Reaction of Cyclopropane, Methylcyclopropane, and Propylene with Hydrogen on the (111) and (110)-(1×2) Surfaces of Iridium

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The hydrogenation, isomerization, and hydrogenolysis of cyclopropane, methylcyclopropane, and propylene have been investigated on the (111) and (110)-(1×2) single-crystalline surfaces of iridium at reactant partial pressures from 0.4 to 10 Torr of hydrogen ($P_H$) and between 20 and 500 Torr of hydrogen ($P_H$) and at surface temperatures from 375 to 700 K. Both the kinetics of the reaction (activation energies and preexponential factors) and the dependences of the rates of reaction on the reactant partial pressures (apparent reaction orders) were examined in detail. Postreaction surface analysis revealed the presence of a carbonaceous residue, the coverage of which was found to vary with the reaction conditions. The reaction of cyclopropane and hydrogen resulted in both hydrogenation to propane and the hydrogenolysis to methane and ethane, with the hydrogenation channel dominating for temperatures below 500 K. The Ir(110)-(1×2) surface was found to be more active than the (111) surface for both the hydrogenation and the hydrogenolysis of cyclopropane. In both cases, the specific activity (per metal surface atom basis) on Ir(110)-(1×2) was greater by a factor between approximately 2 and 10. The hydrogenation of methylcyclopropane on both the Ir(111) and Ir(110)-(1×2) surfaces was found to be dominated by the production of n-butane. This result was interpreted qualitatively by invoking parallel reaction mechanisms for the production of n-butane and isobutane, with the n-butane channel exhibiting a higher apparent activation energy, thus, dominating at the higher temperatures. The hydrogenolysis of methylcyclopropane was found to be similar to that of cyclopropane on both surfaces. However, a selectivity difference was observed between the two surfaces for hydrogenolysis, the product distributions for the major reaction channels were CH$_4$ + C$_2$H$_6$ on Ir(111) and CH$_4$ + C$_3$H$_8$ + C$_2$H$_6$ on Ir(110)-(1×2). The absence of ethane in the major hydrogenolysis channel on the Ir(111) surface can be explained on a stereochemical basis if formation of the appropriate intermediate proceeds through an "edge complex", the formation of which is forbidden sterically on the Ir(111) surface. The Ir(110)-(1×2) surface was found to possess a greater specific activity compared to the Ir(111) surface for the hydrogenation of propylene.

I. Introduction

The reaction of cyclopropane with hydrogen on a variety of transition-metal surfaces has attracted considerable attention since, depending on the reaction conditions, two distinct reaction channels can be observed, namely, "hydrogenation" to form propane and "hydrogenolysis" to form methane and ethane.\(^1\)\(^-\)\(^13\) The hydrogenation pathway might be expected to exhibit some similarities to olefin hydrogenation, whereas the hydrogenolysis pathway might resemble alkane hydrogenolysis. Consequently, from an examination of a relatively simple product distribution (methane, ethane, and propane), two (presumably) fundamentally different reaction pathways can be investigated simultaneously. This idealized view of the two classes of reaction of cyclopropane with hydrogen ignores, however, the obvious differences between cyclopropane and both olefins and alkanes. Whereas evidence has been obtained for the existence of a "pπ-like" nondissociatively adsorbed cyclopropane complex at low temperatures,\(^14\) obviously C−C bond activation (ring-opening) must precede the hydrogenation step. Concerning the hydrogenolysis pathway, unlike alkenes, C−H bond activation in the parent cyclopropane molecule is generally irreversible (and most often preceded by C−C bond activation) as evidenced by the lack of significant exchange between cyclopropane and deuterium over late transition-metal surfaces.\(^15\)

The reaction of cyclopropane with hydrogen has been reported to be slightly "structure sensitive";\(^11\)\(^-\)\(^12\) i.e., the activity and/or selectivity have been found to vary with the morphology (dispersion) of the supported metal. For example, on silica-supported nickel catalysts of varying metallic particle size, the activity for both reaction pathways was found to reach a maximum value for crystallites with an average diameter of 12 Å.\(^12\) The specific activity (per site basis) for this particle size was approximately a factor of 3 greater than that observed with much larger crystallites of average diameters of ≥50 Å. Similar behavior was reported for both alumina- and silica-supported platinum catalysts.\(^11\) This sensitivity of the specific activity to the structure of the surface for supported catalysts has been corroborated by

(15) Deuteriocyclopropanes have been observed from the exchange of cyclopropane and deuterium on tungsten films at temperatures near 275 K.\(^8\) In fact, deuteriocyclopropanes were the major reaction products in this case. Deuterium exchange with the parent hydrocarbon has also been reported on supported rhodium, iridium, and platinum catalysts at temperatures near 375 K.\(^8\) Compared to both the tungsten films\(^8\) and the corresponding rates of propane production on these supported catalysts, the rates of exchange were considerably less on these group VIII metals, e.g., approximately 1% of the rate of propane production at 375 K.
Reaction of Cyclopropanes with H on Ir Surfaces

We have undertaken a fundamental examination of the role of surface structure in the reaction of cyclopropane with hydrogen on two different orientations of iridium single crystals, namely, the close-packed (111) and the corrugated (110)-(1X2) surfaces (cf. Figure 1). Primarily, we present here measurements of the reaction kinetics coupled with postreaction surface characterization via Auger electron spectroscopy. The clean Ir(110)-(1X2) surface reconstructs into a (1X2) superstructure, which contains a large fraction (25%) of low-coordination-number \( \text{C}_{7h} \) edge atoms, whereas a perfect (111) surface contains no such atoms. The (1X2) reconstruction is expected to be stable under reaction conditions, i.e., in the presence of adsorbed hydrocarbon residues and/or surface carbon and hydrogen.

We have considered also the reaction of both methycyclopropane and propylene with hydrogen on these two surfaces of iridium. The study of methycyclopropane provides a more detailed picture of the reaction mechanisms. For example, by examining the relative rates of \( n \)-butane and isobutane production as a function of reaction conditions, particular adsorbed intermediates of the hydrogenation reaction are suggested. On the other hand, the selectivity for the production of methane and propane versus (two molecules) of ethane suggests intermediates relevant to the hydrogenolysis reaction. Finally, the study of the hydrogenation of propylene is useful for a more complete understanding of the mechanism of the hydrogenation reaction of cyclopropane. For example, if both propylene and propane are produced from a common intermediate in the reaction of cyclopropane, a comparison to propylene hydrogenation may implicate the nature of the rate-limiting step (or steps); e.g., the rate-limiting step could involve either the rate of formation of this intermediate or the rate at which the intermediate is hydrogenated.

II. Experimental Procedures

The experiments reported here were performed in a high-pressure stainless steel reaction chamber (total volume \( \approx 600 \text{ cm}^3 \)) linked to an ultrahigh-vacuum (UHV) analysis chamber, similar to that described previously. The chambers, which are pumped separately, are connected by a metal valve, and the base pressure in both is \( 10^{-10} \text{ Torr} \). Facilities are available in the UHV analysis chamber for Auger electron spectroscopy, ion sputtering, and quadrupole mass spectrometry (UTI 100C). The catalyst samples are attached to a long-throw retraction bellows and can be translated vertically to various positions in either chamber. The single-crystalline catalysts of iridium (total surface area, \( \approx 1 \text{ cm}^2 \)) were mounted on tungsten wire leads and were heated resistively.

The temperature was controlled manually and was measured with a W/5% Re–W/26% Re thermocouple spot-welded to the crystal. The crystals were cleaned in the UHV analysis chamber by argon ion sputtering, heating in \( 5 \times 10^{-7} \text{ Torr} \) of oxygen at 700 K and annealing to 1600 K. Surface cleanliness was verified by Auger electron spectroscopy.

The cyclopropane (99.0%) and propylene (99.6%) employed in these experiments were research purity from Matheson. The methycyclopropane was ultrahigh purity (99.999%) from API Standard Reference Materials. The hydrogen was ultrahigh purity (99.999%). The hydrocarbons were purified further by degassing at 80 K, followed by triple distillation from a liquid pentane/solid pentane bath. Reaction products were detected by gas chromatography (GC), which, in this case, is superior to mass spectrometric detection (e.g., there are no complications due to the interpretation of fragmentation patterns). Absolute reaction rates (molecules·cm\(^{-2} \text{-s}^{-1} \)) were calculated by utilizing the measured volume of the reactor, the time of reaction (batch reactor kinetics), and the measured geometrical surface areas of the crystals. Specific rates (molecules·site\(^{-1} \text{-s}^{-1} \)) were calculated by using substrate densities of \( 1.57 \times 10^{15} \text{ cm}^{-2} \) and \( 1.93 \times 10^{13} \text{ cm}^{-2} \) for the (111) and (110)-(1X2) surfaces, respectively. The corresponding saturation coverages of hydrogen, commonly used to determine metallic surface areas of supported catalysts, are within ap-
TABLE I: Carbonaceous Residues following Reactions

<table>
<thead>
<tr>
<th>reactant</th>
<th>fractional carbon coverage, $\theta_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(111) Surface</td>
<td></td>
</tr>
<tr>
<td>cyclopropane</td>
<td>0.48 ± 0.08</td>
</tr>
<tr>
<td>methylecyclopropane</td>
<td>0.52 ± 0.10</td>
</tr>
<tr>
<td>Ir(110)-(1X2) Surface</td>
<td></td>
</tr>
<tr>
<td>cyclopropane</td>
<td>0.49 ± 0.11</td>
</tr>
<tr>
<td>methylecyclopropane</td>
<td>0.54 ± 0.09</td>
</tr>
</tbody>
</table>

*For $P_{H_2} = 100$ Torr. $P_{HC} = 2$ Torr, and $T = 375-700$ K.

Approximately 20% of these substrate densities in each case. However, it should be noted that, if, for example, either the low-coordination-number ($C_1$) or the high-coordination-number ($C_{111}$) surface atoms provide the only "active sites" for a particular reaction (cf. Figure 1), then this normalization will underestimate the specific rate for the Ir(111)-(1X2) surface by a factor of 4.

III. Results

A. Cyclopropane. 1. Ir(111) Surface. Specific rates (product molecules/site-s$^{-1}$) of the reaction of cyclopropane with hydrogen on the Ir(111) surface are shown in Figure 2, plotted in an Arrhenius form. The specific procedure in each case involved the following: reactivating the catalyst into the reaction chamber, filling the chamber with the reactants to the desired partial pressure, heating the catalyst to the desired temperature for the specific time period, cooling the catalyst to room temperature, pumping out the reactant/product mixture for analysis via GC, and then reactivating the catalyst in the UHV chamber for analysis via Auger electron spectroscopy. These data represent steady-state rates, as verified by measuring the total amount of product formed after various times of reaction, typically 50-2000 s, depending on the temperature. No induction periods were detected; i.e., the steady-states were achieved in reaction times <<50 s. To avoid secondary reactions and maintain approximately constant reactant partial pressures, conversions were restricted typically to below 1%. The "standard" reactant partial pressure ratio, $P_{H_2}/P_{HC}$, was 100/2, with a cyclopropane pressure of 2.0 Torr.

Postreaction surface characterization by Auger electron spectroscopy indicated the presence of a submonolayer carbonaceous residue, the fractional coverage of which was essentially independent of temperature ($T = 375-600$ K) for these reactant partial pressures. The measured value of the fractional coverage of carbon on the surface is given in Table I. Postreaction thermal desorption of the surface containing the carbonaceous residue produced only $H_2$, which gave a broad desorption feature from approximately 350 to 800 K, the dominant feature exhibiting a peak temperature of approximately 500 K (see text below and Figure 7). No attempts were made to determine the average stoichiometry ($C_{XH_y}$) of this carbonaceous residue, since it is not representative of the relevant adsorbed reaction intermediates under reaction conditions. This was demonstrated by returning the catalyst to the reaction chamber (after the reactants had been pumped away, maintaining the catalyst at room temperature) and reacting the carbonaceous residue with pure hydrogen at the relevant reaction temperatures. Methane was the only reaction product observed in all cases; i.e., no $C_2$ or $C_3$ products were produced. Moreover, the measured rate of methane production from this titration procedure was at least a factor of 10 smaller than that observed in the presence of 2 Torr of cyclopropane.

As may be seen in Figure 2, the only reaction products observed were methane, ethane, ethylene, propane, and propylene (total $C_3$ product refers to propane and propylene). The two major reaction channels at low temperatures ($T \leq 450$ K) are given by

- $c$-$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6$

i.e., the (dominant) hydrogenation pathway, and

- $c$-$C_3H_8 + 2H_2 \rightarrow CH_4 + C_2H_6$

i.e., the hydrogenolysis pathway. The similarities of the temperature dependence of the reaction rates suggest that the production of ethylene is associated with the hydrogenolysis pathway. It is immediately evident from Figure 2 that the apparent activation energy for the production of propane is much lower than that for the production of methane and ethane (and ethylene). In addition, for $T \leq 450$ K, the rate of hydrogenolysis exceeds that of hydrogenolysis by at least 1 order of magnitude. Extrapolating these rates to lower temperatures clarifies why the hydrogenolysis reaction was not observed on supported iridium catalysts at lower temperatures ($T \leq 375$ K).23,24 The apparent kinetic parameters obtained from the data shown in Figure 2 ($T \leq 450-500$ K) are given in Table II for the two major reaction channels. The apparent activation energy of 9.9 ± 1 kcal-mol$^{-1}$ observed here for the hydrogenation of cyclopropane agrees well with previous work on supported iridium catalysts, where values of 9.8–11.5 kcal-mol$^{-1}$ and 13 kcal-mol$^{-1}$ were obtained. Extrapolating the data of Sinfelt and co-workers24 obtained on a 10 wt % Ir silica-supported catalyst, to our reactant partial pressures and a temperature of 375 K, the predicted specific rate of hydrogenation (to propane) is 0.05 molecules/site-s$^{-1}$, which is in good agreement with the value of 0.017 molecules/site-s$^{-1}$ measured here on Ir(111).

As the temperature is increased above approximately 475 K, a number of changes in the reaction product distribution are observed. Whereas linear Arrhenius behavior is apparent with respect to the total $C_3$ production for temperatures up to approximately 550 K, the selectivity for propylene increases with increasing temperature. The linear Arrhenius behavior suggests that propylene and propane are formed from a common intermediate, whereas the increase in propylene ($T \leq 550$ K) production is best explained by a depletion in the steady-state coverage of hydrogen adatoms with increasing temperature. Above temperatures of approximately 500 K, the relative production of ethane and ethylene decreases, while the production of methane increases. The change in the selectivity of the hydrogenolysis pathway (i.e., $3CH_4 \rightarrow CH_2 = CH_2 + C_2H_6$) is not accompanied, however, by any change in the apparent reaction kinetics. This is evident in Figure 3, where the total rate of hydrogenolysis is plotted in an Arrhenius form in terms of cyclopropane conversion to $C_1$ and $C_3$ products. In particular, a least-squares fit of the data shown in Figure 3 results in, within experimental error, apparent rate parameters identical with those given in Table II (which were fit to $T \leq 500$ K); namely, $k_{app} \approx 1.1 \times 10^{10}$ molecules/site-s$^{-1}$ and $E_{app} \approx 27.3 \pm 2$ kcal-mol$^{-1}$. This observation is unlike that found for alkane hydrogenolysis, where concomitant with the increase in the selectivity for methane, a change was also observed in the apparent reaction kinetics.25 Thus, for cyclopropane, the rate-

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TABLE II: Apparent Rate Parameters* from the Ir(111) Surface

<table>
<thead>
<tr>
<th>temp range</th>
<th>$R(450K)^a$</th>
<th>$k_{app}^{045}$</th>
<th>$E_{app}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>molecules/site-s$^{-1}$</td>
<td>kcal-mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>375–450</td>
<td>0.16</td>
<td>1.0 $\times 10^{10.5}$</td>
<td>9.9 ± 1</td>
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<tr>
<td>400–500</td>
<td>6.8 $\times 10^{-3}$</td>
<td>5.4 $\times 10^{6}$</td>
<td>26.6 ± 2</td>
</tr>
<tr>
<td>375–475</td>
<td>0.92</td>
<td>3.9 $\times 10^{10}$</td>
<td>13.6 ± 1</td>
</tr>
<tr>
<td>375–450</td>
<td>1.1 $\times 10^{-2}$</td>
<td>6.6 $\times 10^{4}$</td>
<td>20.4 ± 2</td>
</tr>
<tr>
<td>425–600</td>
<td>1.0</td>
<td>0.8 $\times 10^{5}$</td>
<td>-0.2 ± 2</td>
</tr>
<tr>
<td>400–500</td>
<td>5.6 $\times 10^{-3}$</td>
<td>1.5 $\times 10^{5}$</td>
<td>23.8 ± 2</td>
</tr>
</tbody>
</table>

*Rate parameters were fit to the total conversion within the specified temperature range by utilizing the expression $R = k_{app}^{045} exp\left(-E_{app}/k_BT\right)$. Reactant partial pressures were 2.0 Torr of hydrogen and 100 Torr of hydrogen. Reaction rate is in terms of total conversion.
The dependence of the specific rates of reaction on the reactant partial pressures has been examined at two different temperatures. Data shown in Figure 4 where reaction rates were measured for variations in both the hydrogen and cyclopropane partial pressures, while maintaining a constant partial pressure of the other and a constant temperature of 450 K. This temperature corresponds to the onset of a detectable rate of propylene production (cf. Figure 2). As may be seen in Figure 4, with the possible exception of the data given by $P_{HC} = 2.0$ Torr and $P_H = 20$ Torr, both decreasing the hydrogen partial pressure and increasing the hydrocarbon partial pressure lead to an increase in the rate of propylene production. Similar behavior is observed for the hydrogenolysis pathway insofar as the rate of ethylene production is concerned. These observations are consistent with a reaction mechanism in which hydrogen and cyclopropane effectively compete for the “same” adsorption sites; i.e., hydrogen adatoms can block the dissociative adsorption of cyclopropane and vice versa. Thus, increasing the temperature, decreasing the hydrogen partial pressure, and increasing the cyclopropane partial pressure act to deplete the steady-state coverage of hydrogen adatoms and, hence, shift the selectivity to the more dehydrogenated products, propylene and ethylene.

The apparent reaction "order" in $P_{HC}$ (i.e., the dependence of reaction rates on the reactant partial pressures) is approximately unity for cyclopropane partial pressures below 2.0 Torr and decreases somewhat at higher pressures for $T = 450$ K and $P_H = 100$ Torr. A maximum is observed with respect to the hydrogen partial pressure, the apparent order decreases from $-1$ to $-1/2$ as $P_H$ is increased for $T = 450$ K and $P_{HC} = 2.0$ Torr. A maximum in the rate of production of propane as a function of the partial pressure for the reaction of cyclopropane and hydrogen has been observed previously on supported iridium catalysts, consistent with our observations here. The $-1/2$ order in $P_{HC}$ for hydrogen partial pressures above 100 Torr is consistent with a mechanism involving competition between the reactants for adsorption sites; i.e., hydrogen is acting to block the adsorption of cyclopropane. The positive order in $P_H$ for pressures below 100 Torr suggests that the hydrogenation step is not rapid with respect to the overall rate of reaction. Similarly, since the total rate of $C_3$ production is a positive order in $P_{HC}$ in this pressure regime, if propane and propylene are formed from a common intermediate, it may be more dehydrogenated than propylene (e.g., a $C_2H_5(a)$ adsorbed species).

Alternatively, the positive order in $P_{HC}$ could involve accelerated removal of a “soft” carbonaceous residue by adsorbed hydrogen atoms, i.e., this residue acting to deplete the active surface area of the catalyst. We believe, however, that this is unlikely for the following reason. As discussed above, the adsorbed hydrogen concentration is depleted by both decreasing $P_{HC}$ and increasing $P_H$. Thus, the coverage of a soft carbonaceous residue would be expected to increase with increasing $P_{HC}$, which would lead to a negative order in $P_{HC}$. As may be seen in Figure 4, negative reaction orders in $P_{HC}$ are not observed for either reaction channel.

In contrast to the hydrogenation pathway, the total rate of hydrocarbon production (i.e., total conversion of cyclopropane to methane, ethane, and ethylene) is only weakly dependent on the reactant partial pressures at $T = 450$ K. The apparent order with respect to $P_{HC}$ is essentially zero, whereas that with respect to $P_H$ is nearly zero for $P_H \geq 100$ Torr and exhibits a small positive value for $P_H < 100$ Torr. These observations should be contrasted with those found for propane hydrogination, where, for $T \leq 500$ K, the reaction rates are approximately first order in hydrocarbon partial pressure and large negative order ($\leq -1/2$) in hydrogen partial pressure. The orders for alkane hydrogenolysis can be rationalized in terms of a pseudoequilibrium between the gas-phase hydride and an adsorbed, dehydrogenated parent hydrocarbon fragment and hydrogen adatoms. The behavior of the hydrogination pathway observed here suggests that this pseudoequilibrium does not occur for cyclopropane.

Rather, formation of the appropriate reaction intermediate is irreversible for cyclopropane.

The sensitivity of the specific rates of reaction on the reactant partial pressures is considerably different at higher temperatures where dramatic changes in the selectivity are observed (cf. Figure 2). This is reflected in the data that are shown in Figure 5, which were measured at a temperature of 575 K. We shall emphasize here the most notable feature of the data shown in Figure 5, i.e., the dramatic shift in the selectivity that is observed for $P_{HC}/P_H$

Figure 3. Specific rates of hydrogenolysis of cyclopropane on the Ir(111) surface, plotted in terms of cyclopropane conversion to methane, ethane, and ethylene. Hydrogenolysis conversion is equivalent to $1/2R_C + 1/3R_C$. The partial pressure of cyclopropane was 2.0 Torr, and that of hydrogen was 100 Torr.

Figure 4. Specific reaction rates for the reaction of cyclopropane and hydrogen on the Ir(111) surface at a temperature of 450 K. (a) The partial pressure of cyclopropane was maintained at 2.0 Torr as the partial pressure of hydrogen was varied. (b) The partial pressure of hydrogen was maintained at 100 Torr as the partial pressure of cyclopropane was varied.

suggests the high-coverage residue is extensively dehydrogenated and high-coverage residues are shown in Figure 1. The coverage of irreversibly bound hydrogen adatoms at 300 K decreases by 400 K. Integration of the spectra is a result of C-H bond cleavage.

Figure 5. Specific reaction rates for the reaction of cyclopropane and hydrogen on the Ir(111) surface at a temperature of 575 K. (a) The partial pressure of cyclopropane was maintained at 2.0 Torr as the partial pressure of hydrogen was varied. (b) The partial pressure of hydrogen was maintained at 100 Torr as the partial pressure of cyclopropane was varied.

< 50. This virtual step-function change in the selectivity from methane (hydrogenolysis) to propylene (isomerization) is accompanied by and probably a consequence of a nearly irreversible transformation in the coverage and/or structure of the carbonaceous residue. Postreaction surface characterization by Auger electron spectroscopy indicates that the fractional carbon coverage increases from a value of \( \theta_C \approx 0.46 \pm 0.1 \) to values of \( \theta_C \approx 0.8-1.0 \pm 0.1 \), as \( P_{H_2}/P_{HC} \) is reduced below a value of 50 at a temperature of 575 K. The specific values for the carbon coverage corresponding to the reaction conditions given by Figure 5 are shown in Figure 6a. The data of Figure 5 are also shown in Figure 6a where they are plotted in terms of a hydrogenation/isomerization (C_3) and a hydrogenolysis (C_1 and C_2) selectivity. Clearly, the hydrogenolysis pathway dominates on the "low"-carbon-coverage surface (\( \theta_C \approx 0.46 \)), whereas the hydrogenation/isomerization pathway dominates on the highly carbonized surface (\( \theta_C \approx 0.8-1.0 \)).

The cause of the selectivity shift may be understood better by considering the nature of the highly carbonized surface. The high-carbon-coverage residue is considerably less reactive to gas-phase hydrogen than the low-coverage residue. For example, reaction of the residue corresponding to \( \theta_C \approx 0.96 \) of Figure 6 with pure hydrogen (~100 Torr) for 300 s at 575 K reduced the carbon coverage by only 10%, whereas a similar treatment of the low-coverage residue produces essentially a clean surface. In addition, postreaction thermal desorption from the high-coverage residue (monitoring H_2) shows that it contains less hydrogen compared to the low-coverage residue. Thermal desorption spectra representative of the low- and high-coverage residues are shown in Figure 7. It is important to realize that the majority of the hydrogen desorbing in these spectra is a result of C-H bond cleavage. In particular, previous work examining H_2 on the clean Ir(111) surface indicates that the coverage of irreversibly bound hydrogen adatoms at 300 K is less than 0.1 monolayers. This hydrogen bound to the Ir metal surface desorbs completely by 400 K. Integration of the spectra shown in Figure 7 indicates that on a per-carbon-atom basis, the high-coverage residue contains approximately one-third of the hydrogen evolved from the low-coverage residue. This result suggests the high-coverage residue is extensively dehydrogenated with virtually all of the carbon atoms bound strongly to the surface.

The lower hydrogen content of the carbonaceous residue and its lower reactivity toward the hydrogen suggest that C-C bonds may be present in the high-coverage carbonaceous residue. However, we do not believe the formation of graphite is significant under these reaction conditions. For example, the density of carbon atoms on the basal plane of graphite is equal to 3.81 \times 10^{15} \text{ atoms cm}^{-2}, which would correspond to a fractional coverage of 2.43 monolayers on the Ir(111) surface. Thus, if graphite were formed at a mean coverage of 1.0 monolayers, it would exist in islands covering 41% of the Ir(111) surface. The most probable effect of this graphite overlayer on the reaction kinetics would be a reduction in the specific activity by a factor of 0.41; i.e., a variation in selectivity would be difficult to reconcile. Consequently, we submit that the high-coverage carbonaceous residue is most likely an uniformly dispersed adlayer consisting of carbon atoms and/or partially dissociated hydrocarbon fragments.
The strongly bound carbonaceous residue, approaching one monolayer in coverage, can be expected to perturb appreciably the ability of the metal surface to bind the relevant reaction intermediates. Although the carburized surface can be expected to lead to a lower steady-state concentration of hydrogen adatoms and, hence, an increase in the relative amount of unsaturated products (propylene), the proper explanation is not that simple. If the hydrogen adatom concentration is the sole cause of the observed behavior, then the selectivity shift should be from propane to ethane. This is not, however, the case. As the hydrogen atom concentration is increased above approximately 500 K, the hydrogenation pathway to form propane and the hydrogenolysis pathway to form methane and ethane is favored. The apparent rate parameters obtained from the data shown in Figure 8 (for $T \leq 475$ K) are given in Table III for the two major reaction channels.

The apparent activation energies observed for the (110)-(1x2) surface are very similar to, although somewhat smaller than, those observed on the (111) surface—the difference being approximately 1 kcal-mol$^{-1}$ for hydrogenation (i.e., on the order of the experimental uncertainty) and 3.5 kcal-mol$^{-1}$ for hydrocarbon conversion (cf. Tables II and III). In terms of absolute activities, at a temperature of 450 K, the (110)-(1x2) surface is more active than the (111) surface for both reaction channels by less than a factor of 4. (Note that this value is dependent on the particular site density chosen for the two surfaces.)

As in the case of the (111) surface, when the temperature is increased above approximately 500 K, the production of ethane decreases, while the production of methane increases. Note that the relative selectivity for ethane begins to decrease at a lower temperature on Ir(111), in agreement with results obtained previously concerning propane hydrogenolysis. Again, this change in the selectivity of the hydrogenolysis channel is not accompanied by any change in the apparent reaction kinetics. This is evident in Figure 9, where the total rate of hydrogenolysis is plotted in terms of cyclopropane conversion to $C_4$ and $C_5$ products. A least-squares fit of these data gives apparent rate parameters of $k_{H_2}^{C_5} = 1.3 \times 10^{10}$ molecules-site$^{-1}$-s$^{-1}$ and $E_{app} = 22.2 \pm 1$ kcal-mol$^{-1}$, identical with those given in Table III, which were fit to $T \leq 525$ K. The decrease in the selectivity for ethane is described best in this case also by an increasing probability of multiple carbon–carbon bond cleavage, due to the decreasing concentration of hydrogen adatoms as the temperature is increased.

The dependence of the specific rates of reaction on the reactant partial pressures has been examined at two different temperatures. Data are shown in Figure 10, for reaction rates measured at 425 K as a function of both the hydrogen and cyclopropane partial pressures, while maintaining a constant partial pressure of the other. Concerning the hydrogenation pathway, the apparent reaction order in $P_{HC}$ is essentially zero, whereas that in $P_{H_2}$ is nearly unity for $P_{H_2} \leq 200$ Torr and evidently becomes negative for hydrogen partial pressures above 200 Torr. As in the case of the Ir(111) surface, a maximum is observed in the rate of propane production as a function of the hydrogen partial pressure.

**Figure 8.** Specific reaction rates for the reaction of cyclopropane and hydrogen on the Ir(110)-(1x2) surface. The partial pressure of cyclopropane was 2.0 Torr, whereas that of hydrogen was 100 Torr.

**Table III: Apparent Rate Parameters$^4$ from the Ir(110)-(1x2) Surface**

<table>
<thead>
<tr>
<th>Temp range, K</th>
<th>$R$ (450 K)$^a$</th>
<th>$k_{app}$ (450 K)$^b$</th>
<th>$E_{app}$ (kcal-mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>375-450</td>
<td>$c$-C$_3$H$_6$ + H$_2$ → C$_3$H$_8$</td>
<td>0.54</td>
<td>7.8 $\times 10^{10}$</td>
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<tr>
<td>400-525</td>
<td>$c$-C$_3$H$_6$ + 2H$_2$ → CH$_4$ + C$_3$H$_4$</td>
<td>2.5 $\times 10^{-2}$</td>
<td>2.4 $\times 10^{-1}$</td>
</tr>
<tr>
<td>375-475</td>
<td>$c$-C$_3$H$_6$CH$_4$ + H$_2$ → $n$-C$<em>5$H$</em>{12}$</td>
<td>3.6</td>
<td>1.2 $\times 10^{-6}$</td>
</tr>
<tr>
<td>375-475</td>
<td>$c$-C$_3$H$_6$CH$_4$ + 2H$_2$ → CH$_4$ + C$_3$H$_4$ + C$_3$H$_6$</td>
<td>1.3 $\times 10^{-2}$</td>
<td>1.3 $\times 10^{-1}$</td>
</tr>
<tr>
<td>450-600</td>
<td>C$_3$H$_4$ + 2H$_2$ → CH$_4$ + C$_3$H$_4$ + (C$_3$H$_4$)</td>
<td>14</td>
<td>0.2 $\times 10^{-1}$</td>
</tr>
<tr>
<td>400-450</td>
<td>C$_3$H$_4$ + 2H$_2$ → CH$_4$ + C$_3$H$_4$ + (C$_3$H$_4$)</td>
<td>1.7 $\times 10^{-2}$</td>
<td>9.3 $\times 10^{-9}$</td>
</tr>
</tbody>
</table>

$^a$Rate parameters were fit to the total conversion within the specified temperature range by utilizing the expression $R = \frac{k_{app}}{T} \exp(-E_{app}/k_BT)$. Reactant partial pressures were 2.0 Torr of hydrocarbon and 100 Torr of hydrogen.$^b$ Reaction rate is in terms of total conversion.

The only reaction products observed on the Ir(110)-(1x2) surface were methane, ethane, and propane. In particular, no unsaturated hydrocarbons (e.g., ethylene or propylene) were produced, in contrast to the observations on the Ir(111) surface. As on Ir(111), the product distribution is described by two major reaction channels for temperatures below approximately 500 K: the hydrogenation pathway to form propane and the hydrogenolysis pathway to form methane and ethane. The apparent rate parameters obtained from the data shown in Figure 8 (for $T \leq 475$ K) are given in Table III for the two major reaction channels.

The apparent activation energies observed for the (110)-(1x2) surface are very similar to, although somewhat smaller than, those observed on the (111) surface—the difference being approximately 1 kcal-mol$^{-1}$ for hydrogenation (i.e., on the order of the experimental uncertainty) and 3.5 kcal-mol$^{-1}$ for hydrocarbon conversion (cf. Tables II and III). In terms of absolute activities, at a temperature of 450 K, the (110)-(1x2) surface is more active than the (111) surface for both reaction channels by less than a factor of 4. (Note that this value is dependent on the particular site density chosen for the two surfaces.)

As in the case of the (111) surface, when the temperature is increased above approximately 500 K, the production of ethane decreases, while the production of methane increases. Note that the relative selectivity for ethane begins to decrease at a lower temperature on Ir(111), in agreement with results obtained previously concerning propane hydrogenolysis. Again, this change in the selectivity of the hydrogenolysis channel is not accompanied by any change in the apparent reaction kinetics. This is evident in Figure 9, where the total rate of hydrogenolysis is plotted in terms of cyclopropane conversion to $C_4$ and $C_5$ products. A least-squares fit of these data gives apparent rate parameters of $k_{app}^{HC} = 1.3 \times 10^{10}$ molecules-site$^{-1}$-s$^{-1}$ and $E_{app} = 22.2 \pm 1$ kcal-mol$^{-1}$, identical with those given in Table III, which were fit to $T \leq 525$ K. The decrease in the selectivity for ethane is described best in this case also by an increasing probability of multiple carbon–carbon bond cleavage, due to the decreasing concentration of hydrogen adatoms as the temperature is increased.

The dependence of the specific rates of reaction on the reactant partial pressures has been examined at two different temperatures. Data are shown in Figure 10, for reaction rates measured at 425 K as a function of both the hydrogen and cyclopropane partial pressures, while maintaining a constant partial pressure of the other. Concerning the hydrogenation pathway, the apparent reaction order in $P_{HC}$ is essentially zero, whereas that in $P_{H_2}$ is nearly unity for $P_{H_2} \leq 200$ Torr and evidently becomes negative for hydrogen partial pressures above 200 Torr. As in the case of the Ir(111) surface, a maximum is observed in the rate of propane production as a function of the hydrogen partial pressure.
Concerning the hydrogenolysis pathway, the apparent reaction order in both $P_{HC}$ and $P_{H_2}$ is essentially zero, in agreement with the observations on Ir(111). The variation in the specific rates of reaction with respect to the reactant partial pressures differs considerably at the higher temperature of 600 K, as may be seen in Figure 11.

The onset of the selectivity shift observed on the Ir(111) surface at $(P_{H_2}/P_{HC} < 50)$ (cf. Figure 5) is apparent on the Ir(110)-(1×2) surface at $P_{H_2}/P_{HC} \leq 10$. As in the case of the Ir(111) surface, the shift is from methane (hydrogenolysis) to propylene (isomerization), as $P_{H_2}/P_{HC}$ is reduced sufficiently. Note, however, that on the Ir(110)-(1×2) surface the selectivity shift from methane to propylene is not complete even at $P_{H_2}/P_{HC} = 10$. That is, these data suggest that the selectivity shift will be complete only upon reducing the hydrogen-to-cyclopropane partial pressure ratio below 10, i.e., experimental conditions not considered here. Postreaction surface characterization by Auger electron spectroscopy indicated that for $P_{H_2}/P_{HC} \geq 25$, the fractional coverage of carbon was approximately constant at $\theta_C \approx 0.59 \pm 0.06$; whereas, for $P_{H_2} = 100$ Torr and $P_{HC} = 9$ Torr, the fractional coverage was $\theta_C = 0.72$ and, for $P_{H_2} = 21$ Torr and $P_{HC} = 2$ Torr, $\theta_C = 0.90$. The fact that this shift occurs on Ir(110)-(1×2) at lower hydrogen-to-hydrocarbon partial pressure ratios ($\sim 10$) compared to the Ir(111) surface ($\sim 50$) indicates that it is more difficult to carburize the (110)-(1×2) surface for this reactant mixture.

B. Methylcyclopropane. 1. Ir(111) Surface. Specific rates of the reaction of methylcyclopropane with hydrogen on the Ir(111) surface are shown in Figure 12 plotted in an Arrhenius form. Conversions were restricted to below 10%. The coverage of the
carbonaceous residue determined via postreaction surface characterization by Auger electron spectroscopy is given in Table I. The coverage of the residue was essentially independent of the reaction conditions considered here (Figure 12) and in text below (Figure 13), and its value is nearly equal to that observed for cyclopropane on this same surface at similar reaction conditions.

As may be seen in Figure 12, a variety of products are observed from the reaction of methylcyclopropane and hydrogen on the Ir(111) surface, namely, methane, ethane, ethylene, propane, propylene, isobutane, n-butane, and a mixture of 1- and 2-n-butenes. The production of isobutane cannot be ruled out due to overlap with the n-butane and 1- and 2-butenes chromatographic peaks. However, a conservative estimate places its rate of production below that of isobutane by 1 order of magnitude. The most notable feature of the data shown in Figure 12 is the predominance of the formation of n-butane (and 1- and 2-butenes) from the hydrogenation channel. The major hydrogenation/isomerization channel on the Ir(111) surface is given by

\[ \text{c-C}_3\text{H}_8 + \text{H}_2 \rightarrow n\text-C_4\text{H}_{10} \text{ or n-C}_4\text{H}_8 \]

whereas the major hydrolysis channel is given by

\[ \text{c-C}_3\text{H}_8 + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_6 \]

The corresponding minor reaction channels involve hydrogenation to isobutane and hydrolysis to ethane. Note that, at a temperature of 425 K, conversion of methylcyclopropane to (2 molecules of) ethane is approximately 1/15 th of that to methane and propane.

The apparent rate parameters obtained from the data shown in Figure 12 are given in Table II for the two major reaction channels. The parameters for the hydrogenation/isomerization pathway were fit to the total n-C_4 (n-butane and 1- and 2-n-butenes) production, whereas those for hydrolysis were fit to the rate of C_1 + C_2 production (methane, propane, and propylene). As with cyclopropane, the relative fraction of unsaturated products increases with increasing surface temperature, consistent with a depletion in the steady-state coverage of hydrogen adatoms as the temperature is increased.

It is of interest to compare our experimental observations (e.g., the large n-butane-to-isobutane selectivity) to previous work on group VIII metals. For example, for similar reaction partial pressures at temperatures near or below 273 K, isobutane has been found to be the major reaction product on both supported platinum (P_{HC} = 50 Torr and P_{H_2} = 50 Torr) and palladium, nickel, and platinum films (P_{HC} = 10 Torr and P_{H_2} = 100 Torr). Similar behavior has been reported for the hydrogenation of gem-dimethyldicyclopropane by several group VIII metal films and supported catalysts, i.e., the relative hydrogenation of gem-dimethyldicyclopropane. This apparent disagreement with the work reported here is readily understood by examining the temperature dependence of the selectivity for n-butane versus isobutane. In particular, the relative selectivity for n-butane increases with temperature, from a value of approximately 1/20 at 275 K to a value of nearly unity at 500–525 K. Our experimental data suggest an even greater temperature dependence of the relative selectivity for n-butane on iridium. Extrapolating our data shown in Figure 12 to lower temperatures indicates that the rates of n-butane and isobutane production should become equivalent at a temperature of approximately 300–325 K. In contrast, the relative selectivity for n-butane is approximately 10^3 at 500 K on Ir(111). The fact that the temperature for which the relative selectivity for n-butane and isobutane is nearly unity is apparently considerably lower for iridium compared to platinum, could be intrinsic, or could be due to differing reaction conditions between our work and previous investigations (e.g., as discussed below, the dependence of isobutane production on P_{HC} and possibly P_{H_2} differs from that for n-butane).

The dependence of the specific rates of reaction on the reactant partial pressures was examined at a temperature of 425 K. These data are shown in Figure 13. The apparent orders in P_{HC} and P_{H_2} are essentially zero with respect to the total production of n-C_4 molecules. Consistent with a decreasing fraction of n-butane production with increasing temperature, the apparent order in P_{HC} for n-butane is positive and is essentially equal to unity. The fact that at a similar temperature of 450 K the order in P_{HC} for the hydrogenation/isomerization of cyclopropane is larger (approximately unity) than that for methylcyclopropane (essentially zero) suggests that the adsorbed methylycyclopropane is bound more strongly to the surface and/or formed more easily (i.e., its coverage is nearer the saturation level, and, thus, the order in P_{HC} is nearly zero). With respect to the minor hydrogenation pathway (the production of isobutane), the order in P_{HC} varies between 1/2 and 1/2 as P_{HC} is increased, whereas the apparent order in P_{H_2} is approximately 1-1/2. Thus, the sensitivity (i.e., the apparent orders) of the two hydrogenation/isomerization pathways differ with respect to each other, suggesting that different intermediates may be involved. Concerning the major hydrogenolysis pathway (the formation of methane, propane, and propylene), the order in P_{H_2} is zero, whereas that in P_{HC} is nearly zero and exhibits a small positive value for P_{HC} < 50 Torr. These observations are consistent with those for cyclopropane hydrogenolysis on this surface where both orders were essentially zero.

2. Ir(110)-(1X2) Surface. Specific rates of the reaction of methylcyclopropane with hydrogen on the Ir(110)-(1X2) surface are shown in Figure 14, plotted in an Arrhenius form. Conversions were restricted to below 10%. The coverage of the carbonaceous residue following the reaction is given in Table I. The coverage of the residue was nearly independent of the reaction conditions considered here (Figure 14) and in text below (Figure 15), and its value is essentially identical with that observed for methylcyclopropane (essentially zero) on Ir(111). The fact that the temperature for which the relative selectivity for n-butane and isobutane is nearly unity is apparently considerably lower for iridium compared to platinum, could be intrinsic, or could be due to differing reaction conditions between our work and previous investigations (e.g., as discussed below, the dependence of isobutane production on P_{HC} and possibly P_{H_2} differs from that for n-butane).

The products observed on the Ir(110)-(1X2) surface were methane, ethane, propane, isobutane, n-butane, and a mixture of 1- and 2-butenes. Again, we estimate that the production of isobutane was smaller than that of isobutane by at least 1 order of magnitude. One additional reaction product, which could not be identified explicitly, was detected. On the basis of the experimental observation that, in the presence of the reaction product mixture and at 300 K, the disappearance of this product was correlated directly with the formation of the parent molecule, methylcyclopropane, we are in doubt, and we shall not discuss the formation of this product further except to note that its rate
n-butane begins to decrease at a higher temperature on the Ir(I10)-(1×2) surface. However, unlike the Ir(I111) surface, there is no dominant hydrogenolysis channel on Ir(I10)-(1×2). Rather, both the production of CH4 + C2H6 and 2C2H4 exhibit similar activities and (possibly fortuitously) similar apparent rate parameters. Recall that the production of CH4 and C2H6 was the dominant hydrogenolysis channel on the Ir(I111) surface.

The apparent rate parameters obtained from the data shown in Figure 14 are given in Table III for the two major reaction channels. The parameters for the hydrogenation/isomerization pathway were fit to the total conversion to n-C4, whereas those for hydrogenolysis were fit to the total rate of conversion to C1 + C2 + C3 products. Comparing the two surfaces for the reaction of methylcyclopropane at a temperature of 450 K, the activities for hydrogenolysis are essentially equivalent, whereas the specific rate of hydrogenation/isomerization is greater on the Ir(I110)-(1×2) surface by approximately a factor of 4.

The product distribution that is observed for the hydrogenolysis pathway on the Ir(I110)-(1×2) surface, i.e., equal amounts of methane, ethane, and propane, can be explained by the following argument. The products from the major reaction channel of hydrogenolysis result from the cleavage of two C–C bonds; i.e., first the ring is opened, and subsequently, a second C–C bond is cleaved in the resulting adsorbed complex, leaving two hydrocarbon “fragments”, which are hydrogenated [or desorbed for the unsaturated species on Ir(I111)] to the observed products. Considering a random scission of two C–C bonds in the parent methylcyclopropane molecule, restricting C–C bond cleavage to the ring carbons, there are three possible combinations; two result in the production of CH4 + C2H6, and one results in the production of 2C2H4. Thus, for a completely random cleavage of two C–C bonds in the methylcyclopropane ring, the expected product distribution is equal amounts of methane, ethane, and propane, exactly what is observed on the Ir(I110)-(1×2) surface. The fact that the production of ethane involves cleavage of the two C–C bonds adjacent to the methyl group and that this pathway is apparently a minor channel on Ir(I111) (i.e., the surface for which the metal surface atoms are relatively more coordinatively saturated) suggests that steric factors may be involved in the observed hydrogenolysis selectivity.

The dependence of the specific rates of reaction on the reactant partial pressures has been examined at a temperature of 425 K. These data are shown in Figure 15. With respect to the total production of n-C4 molecules, the apparent order in both PHC and PH2 are essentially zero. Consistent with a decreasing fraction of n-butane production with increasing temperature, the apparent order in PH2 for n-butane is positive. However, the apparent order in PHC is smaller on the (110)-(1×2) surface compared to the (111) surface for identical reaction conditions. With respect to the minor hydrogenation pathway (the production of isobutane), the order in PHC is between ~1 and ~1/2, whereas the apparent order in PH2 is approximately 1/2–1/3. Again, the differing apparent orders of the two hydrogenation/isomerization pathways suggest that different intermediates may be involved. Concerning the hydrogenolysis pathway, the orders in both PHC and PH2 are essentially zero for all the products observed, suggesting that in agreement with the apparent reaction kinetics, methane, ethane, and propane are formed from a similar intermediate.

C. Propylene. 1. Ir(I111) Surface. Steady-state rates of the reaction of propylene with hydrogen on the Ir(I111) surface are shown in Figure 16a, plotted in an Arrhenius form. Conversions were restricted to below 10%. The coverage of the carbonaceous residue corresponding to these reaction conditions is shown in Figure 16b. There is a significant increase in the coverage of the residue for temperatures above approximately 500 K; i.e., for $T \leq 500$ K, $\theta_c \approx 0.5 \pm 0.1$, whereas, for $T \geq 550$ K, $\theta_c \approx 1.0 \pm 0.1$. Postreaction thermal desorption of the near-monolayer coverage residue produced spectra similar to spectrum b in Figure 7. Note that, for identical reactant partial pressures, the coverage of the carbonaceous residue was independent of temperature for the reaction of cyclopropane on this surface.

The only reaction products observed on the Ir(I111) surface for the reaction conditions considered here were methane, ethylene, and propane. Two major reaction channels were ob-
Reaction of Cyclopropanes with H on Ir Surfaces

T, K

Propylene

$P_{\text{H}_2} = 100 \text{Torr}$

$P_{\text{H}_2} = 100 \text{Torr}$

Methane

Ethane

Ethylene

Propyne

Figure 16. (a) Specific reaction rates for the reaction of propylene and hydrogen on the Ir(111) surface. The partial pressure of propylene was 2.0 Torr, whereas that of hydrogen was 100 Torr. (b) The fractional surface coverage of the carbonaceous residue at the corresponding reaction conditions.

served: hydrogenation to propane and hydrogenolysis to methane and a mixture of ethane and ethylene, the relative selectivity for ethylene increasing with increasing temperature. Compared to cyclopropane on this surface at a temperature of 450 K, the rate of production of propane is approximately a factor of 7 more rapid from propylene, whereas the rate of hydrogenolysis is nearly equivalent for both reactants. The former observation suggests that if cyclopropane and propylene are hydrogenated to propane from a similar intermediate, then the rate of formation of this intermediate from cyclopropane must be less rapid than from propylene.

The specific rate of conversion via both the hydrogenation and hydrogenolysis channels was fit to an Arrhenius expression, and the resulting apparent rate parameters are given in Table II. The apparent activation energy of hydrogenation is nearly zero ($-0.2 \pm 2 $ kcal-mol$^{-1}$), whereas the corresponding apparent preexponential factor is equal to $0.8 \times 10^{64}$ molecules-site$^{-1}$-s$^{-1}$. The former value can be compared to that obtained by Mann and Lien$^{26}$ for a pumice-supported Ir catalyst where the apparent activation energy was found to be 15 kcal-mol$^{-1}$ for temperatures between 333 and 389 K and reactant partial pressures of $P_{\text{H}_2} = 30 \text{Torr}$ and $P_{\text{H}_2} = 60 \text{Torr}$. Unfortunately, these authors made no attempt to measure the surface area of the exposed Ir atoms, and therefore, we cannot compare either the apparent preexponential factors or the specific rates of reaction. On the other hand, the measured rate parameters for propylene hydrogenolysis are similar to those for cyclopropane hydrogenolysis. Unlike cyclopropane, nonlinear Arrhenius behavior is observed in the temperature range examined, $T \approx 400-600 \text{ K}$. The concomitant decrease in the apparent activation energy of hydrogenolysis and increase in the coverage of the carbonaceous residue for temperatures above 500 K suggest that these two events are related.

To obtain supporting evidence for the proposition involving the change in the coverage of the carbonaceous residue, reaction rates were measured as a function of the partial pressure of propylene at a constant partial pressure of hydrogen (100 Torr) and two

Figure 17. Specific reaction rates for the reaction of propylene and hydrogen on the Ir(111) surface at a temperature of 450 K. The partial pressure of hydrogen was maintained at 100 Torr as the partial pressure of propylene was varied.

Figure 18. (a) Specific reaction rates for the reaction of propylene and hydrogen on the Ir(111) surface at a temperature of 575 K. The partial pressure of hydrogen was maintained at 100 Torr as the partial pressure of propylene was varied. (b) The fractional coverage of the carbonaceous residue at the corresponding reaction conditions.

In contrast, as may be seen from Figure 18, as \( P_{H_2} / P_{HC} \) is increased above approximately 200–500 at a temperature of 575 K, there is a shift in both the coverage of the carbonaceous residue and the selectivity. Specifically, as \( P_{H_2} / P_{HC} \) is increased, the coverage of the residue is reduced by approximately a factor of 2, whereas the selectivity shifts from hydrogenation (propane) to hydrolysis (methylene). This behavior, i.e., a dramatic decrease in the hydrogenolysis selectivity on a highly carburized surface, is exactly what was observed for cyclopropane on Ir(111) as shown in Figure 6. The essential difference between these two reactants regarding these phenomena is that smaller partial pressure ratios \( P_{HC} / P_{H_2} \) are sufficient to lead to the highly carburized surface for propylene (~1/20) with respect to cyclopropane (~1/100). This is presumably due to the relative “ease” of chemisorption of propylene compared to cyclopropane.

2. \( \text{Ir}(110)-(1\times2) \) Surface. Steady-state rates of the reaction of propylene with hydrogen on the \( \text{Ir}(110)-(1\times2) \) surface are shown in Figure 19a, plotted in an Arrhenius form. Conversions were restricted to below 10%. The coverage of the carbonaceous residue corresponding to these reaction conditions is shown in Figure 19b. As in the case of the Ir(111) surface, there is a sharp increase in the coverage of the residue that occurs on \( \text{Ir}(110)-(1\times2) \) near a temperature of 550 K. The fact that this adlayer transformation occurs at a higher temperature on \( \text{Ir}(110)-(1\times2) \) implicates again a superior resistance to self-poisoning and carbonization of this surface.

The only reaction products observed for the reaction conditions considered here were methane, ethane, ethylene, and propane. The two major reaction channels were hydrogenation to propane and hydrolysis to methane and a mixture of ethane and ethylene, with the relative selectivity for ethylene increasing with increasing temperature. Compared to cyclopropane on this surface at a temperature of 450 K, the rate of production of propane is a factor of approximately 25 more rapid from propylene, whereas the rate of hydrolysis is nearly equivalent from both reactants. In comparison to propylene on Ir(111) at a temperature of 450 K, the rate of hydrogenation to propane is a factor of approximately 14 greater on the \( \text{Ir}(110)-(1\times2) \) surface, whereas the rate of hydrolysis is more rapid on \( \text{Ir}(110)-(1\times2) \) by approximately a factor of 3.

The specific rate of conversion via both the hydrogenation and hydrolysis channels was fit to an Arrhenius expression, and the resulting apparent rate parameters are given in Table III. Both the apparent activation energy (~3.6 ± 2 kcalmol\(^{-1}\)) and apparent preexponential factor (0.2 × 10\(^{10}\) molecules-site\(^{-1}\)s\(^{-1}\) of hydrogenation and similar to those found on the Ir(111) surface. The rate parameters for propylene hydrolysis compares well to those observed for cyclopropane hydrolysis on \( \text{Ir}(110)-(1\times2) \) and Ir(111) for propylene hydrolysis on Ir(111). In addition, as with the Ir(111) surface, the nonlinear Arrhenius behavior apparent above 500 K can be attributed to the increase in the coverage of the carbonaceous residue.

IV. Discussion

The hydrolysis of cyclopropane to propane has been reported to be slightly "structure-sensitive" on both supported nickel\(^{12}\) and platinum,\(^{13}\) in agreement with the results reported here for two different single-crystalline surfaces of iridium. In particular, the specific activity (for both hydrogenation and hydrolysis) of the \( \text{Ir}(110)-(1\times2) \) surface is greater than that of the Ir(111) surface, the ratio varying between a factor of 2 and 10. This difference in the specific activities is on the order of those reported previously for the supported nickel\(^{12}\) and platinum\(^{13}\) catalysts of varying particle size, where larger specific activities were found for the smaller particles. However, it is significantly less than that reported for the single-crystalline (111) and (100) surfaces of nickel,\(^{13}\) where, under similar reaction conditions, a difference of greater than 1 order of magnitude was found.

With respect to the experimental measurements reported here, the previous results on the supported nickel catalysts of varying metallic particle size are most suggestive. A specific activity (of hydrogenation and hydrolysis) was reported for catalysts with an average crystallite diameter of 12 Å that was a factor of 3 greater than that observed for much larger crystallites with average diameters greater than 50 Å. Previous work concerning the hydrolysis of \( \text{n-butane} \) on these same \( \text{Ir}(110)-(1\times2) \) and Ir(111) surfaces\(^{28}\) led us to compare the results for the iridium single crystals to supported iridium catalysts of varying particle size.\(^{29}\) In making this comparison, "effective particle sizes" were computed for the single-crystalline surfaces by utilizing the ratio of the number of edge (C\(_e\)) atoms to the number of \( \text{Ir}\) atoms (C\(_\text{Ir}\)) as the appropriate criterion (cf. Figure 1). Depending on the particular polyhedral chosen for the crystallite shape, the effective particle sizes are 13–24 Å for the \( \text{Ir}(110)-(1\times2) \) surface and 81–166 Å for the Ir(111) surface. (Utilizing the Ni–Ni lattice spacing, we find that the effective particle size for the \( \text{Ir}(110)-(1\times2) \) surface is 12–22 Å.) Thus, the results presented here [implicating a greater specific activity for the \( \text{Ir}(110)-(1\times2) \) surface] and those obtained on supported nickel catalysts [im-

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(a) Specific reaction rates for the reaction of propylene and hydrogen on the \( \text{Ir}(110)-(1\times2) \) surface. The partial pressure of propylene was 2.0 Torr, whereas that of hydrogen was 100 Torr. (b) The fractional surface coverage of the carbonaceous residue at the corresponding reaction conditions.

![Figure 19](image-url)
The results obtained for cyclopropane on the Ir(111) surface suggested that propane and propylene are formed from a common intermediate (cf. Figures 2 and 4). Although we have presented here only measurements of the reaction kinetics, i.e., direct spectroscopic evidence is lacking, we feel compelled to speculate as to possible reaction intermediates. For example, a reasonable structure for this intermediate is a 1,2-di-σ-bridged C3H6(a) species. However, the observation of a positive order in P3H for the total rate of C3 (propane and propylene) production can be rationalized if the common intermediate is more dehydrogenated than propylene, e.g., a C2H4(a) species. One species that is consistent with the C2H4 stoichiometry is a α-allyl. Addition of a hydrogen atom at the 1 or 3 positions of a α-allyl would produce either the aforementioned 1,2-di-σ-bridged C3H6 or a σ-bridged propylene. Additional hydrogenation would lead to propane, whereas desorption would lead to propylene, consistent with the observations on the Ir(111) surface. This interpretation is obviously not unique. However, there are precedents from organometallic chemistry that involve the reaction of transition-metal homogenous complexes with cyclopropane, which lead to the coordination of a α-allyl ligand, including an Ir(1) complex.36

The hydrogenolysis of cyclopropane to methane and ethene [and ethylene on Ir(111)] was found to be qualitatively different from the hydrogenolysis of propane. For example, over the entire range of temperatures considered on both surfaces (cf. Figures 3 and 9), there was no observable variation in the apparent reaction kinetics. This was corroborated by the lack of any significant variation in the apparent reaction "orders", the order in both PHc and P3H, being essentially zero. These observations can be interpreted by a reaction mechanism involving relatively facile formation of the adsorbed intermediate (i.e., the step that "opens" the ring), with the rate-limiting step being (secondary) C-C bond cleavage in the adsorbed intermediate [i.e., subsequent hydro-}

genation, desorption, and additional hydrogenolysis (i.e., C3 -→ 2C) are rapid with respect to C-C bond cleavage in the adsorbed intermediate]. The major difference between this mechanism and that proposed previously for propane (alkane) hydrogenolysis32 is that formation of the intermediate is both facile and irreversible for cyclopropane.

A reasonable reaction for the first (facile) step is the oxidative addition of cyclopropane to the Ir surface (i.e., ring-opening), forming a "1,3" di-σ-bonded C3H4 species. A likely candidate for the adsorbed species is a metallacycle butane since, for example, the most common route to synthesis of metallacyclic butanes in organometallic chemistry is the addition of cyclopropane to complexes of transition metals in low formal oxidation states.21

Of particular interest here, the fragmentation of metallacyclic butane ligands in homogeneous transition-metal complexes to form olefins and carbenes is well-known23 and, thus, provides an established mechanism for hydrogenolysis. The observation of the production of ethylene from the hydrogenolysis channel on Ir(111) suggests that a metallacycle butane is the dominant intermediate (and mechanism) for hydrogenolysis. The absence of the production of ethylene on Ir(110)-(1×2) (excepting the "severe" reaction conditions of Figure 11) does not necessarily suggest a different mechanism. Rather, it may be a manifestation of a greater specific activity for the hydrogenation of ethylene possessed by the Ir(110)-(1×2) surface.

The most significant result concerning the reaction of methylocyclopropane on these two iridium surfaces is the dominance of the production of n-butane (and 1- and 2-butenes) from the hydrogenation (isomerization) channel. This result can be interpreted qualitatively, as discussed in Section III.B.1, by considering two parallel reaction channels, with the production of n-butane exhibiting a higher apparent activation energy and preexponential factor. In this picture, the C3-C3 bond of methylocyclopropane is cleaved at low temperatures. This interpretation, of course, does not explain why n-butane production dominates at high temperatures. Clues as to the nature of the reaction mechanism that leads to the production of n-butane can be obtained by examining the specific cases for which a high selectivity for n-butane has been observed. For example, Anderson and Avery3 observed a product ratio n-C3H10/C2H6 of 2:1 from the reaction of methylocyclo-

propane with deuterium on tungsten films at temperatures of 290-310 K (P3H = 10 Torr and P3H = 100 Torr). Of particular interest, under identical reaction conditions, the major products were deuteriomethylcyclopropanes, where the exchange with the parent methylocyclopropane was limited to the "ring hydrogens". On the other hand, under similar reaction conditions on palladium, nickel, and platinum films (T = 210-270 K and identical P3H and P3H), the product ratio n-C3H10/C2H6 was always less than 1:10 and no exchange products were detected. Chevreau and Gault16 have reported similar results concerning the reactions of gem-dialkylcyclopropanes. For example, on tungsten films, the major reaction product from 1,1-dimethylcyclopropane was isopentane, and its relative rate of production (selectivity) increased with temperature; e.g., isopentane represented 80% of the products at 275 K and 98% at 575 K. These results suggest that, in cases for which C-H bond activation (apparently) precedes C-C bond activation,31 the ring opens adjacent to the most substituted carbon atom.

Gault and co-workers16 have also examined the reaction of 1,2-cis- and 1,2-trans-dimethylcyclopropanes with hydrogen on platinum, nickel, and palladium films at temperatures between 275 and 325 K (P3H = 5 Torr and P3H = 60 Torr). In all cases, isopentane was the major reaction product. However, n-pentane was detected, and its relative rate of production increased with increasing temperature. Most importantly, on platinum films the relative selectivity for n-pentane was approximately 20% from the cis isomer, whereas it was only 1% from the trans isomer. These results may be interpreted, as they have been recently,28 by invoking a "flat" adsorbed intermediate (or transition state), i.e., the plane of the ring being parallel to the metal surface, for the production of n-pentane, and "edge-on" dissociative adsorption [essentially that described above for metallacyclic butane formation11] for the production of isopentane. It is of interest to note that both of the mechanisms discussed here for the production of n-butane from methycyclopropane—C-H bond activation preceding (or concomitant with) C-C bond activation or a "flat" adsorbed intermediate—would appear to suggest the (eventual) participation of a α-allyl species in the hydrogenation channel.36

The selectivity difference observed between Ir(111) and Ir-

(110)-(1×2) for the hydrogenolysis of methylocyclopropane can be explained on the basis of structural considerations. The presence of propylene from the major (hydrogenolysis) reaction channel on Ir(111) suggests, as was the case for cyclopropane,

(33) C-H bond activation of cyclopropanes has been observed to precede C-C bond activation (i.e., ring-opening) with transition-metal homogeneous catalysts.14
(36) It is of interest to note that, on supported platinum catalysts,37 the major ring-opening products from the reaction of hydrogen (100 Torr) and methylene cyclopropane (50 Torr) have been found to be n-butane (at T = 290 K) and linear butenes (at T = 373 K). Thus, the high selectivity observed here for the production of n-butane and linear butenes from the reaction of methylocyclopropane and the aforementioned (see section III.B.2) possible production of methylocyclopropane would appear to be consistent with the suggestion that C-H (as well as C-C) bond activation is important in the hydrogenation channel.
the involvement of a metallycyclobutane in the hydrogenolysis channel. If the pathway to this intermediate involves an "edge complex," as has been discussed elsewhere,21 then the presence of the methyl group may provide a steric limitation as to the activation of the C-C bond. Since the presence of ethylene (or ethylidyne) from the hydrogenolysis of methylcyclopentane can only be described (for this mechanism) by the fragmentation of a metallycyclobutane that has been formed from the activation of the C-C bond, the selectivity observed for the hydrogenolysis channel should be decisive in determining if a steric limitation exists on such surfaces. In fact, the selectivity is quite different for the major reaction channels on the two surfaces—the product distribution is \( \text{CH}_4 + \text{CH}_3 \text{OH} \) on Ir(111), whereas it is \( \text{CH}_4 + \text{C}_2 \text{H}_6 + \text{C}_2 \text{H}_4 \) on Ir(110)-(1X2). This result can be interpreted readily by considering the stereochemistry of the two surfaces. In particular, an edge complex involving the C-C bond of metallycyclopropane and the C atoms of the Ir(111) surface is precluded by the presence of the methyl group, whereas an edge complex involving the C-C bond may be formed with the low-coordination-number C atoms, which are present (in significant concentrations) only on the Ir(110)-(1X2) surface. Consequently, the absence of ethane in the major hydrogenolysis channel on Ir(111) can be explained purely on a stereochemical basis. It is important to note that, as evidenced by the dominant production of \( n \)-butane, activation of the C-C bond does occur on Ir(111) for the hydrogenation/isomerization channel. The selectivity for hydrogenation of methylcyclopropane being essentially identical with that on the Ir(110)-(1X2) surface. This observation implies that on both surfaces the production of \( n \)-butane from metallycyclopropane does not involve an edge complex; rather, possibly the flat intermediate suggested above.

Finally, comments must be made concerning the apparent superior ability of the Ir(110)-(1X2) surface to hydrogenate surface carbon and/or hydrocarbon fragments. The experimental evidence for this superior ability includes the following observations:

(i) Unsaturated products (ethylene and propylene) are not observed from the reaction of cyclopropane and hydrogen on Ir(110)-(1X2) at the standard reactant partial pressures (\( P_{\text{H}} = 2.0 \text{Torr and } P_{\text{H}} = 100 \text{Torr} \)).

(ii) Higher partial pressure ratios, \( P_{\text{H}}/P_{\text{H}} \), are necessary to carburize the Ir(110)-(1X2) surface from the reaction of cyclopropane and hydrogen.

(iii) Unsaturated hydrogenation products (ethylene and propylene) are not observed from the reaction of methylecyclopropane and hydrogen on Ir(110)-(1X2) at the standard reactant partial pressures (\( P_{\text{H}} = 2.0 \text{Torr and } P_{\text{H}} = 100 \text{Torr} \)). In addition, for identical reaction conditions, the selectivity for \( n \)-butane (with respect to total \( \text{C}_n \text{H}_x \)) is greater on Ir(110)-(1X2).

(iv) The specific rate of hydrogenation of propylene is greater on the Ir(110)-(1X2) surface.

(v) The selectivity for ethylene from the reaction of propylene and hydrogen is greater on Ir(111). In addition, higher temperatures are necessary to carburize the Ir(110)-(1X2) surface for this reaction.

Independent measurements of the adsorption and desorption kinetics of hydrogen on the clean (111) and (110)-(1X2) surfaces of iridium have verified the presence of a higher binding energy adstate on the (110)-(1X2) surface.324 Thus, it might be expected that the hydrogen adatom concentration will be greater on the Ir(110)-(1X2) surface during the reactions reported here, and this could explain a greater rate of hydrogenation on the Ir(110)-(1X2) surface. It must be noted, however, that if one utilizes these clean surface values that describe the kinetics of adsorption and desorption,23,24 the coverage of hydrogen [with respect to vacant sites25] is calculated to be near the saturation level on both surfaces. On the other hand, if both surfaces are "saturated" with hydrogen adatoms, it is difficult to reconcile a positive reaction order for \( P_{\text{H}} \), which is observed for the reaction \( \text{C}_2 \text{H}_2 + \text{H}_2 \rightarrow \text{C}_2 \text{H}_4 \) on both Ir(111) (cf. Figures 4 and 5) and on Ir(110)-(1X2) at 600 K (cf. Figure 1). It is entirely possible that the carbonaceous residue (near a coverage of \( \theta_c \approx 0.5 \)) at the standard reactant partial pressures may perturb the binding energy of the hydrogen adatoms such that the hydrogen coverages are not near saturation, and, thus, do differ significantly. Alternatively, other more subtle effects may be involved. For example, it is also possible that the Ir(110)-(1X2) surface binds olefins more strongly than the Ir(111) surface such that the rate of desorption cannot compete with that of hydrogenation on the (110)-(1X2) surface.

Clues to the plausibility of the preceding arguments would be aided, for example, by a more complete study of the hydrogenation of propylene over the two surfaces, e.g., the apparent reaction orders in both \( P_{\text{H}} \) and \( P_{\text{H}} \). In particular, on Ir(111) and at \( T = 450 \text{ K} \), the reaction order in \( P_{\text{H}} \) is clearly positive, which suggests that the coverage of the adsorbed reaction intermediate [presumably 1,2-di-\( \pi \)-bonded \( \text{C}_2 \text{H}_4(a) \)] is not at this saturation value. Thus, the binding energy (heat of adsorption) of the \( \text{C}_2 \text{H}_4(a) \) species will manifest itself in the apparent reaction kinetics. If we apply the Horiiuti–Pollanyi mechanism,25,26 which describes the hydrogenation of ethylene, to the hydrogenation of propylene, the apparent activation energy will be given by

\[
E_a = E + \Delta H_{\text{ads}}(\delta) + \beta \Delta H_{\text{ads}}(\text{H})
\]

where \( E_a \) is the (negative) heat of adsorption of hydrogen, \( \delta \) is the order in \( P_{\text{H}} \), and \( \beta \Delta H_{\text{ads}}(\text{H}) \) is the (negative) heat of adsorption of propylene. This depends on the apparent reaction orders, the apparent activation energy can be negative, such as is observed here on Ir(110)-(1X2) (cf. Figure 19). Unfortunately, in the absence of a more complete data set, it is impossible to identify explicitly the cause for the different specific activities and apparent reaction kinetics (cf. Tables II and III) for the hydrogenation of propylene on the two iridium surfaces examined here.

V. Conclusions

The hydrogenation, isomerization, and hydrogenolysis of cyclopropane, methylecyclopropane, and propylene have been examined on the Ir(111) and Ir(110)-(1X2) surfaces. These two surfaces were chosen in order to evaluate the role of low-coordination-number metal surface atoms in these reactions. The (110)-(1X2) surface was found to be more active than the (111) surface for both the hydrogenation (to propane) and the hydrogenolysis (to methane and ethane) of cyclopropane. A comparison of these results to those reported previously for both supported nickel2 and platinum3 catalysts suggests that this activity difference could be due to a greater intrinsic activity of the low-coordination-number \( \text{C}_x \) metal surface atoms for these reactions.

Postreaction surface analysis revealed the presence of a carbonaceous residue, the coverage of which was found to vary with both the reaction conditions and the particular reaction (i.e., reactant) examined. For cyclopropane at the "standard" reactant partial pressures (\( P_{\text{H}} = 2.0 \text{Torr and } P_{\text{H}} = 100 \text{Torr} \)) and for temperatures between 400 and 600 K, the fractional coverage of the residue was essentially constant (\( \theta_c \approx 0.5 \)) on both surfaces. However, for temperatures near 575–600 K, as the partial pressure ratio \( P_{\text{H}}/P_{\text{H}} \) was increased sufficiently (>50 on Ir(111), >10 on Ir(110)-(1X2), the fractional coverage of the residue increased dramatically, approaching one monolayer. Concomitant with the transformation in the coverage of the carbonaceous residue, the selectivity of the reaction of cyclopropane and hydrogen was found to shift from methane (hydrogenolysis) to propylene (isomerization). We have associated this selectivity shift with a perturbation in the catalytic properties of the metal surface by the high-coverage carbonaceous residue. This perturbation results in either (or possibly both) a reduction in the binding energy or a change in the structure of the adsorbed reaction intermediate associated with hydrogenolysis. Consequently, the selectivity is shifted to the (relatively facile) isomerization reaction.

On the Ir(111) surface, propane and propylene are formed from a common intermediate from the reaction of cyclopropane. Possible structures for the reaction intermediate have been discussed; one such possible intermediate is an \( \pi \)-allyl. Although

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propylene is not observed for the same reaction conditions on Ir(110)-(1×2), there is no evidence to suggest that a different intermediate is involved [i.e., there is ample evidence that the (110)-(1×2) surface possesses a greater specific activity for hydrogenation reactions]. The hydrogenolysis of cyclopropane was found to be qualitatively different from the hydrogenolysis of propane. In particular, for cyclopropane on both surfaces, there was no variation in the apparent reaction kinetics over the entire temperature range investigated (T ≈ 400–600 K). This difference between cyclopropane and propane is due to the irreversibility of forming the adsorbed intermediate from cyclopropane. The observation of the production of ethylene on Ir(111) from the hydrogenolysis channel, coupled with precedents from organometallic chemistry, suggests that the adsorbed intermediate is a nonnuclear metallacycle butane. The lack of the observation of ethylene on Ir(110)-(1×2) does not exclude the possibility that this mechanism is dominant on both surfaces.

The hydrogenation of methylcyclopropane on both the Ir(111) and Ir(110)-(1×2) surfaces was found to be dominated by the production of n-butane for the reaction conditions considered here. This result was interpreted qualitatively by invoking parallel reaction mechanisms for the production of n-butane and isobutane, with the n-butane channel exhibiting a higher apparent activation energy and, thus, dominating at the relatively high temperatures. Different apparent reaction orders in $P_{\text{H}_2}$ and $P_{\text{H}}$ for the production of n-butane compared to isobutane suggest that different intermediates (mechanisms) may be involved for the two hydrogenation pathways. We suggest that a π-allylic species may be involved in the reaction channel that produces n-butane and "linear" butenes, whereas a 1,3 di-si-bonded intermediate is probably associated with the production of isobutane. The hydrogenolysis of methylcyclopropane was found to be similar to that found for cyclopropane on both surfaces. The observation of the production of propylene on the Ir(111) surface is consistent with the participation of a metallacycle butane in the hydrogenolysis channel. The selectivity difference observed between the two surfaces for the major hydrogenolysis channels would appear to support this mechanism. In particular, the absence of ethene in the major hydrogenolysis channel on the Ir(111) surface can be explained on a stereochemical basis if metallacycle butane formation proceeds through an edge complex, i.e., the presence of the methyl group prevents activation of the C-C bond in methylcyclopropane by the coordinatively more saturated C atoms of the Ir(111) surface.

Finally, the Ir(110)-(1×2) surface was found to possess a greater specific activity with respect to the Ir(111) surface for the hydrogenation of propylene. This observation, coupled with a number of others, implies a greater specific activity of the Ir(110)-(1×2) surface for hydrogenation reactions. One simple explanation for these observations is that the hydrogen adatom concentration is greater on the Ir(110)-(1×2) surface due to the presence of a previously identified higher binding energy adstate for hydrogen on this surface.

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Laser-Induced Activation of Methane at Oxide Surfaces: A Probe of Radical–Surface Interactions

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C–H bond activation was studied via pulsed laser irradiation of oxides in a methane atmosphere. Carbon monoxide was the major product observed at low power densities and room temperature. Significant amounts of C2 products, ethane, ethylene, and acetylene were formed. CO, C2H4, C2H6, and C2H2 are assigned as primary products of the reaction. Laser-induced methane activation produces CH3 and CH2 radical species in the gas phase via a plasma mechanism and is utilized as a tool to study radical–oxide surface interactions. These reactions are surface sensitive as evidenced by the changes in conversion and product selectivity as a function of oxide pretreatment and oxides used.

Introduction

Methane activation is a subject of considerable scientific and practical interest. This is mainly due to the large abundance of methane, a major component of natural gas present in remote areas of the world and the enormous economic gains possible in converting it to easily transportable liquid fuels. In general, thermal routes to methane activation have been inefficient due to the endothermicity of the process.1,2 Commercial processes presently used to convert methane to synthetic crude and gasoline distillate usually involve steam reforming to produce synthesis gas as an intermediate step.3 The substantial capital investments required to implement this process have motivated research into the possibility of more economical, direct methane conversion processes.

Oxidative coupling of methane over oxide catalysts is one approach currently being explored. Keller and Bhasin4 studied the catalytic oxidative coupling of methane to C2 compounds over γ-Al2O3 supported metal oxides. Methane and oxygen were fed into the reactor cyclically to minimize competing gas-phase noncatalyzed reactions. The metal oxide catalyst undergoes a Mars–van Krevelen type mechanism5 with the lattice oxygen participating in a redox cycle. Methyl radicals produced at the oxide surface as a result of hydrogen abstraction react to form C2 compounds. At present, it is not entirely clear whether this reaction occurs primarily in the gas phase or at the oxide surface.

Sofranko et al. found that cyclic redox and methane/oxygen cofed reactions over Mn/SiO2 catalysts resulted in comparable