Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary file

The effect of copper on the redox behaviour of iron oxide for chemical-looping hydrogen production probed by *in situ* X-ray absorption spectroscopy

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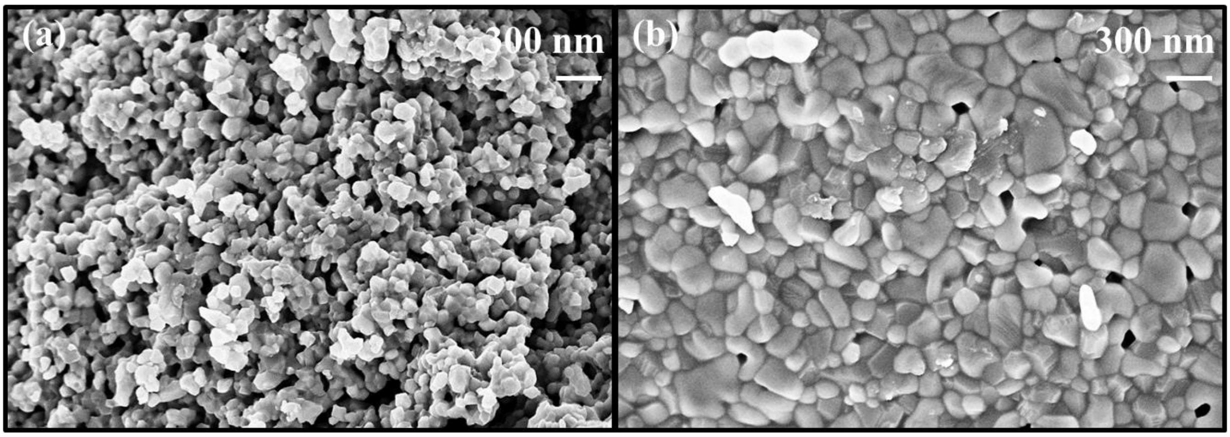

Figure S1: Scanning electron micrographs of the calcined oxygen carriers (a) Fe30Zr70 and (b) Fe30Cu10Zr60.

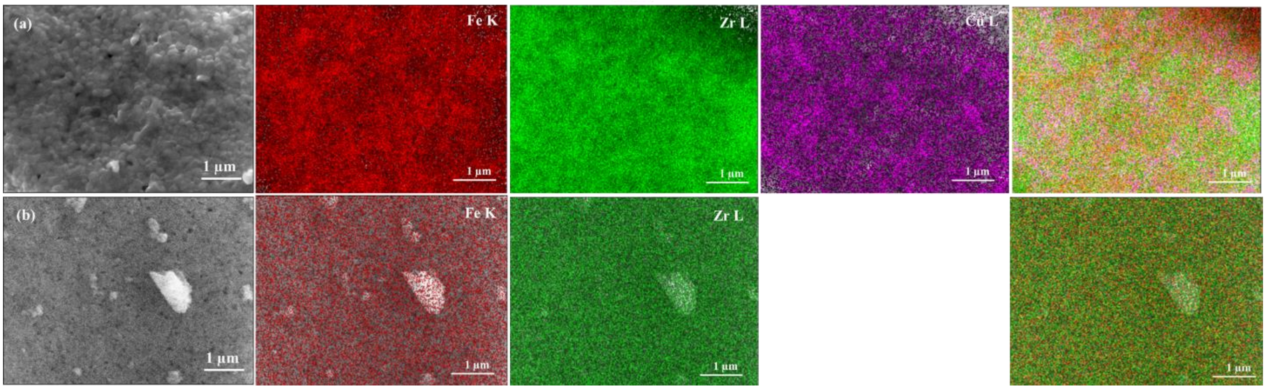

Figure S2*:* EDX maps of calcined (a) Fe30Zr70 and (b) Fe30Cu10Zr60, Copper, zirconium and iron are represented with the colours pink, green and red, respectively.

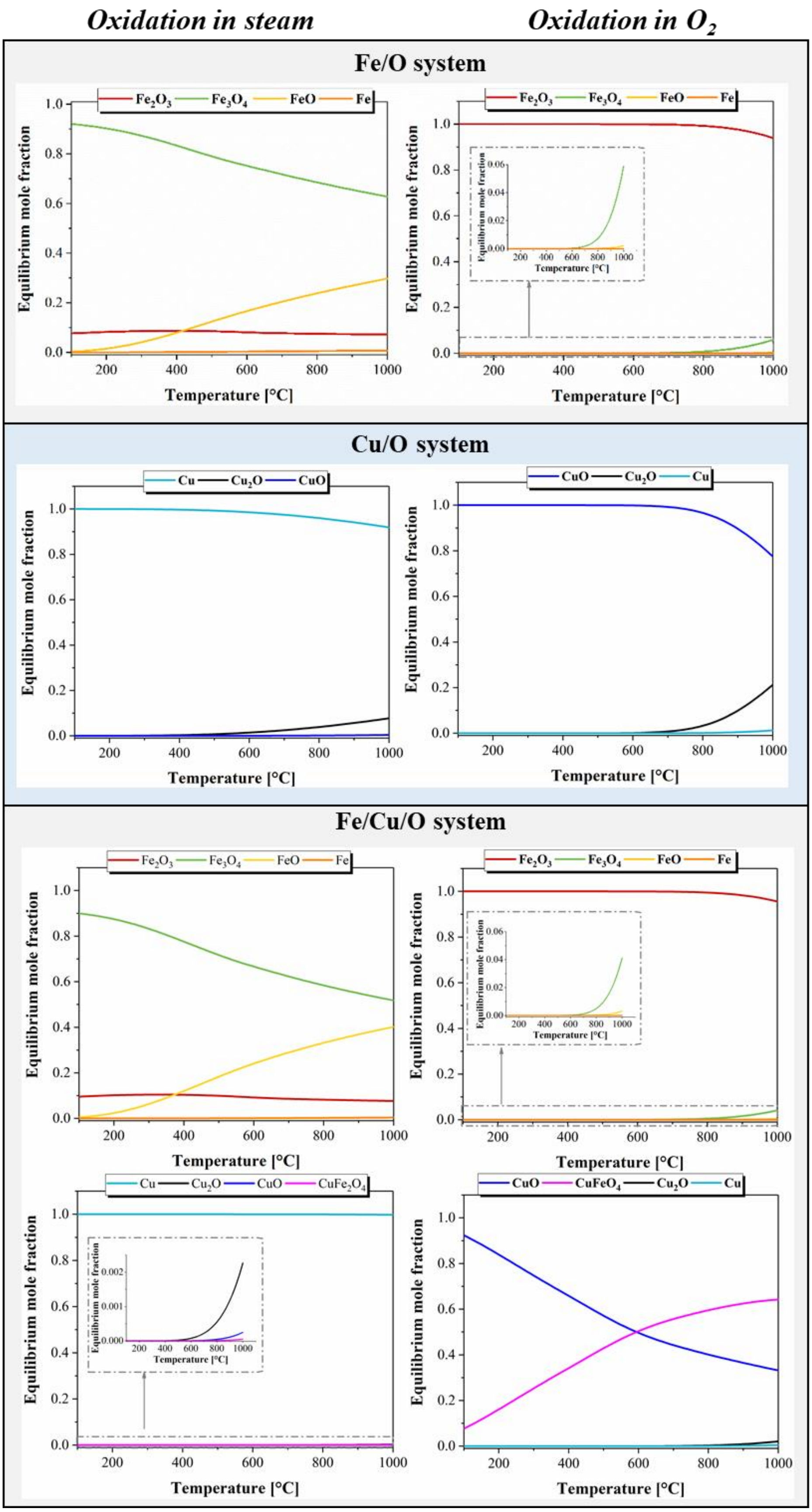

Figure S3: Equilibrium thermodynamics calculations for the Fe/O, Cu/O and Fe/Cu/O systems during oxidative (steam and oxygen) conditions (molar ratio Fe:Cu = 3:1).

A thermodynamic evaluation of the materials is given in Figure S3. The equilibrium mole fractions of the different phases considered (Cu, Cu_2O, CuO, $CuFe_2O_4$, Fe_2O_3, Fe_3O_4, FeO and Fe) were calculated by Gibbs free energy minimization using the HSC chemistry software 6.0 and the thermochemical data of Barin and Platzki.[1] The equilibrium thermodynamics calculations were performed for the i) Fe/O, ii) Cu/O and iii) Fe/Cu/O systems under steam oxidation (molar ratio of Fe:Cu:H_2O = 3:1:100) and oxygen oxidation (molar ratio of Fe:Cu:O_2 = 3:1:100) conditions, as a function temperature.

i. **Oxidation in steam:** In the metallic state, there is no alloy formation between Cu and Fe, in line with experimental evidence (XRD and XANES) and literature.[2] A thermodynamic assessment of the steam oxidation of metallic Fe indicates that Fe can be oxidized up to Fe_3O_4. The steam oxidation of metallic Cu gives only a small quantity of Cu_2O (3 %), with the majority being Cu (97 %), indicating that Cu cannot be oxidized to a sensible extent with steam (i.e. no water splitting reaction using Cu according to equilibrium thermodynamic calculations). In the bimetallic Fe-Cu system, the mole fraction of Cu is not affected by the presence of steam (100 %) and Cu_2O does not form (in line with XRD of Fe30Cu10Zr60 after steam oxidation, Figure S4). Fe is oxidized up to Fe_3O_4, while the formation of $CuFe_2O_4$ or Fe_2O_3 is thermodynamically not favoured under steam oxidation conditions.
ii. **Oxidation in O_2:** For the thermodynamic assessment of the oxidation in O_2, the reactants were Fe_3O_4 and Cu. At 700 °C, Fe_3O_4 is oxidized to Fe_2O_3 (complete oxidation) in the Fe/O system while Cu was oxidized to CuO in the Cu/O system. The formation of Fe_2O_3, CuO and $CuFe_2O_4$ is predicted in the Cu/Fe system.

[1] *I. Barin, G. Platzki, Thermochemical data of pure substances. Wiley Online Library,* ***1989****; Vol. 304.*

[2] *A. Bachmaier, M. Kerberb, D. Setman, R. Pippan, Acta Materialia, 60,* ***2012****, 860-871.*

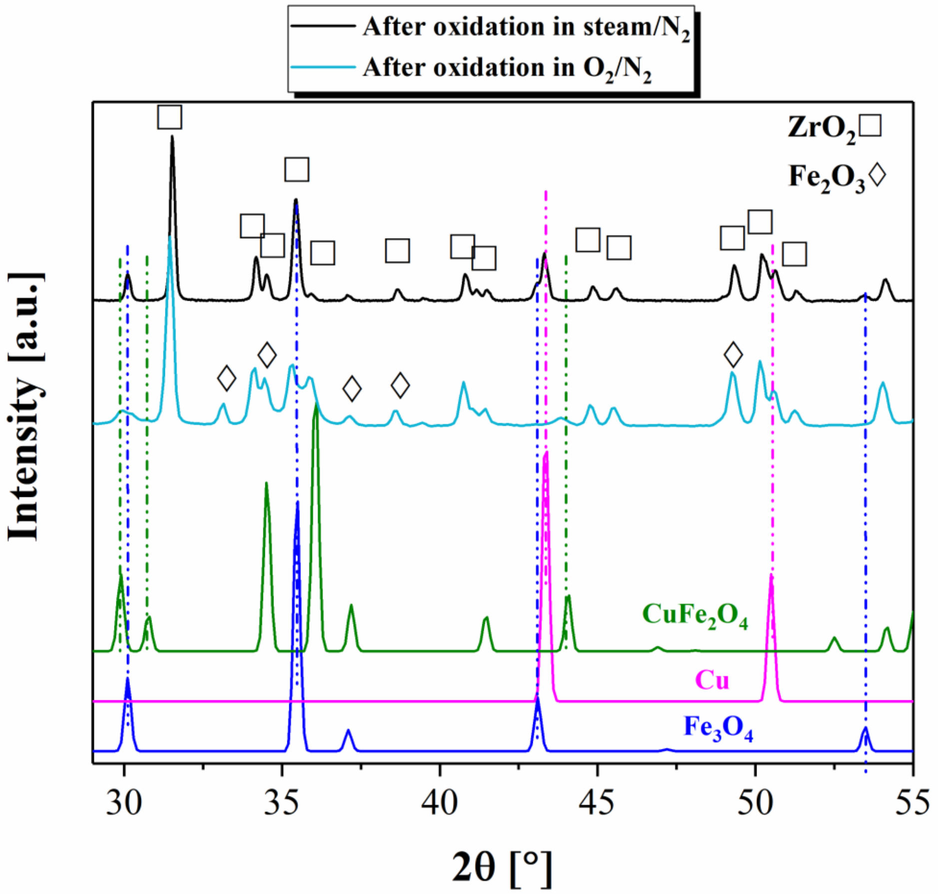

Figure S4: XRD patterns of Fe30Cu10Zr60 (previously reduced in 2.5 % H_2 in N_2) subjected to oxidation in steam/N_2 and followed by O_2/N_2. Cu is in its metallic state after steam oxidation and $CuFe_2O_4$ is formed after oxidation in O_2/N_2 for 20 min.

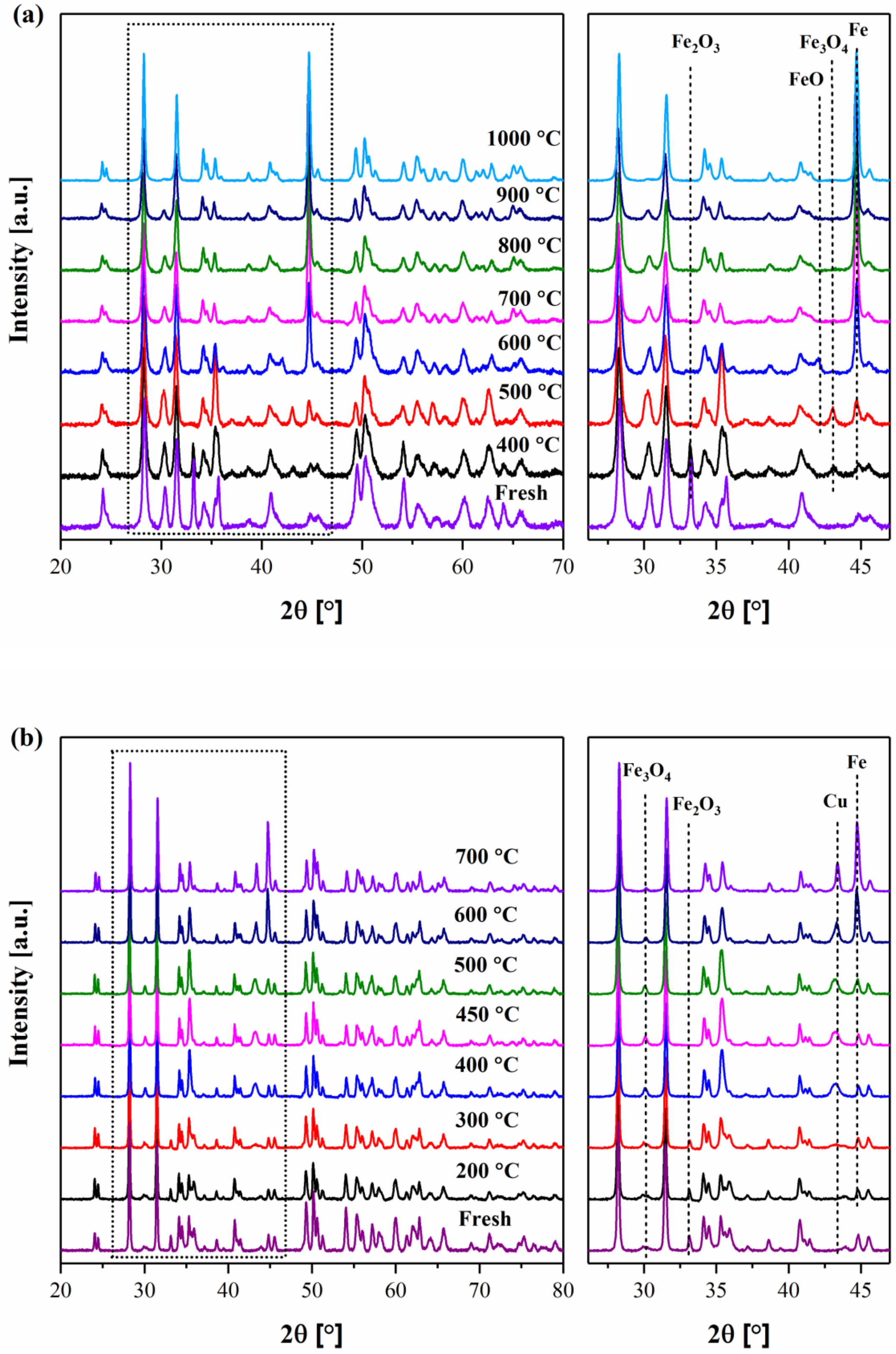

***Figure S5**:* Overall XRD series (a) Fe30Zr70 and (b) Fe30Cu10Zr60 30 at room temperature after H_2 reduction at various temperatures in the temperature range from 25 - 1050 °C.

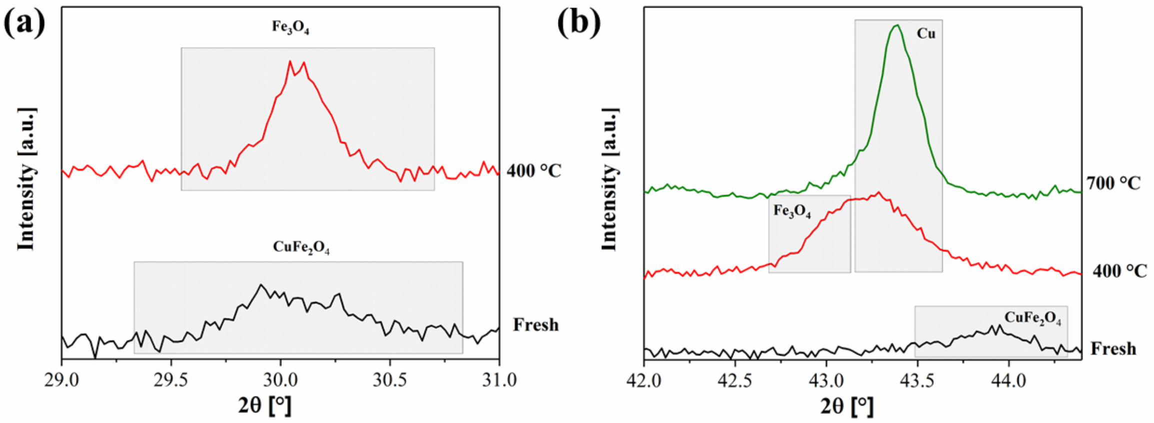

***Figure S6**:* XRD series Fe30Cu10Zr60 at room temperature after H_2 reduction 400 °C representing $CuFe_2O4$ to Fe_3O_4 and Cu transition.

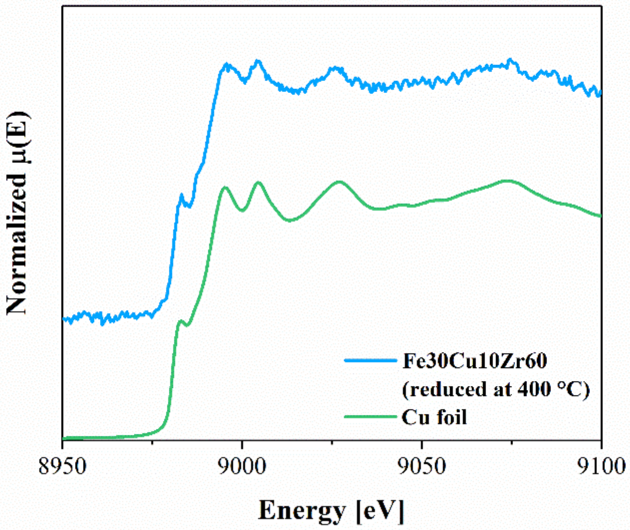

Figure S7: Cu-edge XANES spectra of Fe30Cu10Zr60 together with Cu foil.

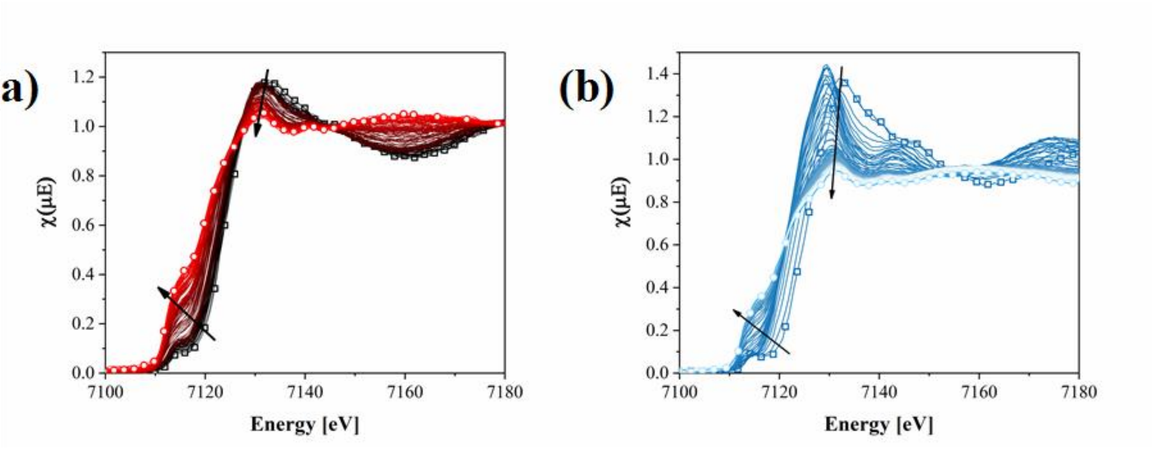

Figure S8: Time-resolved Fe K-edge XANES spectra during reduction of (a) Fe30Zr70 and (b) Fe30Cu10Zr70 at 750 °C using 5 vol.% H_2 in He. The square (□) and circle (○) symbols correspond to the initial and final states, respectively. The arrows indicate the direction of the changes with time.

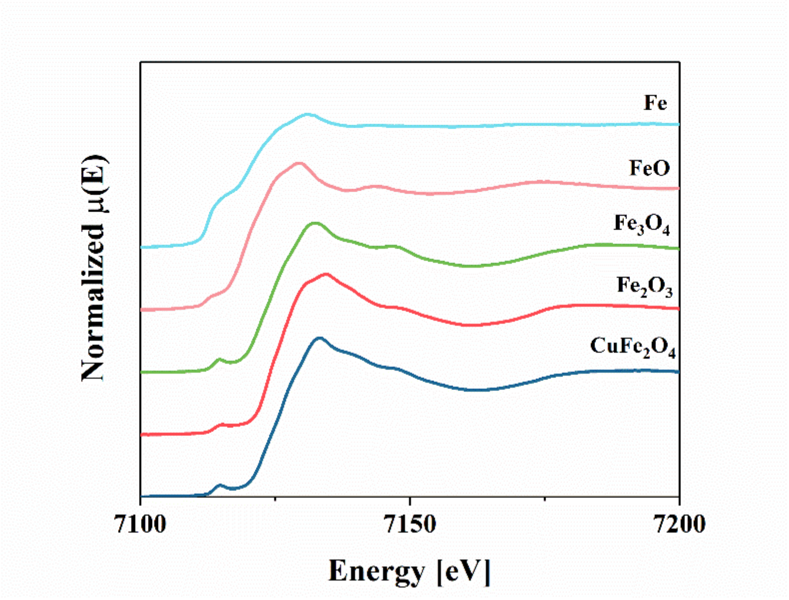

Figure S9: (a) Fe K-edge XANES spectra of (—) $CuFe_2O_4$ reference, (—) α-Fe_2O_3 reference, (—) Fe_3O_4 reference, (—) FeO reference and (—) Fe reference.

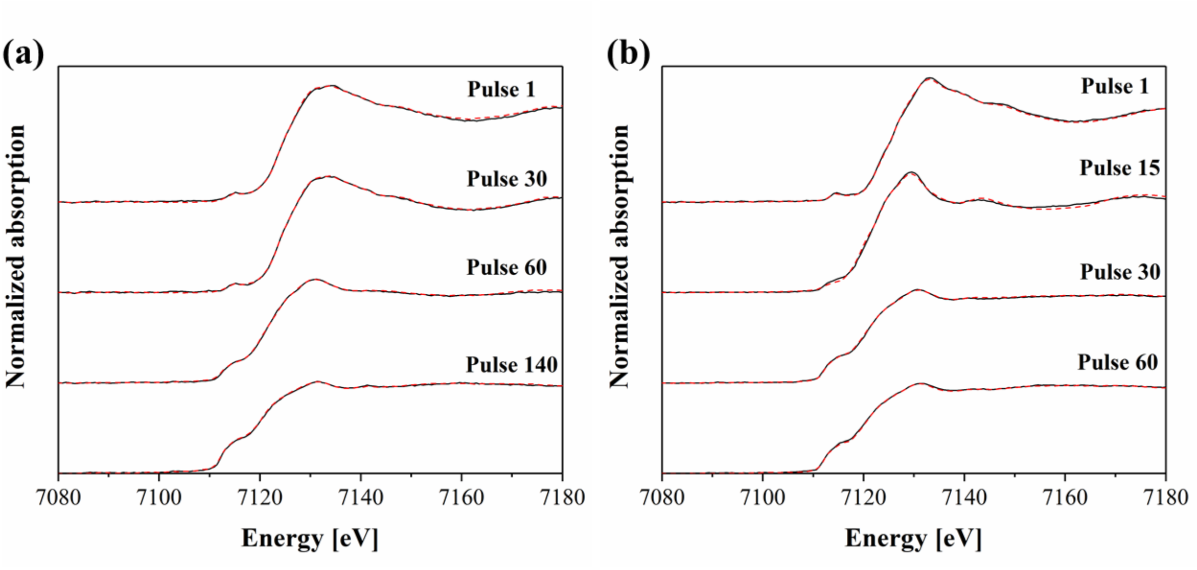

***Figure S10**:* Fe K-edge XANES experimental data (solid black) and corresponding fitting using the least-squares linear combination of standard samples (red dash).

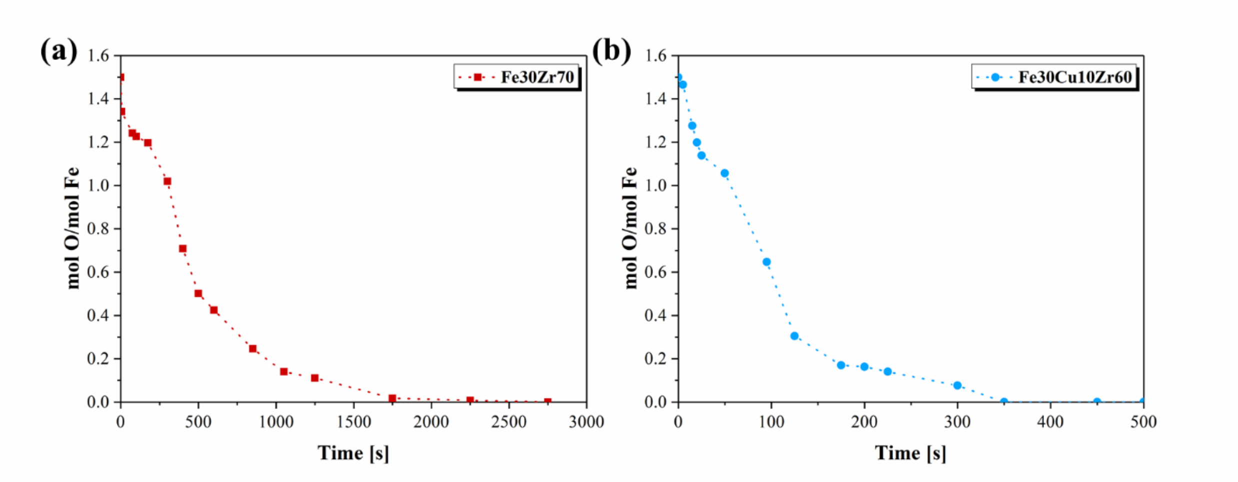

***Figure S11**:* The loss of oxygen in (a) Fe30Zr70 and (b) Fe30Cu10Zr60 as a function of time.

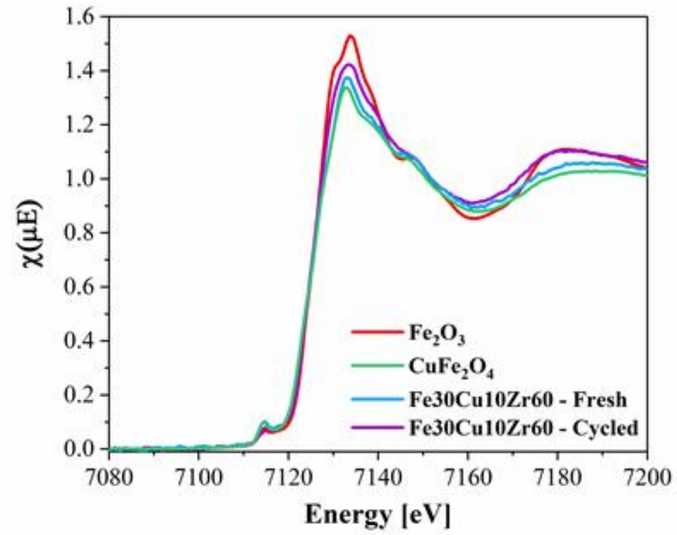

Figure S12: Fe-edge XANES spectra of fresh and cycled Fe30Cu10Zr60 together with α-Fe_2O_3 reference and $CuFe_2O_4$ reference.

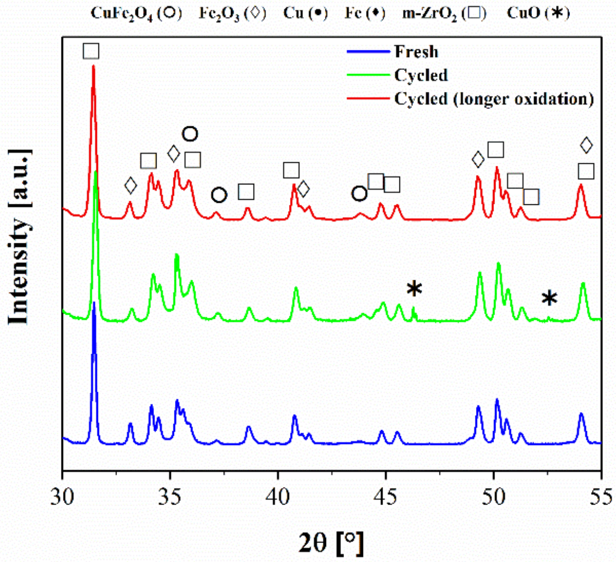

Figure S13: XRD of (—) fresh and cycled and oxidized Fe30Cu10Zr60. The oxygen carrier was oxidized for (—) 5 min. and (—) 20 min after being subjected to 15 redox cycles.