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

Supporting Information

Elucidation of Copper Environment in a Cu-Cr-Fe Oxide Catalyst Through in situ High-Resolution XANES Investigation

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Figure S5. Typical Cu K-edge EXAFS data and associated Fourier transforms collected *in situ* at RT and 773 K are shown here to illustrate the quality of EXAFS and the best fit obtained from the analysis. The data were analysed between 2.7 and 10 $Å^{-1}$ in k-space and fitting range was limited to 0.7 and 2.4 Å in R-space.

Figure S6. Comparison of the *ex situ* calcined samples at 773 K and linear combination of tetrahedral and octahedrally coordinated compounds.

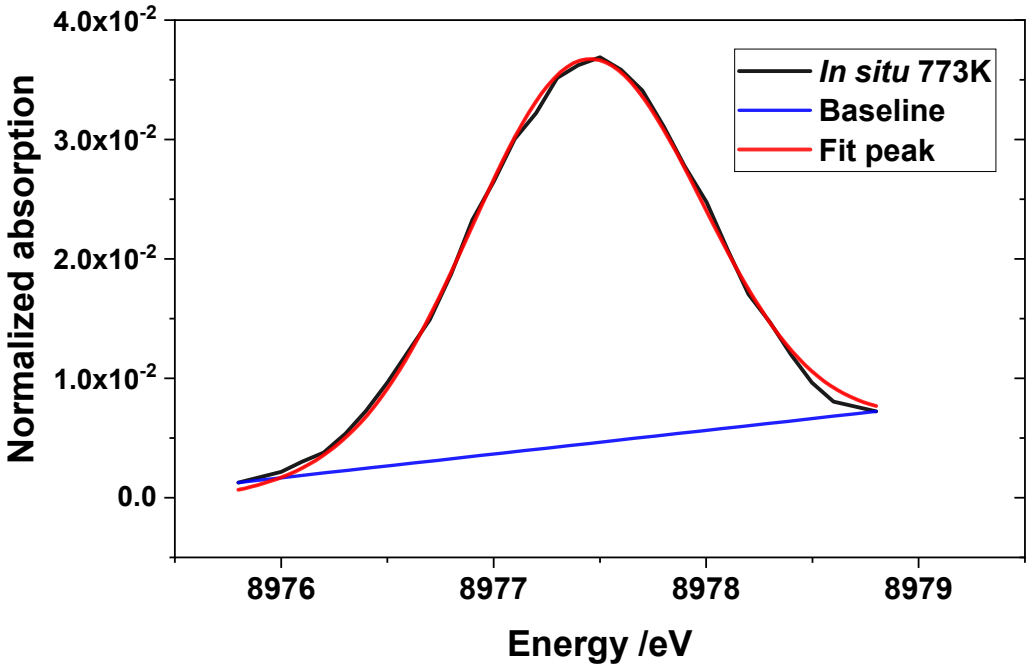

Figure S1. An example of the Cu K-edge pre-edge peak fitting is shown for the *in situ* heated materials at 773 K.

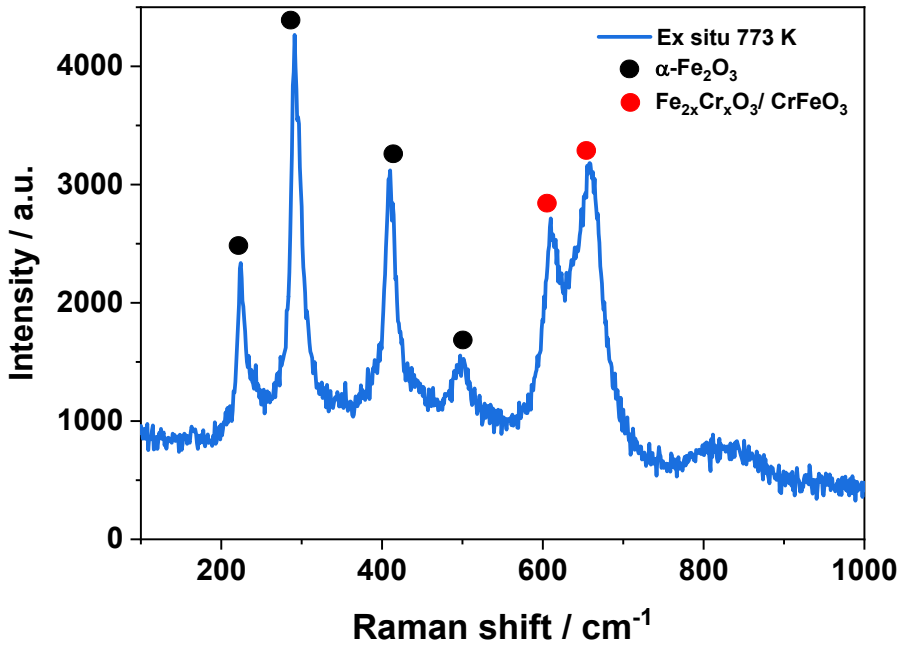

Figure S2. Raman spectrum of Cu-Cr-Fe oxide *ex situ* calcined catalyst at 773 K.

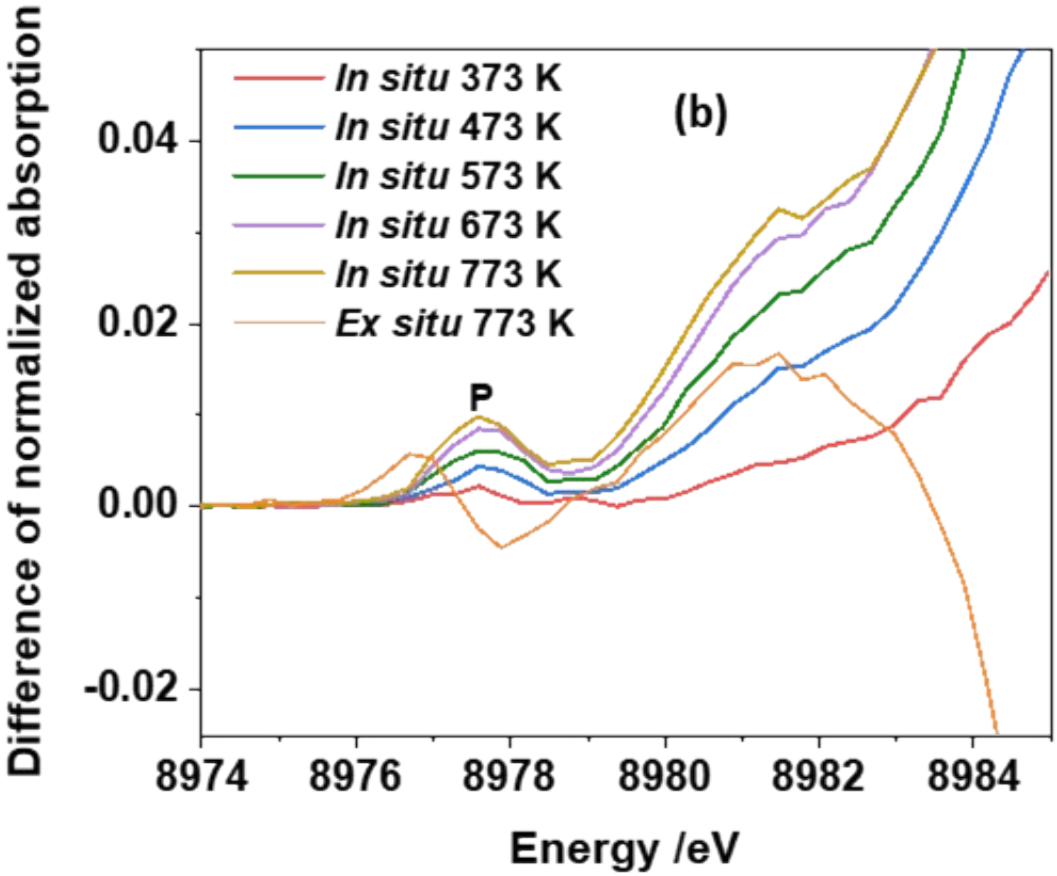

Figure S3. Cu K-edge XANES difference spectra of these systems with respect to starting material of the Cu-Cr-Fe oxide catalyst, measured in situ at various temperatures and an ex situ thermally heated sample, same as the one investigated with XRD, Raman and XPS.

Table S1. The pre-edge energy, its peak area and edge position in energy extracted from XANES data of all the reference compounds, *ex situ* and *in situ* samples are listed.

Sample	Pre-edge peak position (eV)	Pre-edge area	Edge energy (eV) +/- 0.1 eV
As prepared material	8977.40	0.0349	8986.5
In situ 373K	8977.40	0.0357	8986.5
In situ 473K	8977.42	0.0403	8986.4
In situ 573K	8977.43	0.0424	8986.3
In situ 673K	8977.45	0.0435	8986.1
In situ 773K	8977.44	0.0448	8986.1
Ex situ 773K	8977.22	0.0358	8987.2
Cu foil	-	-	8979.1
Cu_2O	-	-	8980.5
CuO	8977.80	0.0299	8984.5
$Cu(OH)_2$	8977.49	0.0353	8986.1
$CuFe_2O_4$	8977.40	0.0290	8987.0
$CuCr_2O_4$	8976.81	0.0975	8986.7

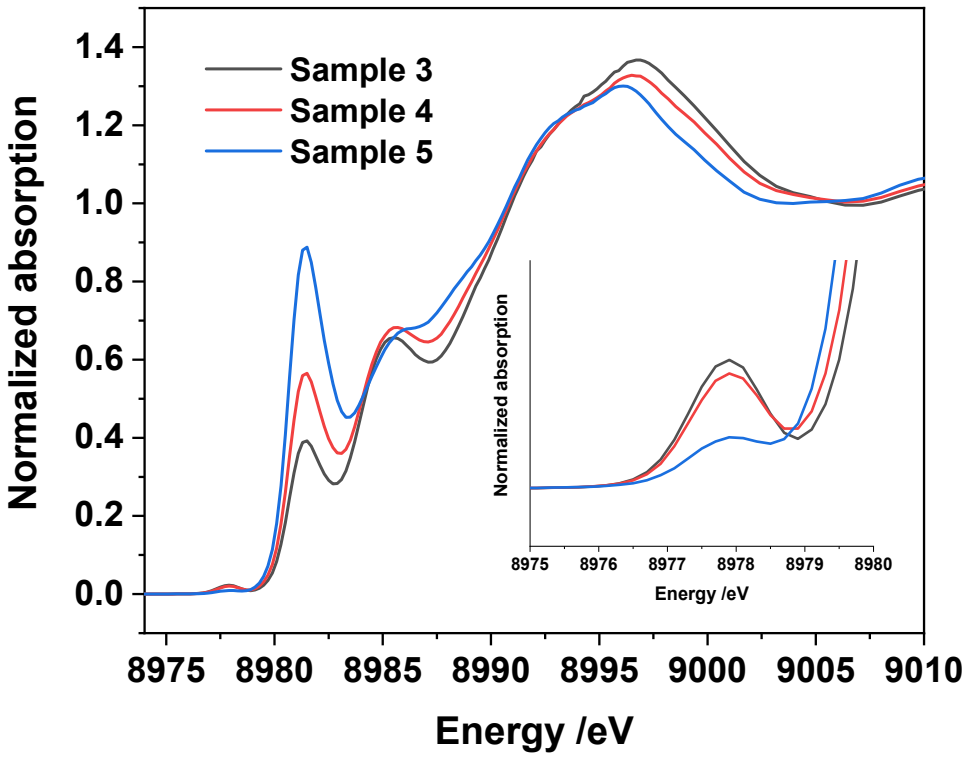

Figure S4. The Cu K-edge XANES of physically combined Cu_2O:CuO, where sample 3 is Cu^{1+}:Cu^{2+} = 28:72, sample 4 is 54:46, and sample 5 is 76:24 by weight.

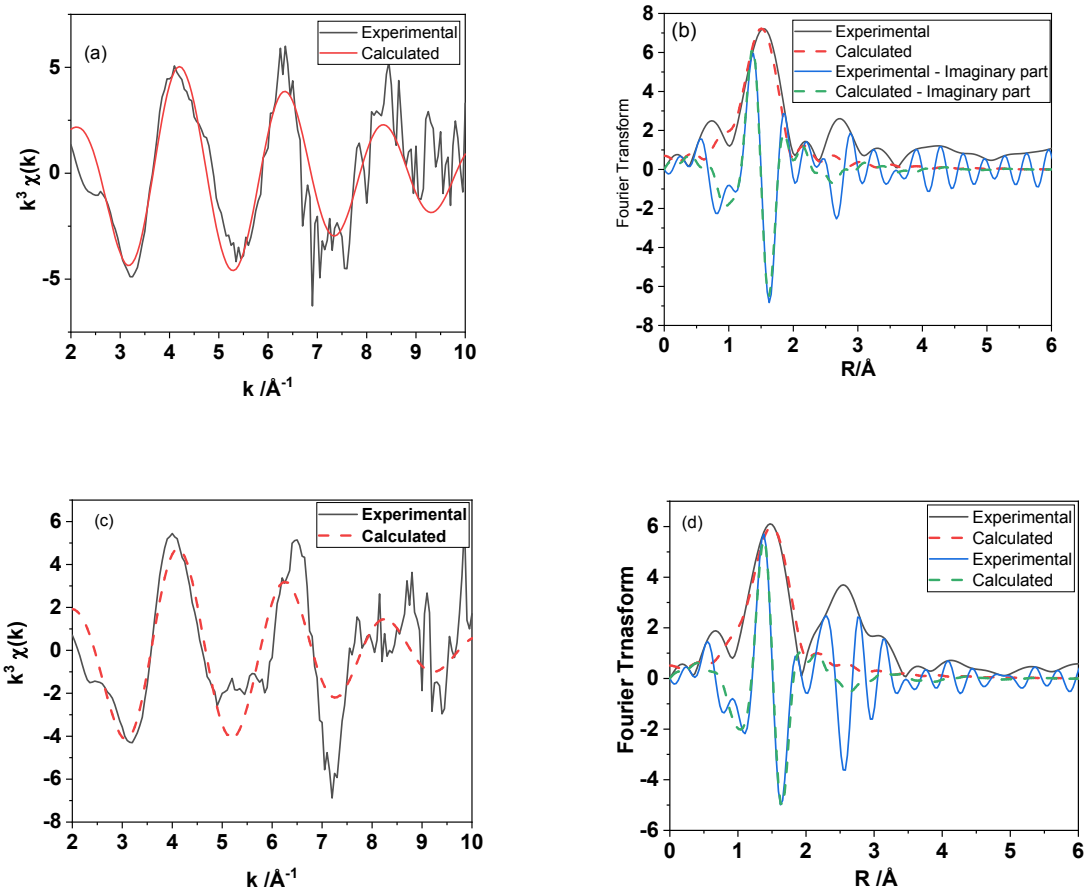

Figure S5. Typical Cu K-edge EXAFS data and associated Fourier transforms collected *in situ* at RT and 773 K are shown here to illustrate the quality of EXAFS and the best fit obtained from the analysis. The data were analysed between 2.7 and 10 $Å^{-1}$ in k-space and fitting range was limited to 0.7 and 2.4 Å in R-space.

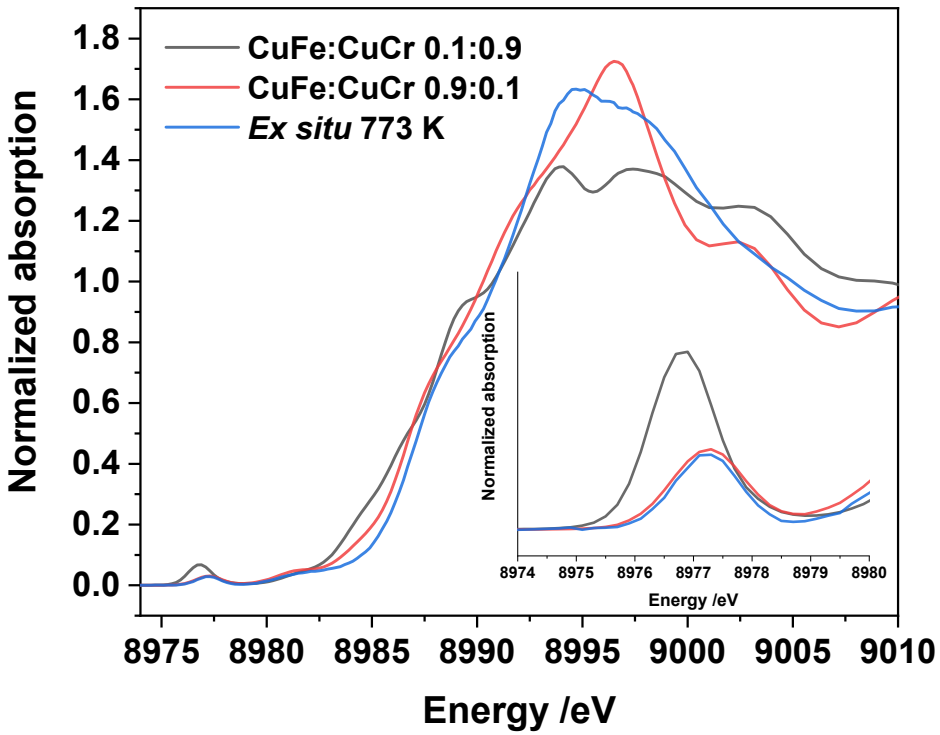

Figure S6. Comparison of the *ex situ* calcined samples at 773 K and linear combination of tetrahedral and octahedrally coordinated compounds are shown here. Although pre-edge intensity and position of the calcined materials are similar to the 10% tetrahedrally coordinated copper mixed with 90% of octahedral compound, it is clear the white line intensity of the calcined material at 773 K is distinctly different.