

# Reaction of Cyclopropane and Hydrogen on the (0001) and (11 $\bar{2}$ 0) Surfaces of Ruthenium

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The hydrogenation and hydrogenolysis of cyclopropane have been investigated on Ru(0001) and Ru(11 $\bar{2}$ 0), and the kinetics of both reaction channels examined in detail as a function of temperature and the reactant partial pressures. The specific activity for propane formation was higher by a factor of 2 on the Ru(11 $\bar{2}$ 0) substrate, whereas the activity for C<sub>2</sub> production on this surface was lower by a factor of 1.3. The higher selectivity for hydrogenation on the Ru(11 $\bar{2}$ 0) surface is attributed to lower hydrogen coverages on this surface and to the intrinsic higher surface carbon levels present during reaction.

## Introduction

The reaction of cyclopropane with hydrogen is a widely used probe reaction for investigating the properties of catalytic systems.<sup>1-3</sup> Depending upon the reaction conditions, either hydrogenation to propane or hydrogenolysis to ethane and methane is observed.<sup>4-14</sup> The hydrogenation pathway can be compared with the hydrogenation of olefins, whereas the hydrogenolysis pathway exhibits similarities to the hydrogenolysis of alkanes. Unlike olefins, C-C bond cleavage must precede the hydrogenation of cyclopropane. The hydrogenolysis of alkanes is also different from the hydrogenolysis of cyclopropane in that the C-H bond activation in the adsorbed cyclopropane molecule is generally irreversible as shown by the lack of significant H/D exchange.<sup>8</sup>

The adsorption and reaction mechanisms for cyclopropane on transition metals have been extensively studied.<sup>15-25</sup> At low temperatures cyclopropane was found to nondissociatively adsorb, forming a  $\pi$ -like-bonded cyclopropane complex.<sup>19,20</sup> Previous investigations have

shown that the reaction of cyclopropane on platinum is a classical example of a structure-insensitive reaction,<sup>24</sup> whereas on iridium the hydrogenation of this hydrocarbon is an example of a structure-sensitive reaction.<sup>26</sup> Reaction rates on the reconstructed Ir(110)-(1 $\times$ 2) surface are greater than on the Ir(111) surface by a factor of approximately 2 for hydrogenation and 10 for hydrogenolysis. The increased activity over Ir(110)-(1 $\times$ 2) for both reaction pathways is attributed to the greater intrinsic activity of the low coordination number (C<sub>7</sub>) metal surface atoms for these reactions. Schwank and co-workers<sup>24</sup> showed that supported ruthenium particles with diameters less than 4-5 nm are very active in catalyzing cyclopropane ring opening. Ruthenium metal particles larger than 5 nm appear to be required for nonselective hydrocracking to methane. Similar results were obtained for supported nickel and platinum catalysts.<sup>12,27</sup>

The adsorption of various molecules on ruthenium single crystals has been investigated, but relatively few studies of hydrocarbon reactions on Ru single crystals have been published. Most of the kinetic studies in the literature have been carried out on supported ruthenium catalysts. In this study, ultrahigh vacuum (UHV) studies on ruthenium single crystals combined with catalytic reactions at elevated pressure conditions (1-200 Torr) address directly the relationship between surface structure and reactivity. The surfaces chosen for this study are the close-packed Ru(0001) surface (Figure 1a) and the more corrugated, open Ru(11 $\bar{2}$ 0) surface (Figure 1b). The kinetics of the hydrogenation and hydrogenolysis of cyclopropane on these surfaces was investigated with emphasis on the relative roles of surface structure, ensemble effects, and electronic contributions.

## Experimental Section

The experiments were carried out in a stainless steel reaction chamber (volume 500 mL), capable of pressures up to 2 atm, which is linked to an UHV surface analysis chamber equipped for Auger electron spectroscopy (AES), temperature-programmed desorption (TPD), ion sputtering, and metal deposition. The separately pumped chambers are connected by a differentially pumped sliding seal.<sup>28</sup> The base pressure in both chambers was 10<sup>-10</sup> Torr.

Schematic drawings of Ru(0001) and Ru(11 $\bar{2}$ 0) surfaces are shown in Figure 1. The ruthenium single crystals were mounted

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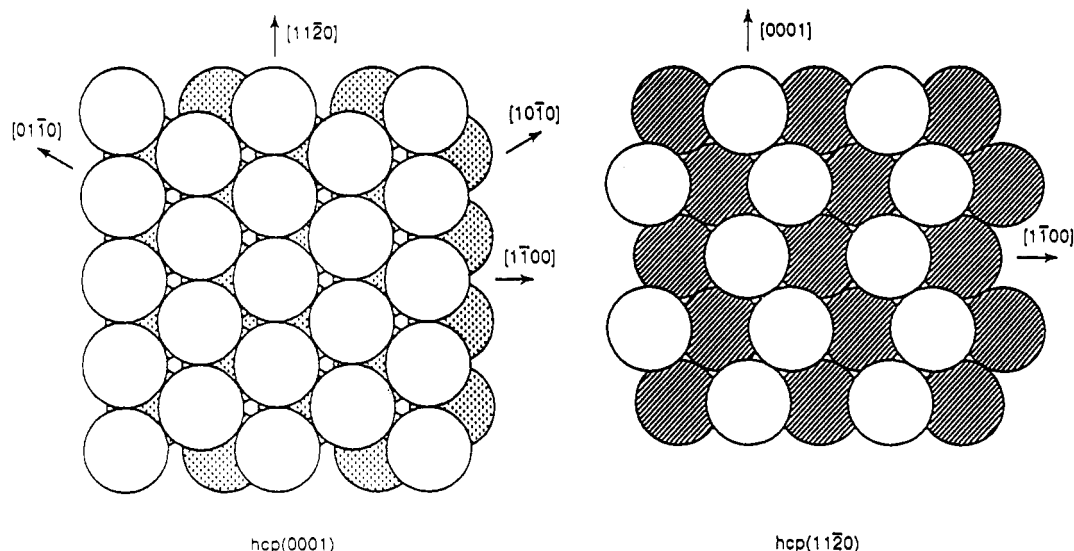


Figure 1. Structures of the hcp (0001) (a) and (11 $\bar{2}$ 0) (b) surfaces of ruthenium.

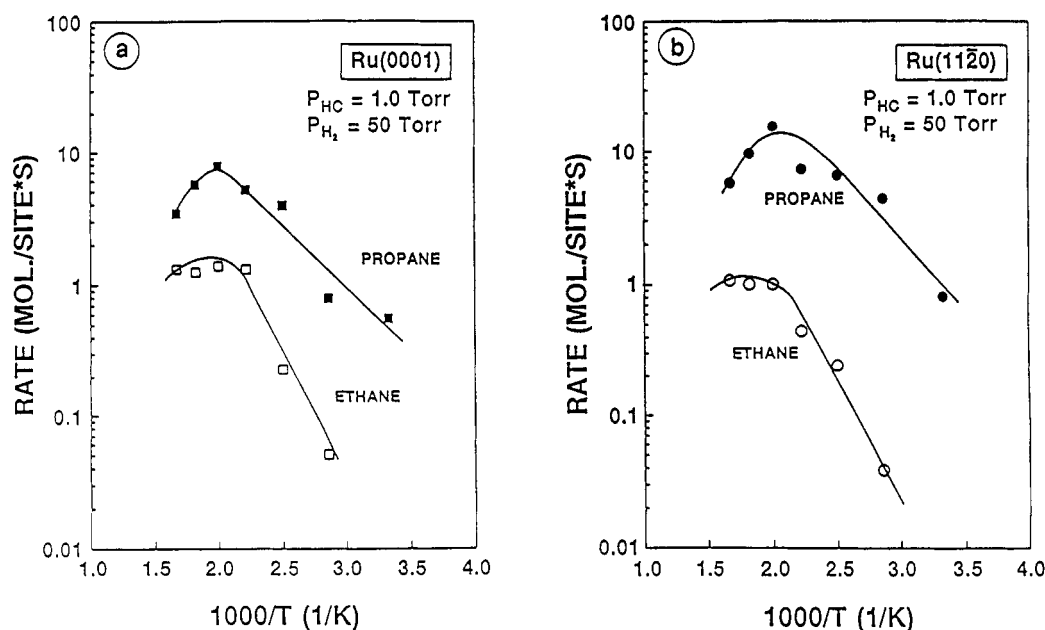


Figure 2. Specific reaction rates (product molecules/(site\*s)) for the reaction of cyclopropane and hydrogen on Ru(0001) (a) and Ru(11 $\bar{2}$ 0) (b) as a function of  $1000/T$ . The partial pressure of cyclopropane was 1.0 Torr, whereas that of hydrogen was 50 Torr.

on tungsten wires for resistive heating, and temperature was monitored with a W/5% Re—W/26% Re thermocouple attached to the backside of the samples. The crystals were cleaned in the UHV chamber with mild argon ion sputtering, heating in  $4 \times 10^{-7}$  Torr of oxygen at 1100 K, and annealing to 1400 K to remove any remaining oxygen. Surface cleanliness was verified by AES. The details of crystal cleaning and characterization have been published elsewhere.<sup>29,30</sup>

The cyclopropane used in the experiments was purified by degassing at 80 K followed by triple distillation from a liquid methanol/solid methanol bath. The hydrogen was Matheson ultrahigh purity (99.999%). Gas chromatography (GC) was used for detection of the reaction products.

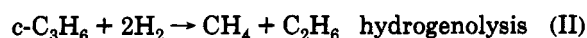
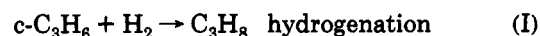
## Results

**A. Ru(0001).** Specific rates of reaction of cyclopropane with hydrogen on Ru(0001) are shown in Figure 2a in Arrhenius form. At 450 K (standard reaction temperature)

no induction period was evident. The specific reaction rates for the C<sub>2</sub> and propane products were constant for reaction times of 30 min; therefore, the data obtained under these conditions represent steady-state reaction rates. At lower temperatures, steady-state conditions were obtained after approximately 10 min. During the induction period decreasing propane rates and increasing C<sub>2</sub> rates were observed.

To avoid secondary reactions and to maintain relatively fixed reactant partial pressures, conversions were restricted to <1%. A reactant ratio of 50 (H<sub>2</sub>/cyclopropane) was used unless otherwise stated.

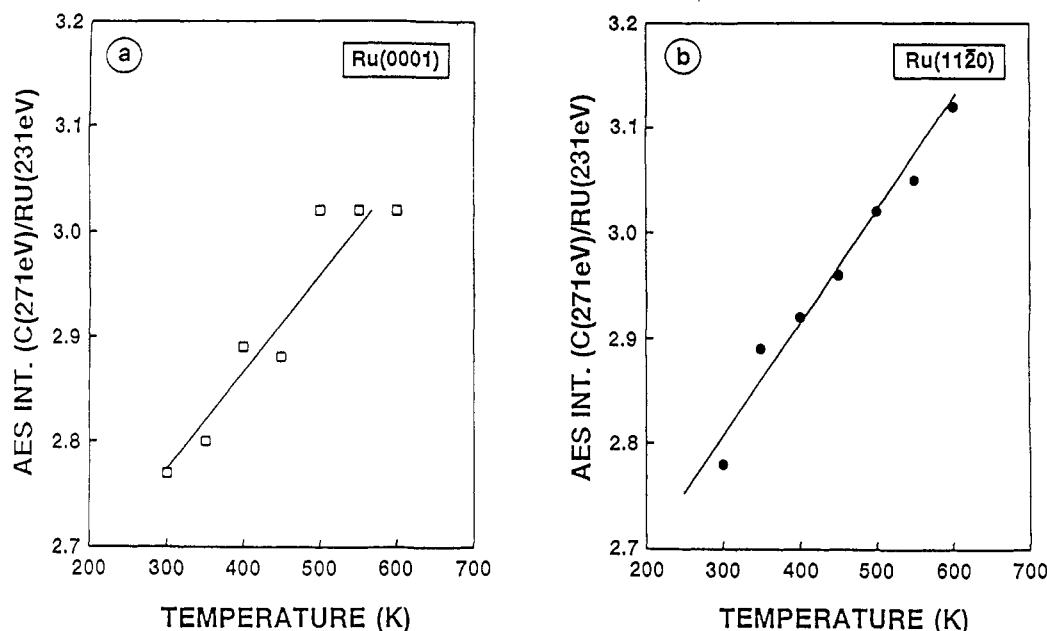
The products observed were propane and ethane, representing the two major reaction channels at low temperatures ( $\leq 550$  K):



At higher temperatures (>600 K) the following reaction

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**Figure 3.** Carbonaceous coverage (Auger ratio of the combined Ru/C peak at 273/271 eV to the ruthenium 231-eV peak) as a function of temperature at a constant cyclopropane/hydrogen ratio of 1/50 (1 Torr of cyclopropane, 50 Torr of hydrogen): (a) Ru(0001), (b) Ru(1120).

became more important:



At 350 K the propane production exceeded the hydrogenolysis by a factor of 10, and for temperatures below 350 K, no  $\text{C}_2$  product was detected.

Within the temperature range 300–450 K, activation energies of  $25.6 \pm 2$  kJ/mol for hydrogenation and  $43.2 \pm 2$  kJ/mol for hydrogenolysis were measured. These values are in agreement with the previous work of Schwank and co-workers<sup>24</sup> on supported ruthenium catalysts. Depending on the support and the ruthenium loading, these workers obtained activation energies between 24 and 48 kJ/mol for propane production and 38 and 51 kJ/mol for hydrogenolysis.

Figure 3a shows that the carbon coverage on the Ru(0001) catalyst after reaction increases substantially with increasing temperature. The carbon coverage was determined from the ratio of the combined Ru/C AES feature at 273/271 eV to the Ru 231-eV peak.<sup>29</sup> Postreaction TPD of the surface containing the carbonaceous residue yielded only hydrogen with desorption features very similar to those found for the clean ruthenium surface. A second reaction (without cleaning) on this surface produced the same specific reaction rates for  $\text{C}_2$  and propane products as for the clean surface.

At 300 K, as noted above, only propane product was observed. With increasing temperature an increasing amount of  $\text{C}_2$  product was found, reaching 28% at 600 K. The highest conversion rate was found at 500 K.

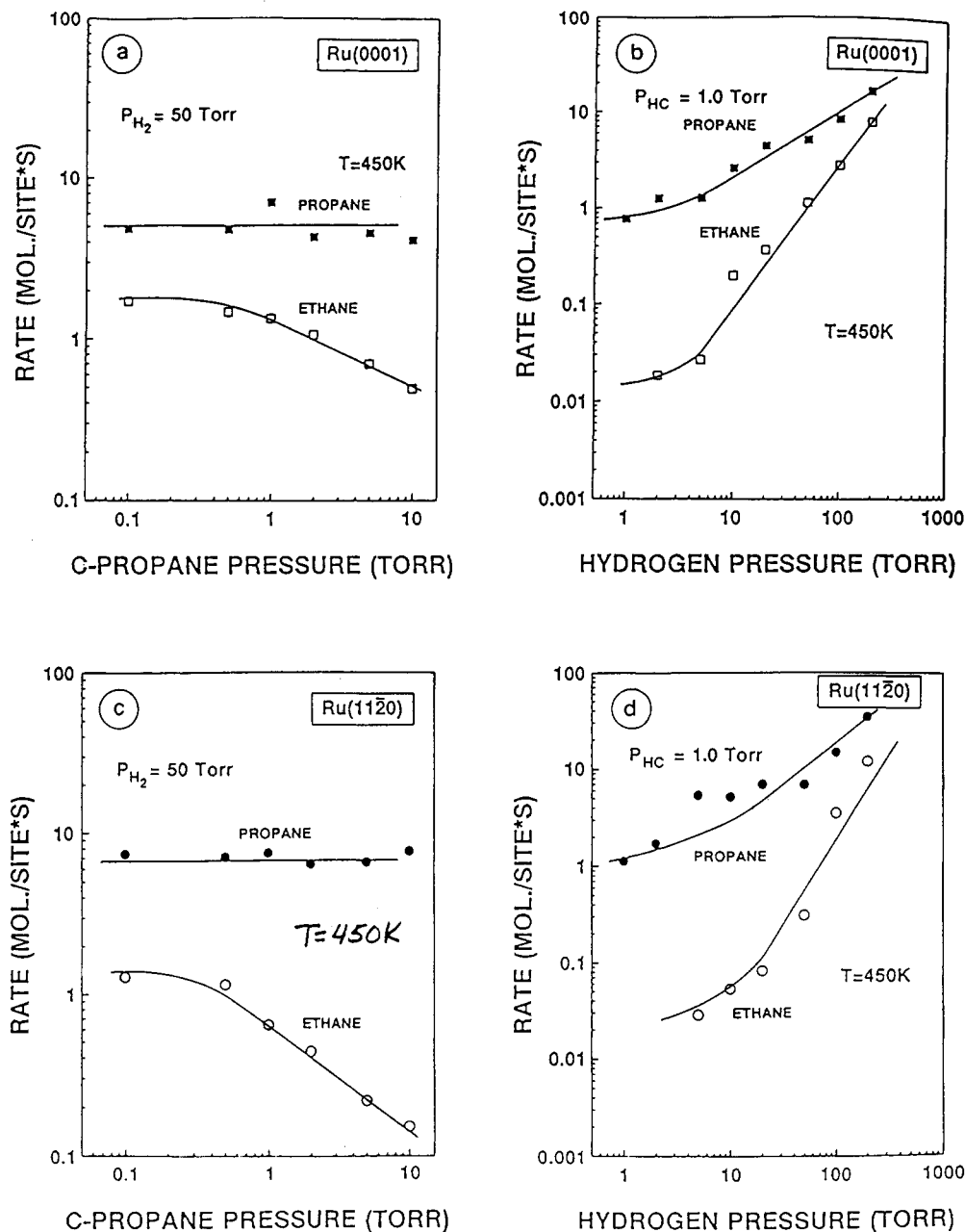
The dependence of the specific rates of reaction on the reactant partial pressures was examined at 450 K. Figure 4a,b shows the reaction rates for propane and  $\text{C}_2$  production as a function of the cyclopropane and the hydrogen partial pressures, while maintaining the hydrogen and cyclopropane pressures fixed at 50 and 1.0 Torr, respectively. The variation of the cyclopropane pressure at constant hydrogen pressure (Figure 4a) had no effect on the rate of propane formation; therefore, the reaction order in cyclopropane for the hydrogenation pathway is essentially zero. On the other hand, the  $\text{C}_2$  production declined with increasing cyclopropane pressure beginning with a pressure

of 0.5 Torr. The reaction order for hydrogenolysis with respect to cyclopropane is  $-0.5$ . This indicates that, with a cyclopropane pressure of approximately 0.5 Torr, the  $\text{C}_2$  formation is inhibited by a lack of available surface hydrogen. That is, at this pressure, the cyclopropane or cyclopropane intermediate coverage is sufficiently high to block adsorption sites for hydrogen. Since hydrogenation requires less available hydrogen than hydrogenolysis, site blocking of molecular hydrogen does not significantly affect the propane formation at these particular reaction conditions (0.1–10 Torr of cyclopropane, 50 Torr of hydrogen). This explanation is verified by the results of subsequent experiments, in which the hydrogen pressure was varied while holding the cyclopropane pressure constant at 1.0 Torr. An increasing hydrogen pressure influences the  $\text{C}_2$  production much more so than the propane product although an increase in both products was observed. A higher hydrogen pressure (at constant cyclopropane pressure) leads to a higher hydrogen coverage, which, in turn, leads to an increase in the  $\text{C}_2$  product.

In Figure 5 the selectivities for  $\text{C}_2$  and  $\text{C}_3$  products as a function of the hydrogen and the cyclopropane pressure are shown. The increase in hydrogen pressure favors the  $\text{C}_2$  formation more than the propane formation; that is, the reaction becomes less selective for propane. Up to a hydrogen pressure of 10.0 Torr, propane was observed almost exclusively; however, the amount of  $\text{C}_2$  product increased to 32% at a hydrogen partial pressure of 200 Torr. The same effect was observed with a decrease in the cyclopropane partial pressure.

The reaction orders with respect to hydrogen (Figure 4a) are 1.8 for  $\text{C}_2$  formation and 0.75 for propane. Since 2 mol of hydrogen is necessary for the formation of ethane and methane and 1 mol of hydrogen for propane, hydrogen adsorption/dissociation appears to be the rate-limiting step. A reaction order of zero with respect to cyclopropane for  $\text{C}_3$  formation suggests that the adsorption of cyclopropane is not the rate-limiting step, but that the formation of an intermediate dehydrogenated species is rate-determining.

As expected, the carbon coverage after reaction increased with increasing cyclopropane partial pressure and de-



**Figure 4.** Specific rates for the reaction of cyclopropane and hydrogen on Ru(0001) (a, b) and Ru(1120) (c, d) at a surface temperature of 450 K. (a, c) The partial pressure of cyclopropane was maintained at 1.0 Torr as the partial pressure of hydrogen was varied. (b, c) The partial pressure of hydrogen was maintained at 50 Torr as the partial pressure of cyclopropane was varied.

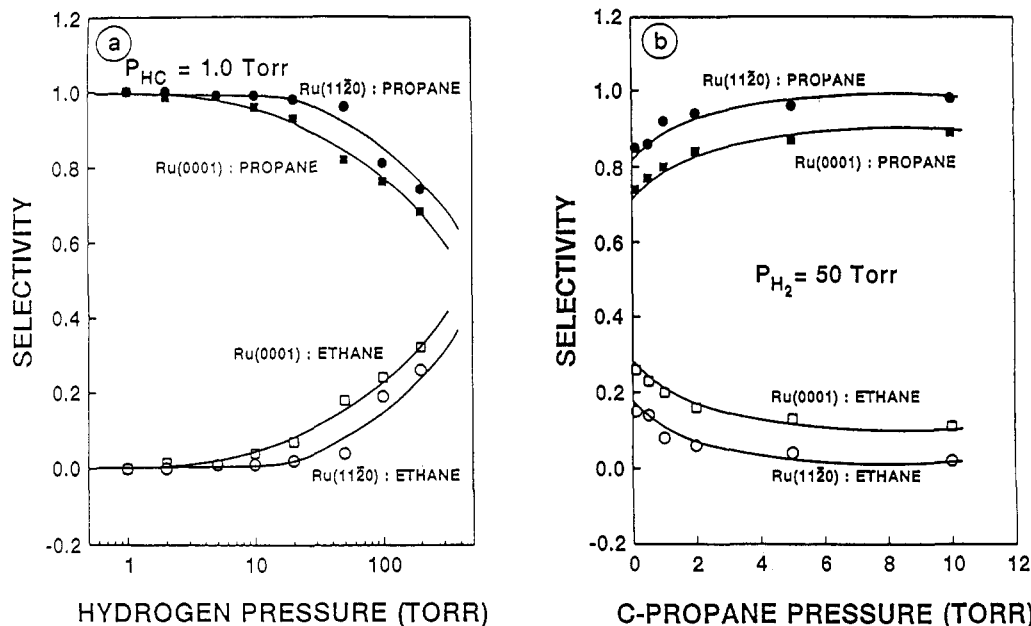
creased with increasing hydrogen partial pressure (Figure 6). Clearly, higher hydrogen coverages as a consequence of higher hydrogen pressures leads to higher hydrogenation activity and, consequently, less carbon residue on the surface.

**B. Ru(1120).** Arrhenius plots for the specific reaction rates of cyclopropane with hydrogen on Ru(1120) to propane and ethane are shown in Figure 2b. These represent steady-state reaction rates obtained for conversions of ~1%. In contrast to the reactions on the Ru(0001) surface a short induction period was observed for C<sub>2</sub> product. During this induction period an increase in the C<sub>2</sub> product was observed, whereas the propane yield remained essentially constant. The reactant partial pressures for cyclopropane and hydrogen were 1.0 and 50.0 Torr, respectively. A rolling over of the rate was observed at ~500 K for propane and ethane. Activation energies of 19.6 kJ/mol for propane formation and 43.3 kJ/mol for ethane formation are derived from Figure 2b.

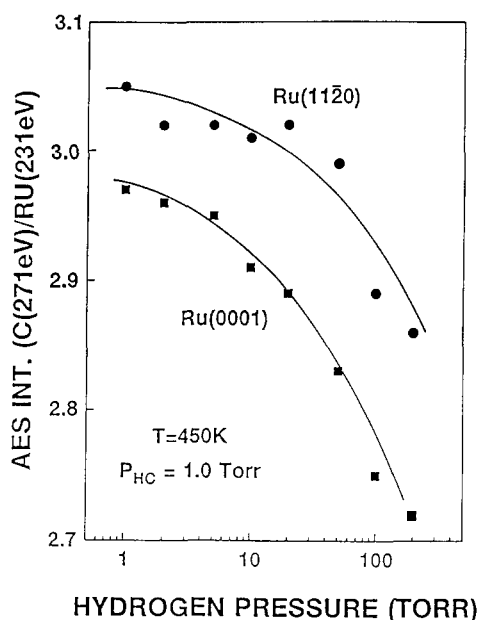
For both hydrogenation and hydrogenolysis, the energies are lower than the corresponding values on the Ru(0001) surface.

The turnover frequencies for propane formation were higher on Ru(1120) by a factor of approximately 2. For example, at 500 K, where the rate reaches a maximum, the turnover frequency is 16 compared with 7.5 on the Ru(0001) surface. The C<sub>2</sub> formation rates at 500 K, on the other hand, are 1.0 on Ru(1120) and 1.35 on Ru(0001). The data of Figure 7 indicate that the selectivity for propane formation is higher on Ru(1120) than on Ru(0001). For example, at 600 K, 84% of the product over Ru(1120) was propane, whereas on Ru(0001), the amount of C<sub>2</sub> product rose to 28% (i.e., 72% propane). These results clearly show the structure sensitivity of cyclopropane reactions on ruthenium.

Generally the carbon coverage following reaction was somewhat higher on Ru(1120). As for the Ru(0001) surface, postreaction TPD produced only hydrogen de-



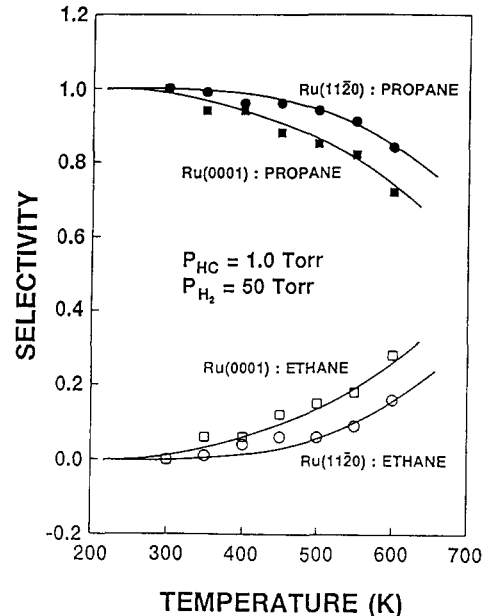
**Figure 5.** Relative selectivity for hydrogenation and hydrogenolysis from the reaction of cyclopropane and hydrogen on Ru(0001) and Ru(1120) at a surface temperature of 450 K: (a) at a constant cyclopropane partial pressure of 1.0 Torr as the hydrogen partial pressure was varied, (b) at a constant hydrogen partial pressure of 50 Torr as the cyclopropane partial pressure was varied.



**Figure 6.** Amount of carbonaceous residues (Auger ratio of the combined Ru/C peak at 273/271 eV to the 231-eV peak of Ru) after reaction on Ru(0001) and Ru(1120) at a temperature of 450 K and a partial pressure of cyclopropane of 1.0 Torr as a function of the hydrogen partial pressure.

sorption with features very similar to those found for the clean surface.

The dependence of the cyclopropane reaction on the partial pressures of cyclopropane and hydrogen was investigated over the Ru(1120) surface. The results of these measurements are shown in Figure 4c,d. Except for the different reaction rates (higher for C<sub>3</sub>, lower for C<sub>2</sub>), the results are very similar to the analogous data for Ru(0001) (Figure 4a,b). For propane the calculated reaction order was zero with respect to cyclopropane over the entire pressure range (1–200 Torr). For ethane a reaction order of –0.6 was observed for cyclopropane between 10 and 0.5 Torr; below 0.5 Torr, the reaction order was zero. The pressure dependence with respect to hydrogen for propane formation was 0.9 and for C<sub>2</sub>, 1.8.



**Figure 7.** Selectivity for hydrogenation and hydrogenolysis from the reaction of cyclopropane and hydrogen on Ru(0001) and Ru(1120) as a function of the reaction temperature. The partial pressure of cyclopropane was 1.0 Torr, whereas that of hydrogen was 50 Torr.

The carbon coverage following reaction on the Ru(1120) surface increased with increasing cyclopropane pressure and decreased with increasing hydrogen pressure. However, as Figure 6 indicates, the total carbon coverage was higher on the Ru(1120) surface than on the Ru(0001) surface. The C<sub>3</sub> selectivity decreased with increasing hydrogen pressure and decreasing cyclopropane pressure. Nevertheless, the cyclopropane reaction on Ru(1120) was more selective for the formation of propane than on Ru(0001) (Figure 5).

### Discussion

Reaction rates for the hydrogenation of cyclopropane are higher on the corrugated Ru(1120) surface by a factor of approximately 2 compared to the smooth Ru(0001)

surface. The rate of hydrogenolysis, on the other hand, is lower by a factor of 1.3 on Ru(11 $\bar{2}$ 0) compared to Ru(0001). For hydrogenation this difference in the specific activities is on the order of those reported previously for Ir(110)-(1 $\times$ 2)/Ir(111),<sup>26</sup> supported nickel,<sup>12</sup> platinum,<sup>27</sup> and ruthenium,<sup>24</sup> where high specific activities were found for relatively small particles. However, in contrast to the results for Ir,<sup>26</sup> the specific activity for the hydrogenolysis pathway on the corrugated Ru(11 $\bar{2}$ 0) is lower compared with the smooth (0001) surface. Since the activation energies for both pathways were found to be somewhat higher on Ru(0001), higher activities might be anticipated for propane and C<sub>2</sub> products on the Ru(11 $\bar{2}$ 0) surface. These differences in the energies of activation are supported by the results found for cyclopropane desorption. Cyclopropane adsorption at 90 K on Ru(11 $\bar{2}$ 0) and Ru(0001) was found to be nondissociative, in agreement with the results of Madey<sup>31</sup> and Felter<sup>20</sup> on Ru(0001). TPD experiments showed a single desorption peak at 155 K on Ru(11 $\bar{2}$ 0), corresponding to an activation energy of desorption of  $38.5 \pm 1$  kJ/mol. On Ru(0001) cyclopropane desorbs at 150 K<sup>20,31</sup> with an activation energy of desorption of  $36.2 \pm 1$  kJ/mol. Ruthenium atoms with lower coordination in the (11 $\bar{2}$ 0) surface are able to form stronger bonds to cyclopropane than the higher coordinated atoms of the (0001) surface.

If cyclopropane and hydrogen adsorption occurs preferentially onto the low coordination site,<sup>28</sup> then the apex atoms in the corrugated (11 $\bar{2}$ 0) surface (Figure 1b) are good candidates for the reaction sites. As indicated in Figure 1b the (11 $\bar{2}$ 0) surface exhibits a row structure. A reaction sequence involving two adsorbed hydrogen atoms and a cyclopropane molecule in hydrogenolysis on this surface should be substantially more difficult than that involving one hydrogen and a cyclopropane molecule for the reaction to propane. Indeed, propane formation is preferred on the (11 $\bar{2}$ 0) surface while the formation of C<sub>2</sub> product is attenuated relative to the (0001) surface. The increase in the carbonaceous residue on Ru(11 $\bar{2}$ 0) likewise is a consequence of the reduced steady-state hydrogen coverage on this surface. A more easily formed and more tightly bound cyclopropane intermediate on Ru(11 $\bar{2}$ 0) reduces the amount of hydrogen on the surface, thus hindering the reaction of adsorbed cyclopropane intermediates to propane, ethane, and methane.

The results obtained for the reaction of cyclopropane with hydrogen on Ru(0001) and Ru(11 $\bar{2}$ 0) indicate a zero reaction order for propane formation at cyclopropane pressures between 0.1 and 10.0 Torr. For the C<sub>2</sub> production on both surfaces, the reaction order was between 0 and 0.5 at low pressures of cyclopropane, and decreased to -0.5 at higher cyclopropane pressures. These results are consistent with a reaction mechanism involving the relatively facile formation of a common surface intermediate, with the rate-limiting step for hydrogenolysis being C-C bond cleavage (e.g., subsequent hydrogenation and desorption are rapid with respect to the C-C bond cleavage in the adsorbed intermediate). A reasonable first step is the addition of cyclopropane to the ruthenium surface, via

formation of a 1,3-diadsorbed species. This adsorption complex, first proposed by Addy and Bond,<sup>7</sup> was also favored by Wallace<sup>32</sup> for the hydrogenation of cyclopropane over ruthenium. On iridium<sup>26</sup> a metallacyclobutane was proposed to be a likely key intermediate. Recent studies by Sakakini<sup>33</sup> of propene adsorption and decomposition on Ru(0001) have shown the existence of an adsorbed propylidene species at 200 K. By annealing the surface to 223 K, these researchers found evidence for both ethylidene and propylidene. The researchers suggest that surface hydrogen is required to efficiently decompose the propylidene species while other adsorbed species may inhibit hydrogen adsorption and therefore hinder the decomposition process. This is in agreement with the results of this study. Another possible explanation is that with increasing cyclopropane pressure the carbon coverage rises and restricts the number of available reaction sites. This increase in carbon coverage then would compensate for any rate enhancement due to the increase in hydrocarbon pressure, thus yielding the apparent zero order in hydrocarbon. Since the carbonaceous residues on both ruthenium surfaces do not influence a second reaction cycle (e.g., a second reaction without surface cleaning), these carbonaceous residues are not graphitic in nature. This postreaction carbonaceous residue likely consists of dehydrogenated intermediates. During a second reaction cycle, sufficient surface hydrogen is available to hydrogenate these residues; thus, no carbon-induced poisoning is apparent. The decrease in the reaction order for the hydrogenolysis indicates a competitive adsorption of cyclopropane and hydrogen; thus, at higher cyclopropane pressures, adsorbed cyclopropane or cyclopropane intermediates exclude hydrogen from the surface.

### Conclusions

The reaction of cyclopropane with hydrogen on ruthenium is structure sensitive. The presence of lower coordinated reaction sites on Ru(11 $\bar{2}$ 0) decreases the activation energy for both hydrogenation and hydrogenolysis. A reduced hydrogen coverage arising from enhanced displacement by cyclopropane and by the concomitant increase in the surface carbon levels leads to higher rates for hydrogenation of cyclopropane and to lower rates for hydrogenolysis on Ru(11 $\bar{2}$ 0) compared to Ru(0001).

The mechanism for hydrogenation and hydrogenolysis on both ruthenium surfaces appears to involve a common cyclopropane-derived surface intermediate. These results are consistent with the rate-limiting step for hydrogenolysis being C-C bond cleavage in this intermediate species. Hydrogen and cyclopropane adsorption is competitive with the resulting coverages dictating the selectivity toward hydrogenation or hydrogenolysis.

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