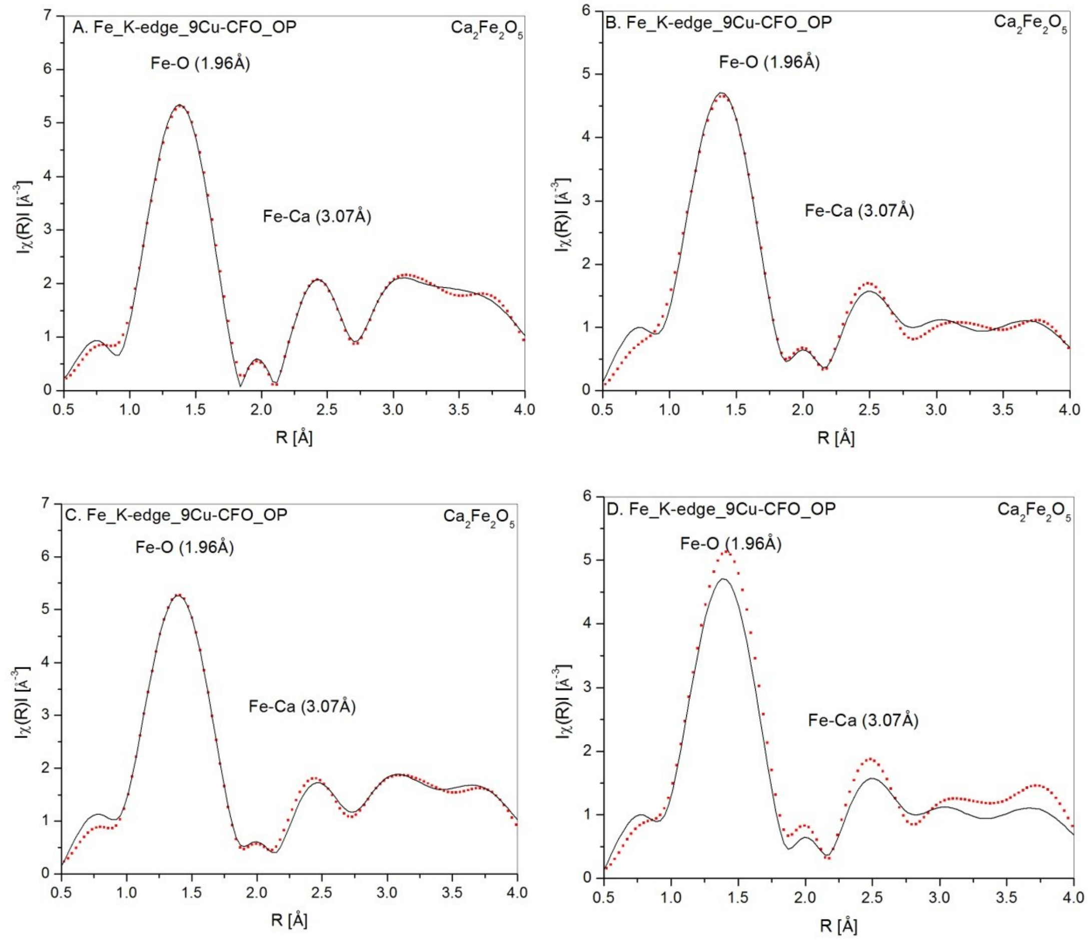


Figure SI 10 Experimental k^3-weighted FT of the $\xi(k)$ function together with the best fit for 40Cu-CFO_OP measured in the Fe K-edge under: **A.** Air at RT; **B.** H_2 at 300^{o}C; **C.** He at RT; **D.** CO/O_2 at 200^{o}C.

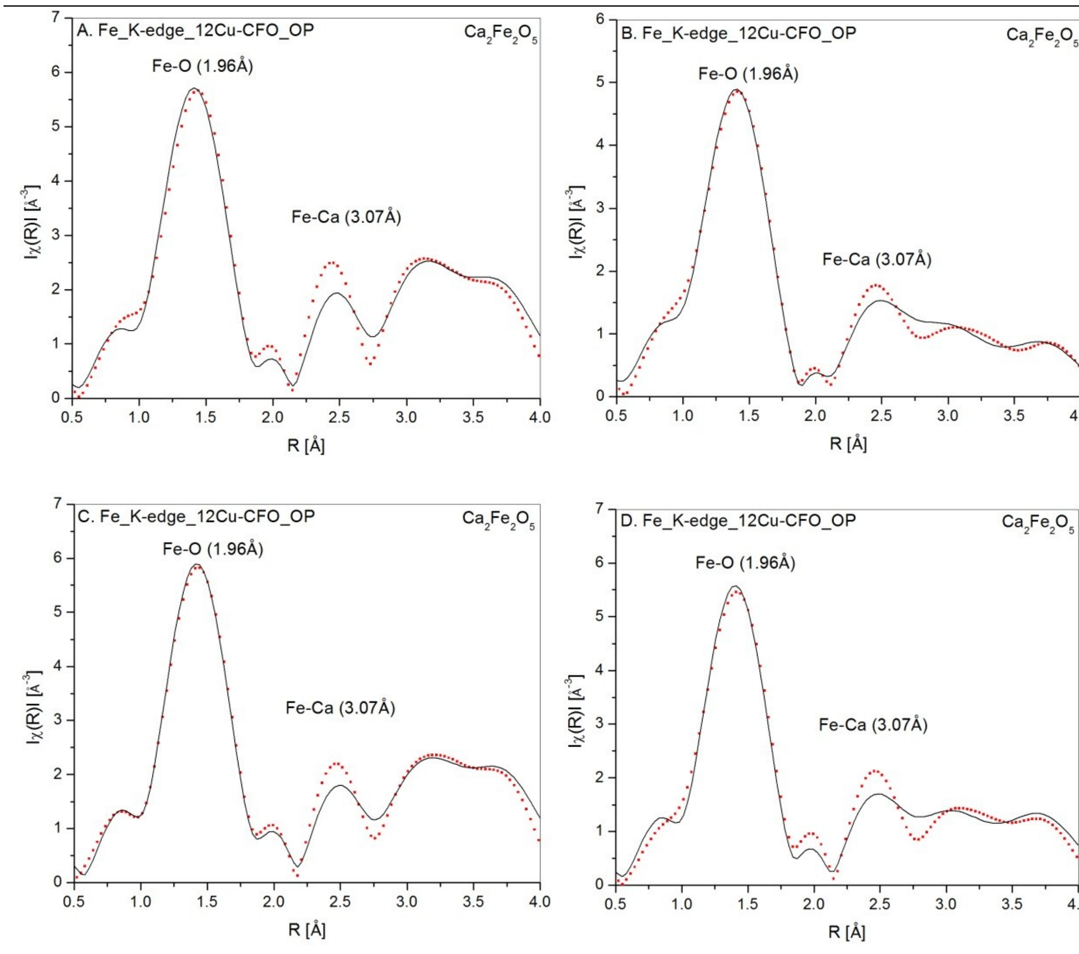


Figure SI 11 Experimental k^3-weighted FT of the $\xi(k)$ function together with the best fit for 12Cu-CFO_OP measured in the Fe K-edge under: **A.** Air at RT; **B.** H_2 at 300°C; **C.** He at RT; **D.** CO/O_2 at 200°C.