Electronic Supplementary Information (ESI) for:

The role of Cu on the reduction behavior and surface properties of Fe-based Fischer-Tropsch catalysts

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Fig. E1 Representative TEM images of the Fe_2O_3 (top), Fe_2O_3 -Cu (middle) and Fe_2O_3 -Cu-K-Si (bottom) materials before treatment.

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Fig. E2 Representative TEM images of the Fe₂O₃ (top), Fe₂O₃-Cu (middle) and Fe₂O₃-Cu-K-Si (bottom) materials after treatment in 0.4 mbar CO/H₂.



Fig. E3 O K-edge XAS spectra of the catalysts before reduction treatment.



Fig. E4 Fe L-edge XAS spectra of the unsupported catalysts after 1 h at 275°C in 0.4 mbar CO/H₂.



Fig. E5 Mass spectrometry data of the product gases during the *in situ* XAS/XPS experiment during CO/H₂ treatment from 180°C to 275°C. Top: m/z = 15 (CH₄), middle m/z = 18 (H₂O) and bottom m/z = 44 (CO₂).



Fig. E6 O K-edge XAS spectra of the catalyst materials after reduction in 0.4 mbar CO/H₂.



Fig. E7 Cu $2p_{3/2}$ and $2p_{1/2}$ XPS spectrum of the Fe_2O_3-Cu catalyst after reduction in 0.4 mbar CO/H_2 at $275^{o}C$



Fig. E8 O 1s XPS spectra of the catalysts during treatment in 0.4 mbar CO/H₂. Top: Fe₂O₃, middle: Fe₂O₃-Cu and bottom: Fe₂O₃-Cu-K-Si.