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HREELS investigations of *trans*-dichloroethene adsorption and chemical reaction on Cu(110)

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The chemisorption and reaction of *trans*-dichloroethene on Cu(110) have been investigated by high-resolution electron-energy-loss spectroscopy (HREELS) as a function of coverage and temperature. At 135 K, both physisorbed and chemisorbed *trans*-dichloroethene are present. Heating to 200 K leads to the formation of acetylene and of a partially dehalogenated intermediate species. By 300 K, the acetylene trimerises to form adsorbed benzene at the surface. Adsorption of *trans*-dichloroethene at 300 K produces benzene directly. Evidence of C–Cl cleavage at temperature as low as 220 K is clearly marked by the emergence of very intense Cu–Cl stretching vibrations which remain even after further heating up to 570 K.

Keywords: HREELS, chemisorption, *trans*-1,2-dichloroethene, DCE, Cu(110)

1. Introduction

The adsorption and chemical reaction study of chlorinated compounds with metallic surfaces is important as a starting point for understanding the hydrodechlorination process and for further defining efficient hydrodechlorination catalysts. Dichloroethene represents a good model system for unsaturated chlorinated compounds but, to date, few surface studies have been published on this adsorbate; these are summarised below.

Near-edge X-ray absorption fine-structure spectroscopy (NEXAFS) and ultra-violet photoemission spectroscopy (UPS) studies by Cassuto et al. [1] show that both multilayer and monolayer adsorption of a series of unsaturated chlorinated molecules (tetrachloroethene, trichloroethene, *iso*-, *cis*- and *trans*-dichloroethene) on Pt(111) and Pt(110) (1 × 2) occurs nondissociatively at 95 K, with the molecules only weakly bonded to the surface in the monolayer range at this temperature. Grassian and Pimentel [2] have reported high-resolution electron-energy-loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS) data on the adsorption and reaction of *cis*- and *trans*-dichloroethene on Pt(111) between 110 and 300 K. This work shows that multilayers formed at 110 K are physisorbed and can be desorbed by warming to about 160 K. In the monolayer and submonolayer range, they conclude that both *cis*- and *trans*-dichloroethene form sigma bonds to the platinum surface with the carbon atoms adopting an sp^3 hybridised structure and the chlorine atoms taking up staggered gauche or trans positions, depending upon whether *cis*- or *trans*-$C_2H_2Cl_2$ was adsorbed. Upon warming above 170 K, partial desorption of the chemisorbed species occurs while dechlorination is initiated at around 200 K leaving acetylene bonded to the surface. Further heating to >400 K is accompanied by further decomposition, with the desorption of chlorine as HCl occurring at about 460 K, leaving carbon residues at the surface. Interestingly, significant photochemical reactivity behaviour of *cis*- and *trans*-$C_2H_2Cl_2$ adsorbed on Pd(111) and Pt(111) has also been observed [3] with dehalogenation under photolysis conditions occurring even at temperatures as low as 120 K. In a recent paper, Yang et al. [4] conclude, from measurements of chloroethene molecules adsorbed on Cu(100) by TDS, NEXAFS and work function change measurements, that no chlorine is present in the hydrocarbon reaction products liberated from the surface and that the degree of thermal dissociation increases with the extent of halogenation. Furthermore, *trans*-dichloroethene was found to produce acetylene and a small amount of benzene, while dissociation of trichloroethene generated acetylene and a carbon residue.

Recently, Laroze et al. [5] have studied the adsorption, reaction and desorption of *trans*-1,2-dichloroethene on a Cu(110) single crystal using RAIRS, TPD and molecular beam experiments. At low temperature, molecular adsorption occurs followed by decomposition at higher temperatures, resulting in the formation of acetylene at the surface. Near room temperature, trimerisation of C_2H_2 occurs to form benzene which is evolved into the gas phase at $\sim$350 K. No desorption of chlorine as Cl_2 or HCl was observed.

In the present study, HREELS investigations have been used to gain further insight into the bonding behaviour and surface reactions of *trans*-dichloroethene on the Cu(110) surface. In particular, the ability of HREELS to probe low-frequency vibrations has been exploited to monitor low-frequency metal–molecule and metal–Cl vibrations, thus obtaining more direct information on metal–adsorbate bonding and the onset of dechlorination processes.

2. Experimental

The HREELS experiments were carried out in an ultrahigh vacuum chamber manufactured by Kurt J. Lesker Co. and equipped with an LK Technologies ELS3000 spectrometer (consisting of a rotating cylindrical double-pass monochromator and a double-pass analyser) and a four-grid LEED optics. The base pressure of the system is 2×10^{-10} Torr. The HREELS chamber is attached to a preparation chamber with a base pressure of $\sim 5 \times 10^{-10}$ Torr, which allowed sample cleaning and heating, as well as XPS studies to be carried out.

The Cu(110) sample (Metal Research Ltd., aligned at $\pm 0.5°$) was polished with decreasing granulometry diamond pastes down to 1/10 μm. After several cycles of ion sputtering (2 kV, 10^{-6} Torr Ar), annealing up to 870 K and XPS analysis, the sample was transferred from the preparation chamber into the HREELS chamber, where it could be heated to 900 K or cooled to 135 K. Crystal temperature was measured with a thermocouple (type N) fixed on the sample holder. The sample, maintained at the low temperature of 135 K, was then exposed to dichloroethene introduced in the chamber at a pressure of 5×10^{-8} Torr through a leak valve. After defined exposures the sample was heated to different temperatures for specific periods of time and then recooled to 135 K before carrying out the HREELS measurements. Exposures at room temperature were conducted in the preparation chamber. The sample was then transferred into the HREELS spectrometer and analysed at 300 K. HREELS experiments were carried out with the incident electron beam set at 5 eV, with an energy resolution at around 4 meV. Both the incidence and scattering angles were 60° from the surface normal.

The liquid *trans*-dichloroethene (99%) was purchased from Sigma–Aldrich. It was outgassed several times through a series of freezing–thawing cycles before introduction into the vacuum chamber. Exposures are expressed in langmuirs ($1\ \mathrm{L} = 10^{-6}$ Torr $\times$ 1 s) where pressures were as indicated on the Bayard–Alpert gauge, i.e., not corrected for gas sensitivity.

3. Results and discussion

The HREELS spectrum obtained after a 10 L adsorption of *trans*-$C_2H_2Cl_2$ on Cu(110) at 135 K is displayed in figure 1(a). For ease of identification the vibrational assignments of liquid *trans*-$C_2H_2Cl_2$ are reported in table 1 based on [6,7]. After obtaining the HREELS spectrum at 135 K (figure 1(a)), the sample was heated for 2 min at 170 K (figure 1(b)) and 220 K (figure 1(c)) and the HREELS spectrum obtained after recooling to 135 K. The spectrum displayed in figure 1(d) was recorded at room temperature.

The spectra obtained at 135 K (figure 1(a)) and 170 K (figure 1(b)) display quite similar structures except for their relative intensities. The C–H stretching vibration is split into two components, at 3055 and 2920 cm^{-1}. The former dominates at 135 K, while the 2920 cm^{-1} vibration appears as the more intense after heating to 170 K. We attribute the presence of two CH stretch vibrations to the presence of some multilayer condensation (3055 cm^{-1}) on top of a chemisorbed monolayer (2920 cm^{-1}). The peak at 2070 cm^{-1} is attributed to a small amount of coadsorbed CO impurity and will not be discussed further. The multilayer phase also gives rise to a very strong loss peak at 905 cm^{-1} and a less intense one at 815 cm^{-1}, assigned, respectively, to a C–H out-of-plane deformation mode and to the C–Cl asymmetric stretching vibration (table 1). As expected, the intensities of all the multilayer bands decrease upon warming (figure 1 (a) and (b)) and this can be used as a criterion for identifying the bands at 280, 425, 640, 1160, 1240 and 2920 cm^{-1} as arising from the chemisorbed first layer. It is noted that the HREELS spectrum attributed to the chemisorbed *trans*-dichloroethene on Cu(110) bears a similarity to that obtained on Pt(111) [2] but differs greatly from the gaseous or condensed phase, indicating significant chemical perturbation of the molecule upon chemisorption. Thus, the in-plane C–H deformations, contributing to the

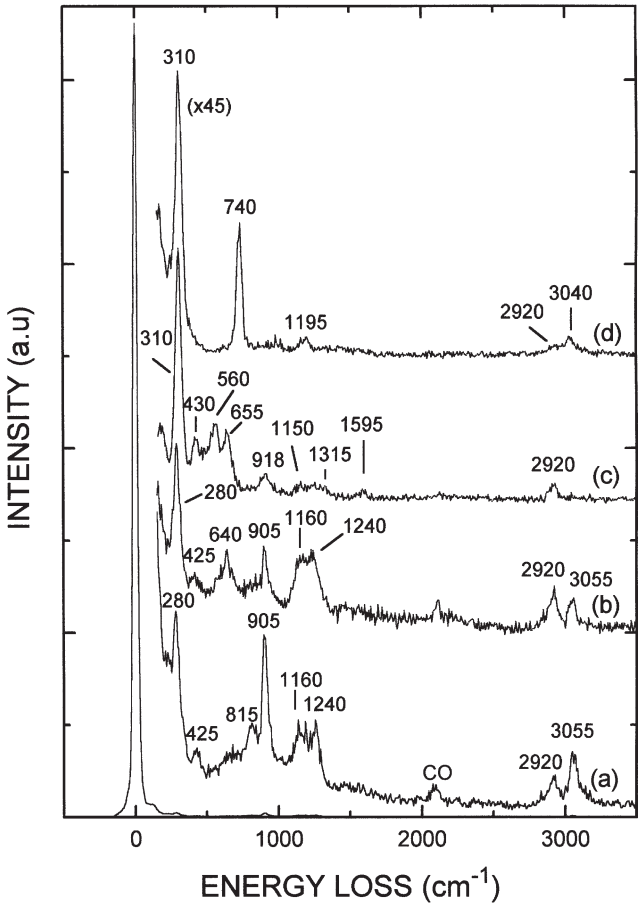

Figure 1. HREELS spectra of 10 L *trans*-$C_2H_2Cl_2$ adsorbed at 135 K on Cu(110) (a) and after successive 2 min heatings at 170 K (b) and 220 K (c). Spectra (a)–(c) have been measured at 135 K. Spectrum (d) has been measured after return to room temperature.

Table 1
Liquid IR and Raman data of *trans*-$C_2H_2Cl_2$ [6,7], as compared with HREELS data of *trans*-$C_2H_2Cl_2$ adsorbed on Cu(110) at 135 and 170 K.

Assignment in the liquid/gas phase	Normal mode description[a] in the liquid/gas phase	Vibrational frequency (cm^{-1})		
		Liquid [6,7]	Physisorbed 135 K (this work)	Chemisorbed 135–170 K (this work)
ν(Cu–C)				425
$\nu_7(A_u)$	γ_s(C–Cl) $-$ γ_s(C–H)	227 (IR)		
$\nu_{12}(B_u)$	δ_{as}(C–Cl) + δ_{as}(C–H)	250 (IR)	280	280
$\nu_5(A_g)$	δ_s(C–Cl) + δ_s(C–H)	350 (R)		
$\nu_8(B_g)$	τ(HClC=CHCl) molecular torsion	763 (R)		
$\nu_{11}(B_u)$	ν_{as}(C–Cl)	817 (IR)	815	640
$\nu_4(A_g)$	ν_s(C–Cl)	846 (R)		
$\nu_6(A_u)$	γ_s(C–H)	895 (IR)	907	
$\nu_{10}(B_u)$	δ_{as}(C–H)	1200 (IR)		1160
$\nu_3(A_g)$	δ_s(C–H)	1274 (R)		1240
$\nu_2(A_g)$	ν(C=C)	1576 (R)		
$\nu_1(A_g)$	ν_s(C–H)	3073 (R)		
$\nu_9(B_u)$	ν_{as}(C–H)	3080 (IR)	3055	2920

[a] γ: out-of-plane bend; δ: in-plane bend; ν: stretch; s – symmetric, as – asymmetric refer to in-phase and out-of-phase vibrations, respectively.

broad structure between 1160 and 1240 cm^{-1} in figure 1 (a) and (b), differ by about -35 to -40 cm^{-1} from the gas phase, while the asymmetric in-plane C–Cl + C–H deformation at 280 cm^{-1} differs by $+30$ cm^{-1} from the gas phase (table 1). The greatest frequency changes, however, are observed for the stretching vibrations. For example, the C–H stretching mode energy of the chemisorbed phase is about 160 cm^{-1} lower than its gaseous/condensed-phase counterpart (see table 1), indicating that the sp^2 bonding of carbon atoms has been modified by chemisorption to resemble an alkane-like sp^3 bonding. This view is further confirmed by the altered frequency of the asymmetric C–Cl stretching vibration which appears at 640 cm^{-1}, some 175 cm^{-1} lower than for the condensed phase, and is similar to that expected for chloroethanes [8]. Therefore, the molecular adsorption of *trans*-$C_2H_2Cl_2$ on Cu(110) can be described in terms of a di-σ-adsorbed species, akin to the types of structures formed by ethene on certain metal surfaces [9]. In this respect, it is interesting to note the influence of the Cl atoms on the bonding interaction of the molecule. For ethene on Cu(110), a weakly interacting π-adsorbed species is formed; the more strongly bonded di-σ ethene species is generally only found on the more reactive Ni, Pt and Ru surfaces [9]. This bonding description of *trans*-$C_2H_2Cl_2$ on Cu(110) also allows the band at 425 cm^{-1}, which has no obvious counterpart in the condensed phase, to be attributed to a Cu–C stretching vibration. The analogous vibration for the di-σ ethene species has been observed to occur in the range 480–400 cm^{-1} [9].

Changes are observed in the HREELS spectra after annealing to temperatures as low as 220 K (figure 1(c)). This thermal treatment results in the disappearance of the higher-frequency C–H stretching component, and a decrease in intensity of the bands between 1100 and 1300 cm^{-1}. New structures are also observed at 430, 560, 655, 918 and 1595 cm^{-1}. Of these, the bands at 430, 655, 918, 1150, 1315 and 2920 cm^{-1} bear a general similarity to the HREELS spectrum of C_2H_2 on Cu(110) [9,10] and can be explained in terms of dehalogenation of the molecule to form acetylene at the surface (table 2). Formation of C_2H_2 at such temperatures has also been demonstrated by RAIRS data [5]. The HREELS data obtained in this work provides further verification of this model by monitoring the emergence of an intense low-frequency peak at 310 cm^{-1} which, as discussed in more detail below, can unambiguously be assigned to the Cu–Cl stretching vibration of adsorbed chlorine atoms. The two main features that remain to be assigned in figure 1(c) are the bands at 560 and 1595 cm^{-1}. One possible suggestion is that at 220 K, some partially dehalogenated species such as a *HC=CHCl intermediate are also present. The 1595 cm^{-1} peak could then be due to the coupling of incident electrons with a C=C stretching mode oriented at an angle with respect to the surface plane, similar to the orientation adopted by vinylidene species at surfaces [11]. The C=C stretching vibration of such a species on Pt(100)(1 × 1) has been observed at 1589 cm^{-1}. The 560 cm^{-1} band, which has no counterpart in known acetylene spectra [9,10], may then be due to the Cu–C stretch of the *HC=CHCl entity, but little data exists on these frequencies, so the assignment remains speculative. However, it is clear that this band is associated with some intermediate species; heating to room temperature leads to the disappearance of this band along with the bands assigned to adsorbed acetylene.

Further heating to 300 K leads to significant changes in the spectrum (figure 1(d)) with a strong band appearing at 740 cm^{-1} and weaker bands at 1170 and 3035 cm^{-1}. These bands can readily be identified as arising from benzene formation [9]. A strong vibrational database exists for this adsorbate, and the peaks at 740, 1195, and 3040 cm^{-1} correspond to the C–H out-of-plane bending, the in-plane C–H deformation and C–H stretching modes, respectively,

Table 2

HREELS results for C_2H_2/Cu(110) [8] in comparison with this work and for adsorbed C_6H_6 (this work) in comparison with values for benzene on Cu(110) and Cu(111) [13,14].

Normal mode description	Vibrational frequency (cm^{-1}) (assignment of species formed at 220 K)		Normal mode description[a]	Vibrational frequency (cm^{-1}) (assignment of species formed at 300 K)		
	This work	C_2H_2/Cu(110) [8]		This work	C_6H_6/Cu(110) [14]	C_6H_6/Cu(111) [13]
ν(Cu–Cl)	310		ν(Cu–Cl)	310		
ν(Cu–C)	430	470				
ν(Cu–*HCCHCl)	560					
γ(C–H)	655	640	γ(CH) (ν_4)	740	685	675
δ_s(C–H)	918	940	β(CH) (ν_{10})	1195		1165
δ_{as}(C–H)	1150	1140				
ν(C–C)	1315	1305				
ν(C–C) of *HCCHCl	1595					
ν(C–H)	2920	2900	ν(CH) (ν_1)	3040		3060

[a] The chosen notation (ν_n) is that proposed by Herzberg [6]. Only the three more significant vibrations relative to benzene and its perturbations are reported in this table: out-of-plane γ_{CH} bending, ν_{CC} ring stretching and symmetric/asymmetric ν_{CH} stretching vibrations.

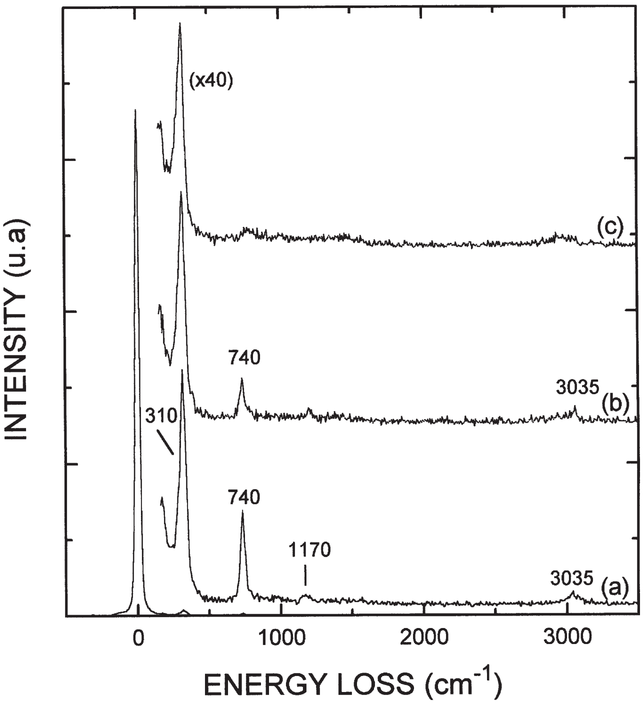

Figure 2. HREELS spectra of 10 L *trans*-$C_2H_2Cl_2$ adsorbed at 300 K on Cu(110) (a) and after subsequent heating at 340 K (b) and 570 K (c) for 2 min. These spectra have been measured at room temperature.

as observed generally on metals [9,12–15]. The small band at 2920 cm^{-1} is attributed to coadsorbed acetylene arising from some readsorption of molecules when cycling down to low temperatures in this experimental run. When the experiment is carried out by exposing a crystal at 300 K to *trans*-$C_2H_2Cl_2$, a clean benzene spectrum is obtained (figure 2(a)). It is, therefore, clear that, by 300 K, the dichloroethene has undergone complete dehalogenation, and that trimerisation of the C_2H_2 ad-species formed at lower temperature is easily achieved at room temperature. Laroze et al., on the basis of their IR data [5], have pointed out that the vibrational frequencies observed for benzene created in this system vary from those observed on clean Cu(110). In particular, the C–H out-of-plane bending vibration appears at 740 cm^{-1}, which is ~57 cm^{-1} higher than on the clean surface [15]. On the basis of analysis by Sheppard [9], this increased frequency can be correlated with a stronger interaction on the Cl-covered surface. This corresponds very well with the fact that benzene is stabilised on this surface up to temperatures of 358 K [5], compared to <300 K on the clean surface [16].

Finally, we turn to the origin of the strong band at 310 cm^{-1} which is observed at >220 K (figure 1 (c) and (d)). In order to investigate this band further, we monitored the thermal evolution of the system for temperatures much higher than 300 K. Figure 2 shows the HREELS spectra obtained after adsorption at 300 K and subsequent heating to 340 and 570 K. From this sequence of spectra, it can be seen that all the bands attributed to adsorbed benzene have decreased after warming to 340 K (figure 2(b)) and, by 570 K (figure 2(c)), have disappeared completely. In contrast, the 310 cm^{-1} peak is still present at the highest temperature. XPS data at this temperature confirm the presence of Cl on the surface with a photopeak (Cl 2p) appearing at a binding energy of 198.0 eV referenced to the Cu $2p_{3/2}$ level at 932.7 eV [5]. We, therefore, associate this low-frequency band to Cu–Cl stretching vibrations, arising from coadsorbed Cl atoms created by the dehalogenation process.

4. Conclusions

HREELS results show that at 135 K, both physisorbed and chemisorbed *trans*-dichloroethene coexist on Cu(110). At 220 K, the physisorbed phase desorbs, while dechlorination occurs as evidenced by a strong Cu–Cl stretching vibration. Both partial and complete dehalogenation occur at this temperature to give C_2H_2 and an intermediate $C_2H_2Cl_{ads}$ species at the surface. Further heating to 300 K leads to the formation of benzene via a trimerisation reaction. This species rapidly dominates on a sample maintained at room temperature and is completely desorbed at $>$360 K.

One can, therefore, summarise the adsorption/reaction of *trans*-$C_2H_2Cl_2$ on Cu(110) as follows:

$T \lesssim 180$ K

$$3C_2H_2Cl_{2\,\mathrm{gas}} \rightarrow 3C_2H_2Cl_{2\,\mathrm{ads}}$$

$180 < T < 220$ K

$$3C_2H_2Cl_{2\,\mathrm{ads}} \rightarrow nC_2H_{2\,\mathrm{ads}} + (3-n)C_2H_2Cl_{\mathrm{ads}} + (n+3)Cl_{\mathrm{ads}}$$

$220 < T < 300$ K

$$nC_2H_{2\,\mathrm{ads}} + (3-n)C_2H_2Cl_{\mathrm{ads}} + (n+3)Cl_{\mathrm{ads}} \rightarrow 3C_2H_{2\,\mathrm{ads}} + 6Cl_{\mathrm{ads}}$$

$T \approx 300$ K

$$3C_2H_{2\,\mathrm{ads}} + 6Cl_{\mathrm{ads}} \rightarrow C_6H_{6\,\mathrm{ads}} + 6Cl_{\mathrm{ads}}$$

$350 < T < 570$ K

$$C_6H_{6\,\mathrm{ads}} + 6Cl_{\mathrm{ads}} \rightarrow 6Cl_{\mathrm{ads}} + C_6H_{6\,\mathrm{gas}}$$

where ($n \leqslant 3$).

Such a reaction scheme is very similar to that proposed by Yang et al. for *trans*-1,2-dichloroethene on Cu(100) on the basis of data gained with the combined use of NEXAFS, TDS and work function change measurements [4] and by Laroze et al. on Cu(110) using RAIRS and TPD techniques [5]. In the latter study, RAIRS data allowed acetylene and benzene at the surface to be monitored and TPD experiments confirmed benzene production via the desorption of mass 78 (C_6H_6) and its cracking peaks (mass 50, 51, 52 and 26) at 373 K. In the work presented in this paper, the greater sensitivity and spectral range of HREELS has allowed further aspects of the adsorption and dechlorination process to be delineated. At low temperatures, the HREELS ability to monitor the weak CH stretching vibrations and the low-frequency C–Cl stretching vibrations enabled the description of the chemisorbed molecule to be made in terms of a di-σ-adsorbed species, with the carbons adopting sp^3 hybridisation. By 220 K, the dehalogenation process was easily identified by the appearance of a strong low-frequency Cu–Cl vibrational band at 310 cm^{-1}. In addition, the HREELS data also showed that both complete and partial dehalogenation processes had occurred at the temperature. It is clear that, after a complete dehalogenation, the ad-species transform into adsorbed C_2H_2 which readily reacts to produce adsorbed benzene. Trimerisation of acetylene into benzene has been frequently observed on many metal surfaces, including on Cu(110) [10,16]. Finally, benzene desorbs at about 360 K [5] leaving a very stable chlorinated surface, as clearly indicated by the Cu–Cl stretching vibration band at 310 cm^{-1} which persists to high temperatures. This is consistent with the known high stability of 3D CuCl crystals.

In conclusion, copper appears to be an extremely good metal for C–Cl bond cleavage, with dehalogenation occurring at very low temperatures, making it a cheap choice of component in a dechlorination catalyst. However, the poor ability of Cu to create H atoms which can be utilised in cleaning the surface via the creation of HCl necessarily leads to the need of incorporating other metals which are capable of performing this function. This has been shown, for example, on Pt(111) [3] where complementary dehydrogenation surface reactions of adsorbed hydrocarbon species open up the possibility of surface dechlorination by the desorption of Cl as HCl at about 460 K.

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