Direct Observation of Extremely Low Temperature Catalytic Dehydrochlorination of 1,1,1-Trichloroethane over Platinum

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Fast X-ray photoelectron spectroscopy reveals that the efficient catalytic destruction of 1,1,1-trichloroethane occurs over Pt{111} surfaces at temperatures as low as 150 K. Decomposition occurs via rapid, sequential C−Cl bond scission to form an alkylidyne surface intermediate that in turn dehydrogenates above room temperature. Atomic chlorine liberated during dehydrochlorination undergoes efficient reaction with surface hydrogen, resulting in the evolution of gaseous HCl and small amounts of ethane, presumably via ethylidyne hydrogenation. Irreversible dehydrogenation of residual hydrocarbon fragments results in significant surface coking above 500 K.

Introduction

The production, consumption, and disposal of compounds that deplete ozone in the stratosphere−notably chlorofluorocarbons (CFCs), halons, carbon tetrachloride, and 1,1,1-trichloroethane (TCA or methyl chloroform)−is tightly regulated under the 1987 Montreal Protocol.[1] As recently as 2000, TCA was widely employed as an industrial solvent; however, it readily evaporates into the air,[2] where it typically persists for 2−12 years.[3] Its low rate of tropospheric decomposition results in ∼10−15% of releases diffusing into the stratosphere,[4] wherein TCA both damages the ozone layer and contributes to global warming. TCA is also classified as a significant nonmethane volatile organic compound (VOC). Specifically, the 1990 London amendment[1] that TCA be completely phased out from member states by 2005 has stimulated intense research into alternative routes to its efficient destuction over current thermal incineration and catalytic oxidation treatments. The hydrodechlorination of TCA has recently been reported at high temperatures (150−350 °C) and pressures (≤50 bar) over supported transition-metal catalysts.[5] A number of issues relating to the active site for dechlorination, requirements for both metal and acidic support functions, and catalyst deactivation have arisen. There is thus an urgent need to develop a detailed mechanistic understanding of the reactivity of TCA over Pt surfaces.

The interaction of TCA over Pt{111} is also interesting from a surface science perspective. Halocarbons exhibit a rich chemistry over many transition metal surfaces,[6] notably copper and silver, wherein iodo- and bromocarbons readily undergo low temperature thermal activation. In contrast, the greater C−Cl bond strength means that the thermal chemistry of less activated chlorocarbons, especially chloroalkanes, is not as extensive. The thermal degradation of chloroethanes/ethenes and chloropropanes have been reported over Cu{100},[7,8] and that of chloroethenes over Cu{110},[9] Pd{110},[10] and Pd{111}.[11] However, although copper surfaces are effective for low-temperature C−Cl dissociation, they have little relevance to catalytic dechlorination processes because copper binds the liberated chlorine too strongly to regenerate active sites and complete the catalytic cycle.[7,8] Indeed, alloying with platinum[12] (or palladium[13]) is

necessary to generate practical group IB dehalogenation catalysts. Furthermore, although a few studies have explored the influence of halogen substitution on the surface reactivity,[8] surprisingly the only investigation of complex (>C_1) 1,1,1-substituted haloalkanes to date is that of chlorofluorocarbons on Pd{111}.[14]

Thermal dissociation of C−Cl bonds over Pt{111} has also proved rather contentious. Jo and co-workers[15] report that chloroethane desorbs molecularly upon heating whereas Freyer et al. suggest it undergoes C−Cl cleavage.[16] Similarly, dehalogenation of *cis*-1,2- and *trans*-1,2-dichloroethene (DCE) has been reported above 200 K on Pt{111},[17] although a more recent synchrotron study by Cassuto et al. found both DCE and 1,1,2-trichloroethene (TCE) simply desorbed without any reaction.[18] A HREELS study of 1,1,2-trichloroethane, the closest chlorocarbon analogue to TCA, only observed photodecomposition over Pt{111}.[19]

In this work we have applied fast XPS to obtain quantitative measurements on the surface chemistry of TCA in real time. This technique allows the direct determination of surface reaction pathways and associated kinetic parameters for both molecular and atomic surface species,[20] and our findings have been correlated with corresponding RAIRS and TPD measurements.

Here we report the efficacy of a Pt{111} model catalyst for the direct, low-temperature catalytic dehydrochlorination of TCA and identify possible deactivation processes.

Experimental Section

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 ultrahigh vacuum (∼1 × 10^{-10} Torr). A saturated monolayer of TCA was obtained from a 3 Langmuir exposure (1 langmuir = 1 × 10^{-6} Torr s). Fast XP spectra were acquired by application of a linear heating ramp (∼0.4 K s^{-1}) to the exposed sample. TCA (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
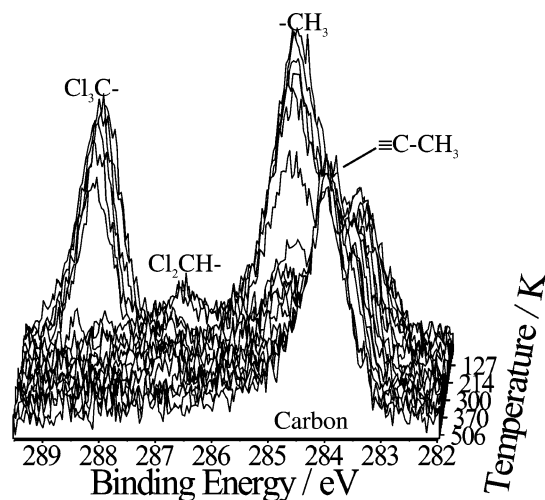

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Figure 1. Temperature-programmed C 1s fast XP spectra of a reacting TCA layer adsorbed at 95 K over a Pt{111} catalyst surface.
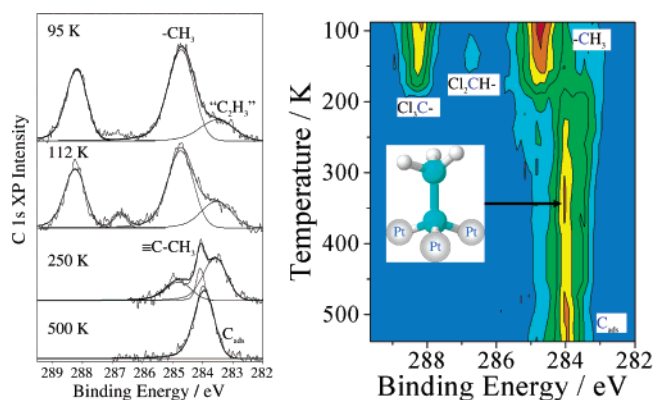

Figure 2. (Left) deconvoluted C 1s XP spectra and (right) C 1s fast XP image map of a reacting TCA layer adsorbed at 95 K over a Pt{111} catalyst surface.

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. A common line shape derived from graphitic carbon was adopted for all C 1s components, on the basis of a Duniach-Sunjic profile convoluted with a Gaussian/Lorentzian (4:1) mix, with a fwhm = 0.5 eV and asymmetry index = 0.062. A similar line shape gave good fits and was employed for all Cl components but with a respective fwhm = 0.74 eV and asymmetry factor = 0.051. Fitting was performed using CASAXPS Version 2.0.35 using the minimum number of peaks required to minimize the R factor. Coverages are defined in terms of monolayers (adsorbates/surface Pt atom) with 1 monolayer (ML) = 1.5×10^{15} atoms cm^{-2}. Temperature-programmed reaction spectra were acquired in a separate ultrahigh vacuum system using a VG 300 amu quadrupole mass spectrometer with a heating rate of ~12 K s^{-1}; spectra are uncorrected for ionization cross-section. Temperatures were measured from a thermocouple spot-welded to the edge of the Pt{111} sample.

Results and Discussion

The thermal chemistry of TCA was investigated over a Pt{111} catalyst surface by fast XPS (Figure 1). At 95 K the adsorbed molecule exhibits two well-resolved C 1s peaks at 284.6 and 288.1 eV corresponding to the respective $-CH_3$ and $-CCl_3$ chemical functions. RAIRS vibrational spectra of TCA (see supplementary information) showed C$-$H modes characteristic of the free molecule,[21] with the symmetric $-CH_3$ deformation occurring ~1380 cm^{-1}, indicating the methyl group is oriented away from the platinum surface. The corresponding C$-$Cl asymmetric stretches (around 725 cm^{-1}) were shifted to lower frequency within the monolayer relative to TCA multilayers, evincing a direct Pt$-$Cl interaction. Comparison of the ν_s(C$-$H) and ν_a(C$-$H) vibrations yields a C$-$C tilt angle of ≤20° to the surface normal, consistent with an almost vertical TCA molecule, bound to the Pt surface via all three Cl atoms. 1,1-Diiodoethane adopts a similar mode over Pt{111}.[22] This adsorption geometry allows a high coverage of 0.4 monolayers of TCA on the catalyst surface. Chemisorbed TCA is stable over platinum up to 130 K, above which it undergoes rapid reaction evidenced by the dramatic changes in the C 1s spectra in Figure. 1. Loss of the CCl$_3$ (288.1 eV) component occurs between 130 and 180 K as a result of efficient cleavage of all three C$-$Cl bonds. Transient formation of a weak state at 286.7

eV, matching that of $-CHCl_2$ observed in 1,1-dichloroethane,[S] suggests dechlorination occurs via stepwise scission of each C$-$Cl bond. No LEED patterns were observed during the reaction of TCA over Pt{111} at any temperature, indicating the resultant atomic chlorine remained randomly distributed over the Pt{111} catalyst surface.

Dechlorination is accompanied by significant changes in the CH$_x$ region, which result in the formation of a stable ethylidyne surface intermediate Pt$_3\equiv$C$-$CH$_3$ at 300 K, with a characteristic binding energy of 284 eV.[23] Zaera and co-workers have previously reported ethylidyne formation during the thermal decomposition of 1,1-diiodoethane over Pt{111}.[22] This extremely low-temperature reaction and the resultant intermediates are highlighted in the associated deconvoluted C 1s spectra and 3D image map shown in Figure 2. RAIRS confirmed the fingerprint symmetric CH$_3$ deformation (1340 cm^{-1}) and C$-$C stretching modes (~1115 cm^{-1}) of ethylidyne[22,24] were present at room temperature and thus retention of the C$_2$ backbone. Kinetic parameters extracted from these spectra (see Supporting Information) yield a surface activation barrier for breaking the first C$-$Cl bond of only 5 ± 1 kJ mol^{-1} and high preexponential factor of $8 \times 10^{13} \pm 0.5$ s^{-1}.

Reaction temperatures >350 K induce the catalytic dehydrogenation of ethylidyne, accompanied by C$-$C bond cleavage to form a variety of strongly adsorbed CH$_x$ moieties. Further dehydrogenation above 500 K results in substantial coking of the platinum surface, with ~0.3 monolayers of carbon deposited during the complete decomposition of TCA.

The fate of liberated surface-bound chlorine atoms is also pivotal in the development of an efficient, robust platinum catalyst for TCA destruction. Strong chlorine adsorption, as occurs over copper surfaces,[7,8] could inhibit the subsequent reaction of further TCA causing rapid deactivation. Our Cl 2p fast XP spectra in Figure 3 show that molecularly adsorbed TCA is characterized by a single chemical environment with a chlorine 2p$_{3/2}$ component at 199.8 eV (spin$-$orbit splitting = 1.56 eV), corresponding to $-CCl_3$. This state diminishes upon heating above 130 K, concomitant with the appearance of a new low binding energy feature at 197.8 eV associated with atomic chlorine.[25] These liberated Cl adatoms are completely removed from the surface of the platinum catalyst at reaction temperatures above 450 K. This results from the extremely efficient reaction between surface H and Cl adatoms above 350 K to form HCl. This reactively formed HCl immediately desorbs into the gas phase.[26]

HCl release is also accompanied by the desorption of a smaller amount of reactively formed ethane at 400 K (Figure

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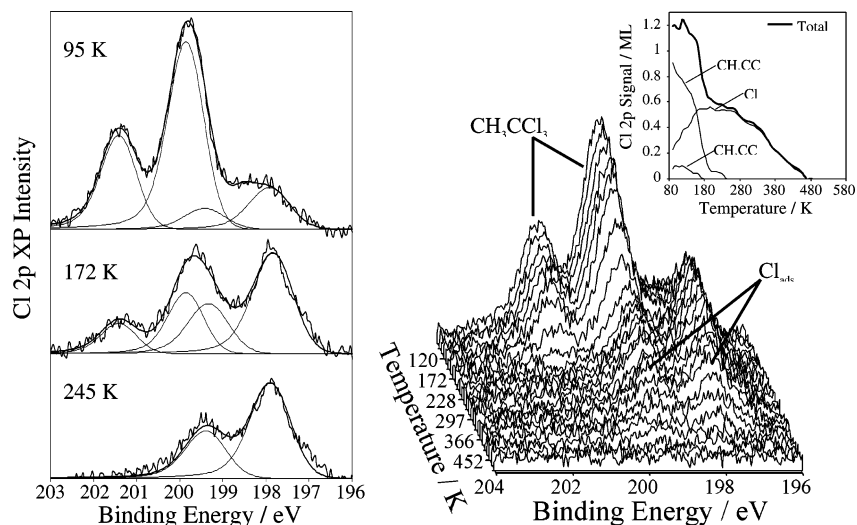*J. Phys. Chem. B, Vol. 108, No. 39, 2004* **14813**

Figure 3. (Left) deconvoluted Cl 2p XP spectra and (right) temperature-programmed Cl 2p Fast XP spectra of a reacting TCA layer adsorbed at 95 K over a Pt{111} catalyst. Inset shows integrated Cl 2p peak intensities.
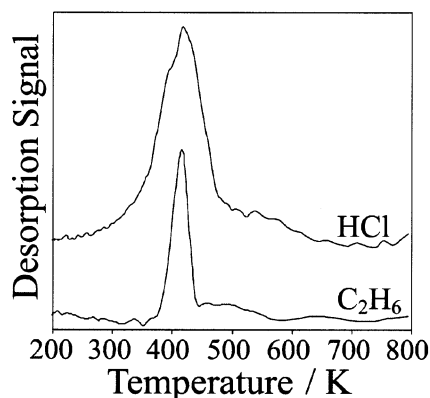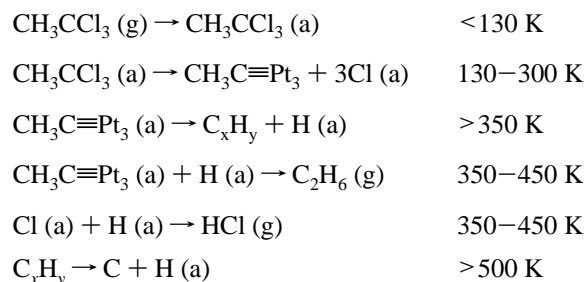

Figure 4. Temperature-programmed desorption spectra from the dehydrochlorination of 3 L TCA adsorbed at 95 K over Pt{111} catalyst surface.

4). Progressive breakdown of the ethylidyne surface intermediate formed from TCA clearly releases surface hydrogen. This reacts with either neighboring Cl or ethylidyne surface species, giving rise to the two principal products. The absence of significant molecular hydrogen desorption is consistent with the initial 1:1 H:Cl stoichiometry in TCA; hydrogen adatom recombination does not compete effectively with clean off of the chlorine already present on the surface. TCA dehydrochlorination is complete by 450 K with atomic carbon the sole surface residue. The C 1s spectrum at this temperature is much broader than that for graphitic carbon, suggesting a carbidic overlayer. The overall reaction mechanism is summarized below:

$$CH_3CCl_3 \text{ (g)} \rightarrow CH_3CCl_3 \text{ (a)} \qquad <130 \text{ K}$$

$$CH_3CCl_3 \text{ (a)} \rightarrow CH_3C\equiv Pt_3 + 3Cl \text{ (a)} \qquad 130-300 \text{ K}$$

$$CH_3C\equiv Pt_3 \text{ (a)} \rightarrow C_xH_y + H \text{ (a)} \qquad >350 \text{ K}$$

$$CH_3C\equiv Pt_3 \text{ (a)} + H \text{ (a)} \rightarrow C_2H_6 \text{ (g)} \qquad 350-450 \text{ K}$$

$$Cl \text{ (a)} + H \text{ (a)} \rightarrow HCl \text{ (g)} \qquad 350-450 \text{ K}$$

$$C_xH_y \rightarrow C + H \text{ (a)} \qquad >500 \text{ K}$$

In summary we have shown that platinum catalysts exposing {111} facets exhibit exceptional activity for the low-temperature dehydrochlorination of TCA. The reaction initiates above 130

K via rapid sequential C–Cl bond scission to form a surface alkylidyne intermediate. Partial dehydrogenation of ethylidyne occurs between 300 and 400 K, which helps remove chlorine and hydrocarbon species from the catalyst surface as reactively formed HCl and C_2H_6. Higher reaction temperatures result in complete, irreversible dehydrogenation of ethylidyne and extensive surface coking. The optimum reaction temperature to facilitate product desorption, while avoiding coking, appears to be ~350–400 K. The introduction of co-fed H_2 should facilitate HCl and ethane production, prolonging catalyst lifetime; we are currently investigating such a hydrodechlorination process.

Supporting Information Available: The fast XP integrated C 1s intensities during TCA dechlorination, along with kinetic analysis of the first C–Cl dissociation step (derived from Figure 1) are available. Reference C 1s XP spectra for 1,1-dichloroethane and ethylidyne, together with RAIR spectra of a TCA multilayer (~10 L at 95 K), low-temperature monolayer (~120 K), and 300 K annealed TCA monolayer are also available. This material is available free of charge via the Internet at http:// pubs.acs.org.

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