The Chemistry of CH$_2$I$_2$ on MoAl Alloy Thin Films Formed on Dehydroxylated Alumina: Insight into Methylene Insertion Reactions

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The chemistry of diiodomethane is explored in ultrahigh vacuum on a MoAl alloy film grown on planar, dehydroxylated alumina by reaction with molybdenum hexacarbonyl. The majority of the diiodomethane forms methylene species below $\sim$250 K, although a small proportion forms CH$_2$I$_{ads}$, which hydrogenates to form iodomethane. The majority ($\sim$90%) of the adsorbed methylene species thermally decomposes to carbon and hydrogen. The remainder undergoes several reactions, including partial hydrogenation to form adsorbed methyl species or total hydrogenation to form methane. The methyl species can couple forming ethane or undergo methylene insertion reactions to form alkyl species up to C$_4$. These form alkenes via a $\beta$-hydride elimination reaction. This chemistry is relatively unique, only having been found previously for Ni(110) surfaces. No such chemistry is found on Ni(100) and Ni(111).

1. Introduction

Mo(CO)$_6$ has been extensively used to deposit molybdenum on oxides to generate catalysts and catalyst precursors. Such a procedure has been applied in ultrahigh vacuum to generate model catalysts supported on planar alumina thin films, where surface-sensitive spectroscopic probes can be used to investigate the surfaces and catalytic reactions. Our recent studies have shown that reacting Mo(CO)$_6$ with aluminum and alumina thin films at 500 K and above forms molybdenum carbide incorporating a small amount of oxygen. Efforts have been made to perform hydrocarbon conversion reactions on these surfaces, and it is found that these surfaces are rather inert. Such inactivity has been found recently by Chen et al. by adsorbing O$_2$ on molybdenum carbide and has been rationalized by site blocking rather than by electronic modification effects. Annealing these films to temperatures higher than 1200 K causes CO desorption through alumina reduction by the carbide carbon and results in molybdenum–aluminum alloy formation.

It has been shown previously that reaction of low exposures of Mo(CO)$_6$ with alumina films above 500 K results in the formation of nanoparticles on the surface, while higher exposures (of $\sim$5000 L of Mo(CO)$_6$) lead to a thin film that completely covers the substrate. The chemistry of hydrogen and CO on MoAl nanoparticles compared with thin films has been investigated to explore particle size effects in these systems.

In the following, the surface chemistry of diiodomethane is investigated on the MoAl alloy film. Such a strategy has been extensively used to examine the surface chemistry of hydrocarbons on surfaces since organic iodides tend to decompose by scission of the C—I bonds at relatively low temperatures to deposit hydrocarbon fragments, along with chemisorbed iodine. The chemistry of iodomethane has recently been explored on the alloy surface where, in addition to hydrogen and methane desorption, the formation of higher hydrocarbons, ethylene, ethane, and propylene, was also found. These products are suggested to form through methylene insertion into alkyl-metal bonds followed by $\beta$-hydride or reductive elimination to form oligomers. In this case, methylene species are formed by partial dehydrogenation of adsorbed methyl species. The chemistry of methylene species is explored directly in the following by studying diiodomethane on the MoAl alloy surface, where methylene species are directly formed by C—I bond cleavage.

The MoAl alloy film formation and characterization has been extensively described. Briefly, it is formed by adsorbing 5000 L of Mo(CO)$_6$ onto a dehydroxylated alumina film grown on a Mo(100) substrate held at 700 K, so that a molybdenum carbide film incorporating a small amount of oxygen is formed. The sample is subsequently annealed to 1500 K to generate a MoAl alloy. Alloy formation is confirmed by X-ray photoelectron and Auger spectroscopies.

The surface chemistry of diiodomethane has been investigated previously on several transition-metal surfaces including Cu, Ag, Mo, Pd, Pt, Rh, Ru, and Ni. Studies have also been performed on Al surfaces. One exception appears to be Ni(110) where up to 10% of alkanes and alkenes, up to C$_4$, are formed. The surface chemistry on aluminum is quite different from that on the transition metals. It has been found that methane coupling reactions occur at $\sim$170 K resulting in ethylene desorption, while neither methane nor hydrogen desorption is observed. On the other hand, AlI$_3$, AlI$_2$, AlI, and CH$_3$Al(H)I desorb at temperatures higher than 400 K, and the surface chemistry is highly dependent on the CH$_2$I$_2$ exposure.

2. Experimental Section

Temperature-programmed desorption (TPD) data were collected in an ultrahigh vacuum chamber operating at a base...
pressure of \(8 \times 10^{-11}\) Torr that has been described in detail elsewhere\textsuperscript{13,17,18} where desorbing species were detected using a Dycor quadrupole mass spectrometer placed in line of sight of the sample. This chamber was also equipped with a double-pass cylindrical mirror analyzer for collecting Auger spectra.

X-ray photoelectron spectra (XPS) were collected in another chamber operating at a base pressure of \(2 \times 10^{-10}\) Torr, which was equipped with Specs X-ray source and double-pass cylindrical mirror analyzer. Spectra were typically collected with a Mg Kα X-ray power of 250 W and a pass energy of 50 eV. The deposited film was sufficiently thin that no charging effects were noted, and the binding energies were calibrated using the Mo 3d\textsubscript{5/2} feature (at 272.4 eV binding energy) as a standard.

Temperature-programmed desorption spectra were collected at a heating rate of 10 or 15 K/s. Temperature-dependent XP and Auger spectra were collected by heating the sample to the indicated temperature for 5 s, allowing the sample to cool to 150 K, following which the spectrum was recorded.

The Mo(100) substrate (1-cm diameter, 0.2-mm thick) was cleaned using a standard procedure, which consisted of argon ion bombardment (2 kV, 1 μA/cm\textsuperscript{2}), and any residual contaminants were removed by briefly heating to 2000 K in vacuo. The resulting Auger spectrum showed no contaminants. Aluminum was deposited onto Mo(100) from a small heated alumina tube, which was enclosed in a stainless steel shroud to minimize contamination of other parts of the system.\textsuperscript{42}

Molybdenum hexacarbonyl (Aldrich, 99%), diiodomethane, and \(d_2\)-diiodomethane (Aldrich, 99%) were transferred to glass vials, were connected to the gas-handling line of the chamber, and were purified by repeated freeze–pump–thaw cycles, followed by distillation, and their purities were monitored using mass spectroscopy. These were dosed onto the surface via a capillary doser to minimize background contamination. The exposures in Langmuirs (1 L = \(1 \times 10^{-6}\) Torr) are corrected to the amu 63 signal. At low CH\textsubscript{2}I\textsubscript{2} exposures (\(\leq 2\) L) the CH\textsubscript{2}I\textsubscript{2} desorption at low exposures. As will be shown below, CH\textsubscript{3}I forms at high CH\textsubscript{2}I\textsubscript{2} exposures and also contributes to the amu 63 signal. At low CH\textsubscript{2}I\textsubscript{2} exposures (\(\leq 2\) L, Figure 3a), no molecular desorption occurs, suggesting complete C–I bond cleavage. At exposures of 3 L and above, two desorption states appear concurrently with desorption peak temperatures of \(\sim 217\) and \(\sim 250\) K, respectively. The high-temperature state saturates at an exposure of \(\sim 10\) L, while the low-temperature state grows indefinitely with exposure so that these are assigned to monolayer and multilayer desorption, respectively. Multilayer

3. Results

Figure 1 displays the Auger spectra of the MoAl alloy film (formed by exposing 5000 L Mo(CO)\textsubscript{6} to dehydroxylated alumina at 700 K and heating to 1500 K\textsuperscript{18}) exposed to various amounts of CH\textsubscript{2}I\textsubscript{2} at 150 K and subsequently annealed to 750 K. The carbon KLL Auger signal at \(\sim 270\) eV kinetic energy following CH\textsubscript{2}I\textsubscript{2} adsorption and annealing suggests that a portion of adsorbed CH\textsubscript{2}I\textsubscript{2} undergoes complete decomposition. The low intensity of the carbon signal does not allow the nature of the deposited carbon (whether it is graphitic or carbidic) to be identified from the line shape. It is found that the intensity of the Al\textsuperscript{0} signal at \(\sim 66\) eV decreases with increasing CH\textsubscript{2}I\textsubscript{2} exposure up to 5 L and stays constant at higher exposures. This strongly suggests that some metallic aluminum is oxidized by iodine. The feature at \(\sim 520\) eV for the alloy film alone indicates that there is a small amount of oxygen initially present in the alloy film. The iodine Auger signal appears at approximately the same energy as oxygen\textsuperscript{19} and the growth in the \(\sim 520\) eV signal with increasing diiodomethane exposure indicates that it has dissociated to deposit carbon and iodine on the surface.

To explore the dissociation of diiodomethane and the subsequent surface chemistry, XP spectra were collected following adsorption of 5 L of CH\textsubscript{2}I\textsubscript{2} on the alloy surface and then annealing to various temperatures, and the results are displayed in Figure 2 where each spectrum was taken after the
desorption commences prior to saturation of the monolayer, and the feature at 180 K at the highest CH₂I₂ exposure (10 L) is due to some desorption from the sample holder.

Figure 3b presents the amu 71 profiles (CH₃I₂⁺) as a function of CH₂I₂ exposure. Zaera has pointed out that 71 amu is due exclusively to CH₃I. This indicates that a portion of CH₂I₂ undergoes C—I bond cleavage and hydrogen addition to form methyl iodide between 200 and 300 K. This reaction has also been found on Ni(110).38

Figure 3c presents the 2 amu desorption profiles. Several desorption states are evident, where the sharp feature at 220 K at high CH₂I₂ exposures is due to fragmentation of the parent molecule in the mass spectrometer ionizer and that centered at ~300 K suggests ethylene desorption. Some ethane (30 amu) desorbs at slightly lower temperatures. Propylene desorption is also observed at ~300 K from the 41 amu signal, but no C₄ hydrocarbons are found to desorb. A similar chemistry is found at higher CH₂I₂ exposures but with some differences. First, some butene (56 amu) desorption is found at ~300 K, and second, an additional ethane (30 amu) desorption state appears at ~210 K, which becomes evident at a CH₂I₂ exposure of 5 L. Especially at CH₂I₂ exposures of 3 and 5 L, the 26, 27, and 30 amu profiles all have high-temperature tails extending up to 600 K, suggesting desorption of some C₂ species at high temperatures. The desorption profiles of 26 and 27 amu signals are slightly different at higher temperatures suggesting aluminum-containing species may also desorb since Al⁺ has an m/e value of 27. The nature of these species will be discussed below together with isotope labeling experiments. The olefin desorption temperatures are exposure independent. Finally, no water was found to desorb from the surface.

The fate of the carbon and iodine adsorbed onto the surface after product desorption (Figures 3 and 4) is explored in Figure 5 by carrying out TPD experiments at a heating rate of 15 K/s following iodomethane adsorption and after annealing to ~750 K, where Figure 5a presents the CO (28 amu) desorption profiles, and Figure 5b presents the iodine (63 amu, I₂⁺) spectra. It is found that CO desorbs at ~1196 K at the smallest CH₂I₂ exposure and increases slightly to higher temperatures with increasing CH₂I₂ exposures. It has been demonstrated previously that this is due to the reaction between deposited carbon and the alumina substrate.18 The desorption peak area is plotted as a function of CH₂I₂ exposure as an inset in Figure 5a. The desorption yield increases almost linearly from 0.5 to 4 L and reaches a maximum at 4 L and then decreases slightly at an exposure of 5 L. Figure 5b shows that iodine desorbs between 800 and 1150 K and that the integrated desorption peak area versus iodomethane exposure is plotted as an inset showing that the iodine coverage increases rapidly at low CH₂I₂ exposures and slows down thereafter.

To better understand the surface chemistry presented above, experiments were also performed using CD₂I₂. Figure 6 presents temperature-programmed desorption profiles as a function of CD₂I₂ exposure, where amu 63 (F⁺) and 72 (CHD₂I⁻) and...
Signals at 73 amu (not shown) mimic those at 72 amu, only with smaller intensities. These desorption profiles are similar to those plotted in Figure 3 for CH₂I₂. However, CD₂I₂ appears to be less reactive compared to CH₂I₂: molecular desorption is observed at CH₂I₂ exposures of 3 L and above, while for CD₂I₂, molecular desorption is detectable at an exposure of 2 L. In this case, saturation of the overlayer (evidenced by the feature at ~250 K) is more evident than in the data of Figure 3a. Again, CHD₂I (CD₂I) formation is observed following monolayer saturation, identical to that found in Figure 3b.

Figure 7a plots the corresponding 2 (H₂), 3 (HD), and 4 (D₂) amu desorption profiles as a function of CD₂I₂ exposure. Apparently H₂ originates from background contamination, while deuterium comes from the dissociation of adsorbed CD₂I₂. The H₂ desorption peak area decreases with increasing CD₂I₂ exposure and the D₂ desorption peak area increases up to an exposure of 5 L and saturates thereafter, consistent with the
spectra shown in Figure 6. The ~210 K state at 3 amu at high CD$_2$I$_2$ exposures is likely due to fragmentation of reactively formed CHD$_2$I.

Figure 7b displays the corresponding 18 (CH$_2$D$_2$), 19 (CHD$_3$), and 20 (CD$_4$) amu desorption profiles. Both CHD$_3$ and CD$_4$ have 18 amu fragments, but this contribution is negligible at low CD$_2$I$_2$ exposures. The desorption profiles of CH$_2$D$_2$ are broader than those of CHD$_3$ and CD$_4$ and extensive desorption occurs below 300 K, while for the latter two molecules, the desorption peak maxima are higher. These suggest that, although CD$_2$ species dissociate at ~200 K (indicated by the low-temperature CD$_4$ desorption), extensive dissociation only occurs above 300 K.

Higher-molecular-weight hydrocarbon desorption was also followed after CD$_2$I$_2$ adsorption, and similar chemistry is found as for CH$_2$I$_2$. For the purpose of simplicity, only the ethylene desorption profiles are plotted (Figure 8). Both C$_2$D$_4$ and C$_2$HD$_3$ desorb from the surface at ~280 K at CD$_2$I$_2$ exposures of 2 L and above. The desorption temperature of both molecules does not vary with CD$_2$I$_2$ exposure. The same behavior has been found for C$_2$H$_4$ desorption shown in Figure 4, suggesting these are not formed by methylene coupling. In cases where methylene coupling does occur, for instance, on Cu(100), ethylene desorption temperature decreases with increasing diiodomethane exposures as expected for a second-order reaction.

The data shown in Figure 7b imply that hydrogen appears to be more reactive than deuterium since CH$_2$D$_2$ desorbs at a lower temperature than CHD$_3$ and CD$_4$. However, this effect may be due to a slower C–D bond cleavage. To address this question, TPD experiments are performed on H$_2$–(D$_2$–) saturated surfaces (20 L exposure), and the results are plotted in Figure 9. Higher methane yields are found in these cases compared with Figures 3d and 7b, confirming methane formation occurs via hydrogenation of methylene species by surface hydrogen. These data indicate that H is more reactive than D in terms of methane formation, especially for reaction between CD$_3$I$_2$ and D$_2$ where the yield of CH$_2$D$_2$ (amu 18) is comparable to that of CD$_4$ (amu 20). It is also clear that CH$_2$I$_2$ dissociates more easily than CD$_2$I$_2$, indicated by the much lower methane yield when CH$_2$I$_2$ is adsorbed on deuterium-covered surface. One last point to mention is that even in the CH$_2$I$_2$ + D$_2$ case, detectable amounts of CHD$_3$ (amu 19) and CD$_4$ (amu 20) are found.

4. Discussion

4.1. Diiodomethane Dissociation. The Auger spectra shown in Figure 1 provide a broad picture of the surface chemistry following CH$_2$I$_2$ adsorption at 150 K and annealing to 750 K. Evidently, a portion of CH$_2$I$_2$ undergoes complete dissociation to deposit carbon and iodine on the surface. It appears that iodine
adsorbs preferentially on aluminum, indicated by the Al\(^0\) (66 eV) signal decrease with increasing CH\(_2\)I\(_2\) exposure up to 5 L. For CH\(_2\)I\(_2\) exposures of 10 and 20 L, no further Al\(^0\) signal intensity decrease is seen suggesting monolayer saturation, and this is confirmed by TPD results (Figure 3a).

XPS and TPD results provide more information on CH\(_2\)I\(_2\) dissociation. No previous XPS studies have been carried out for diiodomethane dissociation on molybdenum surfaces.\(^{22}\) XPS measurements have been performed for CH\(_2\)I\(_2\) adsorbed on aluminum\(^{39}\) where an I 3d\(_{5/2}\) binding energy of 621.3 eV is found following adsorption at 90 K, which decreases to 619.6 eV on heating to 300 K, while the C 1s binding energy is 286.2 eV at 90 K and decreases to 283.5 eV at 300 K. As shown in Figure 2, following CH\(_2\)I\(_2\) adsorption at 150 K and annealing to 200 K, both the C 1s and I 3d\(_{5/2}\) signals do not decrease noticeably in intensity or shift in binding energy, indicating that CH\(_2\)I\(_2\) does not dissociate in this temperature range. This is in accord with the TPD spectra displayed in Figure 9 where methane desorption becomes evident above 200 K. On heating to 250 K, both the C 1s and I 3d\(_{5/2}\) signals attenuate and undergo a binding energy shift, indicating extensive CH\(_2\)I\(_2\) dissociation, where the C 1s binding of 283.4 eV at 250 K implies some CH\(_x\) formation.\(^{38}\) However, it is difficult to determine exactly what species are present on the surface on the basis only of XPS, partly because of the low C 1s photoionization cross section. On heating to 400 K, the C 1s binding energy shifts slowly to 282.7 eV and undergoes an additional shift to 282.5 eV at 500 K and above. These values suggest the presence of carbide (atomic) carbon\(^{17,18}\) indicating extensive C–H bond scission by 500 K. This notion is corroborated by the fact that H\(_2\) desorption diminishes at this temperature (Figure 3c).

An additional reaction pathway, also found on Ni(110),\(^{38}\) is iodomethane formation (Figures 3b and 6b). Iodomethane only

Figure 6. (a) 63 (I\(^2+\)) and (b) 72 (CHD\(_2\)I\(^2+\) and CD\(_3\)I\(_2\)I\(^2+\)) amu temperature-programmed desorption spectra of diiodomethane adsorbed on a MoAl film at 150 K collected using a heating rate of 10 K/s, as a function of CD\(_2\)I\(_2\) exposure. CD\(_2\)I\(_2\) exposures are marked adjacent to the corresponding spectrum.

Figure 7. (a) 2 (H\(_2\)), 3 (HD), and 4 (D\(_2\)) amu and (b) 18 (CH\(_2\)D\(_2\)), 19 (CHD\(_3\)), and 20 (CD\(_4\)) amu temperature-programmed desorption spectra of CD\(_2\)I\(_2\) adsorbed on MoAl film at 150 K collected using a heating rate of 10 K/s, as a function of CD\(_2\)I\(_2\) exposure.

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An additional reaction pathway, also found on Ni(110),\(^{38}\) is iodomethane formation (Figures 3b and 6b). Iodomethane only
forms following diiodomethane saturation. Since iodomethane can only be formed through a CH$_2$I$^-$ (CD$_2$I$^-$) intermediate, it is expected that, at low diiodomethane coverages, this intermediate is not formed. However, at high coverages, diiodomethane may adopt a geometry such that one C–I bond is oriented away from the surface because of surface crowding, thus protecting it from further dissociation as in Scheme 1.

4.2. Formation of Methane and Higher Hydrocarbons. Methane is formed through a stepwise hydrogenation of surface methylene species as indicated by data shown in Figure 7b where, in this case, hydrogen originating from the background incorporates into the desorbing CH$_2$D$_2$ and CHD$_3$. It is found that H reacts with methylene species more easily than deuterium (Figures 7b and 9). This effect has been noted previously and has been ascribed to a large normal kinetic isotope effect, which favors the incorporation of H compared to D. Methane formation commences at ~200 K with a desorption maximum at ~350 K, in case the surface is not precovered with hydrogen (Figure 3d). In the presence of preadsorbed hydrogen, methane desorption still commences at ~200 K but with a lower desorption maximum (Figure 9). The methane yield is also much higher on hydrogen-precovered surfaces. These data taken together demonstrate that methane formation is limited by the availability of surface hydrogen.

It has been found previously that methane is formed from methyl iodide at temperatures that are almost identical to those found here, both on clean and hydrogen-precovered surfaces. This strongly suggests that methyl formation is a facile process, while methyl hydrogenation is the rate-limiting step. Interestingly, it is also found that, when deuterium adatoms are available, either by adsorbing D$_2$ on the surface or by cracking CD$_2$I$_2$, all deuterium-substituted methanes from CH$_3$D to CD$_4$ are formed (Figure 9). This suggests that, although the first step of methylene hydrogenation, that is, methyl formation, is a favored process, the reverse process is not completely blocked.

Higher hydrocarbons are formed on the surface including ethylene, ethane, propylene, and butene (Figures 4 and 8). Ethylene could be formed by two routes: either methylene coupling or methylene insertion into metal–methyl bond followed by β-hydride elimination. Although methylene coupling occurs in most cases, it appears not to be the dominating mechanism on the MoAl alloy. First, and perhaps the most convincing evidence, is that a significant amount of C$_2$HD$_3$ desorbs at approximately the same temperature as C$_2$D$_4$ during thermal activation of adsorbed CD$_2$I$_2$ (Figure 8). Second, being a product from a second-order reaction coupling, the ethylene desorption temperature should decrease with increasing diiodomethane exposures as observed previously, and this is not seen (Figures 4 and 8). This argument depends on the rate of ethylene formation being reaction-rate limited. It is found, however, that molecular ethylene desorbs from the alloy surface at substantially lower temperatures.

It is also proposed that both ethylene and ethane are formed by the same route as propylene and butene; that is, the reaction is initiated by the insertion of methylene species into metal–methyl bond to form a metal–ethyl intermediate. This can undergo β-hydride elimination to form ethylene or hydrogenation to yield ethane. Additional methylenes can insert into the ethyl species to form longer alkyl groups that also undergo β-hydride elimination reactions to produce C$_3$ and C$_4$ olefins. Except at a CH$_2$I$_2$ exposure of 1 L where the ethane desorption temperature is slightly lower than ethylene, at exposures of 3 and 5 L, the desorption temperatures of these two molecules are identical (Figure 4). This suggests that methylene insertion is the rate-limiting step while β-hydride and reductive elimination reactions are fast. The desorption temperatures of propylene and butene, on the other hand, are ~30 K higher than ethylene and ethane. This indicates that higher hydrocarbon formation is limited by the availability of surface methylene species. A typical characteristic for oligomerization by such a methylene insertion mechanism is an exponential decrease of the yield with...
increasing chain length (with a Schulz–Flory distribution). This behavior is shown clearly in Figure 4. The origin of the small amount of ethane that desorbs at \( \sim 210 \, \text{K} \) following 3 and 5 L CH\(_2\)I\(_2\) exposures (Figure 4) is not very clear. Presumably, this is due to methyl coupling considering the facile methyl formation process and the fact that this state increases with increasing CH\(_2\)I\(_2\) exposure, although hydrogenation of the ethyl group cannot be excluded.

### 4.3. High-Temperature Desorption Products

Hydrogen and the majority of the hydrocarbons desorb at below 500 K. However, detectable desorptions at amu 26, 27, and 30 (Figure 4) and amu 31 and 32 (Figure 8) are found between 500 and 600 K. Although such high-temperature desorption states have not been observed on Mo surfaces, organoaluminum desorption is found at these temperatures on aluminum, and the desorption intensity at higher temperatures is assigned to organoaluminum formation. Since this reaction channel is rather minor, it is not possible to discuss these reaction pathways in greater detail.

Iodine desorbs from the surface between 700 and 1100 K (Figure 5b). Iodine desorbs atomically from most transition-metal surfaces at such high temperatures. CO desorbs from the surface at 1100 K and above with a desorption maximum at \( \sim 1200 \, \text{K} \) (Figure 5a), because of reaction between the alumina substrate and carbidic carbon originating from diiodomethane dissociation, and this reaction pathway has been confirmed previously by isotope \(^{18}\text{O}\) labeling TPD experiments. The CO desorption yield decreases at high CH\(_2\)I\(_2\) exposures (inset, Figure 5a), suggesting that iodine adsortion blocks a portion of surface sites where methylene species decompose.

Assuming that the high-temperature CO desorption state removes all carbon originating from complete CH\(_2\)I\(_2\) dissociation (CO\(_2\) desorption is also observed at \( \sim 1000 \, \text{K} \), but the intensity is negligible compared to CO), the percentage of adsorbed methylene species that converts into gaseous products can be estimated where, at a CH\(_2\)I\(_2\) exposure of 5 L, \( \sim 90\% \) of the adsorbed methylene species dissociate completely to hydrogen and carbon. For the remaining \( \sim 10\% \) that converts into gaseous products, higher hydrocarbons comprise \( \sim 40\% \). The overall reaction mechanism, following the above discussion, is summarized in Scheme 2.

### 4.4. Comparison with the Chemistry on Other Surfaces

The thermal chemistry of diiodomethane has been extensively studied on various metal surfaces and in most cases, methylene coupling to form ethylene, decomposition to carbon and hydrogen, and hydrogenation to methane are the major reaction pathways. As has been shown above, methylene insertion reaction requires the coexistence of both alkyl and methylene species on the surface. This is rather difficult since the insertion reaction competes with many other reactions including coupling, hydrogenation, and dehydrogenation. It is therefore not surprising that similar chemistry has only been found for Ni(110). In that case, \( \sim 10\% \) of the adsorbed methylene species converts to higher hydrocarbons up to butene.

On coinage metal surfaces, ethylene appears to be the only hydrocarbon formed from diiodomethane, in these cases, through methylene coupling. Methylene insertion does not occur since methyl species are not formed. This reaction channel can be activated, however, when iodomethane and diiodomethane are coadsorbed on the surface. On molybdenum, methane is the only hydrocarbon product. Lack of CHD\(_3\) and CD\(_4\) desorption when the surface is presod with D\(_2\) suggests that the coexistence of considerable amounts of methyl and methylene species is not achieved. Aluminum has been found to catalyze methylene coupling reaction at rather low temperatures. However, methane insertion reactions are not found.

The unique reactivity of the MoAl for higher hydrocarbon formation may be due to two effects, either electronic or geometric. In the first effect, molybdenum will gain electrons by alloying with aluminum causing larger d-band occupancy, so that it becomes electronically more like a noble metal. Second, it could also be due to the blocking of reactive sites on the surface by coordination to aluminum and the resulting iodine, which inhibits both the deep hydrogenation of the resulting surface methyl species and the deep dehydrogenation of methylene species, allowing the latter to have sufficient time to insert into an alkyl-surface bond.
5. Conclusions

Diiodomethane reacts to form methylene species and adsorbed iodine below \(~250 \text{ K}\) on a MoAl alloy formed from Mo(CO)\(_6\) on dehydroxylated alumina. Approximately 90\% of the adsorbed methylene species decomposes to deposit carbon and evolve hydrogen. A portion of the reactively formed methylene species hydrogenate to methyl species. These can either hydrogenate further to form methane or undergo sequential methylene insertion reactions to form alkyl species. These can react by \(\beta\)-hydride elimination to form alkenes up to \(\mathrm{C}_4\). Some ethane formation is also found, which is formed by either methyl coupling or by hydrogenation of the ethyl species.

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References and Notes