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Low temperature 1,1,1-trichloroethane dehydrochlorination over Pt catalysts: from model surfaces to the real world†

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Fast X-ray photoelectron spectroscopy reveals efficient C–Cl activation of 1,1,1-trichloroethane occurs over platinum surfaces at 150 K, and in the presence of hydrogen, sustained ambient temperature dehydrochlorination to HCl and ethane is possible over supported Pt/Al$_2$O$_3$ catalysts.

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)—is tightly regulated under the 1987 Montreal Protocol.[1] As recently as 2000, 1,1,1-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 non-methane 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 destruction over current thermal incineration and catalytic oxidation treatments. The hydrodechlorination of TCA has recently been reported at high temperatures (150–350 °C) and pressures ($\leqslant$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. Here we report the efficacy of platinum catalysts for the direct, low temperature dehydrochlorination of TCA and identify the reaction pathway and deactivation processes.

The thermal chemistry of TCA was investigated over a Pt{111} catalyst surface by fast XPS (Fig. 1).[6] At 95 K the adsorbed molecule exhibits two well-resolved C states at 284.6 eV and 288.1 eV corresponding to the respective –CH$_3$ and –CCl$_3$ chemical functions. Surface vibrational spectroscopy shows TCA initially adopts a vertical adsorption geometry, bound to Pt *via* the three Cl atoms;† the –CH$_3$ symmetric deformation ~1380 cm^{-1} indicates the methyl group orients away from the surface, while the C–Cl asymmetric stretches ~725 cm^{-1} shift relative to TCA multilayers, evincing a direct Pt–Cl interaction. 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 temperature it undergoes rapid reaction evidenced by the dramatic changes in the C 1s spectra in Fig. 1. Loss of the CCl$_3$ (288.1 eV) component occurs between 130–180 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,† suggests dechlorination occurs *via* stepwise scission of each C–Cl bond. The resulting atomic chlorine remains randomly distributed over the Pt{111} catalyst surface up to room temperature (Fig. 2). Dechlorination is accompanied by significant changes in the CH$_x$ region which result in the formation of a stable ethylidyne–surface intermediate Pt$_3$≡C–CH$_3$ (284 eV) at 300 K.[7] Vibrational spectroscopy confirms retention of the C$_2$-backbone.†

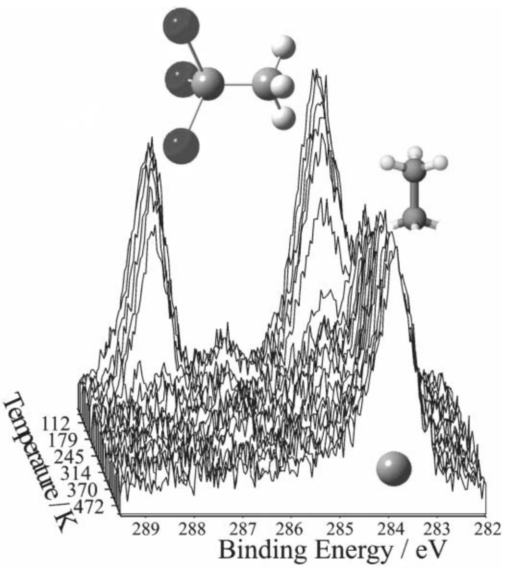

Fig. 1 Temperature-programmed C 1s fast XP spectra of a reacting TCA adlayer over Pt{111}.

Kinetic parameters extracted from these spectra yield a surface activation barrier for breaking the first C–Cl bond of only 5 ± 1 kJ mol^{-1} and high pre-exponential factor of 8 × 10$^{13\pm0.5}$ s^{-1}.†

Higher 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

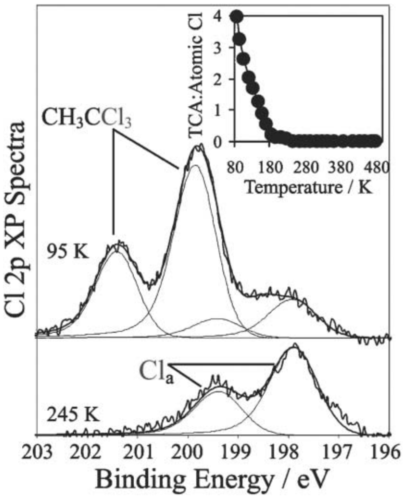

Fig. 2 Temperature-programmed Cl 2p fast XP spectra of a reacting TCA adlayer over Pt{111}. Inset shows switchover to Cl (a).

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† Electronic supplementary information (ESI) available: details of fast XPS experimental and fitting protocols, catalyst preparation and microreactor screening. See http://www.rsc.org/suppdata/cc/b4/b408745c/

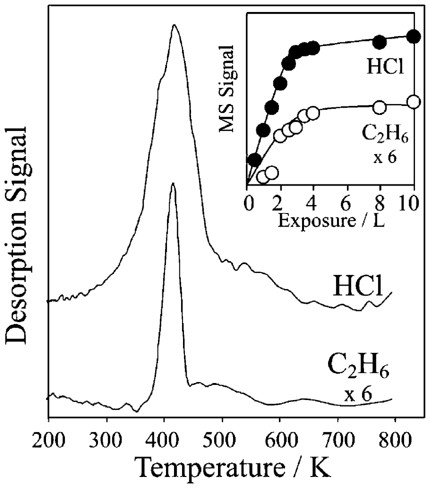

Fig. 3 Temperature-programmed desorption spectra from the dehydrochlorination of TCA over Pt{111}. Inset shows product yields.

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 could inhibit the subsequent reaction of further TCA causing rapid deactivation. Our fast XPS shows that Cl adatoms released above 130 K are completely removed from the surface of the platinum single crystal surface 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 (Fig. 3).[8]

HCl release is also accompanied by the desorption of a smaller amount of reactively-formed ethane above 400 K. Progressive breakdown of the ethylidyne surface intermediate formed from TCA clearly releases surface hydrogen. This reacts with either neighbouring Cl or ethylidyne surface species giving rise to the two products. TCA dehydrochlorination is complete by 450 K with atomic carbon the sole surface residue. The reaction mechanism is summarised below:

$$CH_3CCl_3\ (g) \rightarrow CH_3CCl_3\ (a) < 130\ K$$

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

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

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

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

$$C_xH_y \rightarrow C + H\ (a) > 500\ K$$

Although efficient TCA dehydrochlorination occurs in a *single pass* over a model surface, does the accumulation of adsorbed Cl and/or hydrocarbons block the catalytic cycle and inhibit continuous steady state operation? Is there any evidence that the above mechanism, determined under vacuum conditions, is actually pertinent to practical dispersed Pt catalysts?

These questions were addressed by conducting TCA light-off measurements over a conventionally prepared, high area Pt/Al_2O_3 catalyst (Fig. 4). This catalyst contains Pt particles exposing predominantly {111} facets. In the absence of significant co-fed hydrogen 1,1,1-TCA conversion was extremely poor, and the sole reaction product was HCl.† Introduction of excess H_2 dramatically enhanced TCA dehydrochlorination (>99%), and also resulted in the appearance of reactively-formed C_2H_6. These observations demonstrate that $H_a + Cl_a$ can occur rapidly over Pt/Al_2O_3. However ethylidyne hydrogenation to ethane cannot compete effectively with chlorine where limited surface H_2 is available, and in accord with our model prediction, cokes the catalyst surface. Excess H_2 prevents this coking, permitting rapid, sustained dehydrochlorination above 400 K, precisely the temperature at which C_2H_6 and HCl are desorbed from Pt{111} in Fig. 3.

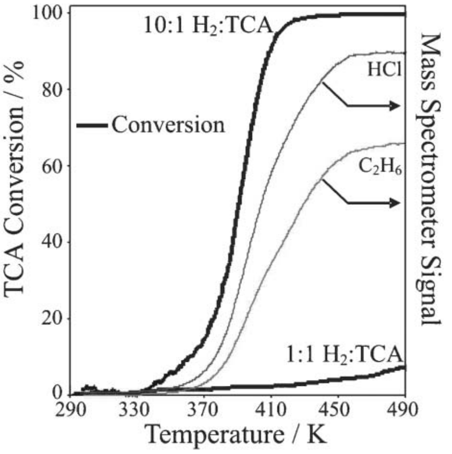

Fig. 4 TCA light-off performance over 9 wt% Pt/Al_2O_3. Catalyst charge = 150 mg; TCA = 6 vol%, balance He; GHSV = 15 000 h^{-1}; 1 bar.

In summary we have shown that platinum {111} facets exhibit high activity for low temperature TCA dehydrochlorination. The reaction initiates above 130 K *via* rapid sequential C–Cl bond scission to form a surface ethylidyne. Partial dehydrogenation of ethylidyne occurs between 300 and 400 K, which helps remove chlorine and (limited) hydrocarbon species from the catalyst surface as reactively formed HCl and C_2H_6. In the absence of additional H_2, higher reaction temperatures result in irreversible dehydrogenation of ethylidyne and extensive surface coking. The rate-limiting step during steady-state operation is C_2H_3 hydrogenation to ethane.

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