Electronic Supporting information (ESI)

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

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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.
Catalyst preparation
A 9wt% Pt/Al2O3 catalyst was prepared by wet impregnation using 1 cm³ of (NH4)4PtCl2 (Johnson Matthey, 55.24 wt% Pt assay) as an aqueous solution per gram of γ-Al2O3 support (Degussa Aluminium Oxide C, 140 m²g⁻¹). The resultant paste was air-dried at 80°C for 12 h and then calcined in flowing O2 at 500°C for 2 h. Catalysts were then reduced in flowing H2 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 % H2/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 cm³ 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 H2:TCA ratios between 1 and 17. Light-off measurements were performed with a ramp rate of 5°Cmin⁻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 C2H6. Blank runs showed negligible gas-phase contributions below 500°C. The systematic error in conversion between repeat runs was ±2%.

![](image)

TCA light-off performance over 9 wt% Pt/Al2O3. H2:TCA = 1:1, balance He; GHSV=15000h⁻¹; 1 bar.
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).
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.
Surface vibrational spectroscopy
RAIRS spectra of an annealed 1,1,1-TCA adlayer.
1,1,1-TCA reaction kinetics

First-order kinetic analysis of leading edge data for the dechlorination of 1,1,1-TCA to CH₃CCl₂ derived from Figure 1.