Evidence of carbon–carbon bond formation on GaAs(100) *via* Fischer–Tropsch methylene insertion reaction mechanism†

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Sequential multiple methylene (CH₂) insertions into adsorbed methyl species on clean gallium-rich GaAs(100)-(4 × 1) occur to form higher alkenes (ethene, propene, butene) and two higher alkyl iodides (iodoethane, iodopropane), not reported for a semiconductor surface previously.

Migratory insertion reactions of methylenes and olefins into alkyl–metal bonds are recognized as a key step in the carbon–carbon bond formation during many surface-catalyzed hydrocarbon conversion reactions. For example, the methylene species is the chain propagator in the Fischer–Tropsch reduction of CO by hydrogen over transition metal catalysts (iron, cobalt, ruthenium) to form higher hydrocarbons.[1] While it is known that some transition metal surfaces, such as gold, copper, silver, Ni(100) and more recently Ni(110), facilitate carbon–carbon bond formation[2–5] *via* methylene insertions into alkyl–surface bonds, semiconductor surfaces have not been shown to exhibit this behavior previously. Our results show that on *clean* GaAs(100) sequential multiple methylene (CH₂) insertions occur to form the higher alkenes, which contrasts with metal surfaces where it is generally the higher alkanes that form, with the exception of oxygen-modified Mo(100) where higher alkenes are formed[6] instead. In this latter case the higher alkenes were shown to form only because of the presence of the co-adsorbed oxygen, and the yields were shown to strongly depend on the oxygen coverage.

In this paper we show that CH₂I₂ on clean GaAs(100) initially forms CH₂ and I species. Following hydrogenation of the CH₂ to CH₃ species, thermal activation leads to three sequential methylene insertions into the CH₃–surface bond to form higher surface alkyls (ethyl, propyl and butyl), which undergo β-hydride elimination to form the respective alkenes. The ethyl and propyl groups also undergo recombination with the surface iodine to form iodoethane and iodopropane, respectively. Interestingly, we do not observe desorption of any gallium or arsenic iodides (GaI_x, AsI_x, x = 1–3) or As₂ etch products, previously known to form during ethyl iodide[7] and trifluoroethyl iodide[8] reactions on gallium-rich GaAs(100). This suggests the rate constant for the formation of the higher alkyl iodides is much higher than the rate constant for the formation of volatile gallium and arsenic halides.

Thermal desorption spectroscopy (TDS) and X-ray photo-electron spectroscopy (XPS) were used to study the surface

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reactions of CH₂I₂ GaAs(100). The descriptions of the UHV spectrometers and experimental procedures used, including the preparation of the gallium-rich GaAs(100) surface and its characterization, are given in detail elsewhere.[9]† XPS showed the clean surface was free of contaminants, and the Ga 3d:As 3d photoemission peak intensity ratio of 1.3:1 confirmed the surface was gallium-rich. The clean surface exhibited the GaAs(100)-(4 × 1) reconstruction, which is thought to be a less-ordered phase of the (4 × 2) reconstruction and is discussed further in reference 8.† CH₂I₂ (99%, Aldrich) was subjected to several freeze–pump–thaw cycles and checked for purity by mass spectrometry before use. All TDS data were acquired with a heating rate of 12 K s⁻¹ following a 10 L CH₂I₂ exposure.

In this paper we present only key TDS results. Fig. 1 shows that the first reaction product detected after thermal activation of CH₂I₂ is ethene, C₂H₄ [monitored *via* C₂H₃⁺ (m/z = 27)]. This desorption trace is broad and asymmetrical, with an *apparent* peak maximum at 510 K. A shoulder is discernable on the low temperature side, suggesting that the trace has mass spectrometer ion source fragment contributions from more than one desorbing species. These contributions are from the higher alkenes (propene and butene) and alkyl iodides (iodoethane and iodopropane) that form during subsequent surface reactions of dissociated CH₂ and I, as we show below. Deconvolution of the C₂H₄ trace in Fig. 1 shows that ethene desorbs at 480 K. We also detected two higher alkenes, propene and butene, using the C₃H₅⁺ (m/z = 41) and C₄H₈⁺ (m/z = 56) ion currents, respectively, for their detection. A deconvolution procedure conducted on the C₃H₅⁺ ion current, to account for the contributions from the desorbing butene and iodopropane, shows that the propene desorbs at 510 K. In the case
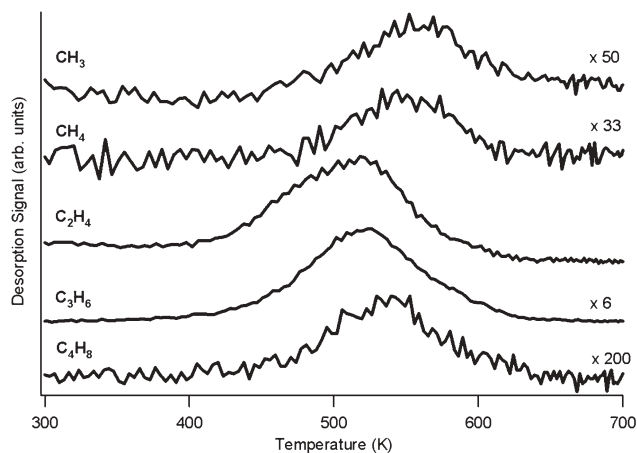

Fig. 1 Desorption spectra monitoring C₂H₃⁺, C₃H₅⁺, C₄H₈⁺, CH₄⁺ and CH₃⁺ ion currents following 10 L CH₂I₂ exposure at room temperature.

of the $C_4H_8^+$ ion current there is no evidence of contributions from higher alkenes and alkyl iodides and we assume that the peak at 540 K is entirely due to butene desorption. A comparison of the peak intensities of the higher alkenes show that the intensity decreases as the carbon length increases, while the desorption temperature maximum shifts progressively to higher temperatures. Uptake curves (not shown) monitoring the ion currents of all higher alkenes and their fragments did not show any shifts in the respective temperature maximum, confirming that these alkenes do not form *via* second-order reactions and, in particular, that ethene does not form by direct coupling of the CH_2 species. The H_2^+ ($m/z = 2$) ion current was monitored but no hydrogen desorption was detected.

Desorption profiles monitoring CH_4^+ ($m/z = 16$) and CH_3^+ ($m/z = 15$) ion currents are also shown in Fig. 1, with peak maxima occurring at 550 K and 560 K, respectively. CH_3 is part of the mass spectrometer fragmentation pattern of both CH_4 (85%) and CH_3I (10%) and calculations reveal that the CH_3^+ ion current is entirely made up of contributions from these desorbing species, with no contributions from desorbing CH_3 radicals. Surface CH_3 forms initially by the reaction between adsorbed CH_2 and H species, the latter being due to adsorption from the background, similar to that observed during CH_2I_2 reactions on clean Ni(110).[4] Calibration experiments to determine the surface hydrogen coverage attainable from a constant background partial pressure of hydrogen for varying exposure times, and the effect on the CH_4 yields were conducted (see ESI†) and showed that, with careful experimental procedures, reproducible surface hydrogen coverages could be attained on a routine basis using this method. We note that the observed CH_4 was not formed in the mass spectrometer by the reaction between background H species and CH_3 radicals as no CH_3 desorption from the surface was detected. The corresponding higher alkanes (ethane, propane, butane) were also monitored but were not detected.

Fig. 2 shows the desorption profiles of the iodine containing products. No parent ion ($CH_2I_2^+$, $m/z = 268$), formed by recombination of dissociated surface species, is detected in the temperature range 300–700 K. No desorption of CH_2^+ ($m/z = 14$) and CH_2I^+ ($m/z = 141$) species (spectra not shown) were detected, confirming that CH_2I_2 dissociates completely upon adsorption to generate surface CH_2 and I species, consistent with previous observations of this molecule on Cu(100),[2] Ni(110),[4] Ag(111),[5] Ru(001)[10] and Rh(111).[11] Fig. 2 also shows desorption profiles monitoring two higher alkyl iodides, iodoethane (C_2H_5I, $m/z = 156$) and iodopropane (C_3H_7I, $m/z = 170$), which desorb at 495 K and 520 K respectively. Other higher alkyl iodides were also monitored but were not detected. Similar to the alkenes, the uptake spectra (not shown) for C_2H_5I and C_3H_7I showed coverage-independent
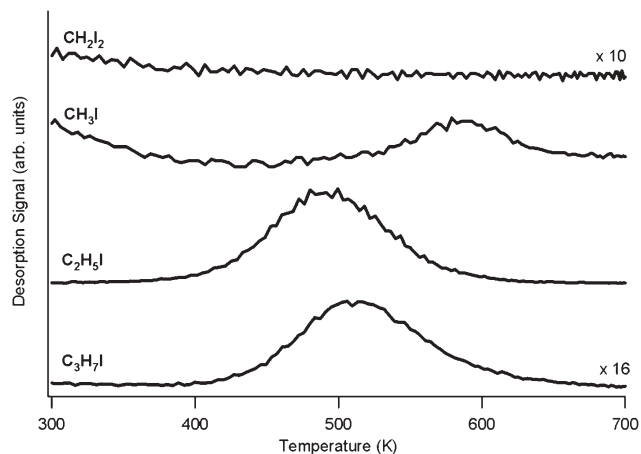

Fig. 2 Desorption spectra monitoring $C_2H_5I^+$, $C_3H_7I^+$, CH_3I^+ and $CH_2I_2^+$ ion currents following 10 L exposure CH_2I_2 at room temperature.

peak positions. Although the alkyl iodides should form by a second-order reaction between the alkyl and iodide species, the pseudo-first order desorption kinetics are observed because the process is reaction-limited, being dependent on the formation of the respective higher alkyl species by the first-order methylene insertion process. The spectrum monitoring CH_3I^+ ($m/z = 142$) shows that desorption occurs at a much higher temperature (585 K) than all other reaction products, suggesting that formation of the higher iodides, higher alkenes and methane are favoured over the formation of methyl iodide. Note that CH_3I formation on Ru(001)[10] occurs at a much lower temperature of 160 K and was observed only for high CH_2I_2 coverages. Lastly, XPS data acquired on completion of each TDS experiment showed a low residual surface concentration of elemental iodine, equivalent to one-tenth of a monolayer, suggesting that not all iodine desorbs as alkyl iodides.

The thermal reactions of CH_2I_2 on gallium-rich GaAs(100) are summarized in Scheme 1. The initiation step in the overall mechanism is the rapid hydrogenation of the CH_2 to CH_3 species, followed by three sequential methylene insertions into the CH_3–surface bond. Two competitive processes can occur for the resulting surface-generated C_2–C_4 alkyls: (i) β-hydride elimination and (ii) reductive elimination with surface iodines. β-Hydride elimination yielding the higher alkene is the preferred route for desorption, consistent with observations on many transition metals, for example Cu(100),[2] Ni(110)[4] and oxygen modified Mo(100).[6] The formation of CH_4 and CH_3I results in the termination of the methylene chain propagation step. The CH_3I forms by a reaction between the surface CH_3 and iodine species, while CH_4 is formed by the reaction between the surface CH_3 and
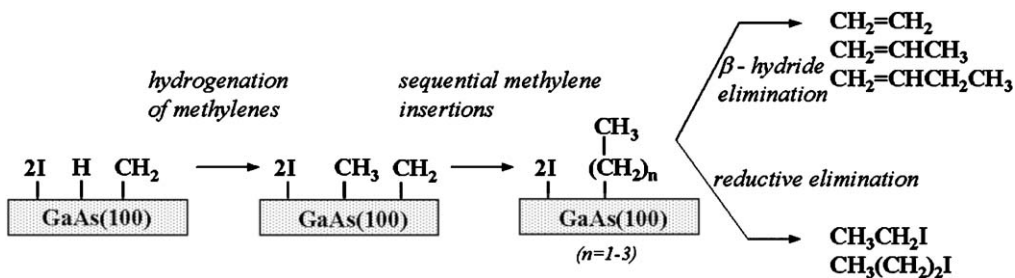
Scheme 1 Proposed scheme for CH_2I_2 reactions on clean gallium-rich GaAs (100)-(4 × 1).

H species, the latter being generated by the β-hydride elimination in the butyl species. The surface CH_3 species for CH_3I formation must be generated by the hydrogenation of the unreacted CH_2 groups for temperatures greater than 500 K, the hydrogens being derived from the consecutive β-hydride eliminations in the ethyl, propyl and butyl species. Since no H_2 desorption, expected at 500 K,[7]† was detected we postulate that there is a direct or through-space transfer of H from the C_2–C_4 alkyl species to the adsorbed CH_2/CH_3 species. The direct transfer mechanism has been previously postulated to account for a lack of molecular H_2 desorption during the disproportionation reactions of C_2–C_4 alkyl iodides on Au(111).[12]

The exponential dependence of the alkene yields on chain length ($C_2 > C_3 > C_4$) that we observe in this study fits well with the Schultz–Flory product distribution observed in the Fischer–Tropsch synthesis[2,13] during successive migratory methylene insertions into the adsorbed methyl species. While we provide no direct spectroscopic evidence for the methylene insertion step, mechanisms invoking methylene insertions have been postulated previously to account for the observed mass spectroscopic product distribution in a number of surface investigations involving chain propagation in adsorbed alkyl groups (see for example references 6 and 13). Moreover, a recent infrared and TDS investigation on Ag(111),[14] involving co-adsorbed CH_2 and CF_3, provides direct spectroscopic evidence that methylene insertions do indeed occur on surfaces, the process being so facile that in the case of CH_2 and CF_3 it was found to occur even at cryogenic temperatures. Hence, the methylene insertion cannot be the rate-limiting step in this study, and it is most likely the β-hydride elimination that controls the overall rate of the reaction.

Reductive elimination of C_2, C_3 alkyls with iodines to evolve the respective alkyl iodides during thermal reactions of CH_2I_2 has been observed only on one other surface, Ni(100),[15] although in that study the reaction surface had been modified with oxygen and the $C_nH_{2n+1}I$ ($n = 1$–3) species were postulated as surface intermediates. We do not observe any CH_2I desorption from GaAs(100) and hence rule out the possibility that the higher alkyl iodides, C_2H_5I and C_3H_7I, are formed via reactions of CH_2I with surface CH_3 and C_2H_5 species, respectively. There are a number of reasons why the higher alkyl iodides cannot be formed by this mechanism. Firstly, CH_2I_2 evolution, expected from any surface CH_2I and I reaction, was not observed. While the formation of C_2H_5I from the surface CH_3 and any CH_2I species could be plausible, as the CH_3 species is stable on the surface to 580 K, formation of C_3H_7I from C_2H_5 and CH_2I is not possible as the C_2H_5 has desorbed from the surface by 500 K. In addition, when the C_2H_5 species are available on the surface they are more likely to undergo the facile β-hydride elimination or be subjected rapidly to another methylene insertion. The low desorption temperature of the C_2H_5 species means no propane (C_3H_8) formation, expected from the direct coupling of the CH_3 and the C_2H_5 species, is observed. In a similar vein, no butane (C_4H_{10}) formation, either by CH_3 and C_3H_7 coupling or the self-coupling of the C_2H_5 species, is observed. We do not see the reductive elimination of the higher alkyls with hydrogens liberated during the β-hydride eliminations, because these hydrogens are directly transferred to the surface CH_2/CH_3 species. Lastly, we propose the two higher alkyl iodides (C_2H_5I and C_3H_7I) and CH_3I are formed by the iodine insertion into the respective alkyl species.

The CH_2I_2 reactions on GaAs(100) show similarities as well as differences to methylene insertion reactions observed on transition metal surfaces. So, for example, three methylene insertions were observed in this study and on Cu(100)[2] and Ni(110),[4] while on oxygenated Mo(100)[6] four methylene insertions were observed. No higher *alkanes* ($>C_2$) were observed in this study or on oxygenated Mo(100), but on oxygenated Ni(110)[14] C_2 and C_3 alkanes formed. On GaAs(100) C_2 and C_3 alkyl iodides are liberated instead, which did not form on clean Ni(110).[5] In comparison with CH_2I_2 reactions on Ru(001)[10] and Rh(111)[11] the differences were more extensive since no methylene insertions were observed and the formation of the only higher hydrocarbon, ethene, occurred *via* self-coupling of CH_2 species. The fact that some similarities in the alkyl coupling behaviour exist between GaAs(100) and two transition metals, Cu(100) and Ni(110), may be attributed to the gallium-rich nature of GaAs(100) used in the experiments, since the surface gallium atoms are more metallic and are expected to be the predominant sites for surface reactions, rather than the sub-surface non-metallic arsenic atoms.[7]

In previous investigations involving ethyl iodide[7] and trifluoro-ethyl iodide[8] on GaAs(100), GaI desorption provided the only pathway for the removal of the surface iodines. In the case of CH_2I_2 we see the surface iodines leave as the C_1–C_3 iodides, implying that the rate constant for this pathway is much higher than that for the formation of gallium iodide etch products. However, since C_2 and C_3 iodides formed before desorption of CH_3I, methylene insertions into the CH_3–surface bond are favoured over the CH_3 reaction with iodine.

In summary we have shown that carbon–carbon bond formation *via* methylene insertions occurs on GaAs(100) to form higher hydrocarbons, and the product distribution suggests high selectivity. The reaction mechanism is similar to the alkyl mechanism[1,12] proposed previously for the Fischer–Tropsch synthesis. Whilst GaAs may prove to be an expensive catalyst for practical purposes, this UHV study provides further under-standing of carbon–carbon bond formation on surfaces, in particular during Fischer–Tropsch synthesis.

Notes and references

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