Supplementary Information

In situ K-edge X-ray absorption spectroscopy of the ligand environment of single-site Au/C catalysts during acetylene hydrochlorination.

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Table S1. Chlorine content in the catalysts, fresh and used, obtained from the raw Cl K-edge XANES and Cl(2p) core-level XPS and spectra.

Catalyst	Cl K-edge (XANES) (a.u.)	Cl 2p (XPS) [at%]
Au/C-AR Fresh	0.29	1.98
Au/C-AR Used	0.21	1.75
Au/C-S$_2$O$_3$ Fresh	0.08	0.25
Au/C-S$_2$O$_3$ Used	0.09	0.42
Au/C-H$_2$O Fresh	0.03	0.28

Table S2. Chlorine content in the carbon support, bare and after treatment with H$_2$O and *aqua regia*, obtained from the Cl(2p) core-level XPS and raw Cl K-edge XANES spectra. (Relative spectra are reported in figure S5 and S6).

Catalyst	Cl K-edge (XANES) (a.u.)	Cl 2p (XPS) [at%]
C	0.01	0.08
C-H$_2$O	0.007	-
C-AR	0.22	1.90

Table S3. Oxygen content obtained from the O(1s) core-level XPS spectra.

Catalyst	O 1s (XPS) [at%]
Au/C-AR Fresh	6.27
Au/C-AR Used	6.47
Au/C-S$_2$O$_3$ Fresh	4.85
Au/C-S$_2$O$_3$ Used	4.13
C	3.75
C-H$_2$O	3.49
C-AR	6.68

Table S4. Sulphur content obtained from the *ex situ* recorded raw S K-edge XANES spectra and S(2p) core-level XPS spectra.

Catalyst	S K-edge (XANES) (a.u.)	S 2p (XPS) [at%]
Au/C-S$_2$O$_3$ Fresh	$1.7 \cdot 10^{-3}$	0.64
Au/C-S$_2$O$_3$ Used	$0.9 \cdot 10^{-3}$	0.43

Figure S1. *Ex situ* Cl K edge XANES of Au/C-AR (-■-), Au/C-S$_2$O$_3$ (-●-) and Au/C-H$_2$O (-▲-).
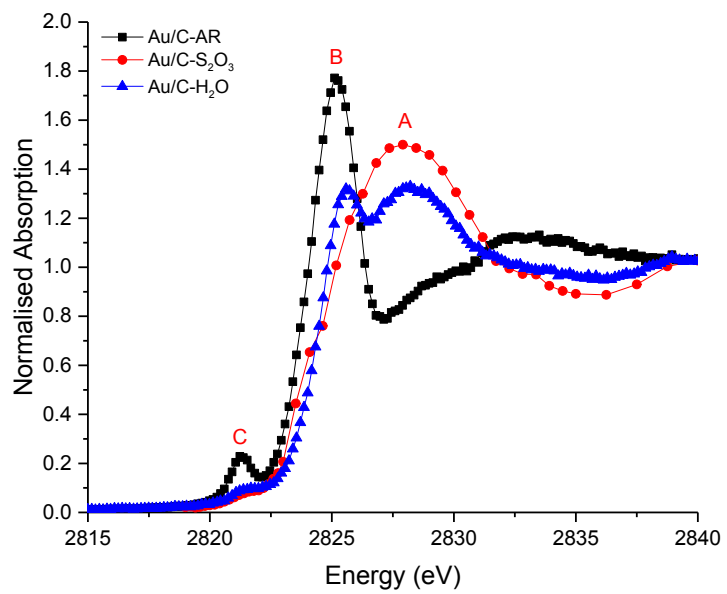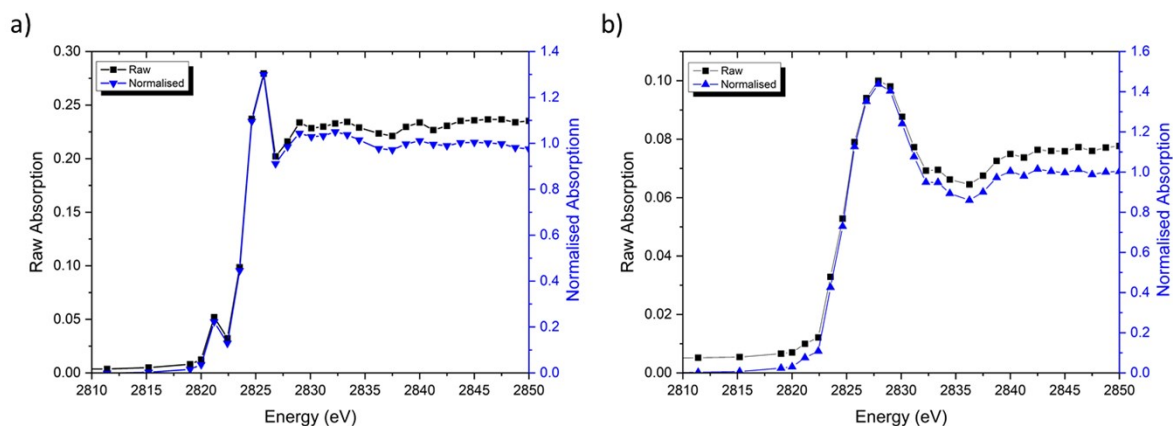
Figure S2. Comparison between raw (-■-) and normalised (-▲-) XANES spectra for the freshly prepared a) Au/C-AR and b) Au/C-S$_2$O$_3$.

All the spectra acquired (*ex situ* and *in situ*) have been initially processed using "PyMca", which has been developed by the Software Group of the European Synchrotron Radiation Facility (ESRF). [1] In particular, all the raw fluorescence spectra which have been initially standardised by the incident beam, and then converted from '.mca' to '.dat' called "Raw fluorescence absorption". Comparisons have been made between raw fluorescence spectra recorded at the same detector position, i.e. *detin* = 99.0. Moreover, when comparing the Cl absorption of the raw fluorescence spectra, the absorption values have been taken at a fixed energy of 2.85 keV.

The pre-edge energy position, intensity and shape have been used to provide information on the character of the bond and associated coordination geometry of the Au-Cl complex.[2] Conventional data reduction [3] of the XANES spectra have been performed using Demeter Software package [4] to obtain the so-called "normalised" spectra.

Figure S3. *Ex situ* Cl 2p XPS of Au/C-H$_2$O catalyst. The first two peaks are associated with "inorganic" Cl (~197 eV), while the other two peaks are associated with "organic" Cl (~200 eV).
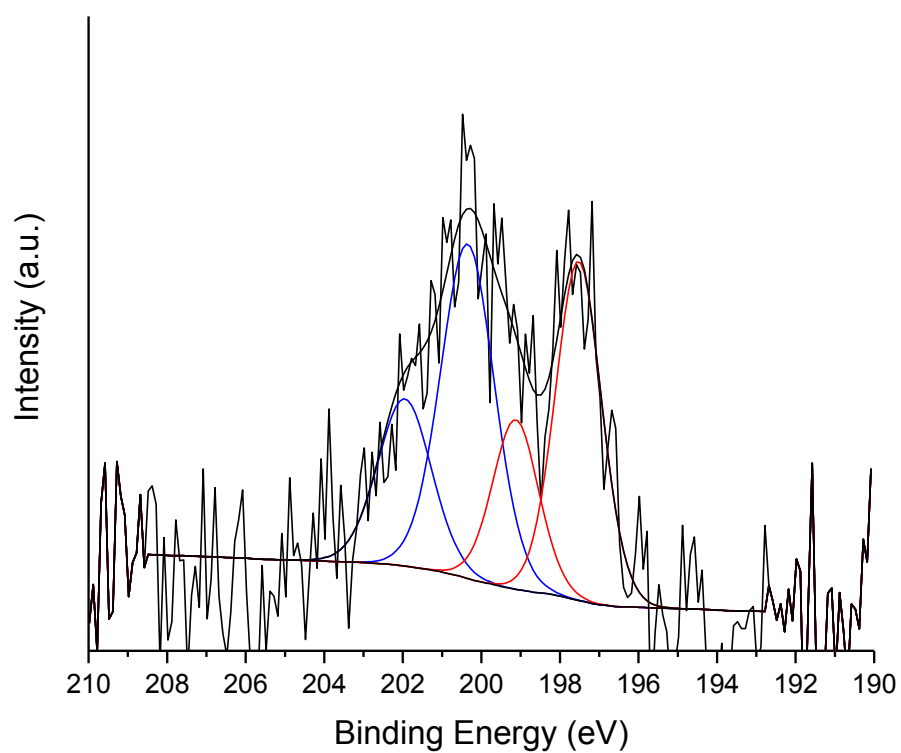
Figure S4. Cl K edge XANES of Au/C-AR (-■-), Au/C-S$_2$O$_3$ (-●-), Au/C-H$_2$O (-▲-) and the reference material, NaCl (-◆-).
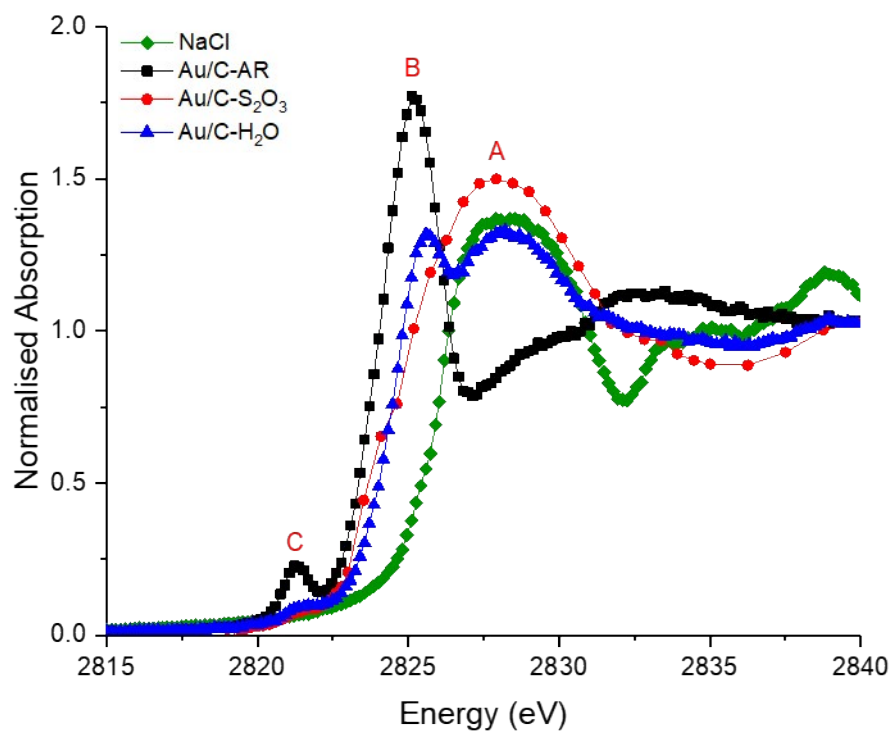
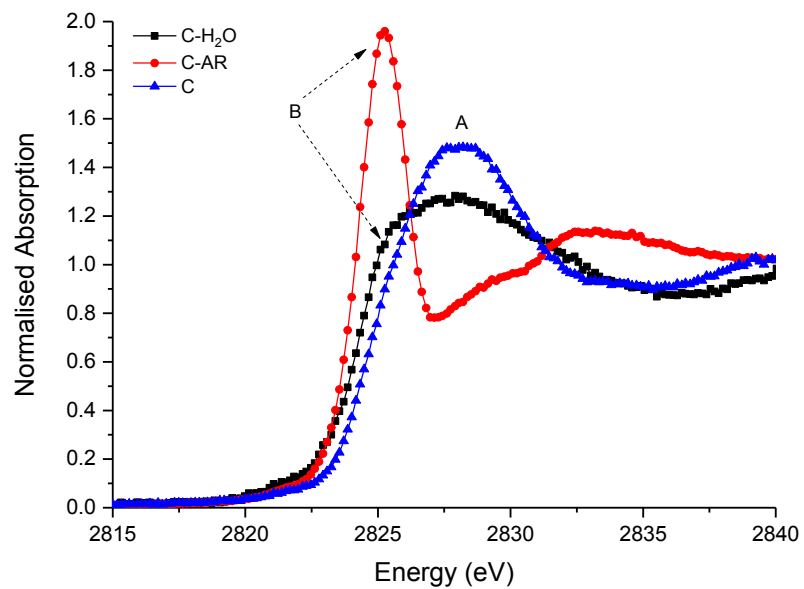**Figure S5.** Cl K edge XANES of bare carbon, C (-▲-) carbon washed with aqua regia, C-AR (-●-) and carbon washed with water (-■-). See Table 2 for quantification of the Cl content.

Figure S6. *Ex situ* Cl 2p XPS of a) the bare carbon and treated with b) water, C-H$_2$O and c) *aqua regia*, C-AR. See table 2 for quantification of the Cl content.
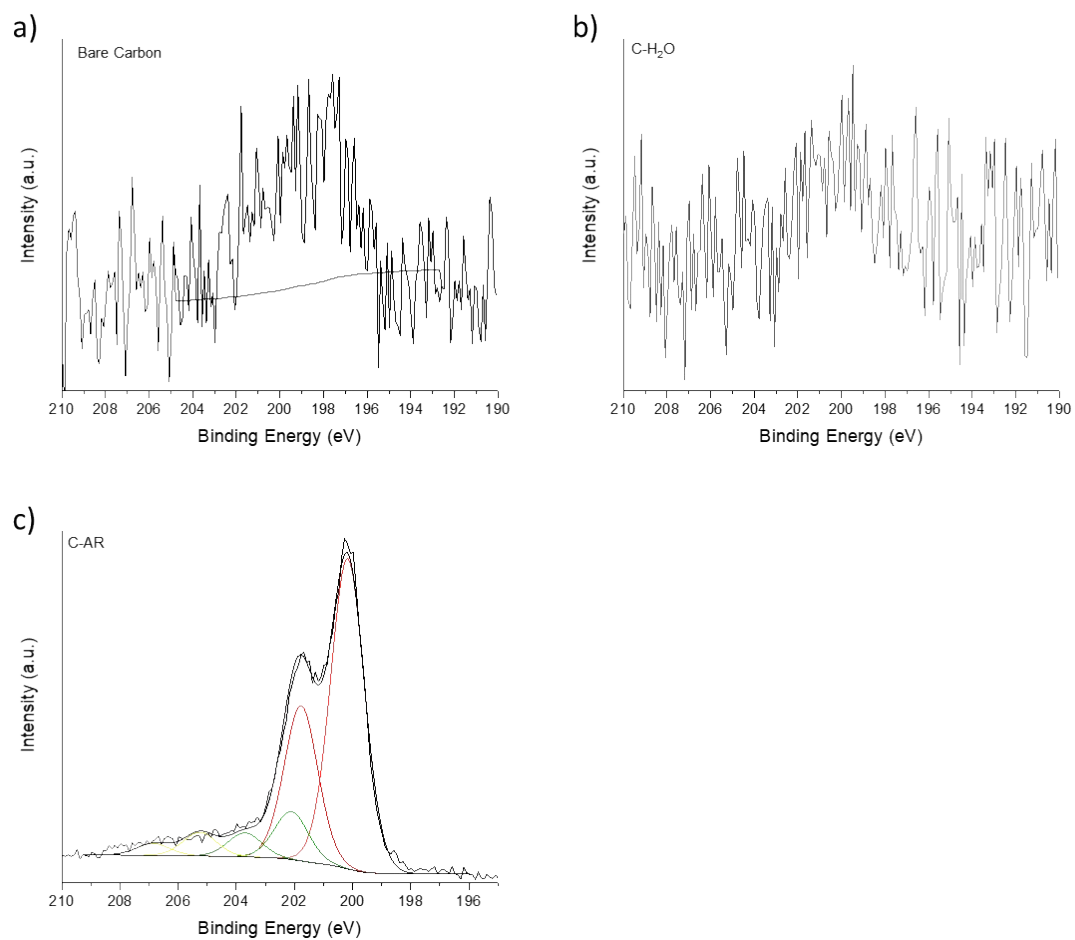
Figure S7. All Cl K edge XANES during heating to 200 °C under helium of a) Au/C-AR and b) Au/C-S$_2$O$_3$ catalysts.
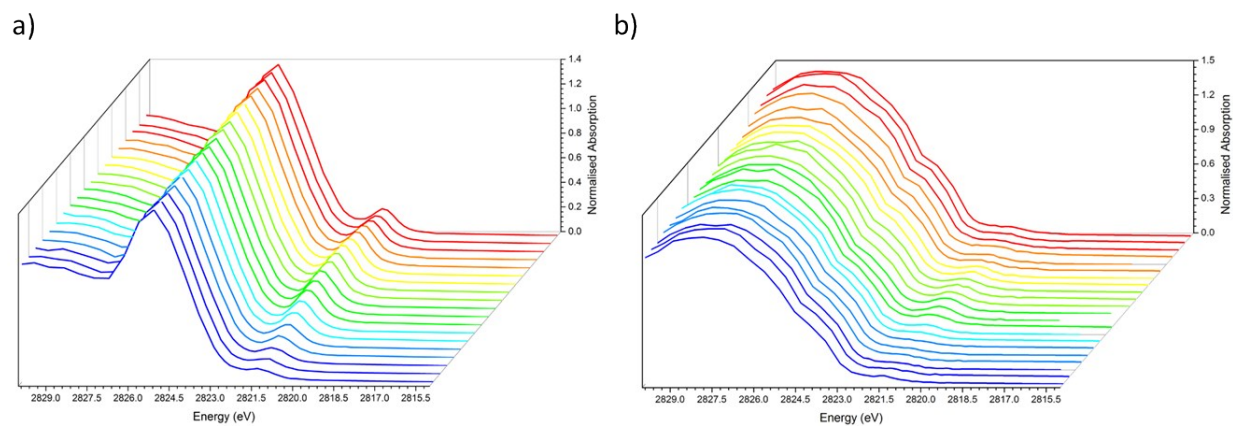
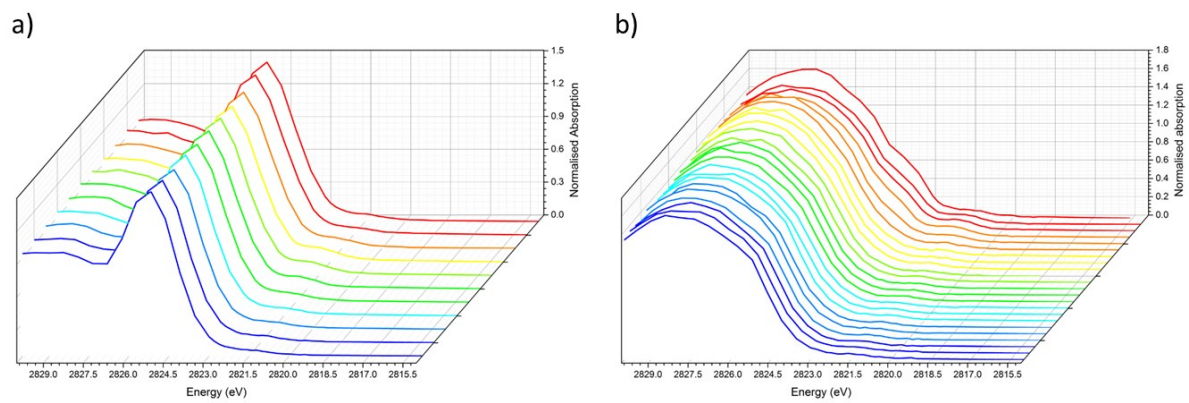**Figure S8.** All Cl K edge normalised XANES during the time-on-line of the a) Au/C-AR and b) Au/C-S$_2$O$_3$ catalysts.

a)

b)

Figure S9. Comparison between raw XANES spectra at the beginning (-■-) and at the end of the reaction time (-●-) of a) Au/C-AR and b) Au/C-S$_2$O$_3$ catalysts.
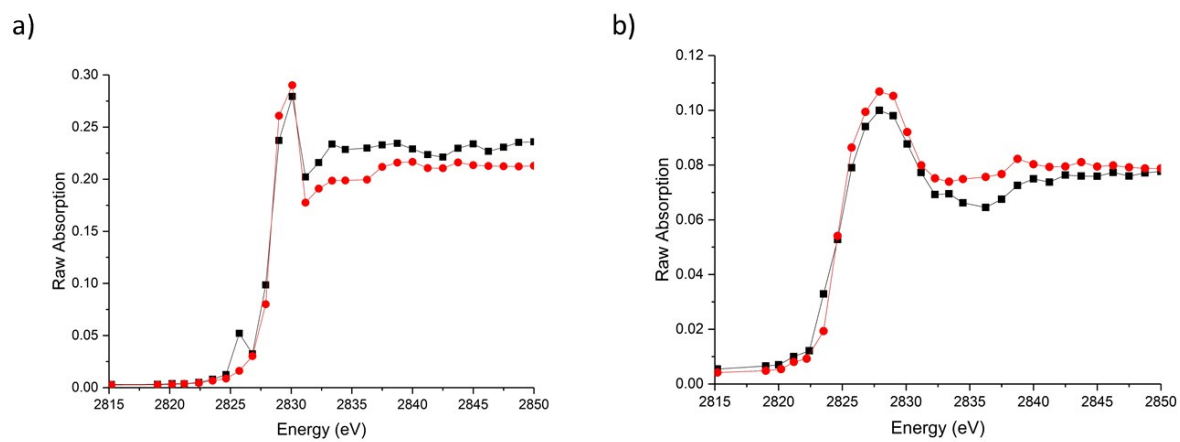
Figure S10. *Ex situ* Cl 2p XPS of the used a) Au/C-AR and b) Au/C-S$_2$O$_3$ catalysts.
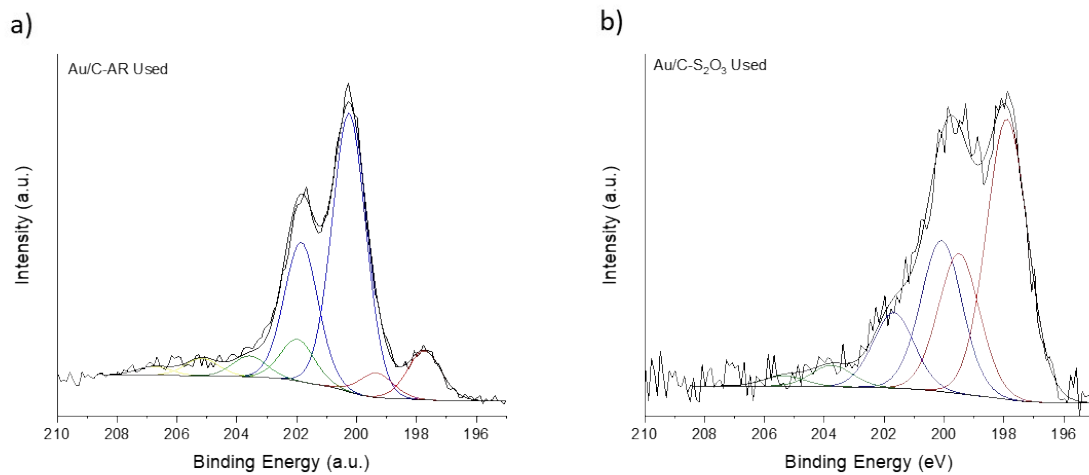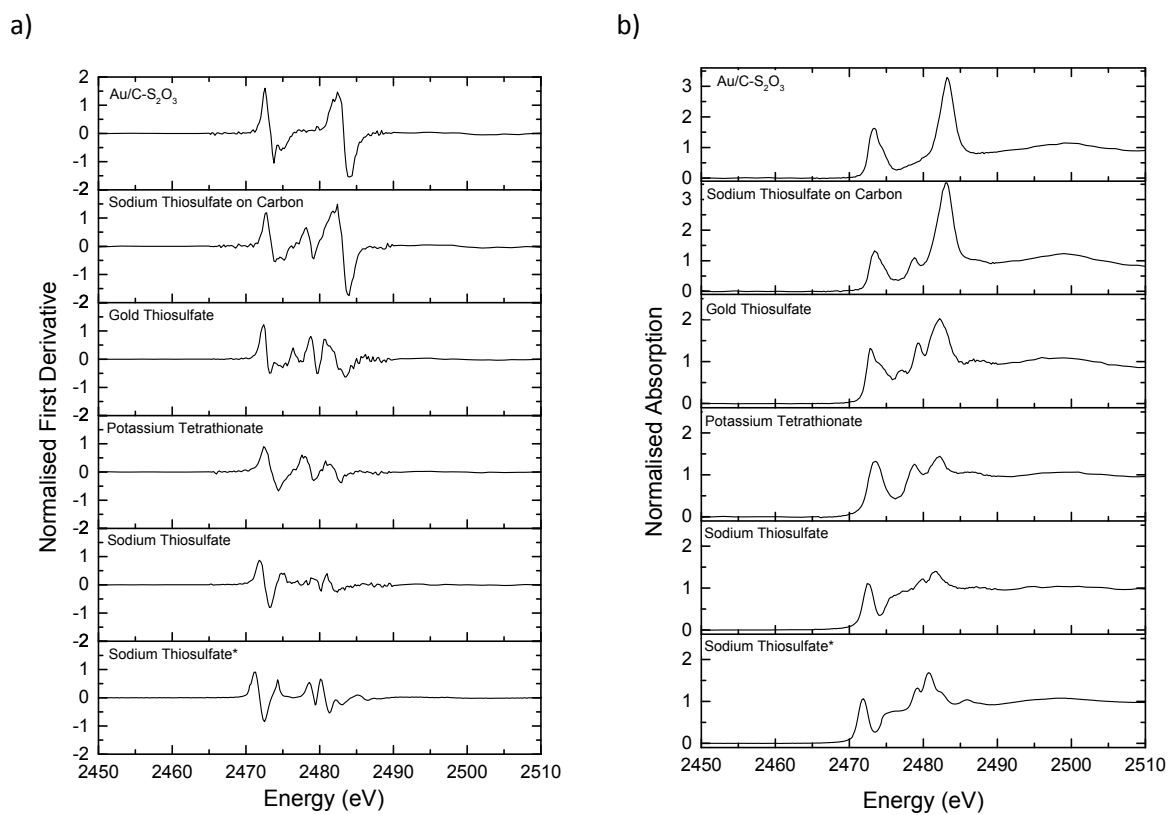See table S1 for quantification of the Cl content.

Figure S11. S K-edge a) normalised absorption and b) normalised first derivative of standards and samples acquired *ex situ*.

(Sodium thiosulfate on carbon has been prepared *via* a "washing step" which reproduced the conventional catalyst preparation method without using the metal precursor. In particular, *ca.* 2 g of carbon, previously grounded, were mixed with *ca.* 5mL of an aqueous solution containing $Na_2S_2O_3$).

Figure S12. a) 2D and b) 3D plot of all *in situ* S K edge XANES normalised absorption spectra of the Au/C-S$_2$O$_3$ catalyst acquired while heating to reaction temperature (200 °C).
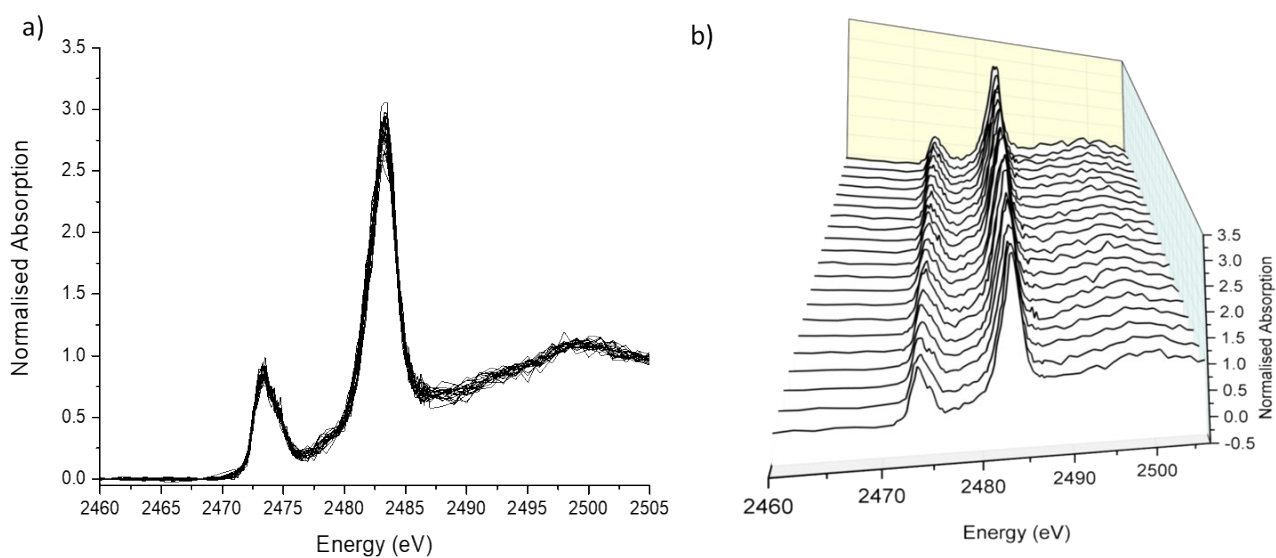
a)

b)

Figure S13. a) 2D and b) 3D plot of all *in situ* S K-edge normalised XANES spectra of the Au/C-S$_2$O$_3$ catalyst during the time-on-line.
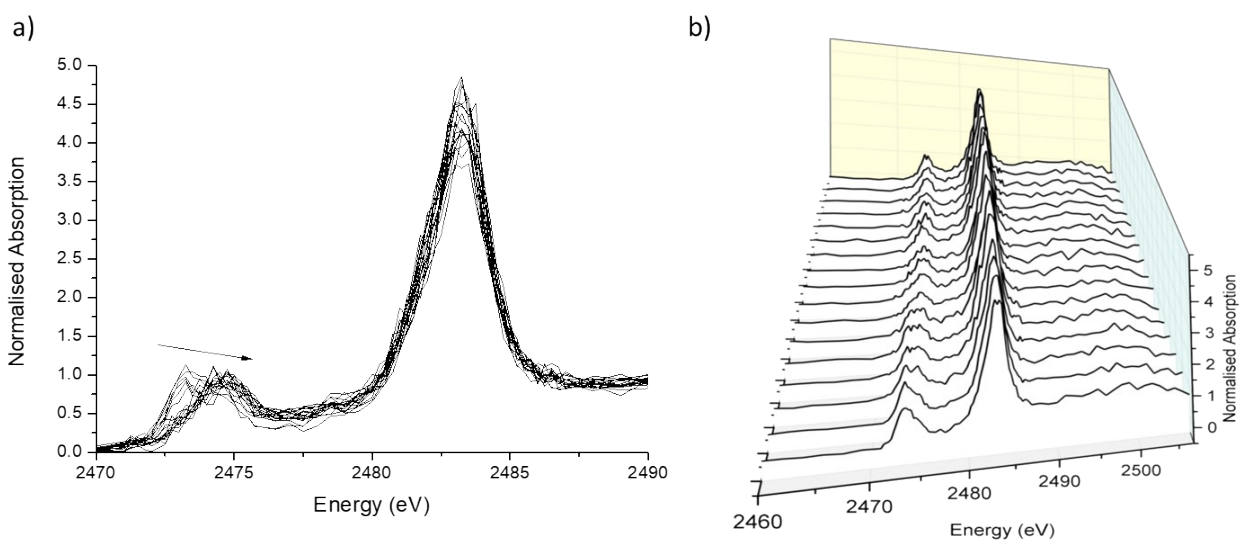
a)

b)

Figure S14. *Ex situ* S 2p XPS of the a) fresh and b) used Au/C-S$_2$O$_3$ catalysts. See table S4 for quantification of the S content.
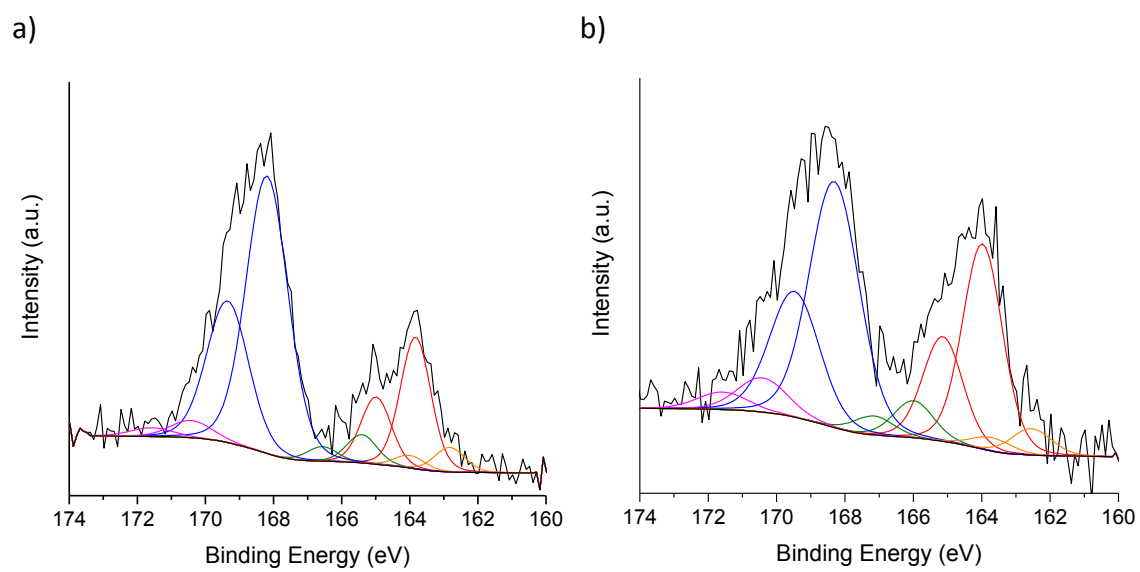
Figure S15. VCM productivity as function of time-on-line during the "accelerated deactivation test" for the Au/C-S$_2$O$_3$ catalyst.

(i) HCl/C$_2$H$_2$/Ar, (ii) HCl/Ar, (iii) second HCl/C$_2$H$_2$/Ar, (iv) C$_2$H$_2$/Ar, and (v) third HCl/C$_2$H$_2$/Ar exposure.

Test conditions: 90 mg catalyst, 23.5 mL min^{-1} C$_2$H$_2$, 23.7 mL min^{-1} HCl and 2.7 mL min^{-1} Ar, 200 °C.
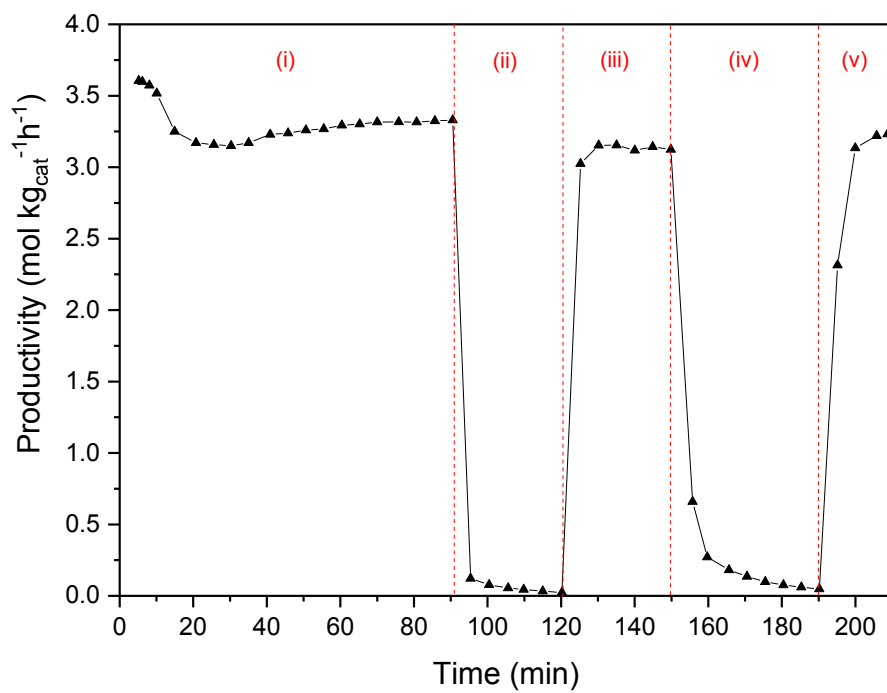
Figure S16. Comparison of the k space for the measured Au L$_3$-edge during step (i) HCl/C$_2$H$_2$/Ar and step (iv) C$_2$H$_2$/Ar of catalyst treatment reported in figure S15.

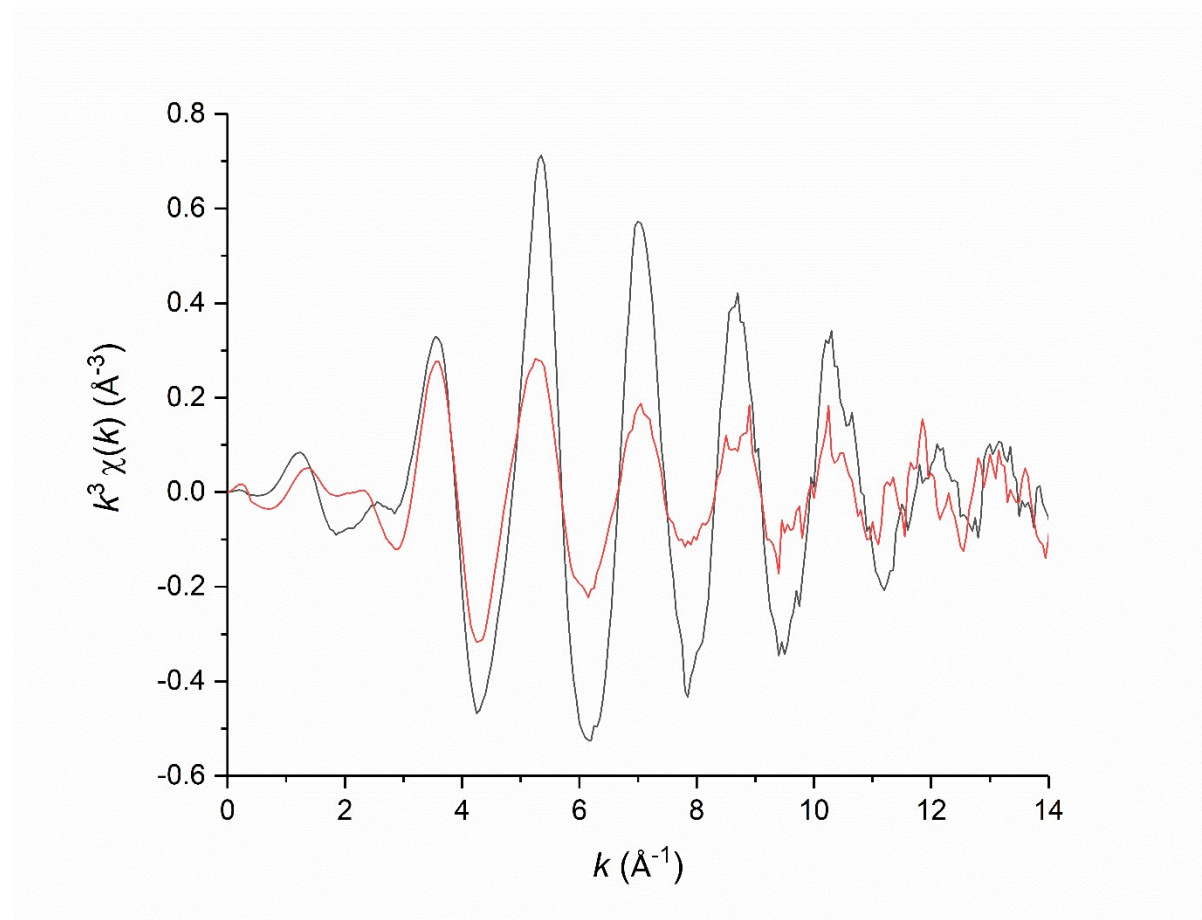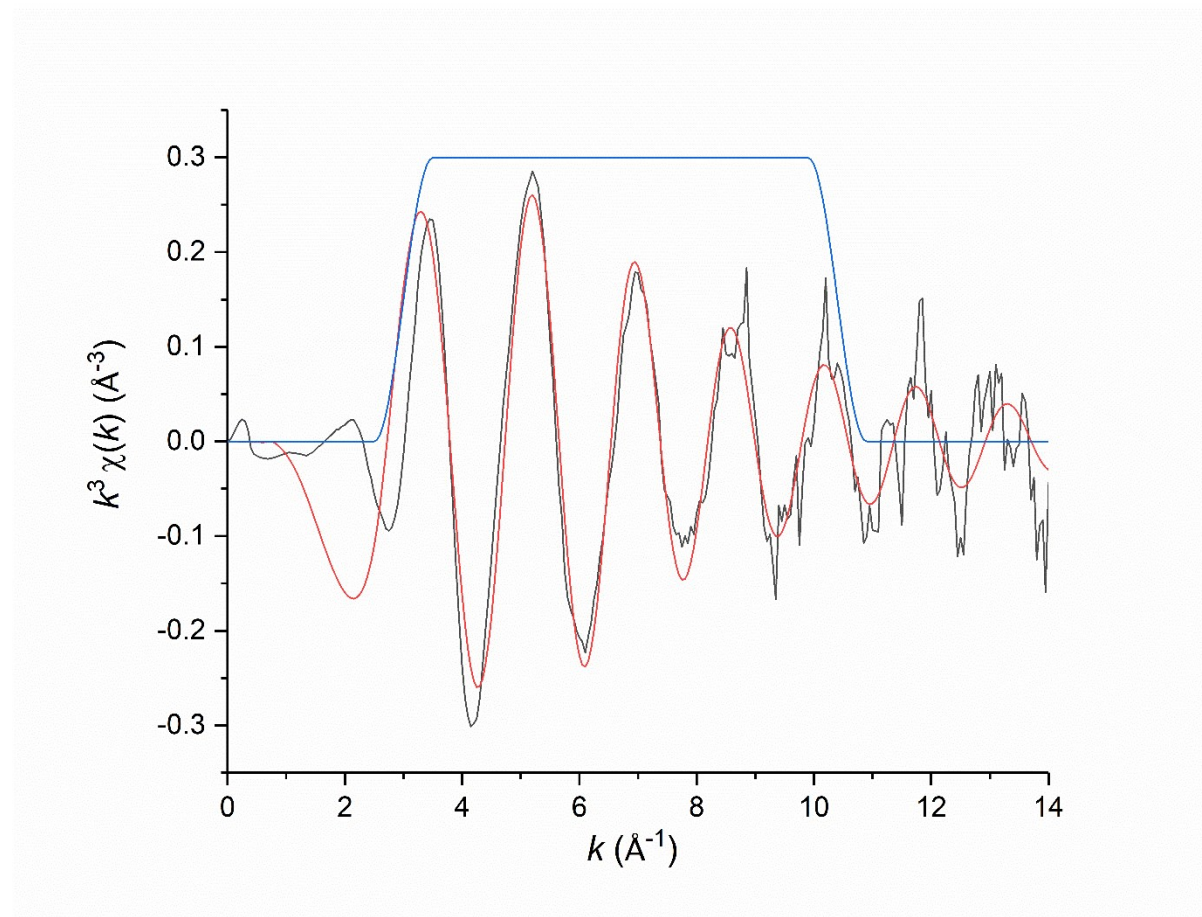*Test conditions: 90 mg catalyst, 23.5 mL min^{-1} C$_2$H$_2$, 23.7 mL min^{-1} HCl and 2.7 mL min^{-1} Ar, 200 °C.*

Figure S17. Comparison of k space for the measured Au L$_3$-edge and fitting model using combined Au-C and Au-Cl paths during step (iv) C$_2$H$_2$/Ar of catalyst treatment reported in figure S15.

Test conditions: 90 mg catalyst, 23.5 mL min^{-1} C$_2$H$_2$, 23.7 mL min^{-1} HCl and 2.7 mL min^{-1} Ar, 200 °C.

References

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2. a) 18. S.E. Shadle, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.,* 1995, **117**, 2259- 2212. b) T. Glaser, B. Hedman, K. O. Hodgson and E. I. Solomon, *Acc. Chem. Res.,* 2000, **33**, 859-868.

3. M. Newville, *Rev. Mineral. Geochem*. 2014, **78**, 33–74.

4. B. Ravel and M. Newville, *J. Synchrotron Radiat.,* 2005, **12**, 537–541.