# Supplementary Material (ESI) for Chemical Communications


# Electronic Supporting information (ESI)

## *Direct observation of extremely low temperature catalytic dehydrochlorination of 1,1,1-trichloroethane over platinum*

Adam F. Lee,* Paul A. Carr and Karen Wilson

Department of Chemistry,
University of York,
Heslington,
York,
YO10 5DD, UK
*afl2@york.ac.uk*

**Fast XPS experimental protocol**:
All XP measurements were performed at the SuperESCA beamline of the ELETTRA synchrotron radiation source using a Pt{111} single-crystal catalyst prepared by standard procedures and maintained under ultra high vacuum (~$1x10^{-10}$ Torr). A saturated monolayer of 1,1,1-TCA was obtained from a 3 Langmuir exposure (1 L = $1x10^{-6}$ Torr s). Fast XP spectra were acquired by application of a linear heating ramp (~0.4 K $s^{-1}$) to the exposed sample. 1,1,1-trichloroethane (Aldrich 99%)was purified by repeated freeze-pump-thaw cycles prior to use and dosed by backfilling the vacuum chamber. C 1s and Cl 2p XP spectra were acquired at a photon energy of 400 eV. The limiting spectral resolution was ~150 meV. Individual spectra were acquired approximately every 30 s during Fast XP measurements and Shirley background-subtracted over the entire elemental region. Temperature-programmed reaction spectra were acquired in a separate ultra-high vacuum system using a VG 300 amu quadrupole mass spectrometer with a heating rate of ~12 $Ks^{-1}$. RAIRS spectra (512 scans averaged) were acquired using a Mattson RS10000 FTIR spectrometer with an MCT detector at 1 $cm^{-1}$ resolution.

**Fast XPS fitting protocol**:
A common lineshape derived from graphitic carbon was adopted for all C 1s components, based on a Duniach-Sunjic profile convoluted with a Gaussian/Lorentzian (4:1) mix, with a FWHM = 0.5 eV and asymmetry index = 0.0618. A similar lineshape gave good fits and was employed for all Cl components but with a respective FWHM 0.74 eV. Fitting was performed using CASAXPS Version 2.0.35 using the minimum number of peaks required to minimise the R-factor.

**Low energy electron diffraction**
No LEED patterns were observed during the reaction of 1,1,1-TCA over Pt{111} at any temperature consistent with a disordered surface.

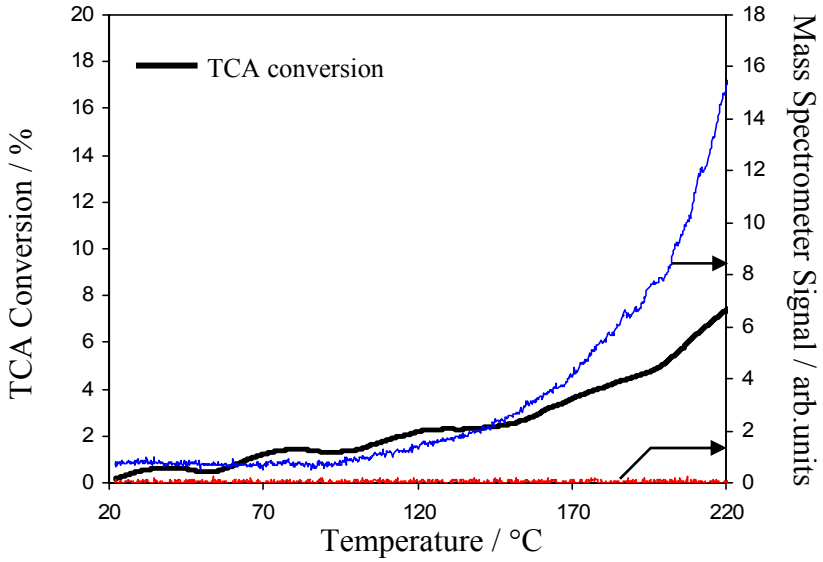
# Supplementary Material (ESI) for Chemical Communications


**Catalyst preparation**

A 9wt% $Pt/Al_2O_3$ catalyst was prepared by wet impregnation using 1 $cm^3$ of (NH4)4PtCl2 (Johnson Matthey, 55.24 wt% Pt assay) as an aqueous solution per gram of $\gamma$-$Al_2O_3$ support (Degussa Aluminium Oxide C, 140 $m^2g^{-1}$). The resultant paste was air-dried at 80°C for 12 h and then calcined in flowing $O_2$ at 500°C for 2 h. Catalysts were then reduced in flowing $H_2$ at 400°C for 2 h. Pt loading was using a Perkin-Elmer P40 emission ICP-MS instrument. Prior to testing the catalyst was pre-reduced at 573 K for 2 h under a 10 vol % $H_2$/He stream (20 $mlmin^{-1}$) and cooled to room temperature under He.

**Microreactor screening**

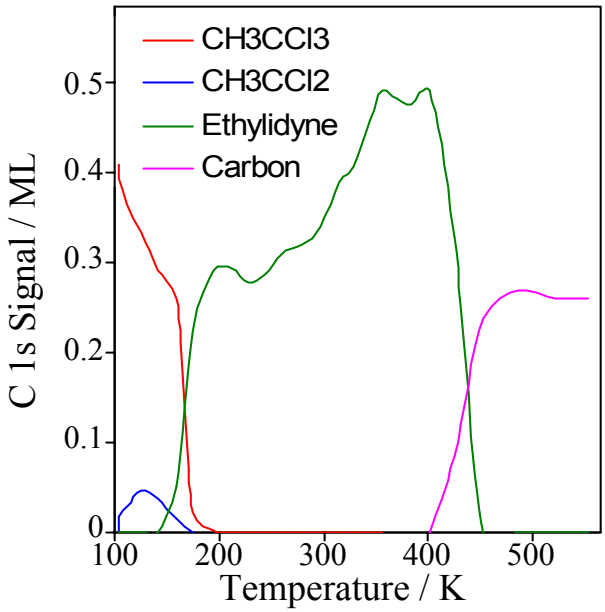
Catalyst testing was performed in a fixed-bed quartz reactor using 160 mg catalyst. The total gas flow rate was 50 $cm^3$ $min^{-1}$). TCA was introduced into a He flow using a syringe pump, equating to 6 vol% TCA. The effect of added hydrogen was also explored for $H_2$:TCA ratios between 1 and 17. Light-off measurements were performed with a ramp rate of 5°C$min^{-1}$ with the catalyst bed temperature measured with a coaxial thermocouple. Reaction was monitored on-line using an MKS Mini-Lab 300 amu quadrupole mass spectrometer. The sole reaction products were HCl and $C_2H_6$. Blank runs showed negligible gas-phase contributions below 500°C. The systematic error in conversion between repeat runs was ±2%.



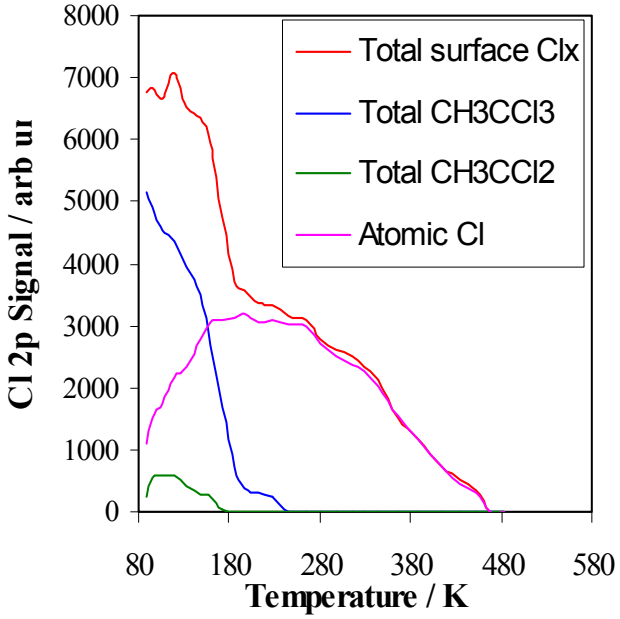

TCA light-off performance over 9 wt% $Pt/Al_2O_3$. $H_2$:TCA = 1:1, balance He; GHSV=15000$h^{-1}$; 1 bar.

# Supplementary Material (ESI) for Chemical Communications


**XPS fits**



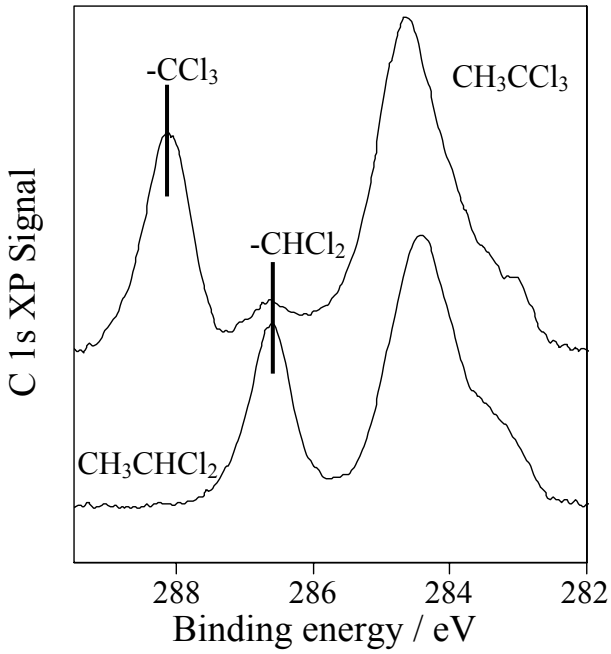

C 1s peak fitted intensities for 1,1,1-TCA adsorbed on Pt{111} at 95 K (Figure 1).




Cl 2p fitted intensities for 1,1,1-TCA adsorbed on Pt{111} at 95 K (Figure 3).

# Supplementary Material (ESI) for Chemical Communications


**1,1-Dichloroethane reference spectrum**

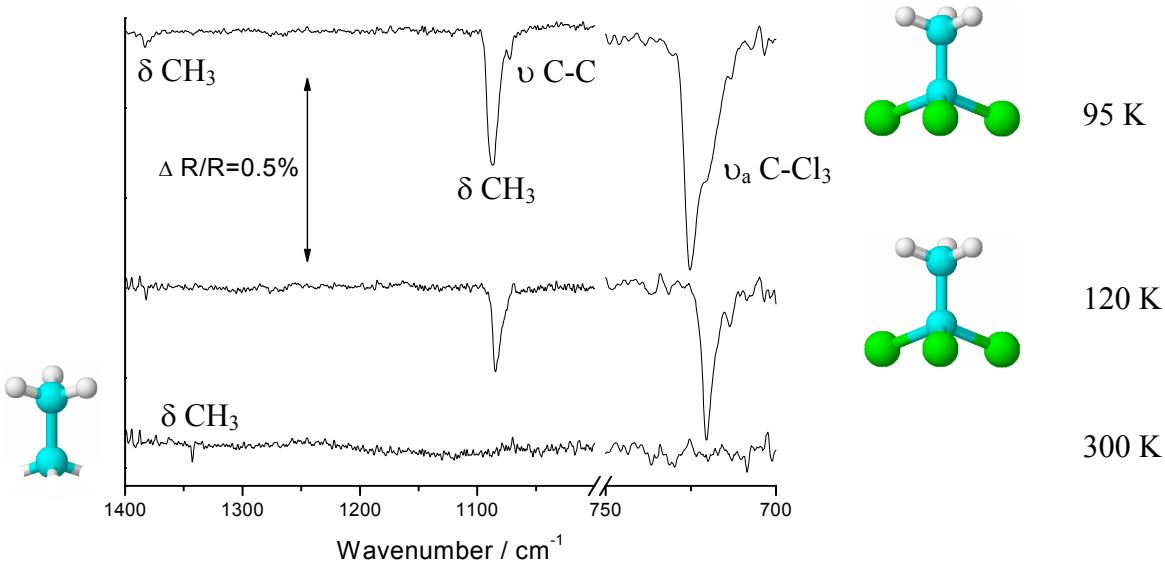



Comparative C 1s spectra of molecularly adsorbed 1,1,1-TCA and 1,1-DCA on Pt{111} at 95 K.

# Supplementary Material (ESI) for Chemical Communications

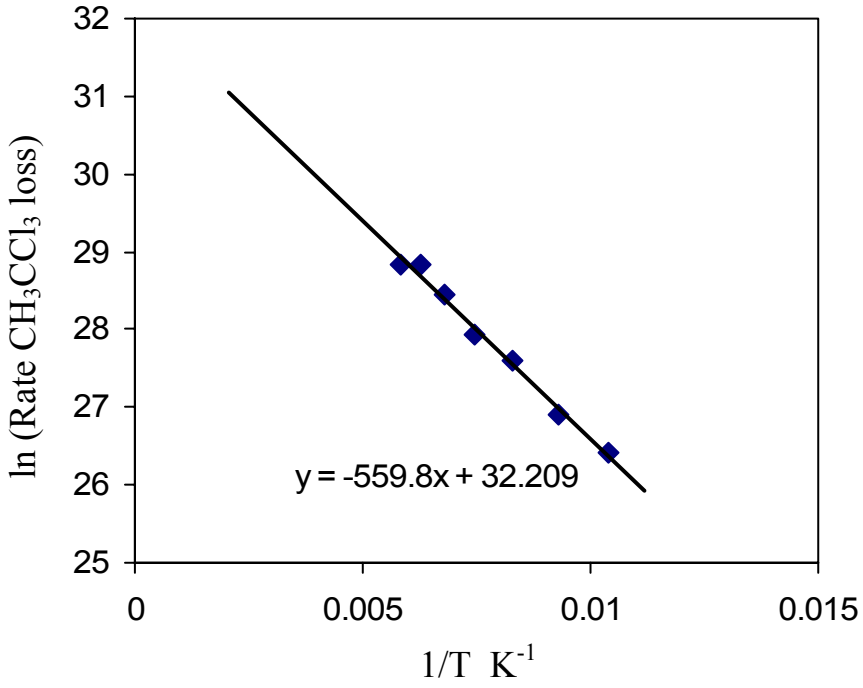

**Surface vibrational spectroscopy**

RAIRS spectra of an annealed 1,1,1-TCA adlayer.



# Supplementary Material (ESI) for Chemical Communications


**1,1,1-TCA reaction kinetics**




First-order kinetic analysis of leading edge data for the dechlorination of 1,1,1-TCA to $CH_3CCl_2$ derived from Figure 1.