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Adsorption and reaction of *trans*-1,2-dichloroethene on copper nanoclusters supported on thin Al_2O_3 films

S. Haq, C. Winkler, A. Carew, J. Ledieu, R. Raval [*]

The Surface Science Research Centre, University of Liverpool, Liverpool L69 3BX, UK

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Abstract

The adsorption and reaction of *trans*-1,2-dichloroethene on Cu nanoclusters supported on a thin Al_2O_3 film grown on NiAl(110) have been studied as a function of temperature and Cu cluster size using molecular beams and temperature-programmed desorption. At 300 K, dechlorination is observed on clusters of all sizes; subsequent desorption yields benzene and acetylene as the main reaction products. The ratio of these is strongly dependent on cluster size; for small clusters only acetylene evolution is observed. With increasing cluster size the probability of trimerisation of acetylene to produce benzene increases, although the desorption of acetylene remains dominant. The adsorption and reaction are compared to previous work on a Cu(110) single crystal where benzene was the main desorption product after adsorption at 300 K. The cluster size-dependent yield of desorption products is attributed to the inability of small clusters to accommodate the dissociation products prior to the trimerisation reaction.

Keywords: Molecular beam; TPD; *trans*-1,2-dichloroethene; Acetylene; Trimerisation; Benzene; Thin alumina film; Cu clusters

1. Introduction

The chemical reactions of chlorinated compounds are of particular interest regarding environmental problems like air and water pollution, as well as for industrial applications. The latter include reactions with or on metallic surfaces, e.g., copper etching in semiconductor fabrication [1], or catalytic processes like the production of the widely used polyvinyl chloride [2]. Since the use of catalysts generally plays an important role in the chemical industry, a good understanding of chemical reactions between chlorinated compounds and metal surfaces provides the basis for improving and developing efficient catalysts.

Due to their simplicity, chloroethenes are good model systems for generating a better fundamental understanding of the reactivity of unsaturated chlorinated compounds with metal surfaces, and a small but growing literature database now exists on these systems. With respect to hydrodechlorination reactions, the group VIII metals, palladium, platinum, and copper, appear to be the most attractive in terms of catalytic activity, selectivity, and stability [3,4]. Therefore, experiments following the reaction of unsaturated chlorinated molecules on Pt(111) and Pt(110) have been reported [5,6], but the scale of the complexity of the reaction-phase space has only recently been demonstrated by Bloxham et al. [7] for *trans*-1,2-dichloroethene on Pd(110). The adsorption of chloroethenes on Cu(100) has been reported by Yang et al. [8] using near-edge X-ray absorption fine structure spectroscopy, and on Cu(110) by Jugnet et al. [9] using high-resolution electron energy loss spectroscopy. We have previously reported on a comprehensive study of the adsorption of *trans*-1,2-dichloroethene on Cu(110) using reflection absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD), and molecular beam adsorption reaction spectroscopy (MBARS) [10]. Specifically, we have shown that the behaviour of *trans*-1,2-dichloroethene on Cu(110) can be divided into three main regimes: Regime 1, which occurs over 85–165 K in which molecular adsorption occurs; Regime 2 in the 170–280 K range in which a sequence of desorption/dechlorination reactions is triggered that leave adsorbed acetylene and Cl atoms on the surface; and, finally, Regime 3 spanning the temperature range 280–500 K is governed by the behaviour of the

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[*] Corresponding author.
E-mail address: R.Raval@liv.ac.uk (R. Raval).

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acetylene intermediate which, when created at low temperatures, trimerises to form benzene that subsequently desorbs at 370 K. However, if created at high temperatures, direct desorption of acetylene competes with the trimerisation reaction.

In this report, we develop on our previous work and try to bridge the “materials gap” that exists between real catalysts and single crystals by studying the adsorption and reaction of *trans*-1,2-dichloroethene on copper nanoclusters supported on a thin Al_2O_3 film, using MBARS and TPD as a function of temperature and mean cluster size. Although still under idealised UHV conditions, this approach allows us to determine the influence of the oxide support and whether the cluster size influences the reaction mechanism, as often seen for gas-phase clusters (an overview can be found in [11]). Additionally, comparison with single crystal work is useful for understanding any differences in reactivity due to the materials gap.

2. Experimental

A detailed description of the experimental procedure used has been reported elsewhere [7,10]. Briefly, all experiments were carried out using standard ultrahigh vacuum (UHV) techniques and conditions. A NiAl(110) single crystal was used to create a model Al_2O_3 film. Copper was evaporated from a bead source made from melting high-purity Cu wire on a tungsten filament. The purity of the liquid *trans*-1,2-dichloroethene (Supelco, 99% purity) was checked by mass spectrometry on admission into the UHV chamber. The thermal molecular beam is generated by expanding the *trans*-1,2-dichloroethene gas from a 0.2-mm quartz capillary and collimated using a 0.3-mm skimmer. The data are shown with the beam initially being reflected from an inert flag in front of the crystal and then striking the sample at time $T = 0$. The uptake is shown using the most intense cracking fragment of *trans*-1,2-dichloroethene, mass 61, whose profile is identical to that of the parent ion of mass 96 (^{35}Cl isotope). Mass 26 is also an intense cracking fragment of *trans*-1,2-dichloroethene and for simple uptake, with no desorbing products, the profile of this is identical to that of masses 61 and 96. However, at certain temperatures this correlation breaks down due to the coincident evolution of acetylene produced from the reaction of *trans*-1,2-dichloroethene with the surface. Therefore, the data shown for mass 26 have been normalised and subtracted accordingly to evaluate the production of acetylene. Additionally, masses 2, 36, 54, and 104 were also measured for desorbing hydrogen, HCl, 1,2-butadiene, and cyclooctatetraene, respectively; these products were not observed and hence not shown. However, where evolution of the reaction product benzene (mass 78) is observed it is shown accordingly. We note that evaporation of Cu from the bead source in the UHV chamber is not directional and leads to changes in the absolute intensity and slope profiles of the mass spectrometer signals of the incident beam; this is due to adsorption onto the Cu evaporated on the surroundings of the manipulator and chamber walls. However, the beam flux remains constant, allowing comparison between the different set of experiments to be valid.

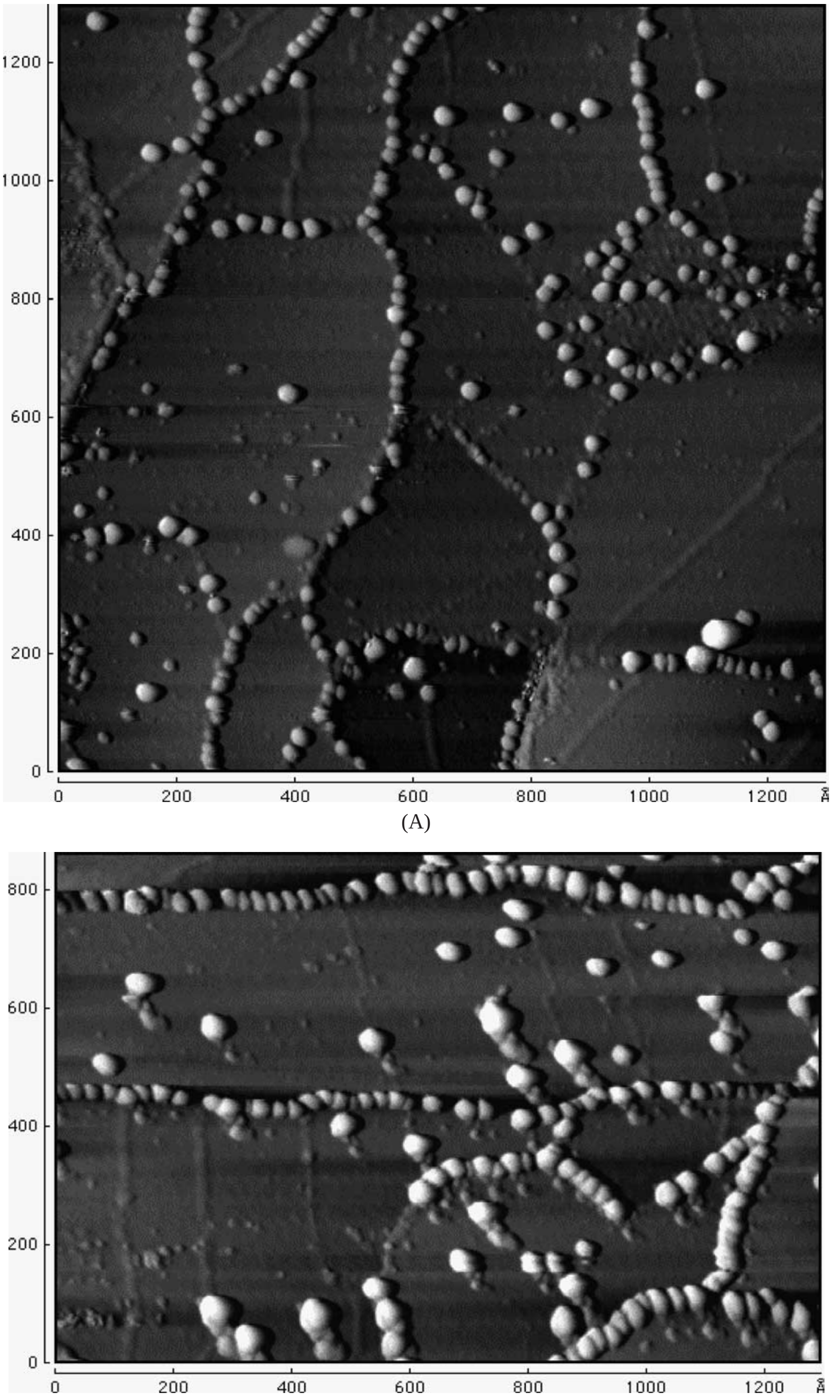
A 5 Å Al_2O_3 film was created by exposing the clean surface to oxygen and heating to 1200 K; this produced a sharp LEED pattern characteristic of the alumina film [12]. The film was then exposed to Cu vapour from the bead source; the exposure determined the mean cluster size and ranged from 60 to 480 s. This work was part of an STM study already reported [13] using the same bead source with as near identical evaporation conditions as possible. In that study it was shown that the growth of the Cu clusters proceeds according to the Volmer–Weber mechanism, with the formation of 3-dimensional islands from the onset of nucleation. The mean cluster size was found to change according to a semilog scaling law with increasing Cu exposure. Representative examples of the size and distribution of the clusters taken from our previous work are shown in Fig. 1 for 0.12 and 0.22 ML of Cu. The nucleation and growth of the clusters occurs at the characteristic defect sites on the alumina film, which can be step edges or reflectional and antiphase domain boundaries. This results in large areas of the alumina surface free of clusters. The clusters range typically in size from 20 to 40 Å diameter and 6 to 8 Å high, and are similar to those reported by others [14,15]. The diameter is uncorrected for any effect that the tip apex may have in measuring the particle shape and size, as it has been shown that depending on the size and shape of the tip, the size of the clusters can be overestimated with STM [16]. With increasing exposure these grow in size and number density, eventually coalescing into 3D chains of clusters. The STM work of Worren et al. [14] has shown that when these clusters are over 40 Å in diameter, the top facet has a (111) orientation.

3. Results and discussion

3.1. Molecular beam data and sticking probabilities

The molecular beam experiments were initially conducted on the clean alumina thin film at several different temperatures. These showed no measurable sticking or uptake of *trans*-1,2-dichloroethene between 300 and 450 K (Fig. 2). This implies that the uptake and reaction products observed in the presence of Cu clusters can be directly attributed to the Cu clusters and not the alumina support. However, this does not necessarily imply that there is no interaction between the incident molecules and the support, only that within the limitations of the experimental technique being used it is not measurable. For comparison, also shown in Fig. 1 is the uptake data measured on Cu(110) at 300 K.

Molecular beam experiments were also conducted on three different Cu nanoclusters/Al_2O_3 systems, created by



(A)

(B)

Fig. 1. STM images of Cu clusters on the alumina thin film, (A) 0.12 ML Cu, 1300 × 1300 Å, and (B) 0.22 ML Cu, 1300 × 850 Å. $I_t = 0.3$ nA and $V_t = 2$ V.

varying the exposure of Cu, and correspond to approximately 0.05, 0.22, and 0.5 ML Cu. The MBARS data from these three systems are shown in Fig. 3. For each Cu cluster sample, experiments were carried out over a range of temperatures. At 300 K, simple uptake is observed for all Cu cluster samples, with no desorbing reaction products. Furthermore, the uptake profiles are consistent with precursor-mediated adsorption. The initial sticking probability, S_0, changes from 0.34 to 0.56 as the number density and size of Cu clusters increase. The variation of S_0 with temperature is shown in Fig. 4; for comparison the data from Cu(110) are also included. On single crystals the sticking probability is a measure of the product of condensation into a physisorbed state and the probability of transfer from this to the chemisorbed state, commonly referred to as precursor-mediated adsorption, and the variation of the sticking probability with temperature and coverage simply reflects changes in these. Trapping into the physisorbed state

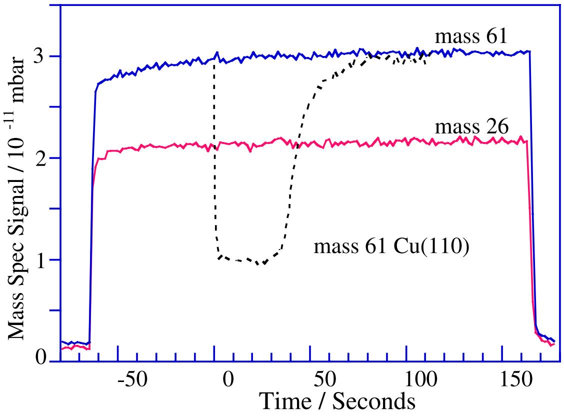


Fig. 2. Molecular beam data showing scattering of *trans*-1,2-dichloroethene from the clean alumina film. The dotted line shows the uptake of *trans*-1,2-dichloroethene on Cu(110) with a beam flux identical to that used in these experiments. In both cases the beam strikes the sample at $T = 0$.

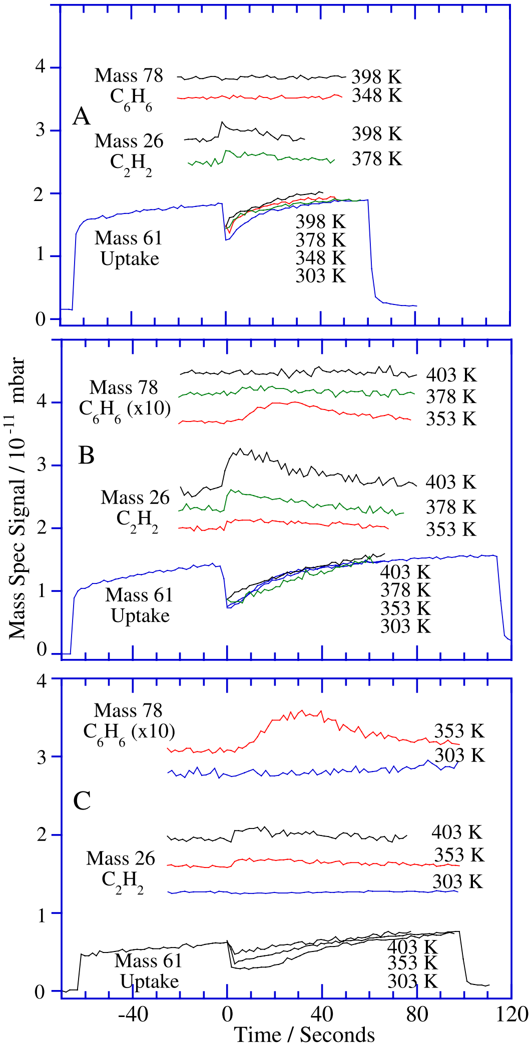


Fig. 3. Molecular beam experiments showing the uptake and product evolution from the reaction of *trans*-1,2-dichloroethene with Cu clusters supported on alumina as a function of temperature. From clusters formed with (A) 0.05, (B) 0.22, and (C) 0.5 ML Cu. The beam strikes the sample at time $T = 0$.

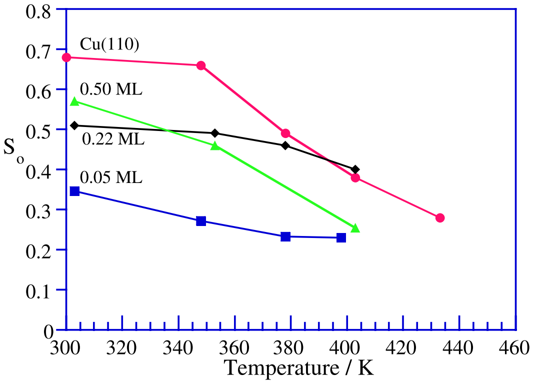


Fig. 4. The variation of the initial sticking coefficient S_0 as a function of temperature. Also included are data from Cu(110).

may itself be classified as being intrinsic or extrinsic, the difference being whether a molecule traps on the clean metal or above an adsorbate-covered surface. For a surface supporting small metal clusters this trapping-adsorption mechanism is equally applicable. However, in these cases, the experimentally measured sticking coefficient is for the combined system of clusters and support. Although the support may be inert with respect to sticking and uptake, as is the case here, accommodation of the incident molecules is still possible and this may be considered as an additional extrinsic precursor state for the combined system. The importance of this becomes apparent for supported clusters that show relatively high sticking coefficients relative to their small number densities. For example, the relatively high value for the initial sticking probability for the lowest Cu cluster coverages suggests that the incident molecules do interact with the alumina film; i.e., the molecules are trapped into a weak adsorption state in which they diffuse across the alumina surface before either desorbing back into the gas phase or finding a reaction site on a Cu cluster. Therefore, the actual sticking probability on these smaller clusters may in fact be higher than that measured for the larger clusters or the single crystal surface. It is interesting to note from Fig. 4 that smaller clusters do indeed show a different temperature-dependent trend for the intial sticking coefficient than the large clusters and Cu(110). This may be due either to the lifetime in the precursor state on the alumina support being less temperature dependent than the metal surface due to a relatively stronger interaction or to smaller clusters having highly reactive sites which show a smaller temperature dependence for adsorption. It is likely that the combination of these factors contributes to the overall adsorption dynamics for the initial sticking, and as the cluster size and number density increase the contributions change accordingly.

3.2. *Reaction pathways at the surface*

3.2.1. *TPD data*

The TPD data measured after the molecular beam experiments at 300 K for the three different Cu nanoclusters/Al_2O_3

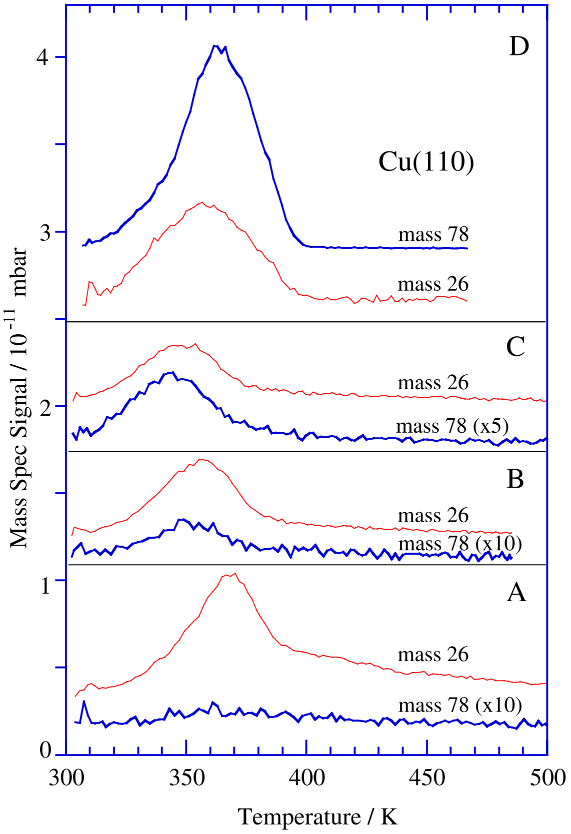


Fig. 5. Desorption spectra showing evolution of benzene (mass 78) and acetylene (mass 26) after adsorption of *trans*-1,2-dichloroethene at 300 K on clusters formed with (A) 0.05, (B) 0.22, and (C) 0.5 ML Cu. For comparison data from Cu(110) are also shown (D).

systems are shown in Fig. 5. Essentially, the desorption products can be associated with two main masses: 26 representing acetylene and 78 representing benzene. This clearly shows that dechlorination of *trans*-1,2-dichloroethene to form acetylene and the subsequent trimerisation of acetylene to form benzene are the major reaction pathways on the Cu clusters. The main acetylene desorption peak shifts from 368 to 346 K with increasing cluster size and number density. Also shown in Fig. 5, for comparison, are the TPD data from Cu(110) measured after exposure to a molecular beam of *trans*-1,2-dichloroethene at 300 K. This latter reference data are important, since on Cu(110) at 300 K, the acetylene intermediate has been shown to almost exclusively trimerise into benzene, which subsequently desorbs at 360 K. Therefore, the sensitivity of our mass spectrometer to benzene and acetylene, and the fraction of mass 26 which arises from a cracking fragment of benzene in the mass spectrometer, can be evaluated. A ratio of the mass 78 and mass 26 integrals is shown in Fig. 6. This clearly shows that whereas the main reaction pathway on Cu(110) is the trimerisation to benzene, the situation is quite different on the clusters where the main reaction pathway is the desorption of acetylene after dechlorination. Some trimerisation into benzene does occur for larger clusters and number densities, but is

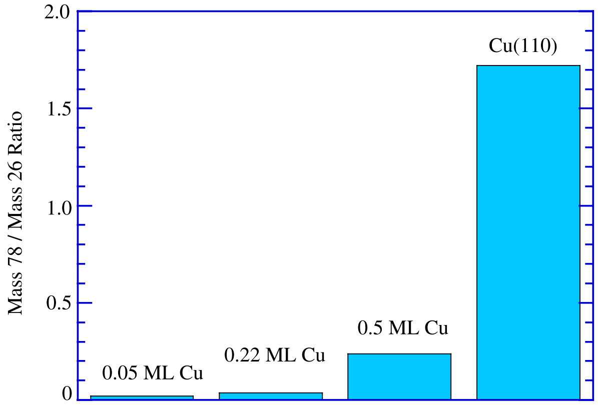


Fig. 6. Ratio of the mass 78 and mass 26 integrals from the desorption data shown in Fig. 4.

almost completely absent for cluster formed from the lowest Cu exposure.

3.2.2. *Molecular beam data above 300 K*

Molecular beam data in Fig. 3 show that above 330 K, the uptake is accompanied by the simultaneous evolution of gas-phase reaction products, benzene and acetylene. Interestingly, the ratio of these products depends on both the Cu cluster size and the temperature. For clusters formed from the smallest Cu exposure, the formation of benzene as a reaction product is not observed at any temperature in these experiments. However, for clusters corresponding to 0.22 ML Cu and above, benzene is clearly evolved, with a maximum rate at about 353 K. In contrast, acetylene is always observed as a reaction product, regardless of Cu cluster size or number density. On clusters where both products are observed, the temperature-dependent ratio of these is very similar to that previously reported for Cu(110). Above 400 K, the behaviour of all the systems converges in that only acetylene is produced into the gas phase. This can be readily understood since the surface is now well above the desorption temperature of acetylene, i.e., the acetylene immediately desorbs on production as its lifetime on the surface is too short to allow trimerisation reactions to occur.

3.3. *Structure sensitivity in reaction pathways*

Overall, it is clear from the TPD and molecular beam data that the adsorption proceeds according to the mechanism outlined below, and the overall behaviour is governed by the relative rates of these reaction steps:

$$C_2H_2Cl_{2(ad)} \rightarrow C_2H_2Cl_{(ad)} + Cl_{(ad)}, \qquad (1a)$$

$$C_2H_2Cl_{(ad)} \rightarrow C_2H_{2(ad)} + Cl_{(ad)}, \qquad (1b)$$

$$C_2H_{2(ad)} \rightarrow C_2H_{2(g)}, \qquad (2)$$

$$2C_2H_{2(ad)} \rightarrow C_4H_{4(ad)}, \qquad (3a)$$

$$C_2H_{2(ad)} + C_4H_{4(ad)} \rightarrow C_6H_{6(ad)}, \qquad (3b)$$

$$C_6H_{6(ad)} \rightarrow C_6H_{26(g)}. \qquad (4)$$

It would seem that process 1, dechlorination, occurs efficiently on all of the Cu cluster surfaces studied, i.e., it is structure insensitive. However, the above data show distinct differences in catalytic reaction processes (2) and (3) between different sizes of clusters, and between these and the Cu(110) single crystal surface. Generally, the catalytic properties of clusters are related to either electronic or geometric structure, although strictly these are interrelated. Geometric structure is defined by cluster size, shape, and surface morphology. Additionally, even for a given morphology, interatomic distances may vary as a function of cluster size, and hence the electronic structure and catalytic activity. The combination of these variables makes the process of relating the catalytic activity of clusters to a specific attribute difficult, especially in this case where a range of cluster sizes exists. However, the physical basis for the differences observed in this work can be established by understanding the reactivity of *trans*-1,2-dichloroethene and acetylene on single-crystal surfaces and translating this to cluster surfaces.

The adsorption of acetylene has been studied on low index faces of Cu(100) [8], (111) [17], and (110) surfaces [18,19]. On these surfaces, acetylene is believed to bond with the surface in a di-σ/di-π coordination [20]. More importantly for this study, acetylene trimerisation to form benzene is very efficient on all three surfaces, on Cu(110) with over 85% conversion [19]. This indicates that, insofar as the low index surfaces are concerned, the trimerisation process is not too sensitive to the surface structure. Furthermore, small Cu clusters supported on MgO(100) also catalyze the trimerisation reaction of acetylene with a high efficiency [21]. However, the trimerisation of acetylene formed from the reaction of *trans*-1,2-dichloroethene on Cu single crystals does appear to be sensitive to surface crystallography, as reports have shown for Cu(110) and Cu(100) surfaces. On Cu(100), Yang et al. [8] report that the acetylene predominantly desorbs without trimerisation and attributes this to the presence of coadsorbed Cl poisoning this reaction pathway. We note that in our own study on Cu(110), atomic Cl had no effect on the trimerisation reaction, and the acetylene produced from the dechlorination reaction trimerised efficiently into benzene, regardless of uptake. Furthermore an efficient trimerisation reaction is observed with excess coadsorbed Cl, as observed from the adsorption of trichloroethene on Cu(110) [22], where the acetylene is formed from the disproportionation of an ethynyl species. Clearly, the presence of the coadsorbed Cl leads to significant reactivity differences on Cu(100) and Cu(110) surfaces. A possible explanation for the difference between these two surfaces may be due to segregation of Cl into its own islands on Cu(110)—we observe a c(2 × 2) LEED pattern at room temperature, which does not change as the benzene desorbs from the surface. This segregation allows the surface to retain Cl-free areas where the trimerisation reaction can proceed. Therefore, the data from these two Cu surfaces may provide a simple explanation for the results from the Cu clusters supported on alumina; i.e., clusters of different sizes expose different surface facets and hence give rise to different catalytic activity. So, in the first instance, clusters where benzene is not evolved may predominantly expose facets that have (100) characteristics, while on larger cluster sizes benzene may be produced from facets that have (110) characteristics. To date, only the top (111) facet for Cu clusters over 40 Å has been directly imaged using STM [14]. However, it is not clear whether all clusters over 40 Å have this surface morphology. Additionally, no direct structural information is yet available for smaller clusters. Furthermore, the vulnerability of small clusters to adsorbate-induced reconstructions may make any comparison based on clean cluster morphology irrelevant.

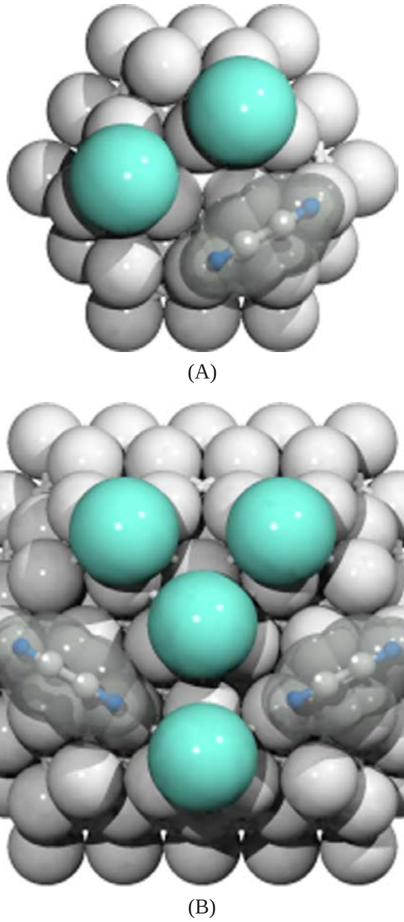


Fig. 7. Hard sphere models using Van der Waals radii showing surface coverage for randomly adsorbed Cl and C_2H_2 on the topmost facet of Cu clusters with (A) 13 Å and (B) 20 Å diameters.

However, the consideration of steric effects between coadsorbed species leads to an alternative and simpler explanation for the size-dependent catalytic activity for acetylene desorption versus trimerisation reactions in this particular system. Unlike the simple adsorption and desorption of molecules like CO, reactive adsorption of *trans*-1,2-dichloroethene requires a critical number of empty sites, as illustrated by Fig. 7, which shows surface coverage according to the Van der Waals radii of the species on clusters of 13 and 20 Å diameter, the latter being typical of the smaller type of cluster we observe by STM. Therefore, when lateral interactions between the resulting adsorbed species are taken into account, a minimum size of cluster is necessary for particular aspects of reactivity to be maintained. Again, it is the influence of the coadsorbed Cl that is critical, and there is evidence that it adversely affects *both* reaction steps (2) and (3). Consider reaction step (2)—the stability of acetylene is increased by the influence of coadsorbed Cl, as evident from the TPD results where the desorption temperature is higher than for clean Cu cluster surfaces (330 K) [21]. For small clusters the desorption shifts to a higher temperature due to the forced proximity of these species increasing the surface stability of acetylene and hence the barrier to its desorption into the gas phase. However, the size of the cluster and the influence of adsorbed Cl become even more critical when step (3), the trimerisation reaction, is considered. Here, the equivalent of six adsorption sites on the cluster is required for adsorbed Cl in addition to the sites required for adsorption of the acetylene molecules prior to trimerisation. Furthermore, for those clusters that can accommodate the minimum number of dissociated species involved in the formation of benzene, there is the additional requirement of sufficient physical segregation of Cl and acetylene to enable trimerisation to occur. For small clusters, these requirements are impossible to fulfils and reaction (3) is completely inhibited, leaving reaction (2) as the only alternative. It is difficult to predict what the critical cluster size needs to be to enable the trimerisation reaction to occur efficiently. The detailed mechanism for the trimerisation of acetylene to benzene has been discussed previously for both Cu and Pd single crystal and cluster surfaces [19,21,23–25]. Of particular relevance to this study is the work of Lomas et al. [19] who, with the careful use of isotope experiments, have suggested that the most probable mechanism on Cu(110) consists of a two-step process. The first step, which is rate limiting, involves the reaction of two acetylene molecules to form a metallopentacycle intermediate, C_4H_4M, step (3a). In the second step, this intermediate reacts with a further acetylene molecule to form benzene, step (3b). The work of Judai et al. [21] has shown that this reaction mechanism also applies to supported Cu clusters, and, furthermore, they were able to detect the desorption of a small quantity of a C_4H_6 species which is produced from unreacted metallopentacylce. Application of this mechanism to this work then sets a minimum size of cluster, such that it allows two acetylene molecules to be accommodated at positions that were not influenced by the coadsorbed Cl to produce the C_4H_4 intermediate. This requirement is obviously difficult for small clusters, and even for the largest clusters studied here, the trimerisation reaction is still highly unfavoured, indicating that accommodation and segregation of the surface species are critical to the overall surface chemistry.

A basic assumption in the discussion above is that there is no substantial spillover of atomic Cl onto the alumina. Although the data and the above arguments clearly indicate this, as otherwise acetylene trimerisation would readily occur as reported for clean Cu clusters [21]. We have additional indirect evidence to support this from RAIRS experiments. In these experiments, at low temperatures the intact monolayer adsorbed on the clusters is observed; however, at 300 K no absorption peaks were observed. This may be due to the sensitivity of RAIRS for this particular adsorption system, as previously we have found that the IR absorption cross sections for benzene and acetylene produced on Cu(110) are extremely small [10]. However, a strong dipole-active phonon mode of the Al_2O_3 thin film at 860 cm^{-1} has been shown to be very sensitive to adsorption onto the film, as we have previously reported [26] and as also discussed by Frank et al. [27]. No change in this mode was observed on adsorption at 300 K, suggesting that spillover of species onto the alumina is minimal.

Finally, we note that the main outcome of the simple considerations laid out above naturally explains the different structural sensitivities we report here compared to our previous work on the adsorption and reaction of NO on similarly sized alumina-supported Cu clusters [26], where the particles shows almost identical reactivity characteristics to that observed on Cu single crystals. This difference can simply be attributed to the unique adsorption and reaction properties of these two systems. The adsorption of nitric oxide shows a complex coverage-dependent reaction mechanism: NO–NO interactions lead to the formation of a dinitrosyl species, which is either stable on the surface or can decompose into atomic O and $N_2O_{(ad)\text{ or }(g)}$, depending on surface coverage. The latter can decompose further into O and $N_{2(g)}$ depending on the availability of surface sites. Overall, the key reaction is conversion of the monomer into the dimer, which may be sensitive to particle surface crystallography but is less demanding of cluster size, requiring at most two to three adjacent sites. In contrast, the trimolecular reaction for the conversion of acetylene to benzene, plus the steric influence of adsorbed Cl, requires a relatively more complex arrangement of the adsorbed species, and therefore a larger surface area for the reaction to proceed.

4. Conclusions

The adsorption and reaction dynamics of *trans*-1,2-dichloroethene on Cu clusters supported on a thin Al_2O_3 film grown on NiAl(110) are found to be size dependent. Although precursor-mediated adsorption is observed for all cluster sizes and number densities, small clusters show subtle differences that can be related to the interaction of the incident molecules with the oxide support and a higher adsorption probability on these clusters. At 300 K and above, dechlorination is observed on clusters of all sizes with the formation of benzene and acetylene as the main reaction products. The ratio of these is strongly dependent on cluster size; for small clusters only acetylene evolution is observed.

With increasing cluster size the probability of trimerisation of acetylene to produce benzene increases, although the desorption of acetylene remains dominant. The adsorption and reaction are compared to previous work on a Cu(110) single crystal where benzene was the only desorption product after adsorption at 300 K. The cluster size-dependent yield of the desorption products is attributed to the inability of small clusters to accommodate and segregate the dissociation products in order for the trimerisation reaction to proceed.

Acknowledgments

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