The Chemistry of Alkyl Iodides on Copper Surfaces. 2. Influence of Surface Structure on Reactivity[†]

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The thermal chemistry of iodomethane, iodoethane, 1-iodopropane, 1-iodobutane, and 2-iodohexane on copper (100), (110), and (111) single-crystal surfaces was characterized in this and previous studies by temperature-programmed desorption (TPD) spectroscopy. The main decomposition pathway available to the methyl surface moiety that results from C−I bond activation in adsorbed iodomethane is α-hydride elimination to methylene, a step that occurs around 460−470 K on all three surfaces. Some methylene dimerization to ethane is also seen at higher coverages, at a rate that depends significantly on surface structure; ethane desorption peaks at 400 K on Cu(110), but only above 440 K on Cu(100) and Cu(111). Ethyl groups produced by iodoethane decomposition react at much lower temperatures and mostly undergo β-hydride elimination to ethylene. The ethyl dehydrogenation reaction is structure sensitive as well, a fact illustrated by the different ethylene desorption peak maxima observed in the TPD experiments, at 225, 247, and 255 K on Cu(110), Cu(111), and Cu(100), respectively (at saturation). Perhaps the more telling observations are the difference in feasibility of H−D scrambling in the ethylene resulting from conversion of a 1:1 mixture of normal and perdeutero iodoethane, a reaction viable on Cu(100) but not on Cu(110), and the 10-fold difference in ethane yield between those two crystals. Additional studies with 1-iodopropane and 1-iodobutane provided some information on the effect of chain length on reactivity, and experiments with 2-iodohexane attested to the high selectivity for removal of internal hydrogen atoms during β-hydride elimination from alkyl species.

1. Introduction

The reactivity of adsorbates on solid surfaces is often controlled by the nature of the reactant and/or the structure of the substrate. This dependence is more significant in systems with complex chemistry, because the selectivity among several possible pathways is particularly sensitive to subtle changes in relative rates. The dependence of reaction selectivities on surface structure is critical in the design of catalysts for industrial processes.[1] This so-called ensemble effect has been used to explain many catalytic observations.[2−6]

The structure sensitivity of hydrocarbon conversion processes in particular has been studied extensively by using conventional catalyst characterization techniques. Specifically, changes in activity and selectivity in supported catalysts as a function of particle size are often taken as a sign of the influence of surface structure on reactivity.[7] It has generally been concluded that while hydrogenation and dehydrogenation steps are almost insensitive to the topography of the surface,[8−10] C−C bond-breaking and skeletal rearrangements depend strongly on it.[6,11] Unfortunately, studies with supported catalysts are limited by the complexity of those systems; many parameters change with changing preparation procedures, so supported catalysts display a mixture of particles with different sizes, shapes, and composi-

tions. Catalytic studies on single-crystal surfaces have shed some additional light into the microscopic details of this dependence of reactivity on structure,[5,12−14] but more needs to be done to develop a complete understanding of the factors involved in such correlations.

An alternative route to an atomic-level understanding of catalytic reactions on surfaces is the study of elementary steps on well-defined single-crystal surfaces under vacuum conditions.[15,16] In terms of hydrocarbon conversion processes, alkyl groups are crucial intermediates in many reactions associated with hydrogenation, dehydrogenation, cracking, and reforming, among others.[17−21] The recent development of preparation methods for alkyl groups on metal surfaces via the activation of alkyl halide precursors has advanced these studies considerably.[15,16,22,23] Specifically, activation of alkyl groups by copper leads to β-hydride elimination to the corresponding olefin,[24−28] the same as in more reactive transition metals such as platinum[29−31] and nickel,[32−34] and also to other hydrogenation and coupling steps.

The previous accompanying report probed the dependence of adsorption structure on surface coverage and the relation between those changes and the subsequent reactivity of the adsorbates.[35] In this paper, temperature-programmed desorption (TPD) data are presented for a number of alkyl iodides adsorbed on Cu(100), Cu(110), and Cu(111) single-crystal surfaces (Figure 1) to illustrate the changes induced by changing surface structure on the rates of some key thermal conversion elementary steps. Specific rate changes were identified for methylene
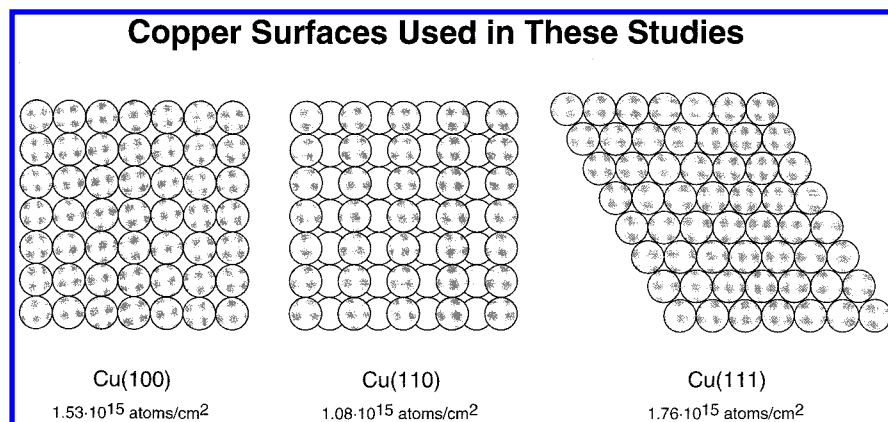
Figure 1. Schematic representation of the three crystallographic orientations of the copper single-crystal surfaces used in the studies reported here.

insertion and β-hydride elimination steps which indicate that both reactions are facilitated by open structures such as that in Cu(110); important selectivity shifts were observed as a consequence of these relative variations between olefin and alkane production rates among the different copper crystallographic orientations. The possibility of suppressing H−D exchange and other isotope scrambling processes by choosing the appropriate catalyst structure was also proven. Additional studies on reactivity versus alkyl chain length and branching are also reported.

2. Experimental Section

The experiments reported here were performed in two ultrahigh vacuum (UHV) chambers pumped with ion and titanium sublimation pumps and equipped with sample manipulators capable of moving in the x, y, z, and θ directions, cooling the samples to 115 K, and resistively heating them to over 1000 K.[26,36] These apparatii also contain an Auger spectrometer, low-energy electron diffraction optics, and an ion sputtering gun for sample cleaning. A VG-SPX300 0−300 amu quadrupole mass spectrometer differentially pumped and shielded from the chamber by a stainless steel tube which terminates in a 2 mm diameter aperture skimmer was used to perform the temperature-programmed desorption (TPD) studies described in this paper.

The copper single crystals were cut in the (100), (110), and (111) orientations, polished to a mirror finish using standard procedures, and mounted on the sample holder as described before.[26] The temperature was measured to an accuracy of ±5 K with a chromel−alumel thermocouple inserted into a hole on the side of the crystals. The samples were routinely cleaned by cycles of sputtering with Ar$^+$ ions, first at 850−920 K and then at room temperature, followed by annealing in vacuum at 950 K. Iodine was removed from the surface between experiments by flashing to 950 K. All the compounds used here were purchased from Aldrich (99+% purity) except for the 2-iodohexane and *cis*-2-hexene, which were obtained from Pfaltz and Bauer, respectively. After purification by filtration through an alumina column, the iodoalkane samples were stored in glass ampules and shielded from light to avoid any photodecomposition. These iodoalkanes were then subjected to several freeze−pump−thaw cycles before introduction into the vacuum chamber, and were often passed over an in-line alumina plug to remove any traces of HI. The purity of the reagents was checked periodically by mass spectrometry. Gas exposures were performed by backfilling the vacuum chamber using leak valves, and are reported in langmuirs (1 L $\equiv 10^{-6}$ Torr s), not corrected for differences in ion gauge sensitivities.

3. Results

3.1. Iodomethane. Most of the thermal chemistry of iodomethane on (100),[37,38] (110),[36] and (111)[39,40] copper single-crystal surfaces has been published already, so only the key data needed to discuss structure sensitivity issues will be presented here. The main desorbing products in TPD experiments with methyl iodide on copper are methane, ethylene, and ethane, although some propylene is also seen in some cases. Interestingly, hydrogen desorption is rarely seen from these systems, and no carbon is left behind after high-temperature heating either. The left panel of Figure 2 displays the methane TPD traces obtained for 1.0 L of CH$_3$I on all three Cu(111), Cu(100), and Cu(110) surfaces, while the right frame shows the traces recorded for ethane desorption after higher (3.0 L) exposures. It can be seen here that the differences in the desorption spectra for methane among the three crystals are subtle, the desorption maximum appearing at 460, 468, and 470 K on the (111), (110), and (100) surfaces, respectively. It is important to note that the presence of different amounts of iodine on the surface leads to changes in peak temperatures larger than those reported here as a function of surface structure.[41]

Ethylene production from iodomethane thermal activation follows quite closely that of methane formation on all three surfaces in terms of both peak shapes and yield changes with coverage. Ethane formation, on the other hand, displays a significantly different behavior. For one, the peak maximum for ethane desorption shifts in all cases to low temperatures with increasing initial CH$_3$I coverage. For instance, on Cu(110) that feature shifts from 450 K after a 1.25 L dose to about 400 K after a 3.0 L exposure,[36] and on Cu(100) it drifts from approximately 460 K at 1.0 L to 440 K at 2.0 L.[38] Furthermore, ethane production is only observable at high coverages, above 1.0 L, but becomes dominant at saturation. Finally, there is a clear trend in terms of the ease with which this reaction takes place on the different surfaces. As Figure 2 shows, ethane desorption at high coverages peaks at 400, 440, and 450 K on Cu(110), Cu(100), and Cu(111), respectively. Figure 3 displays another manifestation of this trend, in this case in terms of the ethane/(methane + ethylene) yield ratio from these TPD experiments. Again, the data in Figure 3 indicate that more ethane is produced on surfaces where its desorption occurs at lower temperatures. Notice that the yield ratio is a more sensitive parameter for comparing relative rates between competitive reaction pathways: besides the clear different behavior of the Cu(110) surface already mentioned, Figure 3 also shows that Cu(100) is somewhat better at promoting the methyl−methyl coupling reaction than Cu(111).
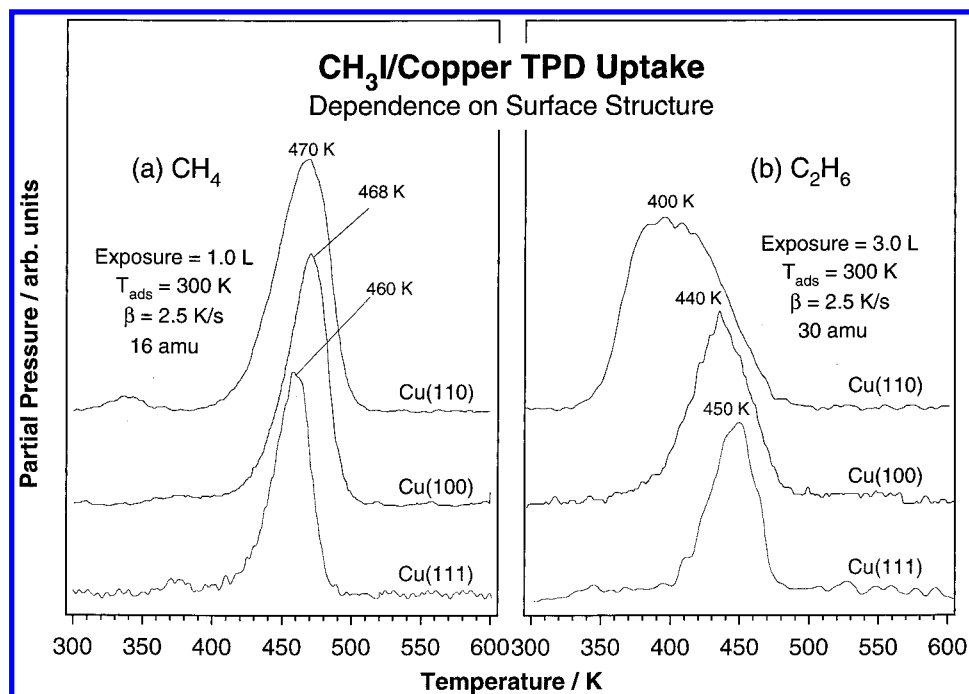
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Figure 2. Methane (left) and ethane (right) temperature-programmed desorption (TPD) traces from iodomethane adsorbed on Cu(111), Cu(100), and Cu(110) surfaces at 300 K. The initial exposures and other experimental conditions are provided in the figure. Methane formation, a reaction limited by α-hydride elimination from surface methyl groups, occurs at approximately the same temperature on all three surfaces, but C−C coupling to ethane is significantly faster on Cu(110).
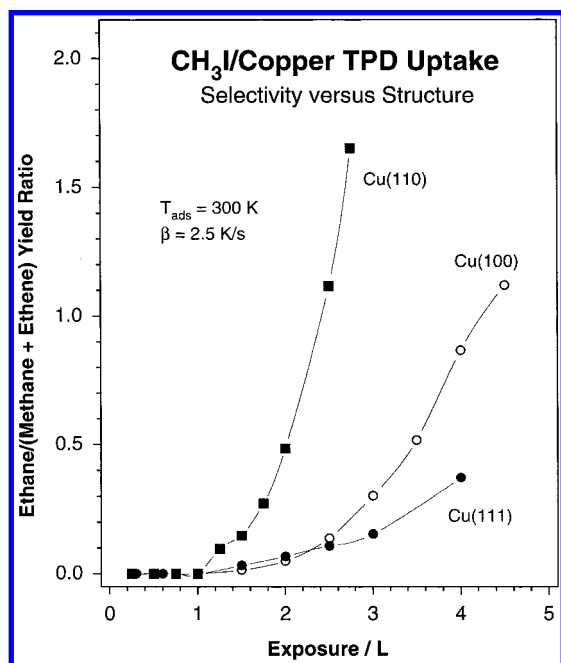

Figure 3. Yield ratio of C−C coupling to ethane against α-hydride elimination to methane and ethylene as a function of initial exposure from TPD experiments with iodomethane on the three copper surfaces used in this report. The increases in relative ethane yield with coverage on all surfaces reflect the second-order nature of the C−C coupling step. Also, the higher ethane relative yield for the case of Cu(110) is an indication of the ability of that surface to promote the coupling reaction preferentially.

3.2. Iodoethane. The thermal chemistry of iodoethane was studied by TPD on the three copper surfaces referred to above as well. Molecular desorption from Cu(110) is only observed after exposures above 2.0 L (data not shown), indicating that all of the chemisorbed iodoethane decomposes on the surface at lower coverages. A peak is seen at 145 K for the 4.0 L exposure on that surface, which we attribute to monolayer iodoethane molecular desorption.[25] On Cu(100), molecular desorption from the first layer occurs at 165 K.

Thermal activation of ethyl groups formed via dissociative adsorption of iodoethane on copper surfaces leads to the formation of a number of hydrocarbon products, the same as in the case of propyl species.[26] In particular, the thermal reactivity of ethyl moieties is dominated by ethylene formation via β-hydride elimination. This is a common reaction in systems involving alkyl groups, and has been seen on a large number of surfaces as well as with a good number of alkyl groups.[15,16,21,22,24,27,28,30,32−34,42] Figure 4 shows ethylene TPD data obtained from iodoethane chemisorbed on Cu(110) (left panel), Cu(111) (middle), and Cu(100) (right) as a function of exposure. Notice that, again, the peak temperature maxima change with surface structure, going from 225 K on Cu(110) to 247 and 255 K on Cu(111) and Cu(100), respectively, at saturation. Also, the desorption peak from the (110) surface displays an approximately symmetrical shape and the same constant maximum at all coverages (a behavior associated with simple first-order kinetics), but more complex behavior is seen on both Cu(111)[43] and Cu(100),[27] where the peaks are skewed and the maxima shift to higher temperatures with increasing iodoethane exposures.

Additional minority products are detected upon heating iodoethane on copper surfaces. In particular, some ethane is produced at high coverages via reductive elimination of ethyl surface groups with the hydrogen atoms produced by the β-hydride elimination step.[15,16,22,23] Figure 5 shows ethane TPD traces obtained for the case of Cu(100) as a function of iodoethane dose. Desorption in that case starts only above 2.0 L, and its maximum shifts from 250 K after that exposure to 237 K at saturation. A small amount of ethane is also produced on Cu(110), but again only at high coverages. C−C coupling to butane (reductive elimination of two ethyl groups) is possible on Cu(110) and Cu(111) as well, but it is not seen in TPD experiments with Cu(100). Some hydrogen desorbs from the Cu(110) surface around 315 K (a desorption-limited process),
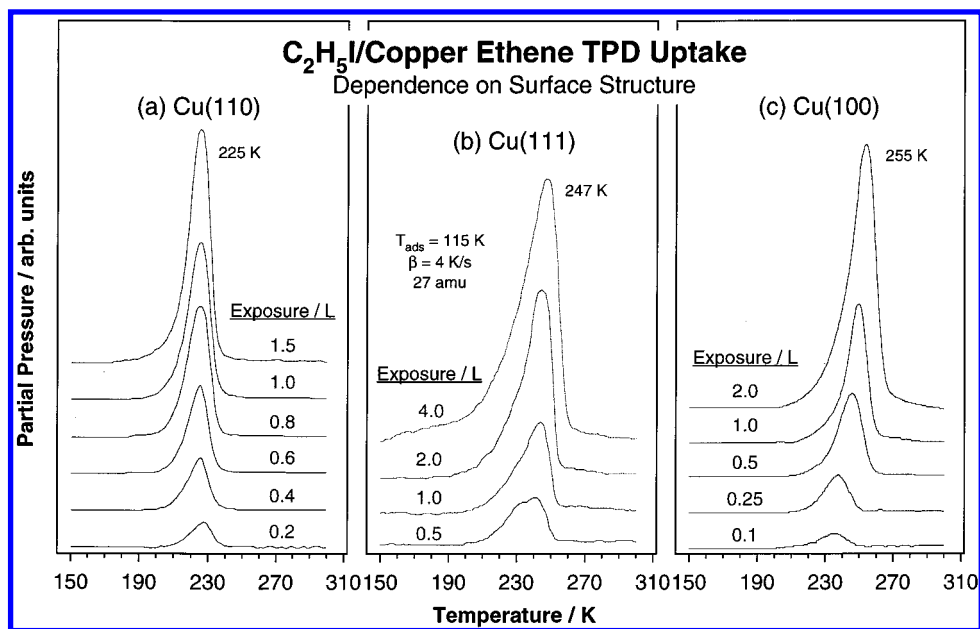
Figure 4. Ethylene TPD as a function of exposure for iodoethane adsorbed on Cu(110) (left), Cu(111) (center), and Cu(100) (right). Ethylene formation shifts to higher temperatures with increasing coverages in the Cu(111) and Cu(100) cases, presumably because of cage effects, but not on Cu(110). Cu(110) also promotes the β-hydride elimination step at lower temperatures.
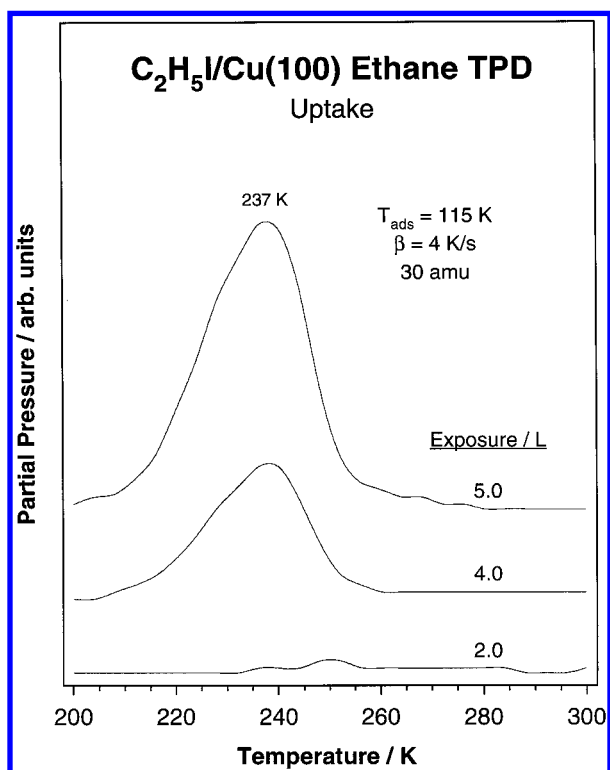

Figure 5. Ethane TPD as a function of exposure for iodoethane on Cu(100). Ethane is only produced after doses above 2.0 L and desorbs at about 237 K at saturation.

but no significant amounts of carbon are left behind on any of the three copper surfaces after heating above 300 K.

The relative carbon-containing product yields from decomposition of iodoethane on Cu(110) (left) and Cu(100) (right) are shown as a function of exposure in Figure 6. As stated before, ethylene production dominates at all coverages, but its importance is more marked at low surface concentrations. For instance, in the case of Cu(110), the ratio of ethylene to ethane produced after a 2.0 L iodoethane dose is 99:1, whereas the percentage of each product formed at 3.0 L is as follows: butane, 1%; iodoethane, 18%; ethylene (235 K desorption), 66%;

ethylene (390 K desorption), 12%; and ethane, 3%. Auger electron spectroscopy was used for absolute coverage calibration. It was determined that only iodine remains on the surface above 450 K and that the iodine atoms can be removed from the surface by annealing above 950 K. The density of iodine atoms left on the Cu(110) surface after saturation exposures of iodoethane was estimated to be 5×10^{13} iodine atoms/cm^2.[25,44] This represents a saturation coverage for iodoethane on Cu-(110) of only about 0.05 monolayers (ML), much less than the approximately 0.25 ML seen on Ni(100)[32,34] and Pt(111).[29] This value provides an absolute scale for the yields in Figure 6 (approximately the same iodoethane saturation coverage was assumed for both (110) and (100) surfaces).

The reversibility of β-hydride elimination on Cu(110) was probed next. This was done in two ways: (1) by coadsorbing ethylene with deuterium atoms on that copper surface and searching for deuterium incorporation in the desorbing hydrocarbon products and (2) by preparing mixed monolayers of iodoethane-d_0 and iodoethane-d_5 on Cu(110) and looking for isotopic scrambling in the ethylene that forms upon thermal activation. Neither approach, described in more detail below, produced any evidence for the kinetic reversibility of the β-H elimination reaction on Cu(110) under ultrahigh vacuum conditions, in contrast with the case of Cu(100), for which such reversibility was previously reported.[27]

The experiments with coadsorbed ethylene and deuterium were attempted first. Since the dissociative adsorption of molecular hydrogen on clean copper surfaces is an activated process,[45] the deuterium atoms were deposited on the surface by backfilling the chamber with D$_2$ and by using a hot tungsten filament to dissociate the molecules in front of the crystal, which was held at 115 K. It was determined that a 20 L of D$_2$ exposure (the amount used in our studies) leads to a D atomic coverage of roughly $^2/_3$ of saturation. The rational behind the ethylene + deuterium coadsorption studies is that if the rate of the single incorporation of surface hydrogen into ethylene to form ethyl moieties (the reverse of the β-H elimination reaction) is significant compared to the rate of ethylene desorption, then the formation of some deuterated ethylene (ethylene-d_1, 29 amu) should be detected. No evidence of this was obtained in our

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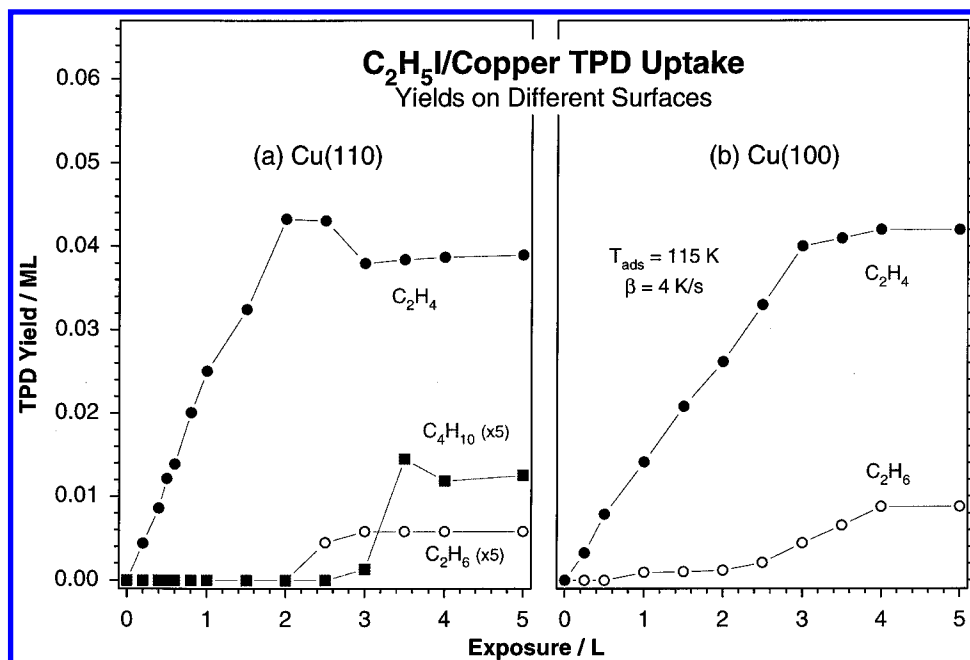*J. Phys. Chem. B, Vol. 104, No. 14, 2000* **3021**

Figure 6. TPD yields from iodoethane activation on Cu(110) (left) and Cu(100) (right) surfaces as a function of initial exposure. Absolute coverages were calculated by iodine Auger experiments, as mentioned in the text. Ethylene desorption dominates in both cases at all coverages, but detectable amounts of ethane are also produced after high doses. Hydrogenation to ethane is significantly more favorable in relative terms on Cu(100) than on Cu(110), but C−C coupling to butane is only seen on Cu(110).

studies (data not shown here but reported in ref 25). Note, however, that this experiment only probes the reversibility of β-hydride elimination up to ~180 K, the temperature at which ethylene desorbs.

To investigate the reversibility of the β-H elimination reaction up to the temperature at which the forward reaction proceeds (220 K), additional TPD studies were performed using a 1:1 mixture of iodoethane-d_0 and iodoethane-d_5. In this case, the reversibility of the β-hydride elimination step should become evident either by deuterium incorporation in the adsorbed C_2H_4 that results from initial dehydrogenation of C_2H_5I or by hydrogen incorporation in the C_2D_4 from C_2D_5I. On the basis of the cracking pattern of the different deuterated ethylenes,[46] 29 and 31 amu were chosen in our experiments to follow the potential formation of C_2H_3D and C_2D_3H, respectively. Once again, no evidence for isotope crossover was obtained in these experiments (Figure 7). Specifically, there is no production of either monodeuterioethylene from iodoethane-d_0 or trideuterioethylene from iodoethane-d_5 on the surface dosed with the isotopic mixture. In other words, the top trace in Figure 7, the TPD for the 1:1 mixture, can be entirely accounted for by the chemistry of the two individual compounds illustrated in the bottom and middle traces. This indicates that β-hydride elimination is effectively irreversible on Cu(110) under ultrahigh vacuum conditions. One other thing that becomes clear from the data in Figure 7 is that there is a marked kinetic isotope effect in the β-hydride elimination reaction: the removal of deuterium atoms occurs at 233 K, a temperature about 15 K higher than that of normal hydrogen.

3.3. Other Iodoalkanes. The thermal chemistry of heavier iodoalkanes on copper surfaces was briefly probed here as well. In general, the chemistry observed on Cu(110) surfaces matches qualitatively that seen on Cu(100)[47] and Cu(111),[43] and also that reported for other metals.[16,33,34,48,49] In particular, the dominant decomposition reaction is (when possible) β-hydride elimination. A summary of the TPD yields from activation of iodoethane, 1-iodopropane, and 1-iodobutane on Cu(110) at saturation are provided in Table 1, and the desorption traces
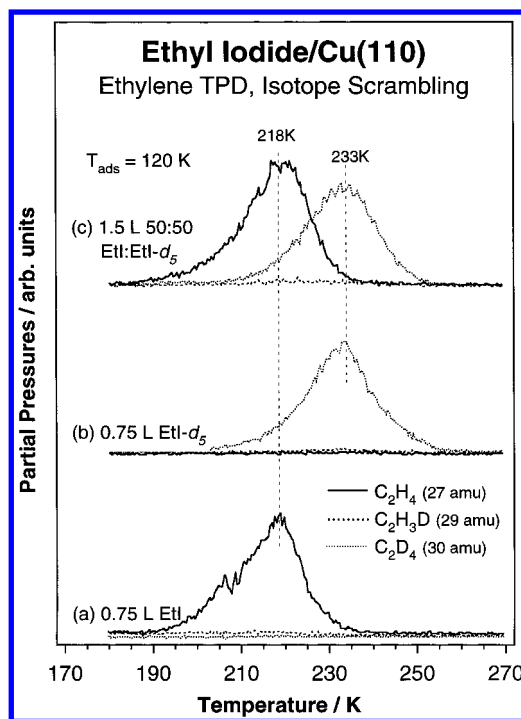

Figure 7. (top) Ethylene TPD from a 1:1 normal + perdeutero iodoethane mixture on Cu(110), used to test the reversibility of the β-hydride elimination step. The 27, 29, and 30 amu signals were used to identify C_2H_4, C_2H_3D, and C_2D_4 desorption, respectively. The traces from experiments with pure iodoethanes-d_0 and -d_5 are shown in the bottom and middle sections, respectively, for reference. The lack of formation of mixed-isotope ethylenes in the experiments with the mixture attests to the absence of any ethylene rehydrogenation.

for propylene and butene from thermal activation of 1-iodopropane and 1-iodobutane on Cu(110), respectively, are shown as a function of exposure in Figure 8. With both 1-iodopropane and 1-iodobutane, the desorption of the olefin shifts toward higher temperatures as the surface coverage is increased. In the case of 1-iodobutane, one single peak is seen in all cases, skewed

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TABLE 1: Relative Yields for the Hydrocarbon Produced by Thermal Activation of Iodoethane, 1-Iodopropane, and 1-Iodobutane on Cu(110) at Saturation Coverages

	yield (%)		
	iodoethane	1-iodopropane	1-iodobutane
alkene	78	79	73
alkane (hydrogenation)	3	1	9
alkane (C–C coupling)	1	2	0
molecular desorption	18	18	17

toward the low-temperature side, and peaking at a temperature whose maximum goes from 225 K after a 1.0 L dose to 245 K at saturation (5.0 L). The case of 1-iodopropane is a bit more complex, since there seem to be two features in the spectra for the middle doses. The main feature shifts gradually to higher temperatures, from 200 K at 2.0 L to 221 K after a 6.0 L dose, and a second peak grows above 3.0 L and goes from a maximum at 220 K at that exposure to about 225 K at saturation. It is worth remembering that in the case of iodoethane there is only one symmetrical ethylene TPD peak which does not shift with coverage.

Finally, the regioselectivity of the β-hydride elimination step was probed by TPD studies with 2-iodohexane. The main frame of Figure 9 displays the hexene TPD traces obtained for the 2-iodohexane/Cu(100) system as a function of initial dose. One peak appears around 265 K at exposures as low as 0.75 L that grows and shifts to higher temperatures until saturating about 2.0 L. A second feature starts to grow at 200 K above 1.0 L doses and dominates the spectra at higher coverages. The identity of this olefin as 2-hexene was made with the aid of the cracking patterns of 1- and 2-hexenes taken with our same mass spectrometer. The inset of Figure 9 compares the relative signal intensities of those two olefins against the integrated intensities of the desorption peaks from the TPD experiments with 2-iodohexane for a number of selected fragment masses. Notice in particular the large discrepancy in the 56/55 amu ratio between the TPD data and the mass spectrum of 1-hexene.
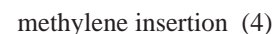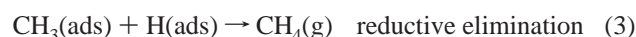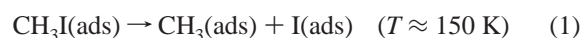
4. Discussion

4.1. General. The chemistry of alkyl iodides on copper surfaces reported here displays the general behavior seen on other alkyl halide/transition metal systems.[15,16,22,23] Specifically, most alkyl halides adsorb molecularly at low temperatures but decompose via a carbon–halide bond scission step around 120–160 K to form surface alkyl groups. Further thermal activation of the resulting alkyl moieties proceeds mainly via β-hydride elimination to the corresponding olefin. Reductive elimination steps, either hydrogen incorporation to the alkane or, as in other late transition metals, C–C coupling to form the dimer, compete to some extent. A more detailed discussion of these issues follows.

4.2. Iodomethane Thermal Chemistry. Iodomethane is unique among the alkyl iodides studied here in that it only contains α-hydrogens. Since α-hydride elimination is considerably slower than β-hydride elimination,[21] methyl groups are particularly stable on metal surfaces. On copper (as on many other metals), the dissociation of the C–I bond in adsorbed alkyl iodides, iodomethane included, takes place about 150 K and yields alkyl surface groups;[35,43,50] the resulting methyl species are then stable to temperatures of 400 K or higher. It has been determined that methyl decomposition on copper surfaces is limited by its first dehydrogenation step.[36]

As mentioned in the Results section, methane and ethylene production from methyl iodide on copper follow the same kinetic behavior, which is to say that they share the same rate-limiting step. Furthermore, the CH_4 and C_2H_4 TPD peaks appear at approximately the same temperature for all methyl iodide coverages, a strong indication of first-order kinetics. All this is consistent with our previous proposal that the production of methane and ethylene are both initiated by a rate-limiting (rls) α-hydride elimination step to methylene. Interestingly, it appears that subsequent ethylene formation is achieved not by the direct coupling of two methylene species, but by methylene insertion into a copper–methyl bond followed by β-hydride elimination of the resulting ethyl moiety.[36] The overall mechanism for these reactions can be summarized as follows:

$$CH_3I(ads) \rightarrow CH_3(ads) + I(ads) \quad (T \approx 150 \text{ K}) \quad (1)$$

$$CH_3(ads) \rightarrow CH_2(ads) + H(ads)$$
$$\alpha\text{-hydride elimination, rls } (T \approx 460 \text{ K}) \quad (2)$$

$$CH_3(ads) + H(ads) \rightarrow CH_4(g) \quad \text{reductive elimination} \quad (3)$$

$$CH_3(ads) + CH_2(ads) \rightarrow CH_3CH_2(ads)$$
$$\text{methylene insertion} \quad (4)$$

$$CH_3CH_2(ads) \rightarrow CH_2=CH_2(g) + H(ads)$$
$$\beta\text{-hydride elimination} \quad (5)$$

On the basis of the results shown in Figure 2, it can therefore be concluded that α-hydride elimination from methyl groups is approximately structure insensitive; that is, its rate is not affected significantly by the structural details of the copper surface. This could be understood at least in part by realizing that such a dehydrogenation step is unimolecular and may therefore require a small ensemble of metal atoms. It is tempting to suggest based on this result that the methyl groups coordinate to one single copper atom on all three surfaces, hence the insensitivity of its decomposition to the structure of its immediate surrounding. However, the low values of the metal–methyl stretching frequency (370 cm^{-1}) obtained by high-resolution electron energy loss experiments[38,39] suggest a nested adsorption geometry in three- or four-fold hollow sites instead. It is also not clear how methane and ethylene formation can follow similar kinetics on all (100), (110), and (111) surfaces but be strongly affected either by the coverages of the surface species or by the presence of coadsorbed iodine.[51] This latter effect has been previously explained in terms of the need for an additional adsorption site to accommodate the salient hydrogen atom, but that argument should also apply to changes in surface structure. More research is needed to settle this issue.

Ethane formation from methyl iodide on copper surfaces probes another family of elementary steps for chemisorbed alkyl groups, namely, alkyl (methyl) coupling. The lower temperatures at which ethane desorbs compared to those needed for methane or ethylene production provides an indication of the facile nature of the former reaction relative to the latter. The shifts in the C_2H_6 TPD peaks toward lower temperatures and their increase in relative yield with increasing coverage are also expected given the second-order nature of the coupling step. What is somewhat surprising is the significant difference seen for this reaction on Cu(110) as compared with either Cu(100) or Cu(111). In particular, ethane desorption at saturation is seen about 400 K on the former surface, but only above 440 K in the latter. This represents a difference of about 2 orders of magnitude in reaction rate. In addition, the coverage dependence is the most dramatic on the (110) surface, where the ethane TPD peak maximum shifts from about 450 K at 1.25 L to 400 K after a 3.0 L dose,
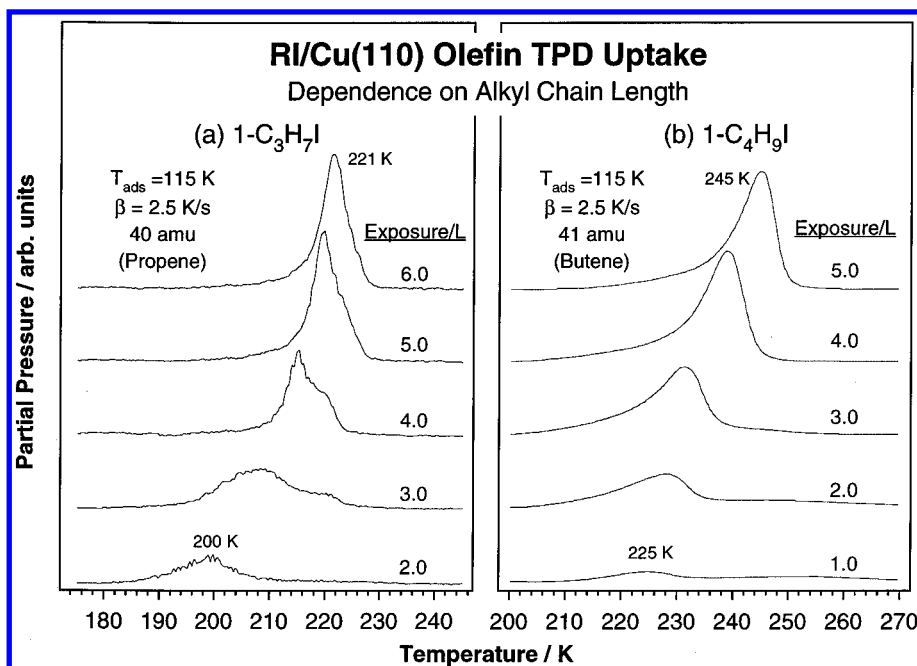
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Figure 8. Alkene TPD from 1-iodopropane (left) and 1-iodobutane (right) on Cu(110) as a function of initial exposure. The TPD peak maxima shift to higher temperatures with increasing dose in both cases, but propylene desorption from 1-iodopropane peaks somewhere between 200 and 221 K depending on coverage, while butene production maximizes between 225 and 245 K. Also, propylene desorption displays a more complex behavior, with a second peak that starts about 220 K at 3.0 L and slowly merges with the main feature at saturation.
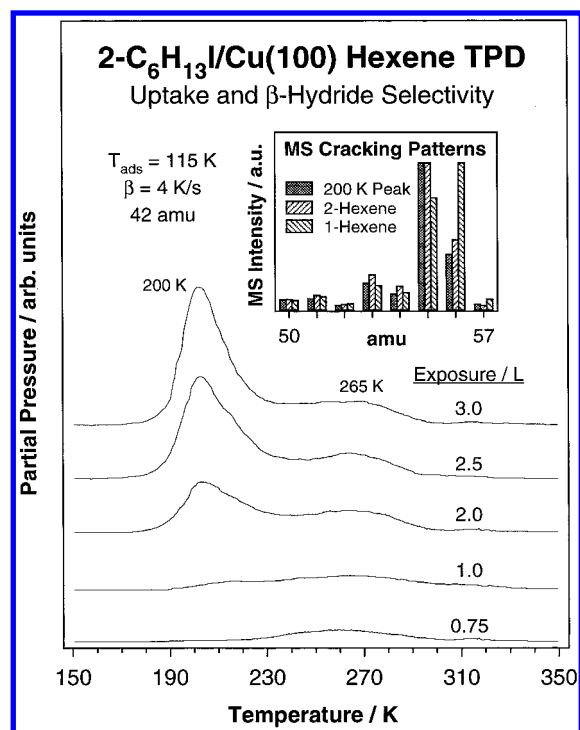

Figure 9. Hexene TPD traces from 2-iodohexane on Cu(100) as a function of initial exposure. Hexene from β-hydride elimination is produced in two stages, one around 265 K at all coverages and a second at 200 K which develops after exposures above 1.0 L. The identity of the desorbing product was determined to be 2-hexene by comparison with the cracking patterns of the 1- and 2-hexene isomers in our mass spectrometer, as shown in the inset. This result attests to the preference for the formation of olefins with internal double bonds.

a 50 K temperature difference; the same change only results in a shift of less than 20 K on Cu(100).

The observations discussed in the previous paragraph attest to the strong dependence of alkyl coupling reactions on surface structure, in particular to the significant ease with which they occur on open surfaces such as Cu(110). It is interesting to notice that this trend is paralleled by β-hydride elimination reactions, which are also slightly more favorable on Cu(110), but is the exact opposite to that seen for methylene insertion reactions, which are about 2 orders of magnitude *slower* on Cu(110) versus either Cu(100)[38] or Cu(111).[39] It is not clear at present why methyl coupling displays a structure sensitivity opposite to that of methylene coupling.

To the best of our knowledge, previous studies on the structure sensitivity of the conversion of adsorbed methyl iodide has only been carried out for nickel.[52-54] Only methane and hydrogen are seen to evolve from that surface; no coupling or insertion steps are ever observed there. The conversion of methyl groups also occurs at much lower temperatures, because nickel is particularly efficient for the promotion of dehydrogenation reactions.[6,21] On Ni(100), methane is formed around 250 K by an initial rate-limiting α-hydride elimination step, the same as on copper.[52,53] The chemistry on Ni(111) is quite similar, except that methane desorption is detected at a slightly higher temperature, about 260 K, and only starts after exposures of 2.0 L or more.[54] This order is the reverse from that seen on copper, where methane formation on the (111) plane maximizes at about 10 K *lower* than on the (100) surface, but, as mentioned above, this difference may not be significant in light of the larger effects exerted by changes in coverage or iodine coadsorption. Also, no significant shifts in the peak maximum are seen as a function of coverage in either nickel crystal, implying the same first-order kinetic nature of the α-elimination step observed on copper. On the other hand, it is clear that methylene species are not stable on nickel.[55] Methylene does form on Pt(111),[56] but interconverts reversibly to methyl and methylidyne until rehydrogenating to methane.[57-59]

4.2. Thermal Chemistry of Ethyl Surface Groups. As in the case of iodomethane, heating adsorbed iodoethane on copper produces chemisorbed ethyl moieties below 200 K, and further temperature increases on those surfaces induce a number of ethyl conversion reactions. The extensive organometallic and surface

science literature available to date provides evidence for three main decomposition pathways: β-hydride elimination to ethylene, reductive elimination with surface hydrogen (hydrogenation) to ethane, and reductive coupling to *n*-butane.[15,16,22,34,60] All three reactions are observed on copper, ethylene production being the dominant path in all cases and under most conditions. β-Hydride elimination is known to take place exclusively during alkyl conversion chemistry on most metal surface,[21,31−34,42,61,62] but on coinage metals coupling becomes important,[63] competing with dehydrogenation steps on copper[36,64] and gold surfaces[65,66] and dominating completely on silver.[48]

The chemistry reported here for iodoethane on copper falls nicely within this previously reported trend, at least in a qualitative sense. As mentioned above, β-hydride elimination, reductive elimination, and coupling reactions are all observed on the three copper surfaces, with the first dominating the overall process. β-Hydride elimination from alkyl groups on Cu(110) occurs at ~220 K, i.e., with an activation energy of approximately 14 kcal/mol, a barrier comparable to that for β-hydride elimination on Pt(111),[22,31,67] Ni(100),[22,32,34] and Fe-(111).[68] This fact may appear surprising at first since copper is generally thought to be no good for processes involving C−H bonds, but is easily explained once it is realized that the lack of activity of copper catalysts for hydrocarbon conversion is only due to their inability to activate the original reactants (typically saturated hydrocarbons). Stable hydrocarbons such as paraffins interact quite weakly with copper ($\Delta H_{ads} < 10$ kcal/mol) and, as a result, desorb intact below the temperature required for any C−H bond scission. Alkyl groups bind much more strongly to copper (the Cu−C bond energy amounts to 33 ± 6 kcal/mol[16]) and thus remain on the surface up to the temperatures required for C−H bond activation. The binding energies of both reactants (alkyl groups) and products (alkenes and H atoms) on copper may be lower than those on other metals, but the two counteract each other so the reaction thermodynamics on Cu are comparable to those for β-H elimination on Pt and Fe, where $\Delta H_{rxn} \approx 7$ kcal/mol.[15,16]

In addition to β-hydride elimination, reductive elimination is feasible on copper surfaces as well. Two types of reactions are seen in connection with this, ethyl hydrogenation to ethane (reductive elimination of one ethyl group with surface hydrogen) and C−C coupling to butane (reductive elimination of two ethyl groups). Some similarities are seen here with the case of iodomethane. For one, reductive elimination products are only seen at high coverages; β-hydride elimination is observed after low iodoethane doses exclusively. Furthermore, the ethane TPD peak shifts to lower temperatures with increasing coverage (Figure 5), a behavior typical of second-order kinetics. Lastly, hydrogenation and coupling steps appear to display lower activation energies, and to occur at lower temperatures, than dehydrogenation reactions. For instance, ethane formation on Cu(100) peaks at 235 K, while ethylene formation on the same surface at comparable iodoethane coverages only starts about 255 K. A more dramatic example of this is that of butane versus ethylene production on Cu(111), which take place at 120 and 247 K, respectively.[69]

Another aspect of the chemistry of ethyl groups on copper relevant to our studies is that concerning the reversibility of the β-hydride elimination step. This was probed here on Cu-(110) by the experiments illustrated in Figure 7. First, it needs to be pointed out that ethylene desorption from iodoethane on copper is reaction limited; the C−I bond in ethyl iodide breaks at a much lower temperature (see above), and ethylene molecular desorption also occurs below 200 K.[51] This means that the

temperature of the ethylene desorption peaks reflect the kinetics of the β-hydride step from adsorbed ethyl species. The data in Figure 7 show that thermal activation of normal and perdeutero iodoethane mixtures only yield ethylene-d_0 and ethylene-d_4, a clear proof that no scrambling takes place between the two isotopically labelled reactants. This means that the hydrogen (deuterium) atoms released by β-hydride elimination from normal (perdeutero) ethyl species do not incorporate back into the resulting ethylene molecules, and consequently, that the dehydrogenation step is not reversible on this surface. In contrast, reversibility of that step does occur on Cu(100) (see below).

Figure 7 not only shows the lack of H−D exchange in ethyl and ethylene species adsorbed on Cu(110), but also points to a normal kinetic isotope effect for the β-hydride elimination step which manifests itself as a shift from 218 to 233 K. This kinetic isotope effect is quite large, amounting to a factor of almost 10 at 210 K, as seen directly from Figure 7 by measuring the relative heights of the TPD traces for C$_2$H$_5$I and C$_2$D$_5$I on Cu-(110) at that temperature. The larger than usual value of the ratio of the rates with H versus D can be explained by secondary isotope effects due to the negative ion character of the leaving hydride group in the β-hydride elimination step.[28]

4.3. Structure Sensitivity. As mentioned above, the chemistry of ethyl groups on copper is roughly that expected from the position of that metal in the periodic table. Nevertheless, there are interesting subtle differences in the details of the conversion of ethyl on Cu(110), Cu(111), and Cu(100) indicative of a structure sensitivity in at least some of the reactions mentioned above. In particular, there are clear differences in the relative yields from ethyl iodide conversion between the Cu(100) and Cu(110) surfaces: the relative yield for ethane formation on Cu(100) is 17% at saturation,[27] whereas on Cu-(110) it is only 3% (Figure 6). We believe that the larger extent of alkane production on Cu(100) reflects a difference in rates for the β-hydride elimination between the two surfaces. Indeed, β-hydride elimination is significantly slower on Cu(100), where ethylene formation is maximum at 255 K, than on Cu(110), where the ethylene evolution peaks at 225 K; this represents a difference of more than an order of magnitude in the reaction rate constant at any given temperature in that range. The Cu-(111) case seems to lie somewhere in between, since ethylene desorption from that surface is observed at an intermediate temperature of 245 K, although this comparison must be done with some caution, because the Cu(111) data correspond to studies with bromoethane (not iodoethane); the decomposition of the parent molecule in that case could take place on defect sites.[43]

When contrasting the conversion of ethyl iodide to ethylene among the different copper surfaces, it is also noticed that there is an apparent peak shift toward higher temperature on Cu(100) and Cu(111) with increasing iodoethane coverage which is not observed on Cu(110). A similar shift has been seen previously for iodobutane on Cu(110),[70] in which case it was explained by complex kinetics involving site blocking. In essence, this argument is based on the fact that β-hydride elimination may not be a first-order process, but it may require an additional empty surface site adjacent to that where the alkyl is coordinated to the surface in order to accommodate the leaving hydride. As the alkyl coverage is increased, more sites become unavailable and the reaction slows down. However, it is interesting to note that this effect is detected on a corrugated and more open Cu-(110) surface but not on the square closed-packed and atomically flat Cu(100). Electronic effects could also play a role in the

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changes in reactivity and selectivity seen here, since the work function of copper varies significantly with surface structure, from 4.48 eV on Cu(110) (atomic density = 1.08×10^{15} atoms/cm^2) to 4.59 eV on Cu(100) (1.53×10^{15} atoms/cm^2) and 4.98 eV on Cu(111) ($1.76 \cdot 10^{15}$ atoms/cm^2).[71] Clearly, there is a need for the determination of the specific coordination geometry of both the alkyl and olefin moieties to the surface atoms to resolve this issue.

As mentioned before, β-hydride elimination may dominate the thermal chemistry of alkyl groups on copper surfaces at low coverages, but it competes to some extent with reductive elimination and C−C coupling steps at saturation. Nevertheless, the yield of reductive elimination with coadsorbed hydrogen is always small, less than 10%. That may be justified at least in part by the low coverage of the co-reactant (H atoms), which needs to be produced by β-hydride elimination of the alkyl groups. Surprisingly, though, more ethane is produced on Cu-(100) than on Cu(110), although dehydrogenation on the former occurs at about 30 K higher temperature than on the former. Furthermore, notice that C−C coupling is also a minority path on all surfaces (nonexistent on Cu(100)), even though no hydrogen is needed there and even though the desorption temperature for the resulting alkyl dimer is quite low, below 150 K.[69] Given that both reductive elimination reactions (with hydrogen and via C−C coupling) are seen only at high coverages, the most likely explanation for their low yield is the second-order nature of the kinetics involved.

In addition to the changes in rate for the β-hydride elimination step from alkyl groups with changing surface structure, our previous discussion also points to a difference between the relative rates of ethylene desorption and its partial hydrogenation to ethyl groups, as manifested by the reversibility of the ethylene formation step seen on Cu(100)[27] but not on Cu(110). It is interesting to speculate about the reason for this. One possible explanation is that ethylene hydrogenation may occur with comparable rates on both surfaces, and that the differences are all due to differences in the rate of dehydrogenation. Notice that while β-hydride elimination from normal iodoethane peaks around 220 K on Cu(110) (Figures 4 and 7), it requires temperatures on the order of 250 K on Cu(100). Given the estimated 8 kcal/mol energy barrier for the incorporation of hydrogen on ethylene chemisorbed on Cu(100),[27] this 30 K temperature difference for ethyl dehydrogenation between the two surfaces amounts to approximately an order of magnitude difference in the rate of ethylene hydrogenation. Hence, the latter reaction is expected to not be important on Cu(110) (because of the low temperature of the ethylene production step), but to become quite relevant at the higher temperatures needed on Cu-(100).

The explanation provided above also helps understand the higher yield for ethane production on Cu(100), another reaction involving the incorporation of surface hydrogen atoms. Notice, however, that ethylene molecular desorption occurs at much lower temperatures on Cu(100) (120 K) than on Cu(110) (180 K).[25] This means that, for the H−D scrambling to occur on Cu(100), the rate of hydrogen incorporation on adsorbed ethylene (ethylene insertion into a metal−hydrogen bond, the reverse of β-hydride elimination) must be quite fast, since it needs to compete favorably against ethylene desorption. It could therefore be inferred that hydrogenation of ethylene to ethyl species may be faster on Cu(100) than on Cu(110). The slower ethyl β-hydride elimination and the faster ethylene hydrogenation on Cu(100) are related (the two steps being the reverse of each other) and work together to make H−D exchange possible.

One interesting aspect of alkyl halide conversion processes such as those addressed in this report is the role that the halide atoms play once they are liberated from the molecules and deposited onto the metal surface. An initial concern when alkyl halides were introduced as potential precursors for the preparation of alkyl surface intermediates was the potential effect that the halogen byproduct may have in modifying the electronic nature of the metallic surface.[22,23] Subsequent experiments using alternative methods of preparation of alkyl intermediates, however, have shown that this is not a serious problem, at least for the case of alkyl iodides.[15,16] There is still the issue of site blocking, which manifests itself in a particularly noticeable form when considering selectivities between unimolecular and bimolecular elementary steps.[59,70,72] The role of iodine site blocking in controlling surface reactions is in fact evident in the data reported here, since it is quite apparent that such effect is responsible, at least in part, for the low efficiency of some of the hydrogenation and C−C coupling steps. Finally, it is interesting to point out that halide atoms can facilitate atomic mobility and reconstruction on copper surfaces,[73] which means that the results of structure sensitivity studies done by changing the crystallographic orientation of the exposed surface of the metal (as we did here) need to be interpreted with some caution.

Finally, it may be informative to compare the structure sensitivity on copper reported in this paper with that seen before on gold surfaces. Alkyl iodides are less reactive on gold than on copper, so considerable molecular desorption is seen on the former metal.[65] Moreover, the alkyl groups resulting from the activation of the C−I bonds tend to follow coupling rather than dehydrogenation reactions. Previous work has already established that hydrogenation−dehydrogenation reactions in adsorbed alkyls are favored on most transition metals,[31,53,55,57,59,74] but that coupling becomes competitive on coinage metals, particularly on silver.[48] Nevertheless, the structure sensitivity seen on gold follows the same general trends than those observed on copper substrates. Specifically, while ethyl coupling to butane occurs at the same temperature (260 K) on both Au-(100)[66] and Au(111),[65] the formation of both ethylene and ethane (which are limited by the same β-hydride elimination step) occurs at 265 K on Au(111) but only at 310 K on Au(100). Again, the (100) surface seems to disfavor the dehydrogenation step.

4.4. Thermal Conversion of other Alkyl Groups. The effect of changing alkyl chain structure on reactivity was probed briefly. A more detailed study of this on Cu(100) surfaces has in fact been published by our group already.[47] Here, we investigated the reactions of iodomethane (Figure 1), iodoethane (Figure 4), 1-iodopropane (Figure 8, left), and 1-iodobutane (Figure 8, right) on Cu(110). β-Hydride elimination was found to dominate in all cases but iodomethane (where that step is not possible). The kinetics of desorption of the resulting olefin was also determined to be somewhat complex. For instance, the desorption maximum was seen to shift to higher temperatures with increasing coverages for 1-iodopropane and 1-iodobutane but not for iodoethane. Moreover, in the case of 1-iodopropane two peaks were seen in the propylene TPD at low coverages which converge toward saturation. A slight increase in temperature maximum was detected as the alkyl chain was made larger, from about 220−225 K for ethylene and propylene desorption from ethyl and propyl species, respectively, to approximately 245 K for the 1-iodobutane case. This dependence of dehydrogenation temperature on chain size is small, and displays a trend opposite to that reported for Cu(100).[47] However, it is dangerous to read much into these changes because of the significant peak

shifts in the TPD traces induced by varying coverages. Notice that there are no significant changes in relative yields among the different products as the chain size is increased (Table 1). An increase in activation energy for β-hydride elimination with chain size was also seen on Ni(100).[34]

Finally, the selectivity between internal and external hydride abstraction from alkyl chains was probed here via the identification of the isomer of hexene produced by thermal activation of 2-iodohexane on Cu(100). The nice aspect of the iodohexane case is that there are easy to identify differences between the mass spectrometer cracking patterns of 1- and 2-hexenes, the two products expected from β-hydride elimination in this system (Figure 9, inset). The TPD data shown in Figure 9 clearly indicate that only 2-hexene is produced from 2-hexyl surface groups on Cu(100). An analogous result for the case of 2-pentyl moieties was reported by our group before.[47] It appears that in this reaction the removal of internal hydrogens is highly favored, perhaps because of the higher thermodynamic stability of 2-alkenes relative to their 1-alkene counterparts.

4.5. Summary. Several aspects of the surface chemistry of alkyl groups on copper surfaces were highlighted by the study reported here. Special emphasis was placed on the role of surface structure on reactivity, but a few additional issues were addressed in terms of alkyl chain length and dehydrogenation regioselectivity. Below we provide a list of some of the key observations from this work.

(1) α-Hydride elimination reactions appear to be reasonably insensitive to the structure of the copper surfaces.

(2) Reductive elimination steps such as β-hydride elimination and C−C coupling, on the other hand, are significantly faster on more open surfaces; these reactions are much faster on Cu-(110) when compared with either Cu(100) or Cu(111).

(3) Methylene coupling display the opposite trend, namely, this reaction is a couple of orders of magnitude slower on Cu-(110) than on either Cu(100) or Cu(111).

(4) H−D scrambling within alkyl groups coadsorbed with atomic deuterium is feasible on Cu(100) but not on Cu(110). This is explained by a faster rate for olefin hydrogenation on the former surface.

(5) Ethylene molecular desorption is significantly faster on Cu(100) than on Cu(110).

(6) Alkyl chain length appears to have little or no effect on the rates of either reductive or β-hydride eliminations.

(7) β-Hydride elimination of internal hydrogen atoms is favored over the removal of those hydrogens at the end of the alkyl moieties (from the terminal methyl groups).

5. Conclusions

The dependence of the reactivity of adsorbed alkyl groups on the structure of copper surfaces was probed by comparing their behavior on Cu(100), Cu(110), and Cu(111) single crystals. Temperature-programmed desorption experiments with io-domethane indicated that there is only a small change in reaction rate for α-hydride elimination steps with changing surface structure; methane and ethylene are both produced between 460 and 470 K on all three surfaces. C−C coupling to ethane, on the other hand, appears to be facilitated by the more open Cu-(110) surface. For the case of larger alkyl chains, β-hydride elimination dominates the chemistry on all three copper surfaces, but a structure sensitivity of that step is again evident by the changes in relative yields for ethylene and ethane as well as by the significant isotope scrambling in the resulting ethylene on Cu(100) not viable on Cu(110). Carbon−carbon coupling is seen on Cu(110), but not on Cu(100), at high coverages; as with

methyl groups, C−C bond formation is enhanced by open surface structures. Finally, the preferential extraction of internal hydrogens during the dehydrogenation of alkyl surface groups was proven by the selective formation of 2-hexene from 2-iodohexane on Cu(100).

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