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## Title

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## Author

Castner, D.G.

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D. G. Castner, R. L. Blackadar and G. A. Somorjai

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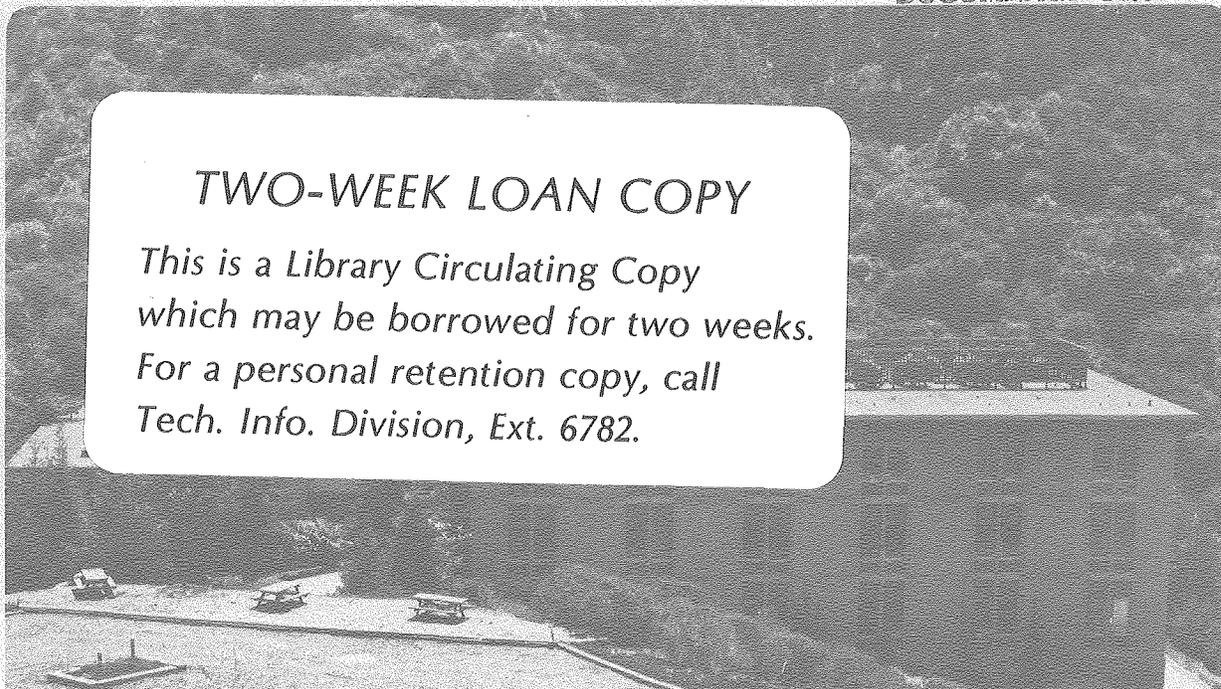
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FOIL AND SINGLE CRYSTAL CATALYSTS. CORRELATIONS  
OF CATALYST ACTIVITY, SELECTIVITY AND SURFACE  
COMPOSITION

D.G. Castner,\* R.L. Blackadar and G.A. Somorjai

Materials and Molecular Research Division  
Lawrence Berkeley Laboratory and Department  
of Chemistry, University of California,  
Berkeley, CA 94720

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\*Present Address: Chevron Research Company, P.O. Box 1627, Richmond, CA 94802.



## Abstract

CO hydrogenation at 6 atm over Rh polycrystalline foil and single crystal (111) catalysts was investigated in a system where the surface structure and composition of the catalysts could be characterized both before and after the reaction. The reaction conditions (H<sub>2</sub>:CO ratio, reaction temperature, surface pretreatment and gas phase additives) were systematically varied to determine the conditions for the formation of oxygenated hydrocarbons. Initially clean Rh catalysts showed no structure sensitivity, primarily produced methane (90 wt %) at an initial rate of 0.15 molecules•site<sup>-1</sup>•sec<sup>-1</sup> at 300°C, and did not produce detectable amounts of oxygenated hydrocarbons. Preoxidation of the Rh (100 torr O<sub>2</sub>, 600°C, 30 min.) resulted in dramatically increased initial rates, a larger fraction of higher molecular weight hydrocarbons in the product distribution, formation of methanol, ethanol and acetaldehyde, and some structure sensitivity. The different Arrhenius methanation pre-exponential factors and activation energies over the clean and preoxidized Rh foils indicate the methanation mechanism is different on these two surfaces. Decreasing the reaction temperature or H<sub>2</sub>:CO ratio increased the C<sub>2</sub>H<sub>4</sub> to C<sub>2</sub>H<sub>6</sub> ratio and shifted the product distribution towards the higher molecular weight hydrocarbons. The addition of 1 mole % of CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH or C<sub>2</sub>H<sub>6</sub> to the H<sub>2</sub>:CO reaction mixture caused only a small increase in the fraction of higher molecular weight hydrocarbons.



## I. Introduction

The reaction of  $H_2$ -CO gas mixtures over the group VIII metals produces a wide range of products, including alkanes, olefins and oxygenated hydrocarbons. The reaction rates and product distributions resulting from CO hydrogenation depend both on the reaction conditions and the catalyst. Recent investigations on supported Rh catalysts<sup>1-4</sup> have reported the existence of a large percentage of oxygenated hydrocarbons (methanol, ethanol, acetaldehyde and acetic acid) in the product distribution. The relative amounts of oxygenated hydrocarbons produced depend on the catalyst support and method of depositing the rhodium on the support. These results are in contrast to earlier results over Rh foils<sup>5</sup> and supported Rh on  $Al_2O_3$ <sup>6</sup> at 1 atm, where the formation of oxygenated products was not detected.

We have investigated CO hydrogenation over polycrystalline Rh foil and Rh(111) single crystal catalysts at 6 atm total pressure. The reaction conditions ( $H_2$ :CO ratio, reaction temperature, surface pretreatment and gas phase additives) were systematically varied to determine the optimum conditions for production of oxygenated hydrocarbons over these Rh catalysts. Results will be presented for  $H_2$ :CO ratios from 3:1 to 1:3, reaction temperatures from 250 to 400°C, over clean and preoxidized Rh catalysts, and the effects of the addition of 1 mole % of  $CH_3OH$ ,  $CH_3CH_2OH$  and  $C_2H_4$  to the  $H_2$ -CO reaction mixture. The surface structure and composition of the catalysts were characterized before and after a reaction, using low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Thus, correlations between catalyst activity, selectivity and surface composition could be made. Our results will be compared to the previous results for Rh and Fe catalysts.

## II. Experimental

The apparatus employed in these experiments has been described in detail elsewhere.<sup>5,7</sup> Briefly, it consists of a diffusion pumped ultrahigh vacuum (UHV) bell jar equipped with a high pressure (1-20 atm) isolation cell, retarding field LEED and AES, an ion sputter gun, and a quadrupole mass spectrometer. With the cell open, the catalysts ( $\sim 1 \text{ cm}^2$ ) were characterized by LEED and AES, and cleaned by Ar ion bombardment and annealing, as described previously,<sup>8</sup> When the cell was closed the apparatus could be operated as a stirred batch reactor (160  $\text{cm}^3$  volume) or a catalyst pretreatment chamber.

In the batch reactor mode the cell was closed and first the  $\text{H}_2$ , then the CO was admitted to the cell loop. The CO (Matheson, 99.95%) was passed through a dry ice trap to remove carbonyls; the  $\text{H}_2$  (Liquid Carbonic Corp., 99.995%) was used without further purification. In the gas phase additives experiment the additives were admitted to the cell loop before the  $\text{H}_2$  and CO. Once the reaction mixture was placed in the cell it was circulated for several minutes to insure adequate mixing of the gases. During the admitting and mixing of the gases the Rh catalysts were at room temperature. The reaction was started by heating the crystals to the desired reaction temperature. The crystals were heated resistively and the reaction temperature monitored with a Pt-10% Rh/Pt thermocouple spot welded to the edge of the crystal. The buildup of reaction products during the reaction was monitored with a gas chromatograph (Perkin-Elmer Model 3920B) equipped with a flame ionization detector, Chromasorb 102 column and peak area integrator (Spectra-Physics Minigrator 23000). After a reaction the crystal was cooled to near room temperature, the gases pumped away and the cell opened. Pumpdown from 6 atm to UHV conditions

took only a few minutes. The reactions typically lasted three hours, but some reactions were ended earlier or later, so the surface composition of the catalyst could be determined at various stages of the reaction.

Preoxidization of the Rh catalysts was carried out by heating them at 600°C for 30 minutes in 800 torr of O<sub>2</sub>. This caused the formation of an epitaxial oxide layer on the Rh crystals and the dissolution of oxygen into the Rh lattice.<sup>10</sup> The oxide layer produced under these conditions was amorphous and generally had an O<sub>510</sub>/Rh<sub>302</sub> peak-to-peak ratio of 0.5 to 0.6. Considerably higher O<sub>510</sub>/Rh<sub>302</sub> ratios were obtained by oxidizing Rh catalysts having more than a monolayer of carbon on the surface.

The initial turnover numbers (TN) were determined from a least squares fit to the initial slope of the product concentration versus time curves. In determining the product concentration (molec•site<sup>-1</sup>) the atom density of the Rh(111) surface (1.6x10<sup>15</sup> atoms•cm<sup>-2</sup>) was taken as the active site density. For the clean surfaces, this procedure should result in a conservative estimate of the TN since it assumes all of the rhodium atoms in the surface are active. The same procedure was used for the preoxidized surfaces, thus ignoring possible increases in surface area as well as the reduced Rh surface density on the oxide.

### III. Results

#### A. CO Hydrogenation Over Clean Rh Catalysts.

The buildup of reaction products during a typical three-hour CO hydrogenation experiment at 300°C, 6 atm and 3H<sub>2</sub>:1CO over the clean Rh catalysts is shown in Fig.1. Under these reaction conditions the Rh catalysts produced primarily methane (90 wt %) at an initial rate of 0.15 molecules•site<sup>-1</sup>•sec<sup>-1</sup>. Small amounts of C<sub>2</sub> and C<sub>3</sub> hydrocarbons were also formed, but no oxygenated

hydrocarbons were detected, CO hydrogenation over the clean polycrystalline Rh foil and Rh(111) single crystal yielded the same results. Although this apparent lack of structure sensitivity is partly due to the large fraction of (111) facets expected to be present on the annealed polycrystalline foil, it does imply that surface imperfections such as grain boundaries do not play an important role in CO hydrogenation over the clean Rh surfaces.

As the reaction progresses the  $\text{CH}_4$  TN and the ratio of  $\text{C}_2\text{H}_4$  to  $\text{C}_2\text{H}_6$  decrease, indicating the catalyst activity and selectivity are changing during the reaction. AES showed that small amounts of sulfur and chlorine and about 1 monolayer of carbon were present on the surface after a three-hour reaction (Fig.2). The C and Cl AES signals increased to the values shown in Fig.2b during the first 30 minutes of reaction and remained constant during the remainder of the reaction. The majority of the increase in the S AES signal occurred during the first 30 minutes, but it did increase slightly during the remainder of the reaction. The close proximity of Rh 256 and 302 AES peaks to the C 272 AES peak prevented analyzing the lineshape of the C peak to determine whether a change in the chemical state of the carbon overlayer was occurring during the reaction. Thus, no major changes in surface composition were detected by AES when changes in the catalyst activity and selectivity were occurring.

#### B. CO Hydrogenation over Preoxidized Rh(111).

Preoxidation of the Rh(111) crystal resulted in a large increase in the initial TN, a slight shift in the product distribution toward the higher molecular weight hydrocarbons, and the formation of methanol, ethanol and acetaldehyde. The results of CO hydrogenation over a preoxidized Rh(111) crystal at  $300^\circ\text{C}$ ,  $3\text{H}_2:1\text{CO}$  and 6 atm are shown in Figs. 3 and 4. The TN's decreased

markedly during the first 30 minutes, then slowly decreased until they reached a fairly constant value by three hours. Even after three hours the  $\text{CH}_4$  TN over the preoxidized Rh(111) crystal was higher than the initial  $\text{CH}_4$  TN over the clean Rh(111) crystal. The TN decrease could be correlated with the oxygen and carbon concentrations in the near surface region. During the first 30 minutes of CO hydrogenation the oxygen AES signal decreased and carbon AES signal increased to their steady state levels shown in Fig.5b. Thus, the highest activity was observed at the highest oxygen concentration and after the steady state concentration of carbon and oxygen were reached, the catalyst activity decreased to a constant value. Oxygenated hydrocarbons were produced during the entire three hours of CO hydrogenation, including the steady state period, which suggests that the oxygen atoms in the product molecules originated from the CO molecules and not from the surface oxide. This interpretation is explored further at present by using isotope labeled oxygen atoms,

The selectivity changes caused by preoxidation resulted from different degrees of enhancement of the TN. Initially increasing the oxygen concentration to  $\text{O}_{510}/\text{Rh}_{302}=0.6$  resulted in larger increases in the  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  TN than in the  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  TN. This yielded the lower  $\text{CH}_4$  percentage and  $\text{C}_2\text{H}_4$  to  $\text{C}_2\text{H}_6$  ratio. Further increase of the  $\text{O}_{510}/\text{Rh}_{302}$  ratio to 2.6 slightly increased the hydrocarbon TN while the production of methanol, ethanol and acetaldehyde was markedly increased. This resulted in an even further decrease in the percentage of  $\text{CH}_4$  in the products.

Decreasing the  $\text{H}_2:\text{CO}$  ratio and reaction temperature shifted the product distribution toward the higher molecular weight hydrocarbons and increased the  $\text{C}_2\text{H}_4$  to  $\text{C}_2\text{H}_6$  ratio (Figs.6 and 7). These changes are due to a

decrease in the  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  TN, while the  $\text{C}_2\text{H}_4$  and  $\text{C}_2$  TN remained relatively constant. During the CO-rich reactions, the only oxygenated hydrocarbon produced was acetaldehyde. Also two to four monolayers of carbon were deposited on the Rh surface (Fig.5c) and the TN's decreased more rapidly with reaction time. The increased amount of carbon deposited during the CO-rich reactions was probably responsible for this increased poisoning rate.

### C. CO Hydrogenation over Preoxidized Rh foils.

Preoxidation of the Rh foil resulted in a large increase in the initial TN's, a slight shift in the product distribution toward the higher molecular weight hydrocarbons and the formation of methanol, ethanol and acetaldehyde, as was observed for preoxidation of the Rh(111) crystal. Fig.8 shows the CO hydrogenation results over a preoxidized Rh foil at  $300^\circ\text{C}$ ,  $3\text{H}_2:1\text{CO}$  and 6 atm. Unlike the clean Rh catalysts there was evidence for some structure sensitivity on the preoxidized Rh catalysts. On the preoxidized Rh foil the increases in the  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  TN were smaller, the  $\text{C}_2\text{H}_4$  to  $\text{C}_2\text{H}_6$  ratio was larger, and a lower percentage of ethanol was produced when compared to the preoxidized Rh(111) crystal surface. The two preoxidized surfaces showed a similar variation of surface composition during the reaction in the  $\text{H}_2$ -rich mixtures, namely a large decrease in the oxygen concentration and the deposition of about one monolayer of carbon on the surface (Figs. 5a and 5b). The only difference was that more boron segregated to surface during preoxidation of the Rh foil.

The variation of the product distribution with reaction temperature for the preoxidized Rh foil (Fig.9) was the same as observed for the preoxidized Rh(111), i.e. increased  $\text{C}_2\text{H}_4$  to  $\text{C}_2\text{H}_6$  ratio and percentage of higher weight products as the temperature was decreased. From an Arrhenius plot of the

of the initial  $\text{CH}_4$  TN versus  $1/T$  the activation energy ( $E_a$ ) of methane formation over the preoxidized Rh foil was determined to be  $12+3$  kcal/mole. Since the initial  $\text{CH}_4$  TN was used in this determination, this  $E_a$  should be representative of methane formation over a heavily oxidized Rh surface. The value of  $E_a$  for the preoxidized Rh foil (12 kcal/mole) is significantly lower than the value for the clean Rh foil<sup>5</sup> (24 kcal/mole), suggesting that methane formation proceeds by different mechanisms over the two Rh surfaces. The change in mechanism is also suggested by the Arrhenius pre-exponential factor which decreases by more than a factor of  $10^3$  upon preoxidation of the Rh foil. Decreasing the  $\text{H}_2:\text{CO}$  ratio over the preoxidized Rh foil resulted in an increase in the  $\text{C}_2\text{H}_4$  to  $\text{C}_2\text{H}_6$  ratio and the percentage of higher weight products, as was observed over the preoxidized Rh(111) crystal. Again the only oxygenated hydrocarbon formed under CO rich conditions was acetaldehyde. The major difference between the two preoxidized Rh catalysts under CO rich conditions was that more carbon was deposited on the preoxidized foil and poisoning was correspondingly faster.

#### D. CO Hydrogenation with Gas Phase Additives

The selectivity change resulting from addition of ~1 mole % of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{C}_2\text{H}_4$  to a  $3\text{H}_2:1\text{CO}$  reaction mixture at  $250^\circ\text{C}$  and 6 atm over a preoxidized Rh(111) crystal is shown in Fig.10. Because the amount of gas phase additive completely overshadowed the amount of that particular product <sup>formed</sup> / by the Rh catalyst, oxygenated hydrocarbons or  $\text{C}_2$  hydrocarbons produced by the catalyst could not be measured when their respective additives were present. All three additives produced similar results--a small increase in the higher molecular weight fraction, especially  $\text{C}_3$ . The absolute amount

of methane produced and the initial  $\text{CH}_4$  TN were not significantly affected by the presence of the gas phase additives, thus the decrease in the  $\text{C}_1$  fraction is due to the increases in the higher weight hydrocarbon fractions.

#### IV DISCUSSION

Preoxidation of the Rh catalysts produces pronounced changes in catalyst activity and selectivity, indicating that the chemical environment of the Rh atoms plays an important role in determining the catalytic properties of Rh catalysts. This is consistent with previous investigations of Rh catalysts. Below 1 atm, CO hydrogenation over supported Rh catalysts formed by decomposition of Rh carbonyls produce primarily methanol on MgO, ZnO, BeO and CaO supports<sup>1</sup> and primarily ethanol on  $\text{Ca}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ThO}_2$ ,  $\text{ZrO}_2$  and  $\text{CeO}_2$  supports.<sup>2</sup> CO hydrogenation over supported Rh catalysts formed from  $\text{RhCl}_3$  impregnation on  $\text{La}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  supports<sup>36</sup> and Rh carbonyl decomposition on  $\text{SiO}_2$ ,  $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  supports<sup>1</sup> produces primarily hydrocarbons at reaction pressures of 1 atm and below. Thus, the product distribution obtained over these Rh catalysts changes significantly with changes in the rhodium chemical environment.

The  $\text{CH}_4$  TN over the unsupported Rh catalysts depends directly on the oxygen concentration in the near surface region as shown in Table I. The lowest initial  $\text{CH}_4$  production rate is obtained during CO hydrogenation over clean catalysts and the highest during CO hydrogenation over the catalysts with an epitaxial oxide. An intermediate rate is given by preoxidized surfaces which are flashed in vacuum prior to CO hydrogenation,<sup>5</sup> resulting in a low near-surface oxygen concentration.<sup>10</sup> The fact that  $\text{CO}_2$  hydrogenation

gives a higher  $\text{CH}_4$  TN than  $\text{CO}$  hydrogenation under the same reaction conditions suggests that  $\text{CO}_2$  is oxidizing the catalysts during hydrogenation.  $\text{CO}_2$  has been shown to dissociatively adsorb on Rh surfaces<sup>8,9,11</sup> and an oxygen AES signal was detected in the early stages of  $\text{CO}_2$  hydrogenation over the Fe catalysts.

The dramatic changes in the Arrhenius pre-exponential factor and activation energy, shown in Table II, strongly indicate that a change in mechanism is the cause of the increased  $\text{CH}_4$  TN on preoxidized surfaces. In particular, a simple effect of surface area or site density change can be ruled out. The activation energy on the oxygen treated surfaces, 12 kcal/mole, is half that on the clean surfaces, 24 kcal/mole, and within experimental error of the value for  $\text{CO}_2$  hydrogenation on clean Rh, again suggesting oxidation by  $\text{CO}_2$ . Preexponential factors show a similar trend.

Our results for  $\text{CO}$  hydrogenation at 6 atm over the clean, unsupported Rh catalysts agree well with previous results for the supported Rh catalysts which primarily produce hydrocarbons<sup>1,2,6</sup> and Rh foils<sup>5</sup> at 1 atm. This agreement indicates that Rh foils and single crystals are good model catalysts for non-oxygenated hydrocarbon formation over supported Rh catalysts and that either metallic Rh or a Rh-carbon complex is active in this process. Conversely, the total absence of oxygenated hydrocarbons over the clean Rh catalysts indicates that an environment other than Rh or Rh-C is necessary for their production at low pressures over Rh supported on basic metal oxides.<sup>1,2</sup>

We did observe oxygenated hydrocarbons in amounts up to about 10% on surfaces pretreated with oxygen, suggesting that a higher oxidation state of the Rh atoms may be crucial to this process.  $\text{CO}$  is believed to be the

source of oxygen in the products because oxygenated species are still produced after near-surface oxygen concentration has reached its low steady-state value, but the diffusion of oxygen from subsurface layers cannot be ruled out at present as the possible source of oxygen that appears in the oxygenated products. <sup>18</sup>O labeling studies are needed to resolve this question.

In the pressure range of 25 to 200 atm oxygenated products have been observed over Rh/SiO<sub>2</sub> catalysts.<sup>3,4</sup> If clean unsupported Rh serves as a good model for these catalysts, as suggested above, then similar behavior should be observed in our system at high pressures. Increasing pressure from 1 atm<sup>5</sup> to 6 atm (present study) did not significantly change the product distribution, showing that pressures higher than 6 atm are necessary for production of oxygenated products on clean, unsupported Rh.

There were two minor differences between our results and the previously reported results for Rh foil at 1 atm.<sup>5</sup> The percentage of C<sub>2</sub>H<sub>6</sub> in the C<sub>2</sub> fraction after three hours of CO hydrogenation was larger in our experiments, possibly due to the higher H<sub>2</sub> partial pressure at 6 atm causing increased C<sub>2</sub>H<sub>4</sub> hydrogenation. We observed catalyst poisoning at 6 atm which was not seen at 1 atm.<sup>5</sup> It is possible at 6 atm the effect of the S and Cl impurities is more pronounced or the carbon overlayer is being transformed from an active to a nonreactive layer.

The selectivity changes observed from variation of the reaction temperature and H<sub>2</sub>:CO ratio were reasonable. The free energies of formation,  $\Delta G_f$ , of the higher molecular weight hydrocarbons decrease more rapidly than those of the lower molecular weight hydrocarbons as the temperature is decreased.<sup>13</sup> Also, at the lower temperature the olefin  $\Delta G_f$ 's approach the paraffin  $\Delta G_f$ 's.<sup>13</sup>

Thus, a larger percentage of higher weight hydrocarbons and olefins should be present at the lower reaction temperatures, in agreement with the experimental results. Decreasing the  $H_2:CO$  ratio will reduce the amount of hydrogen available for incorporation into the reaction products and reduce the hydrogenation of the reaction products. Thus, CO rich mixtures will produce larger percentages of olefins and aldehydes, in agreement with the experimental results.

A comparison between our CO hydrogenation results over Rh catalysts to previous results over Fe catalysts<sup>12-14</sup> reveals several differences. The Fe catalysts are more active initially but poison more rapidly due to a large buildup of carbon on the surface. During this initial, active period the Fe catalysts produce hydrocarbons at higher rates and higher average molecular weight than the Rh catalysts, but after a multilayer of carbon has been deposited on the Fe catalysts, only  $CH_4$  is formed and at a significantly lower rate. Thus, the Fe catalysts are more active than the Rh catalysts, but the Rh catalysts maintain their Fischer-Tropsch (FT) activity for a longer period of time. During the FT active period both metals are covered by about one monolayer of carbon under  $H_2$ -rich conditions. Upon pretreatment with oxygen, both Fe and Rh catalysts show increased TN, a higher molecular weight distribution of products and formation of oxygenated hydrocarbons, the last effect being more pronounced on Rh. Gas-phase additive studies show that readsorption of the initially formed olefinic products, such as  $C_2H_4$  and  $C_3H_6$  is important for hydrocarbon chain growth on Fe,<sup>14</sup> while the effect for Rh is small. Thus for Rh, unlike Fe, our product distributions obtained at low CO conversions (<1%) without gas phase additives should be

representative of results at higher conversion.

#### V Conclusions

1. No structure sensitivity or oxygenated hydrocarbon formation was observed over the clean Rh catalysts during the catalyzed hydrogenation of CO.
2. Preoxidation of the Rh catalysts resulted in higher TN, the production of oxygenated hydrocarbons and some structure sensitivity.
3. Activation energy for methanation on preoxidized Rh was significantly less than on clean Rh, indicating a different mechanism.
4. The readsorption of the initial reaction products affects the product distribution to a lesser extent on Rh catalysts than on Fe catalysts.

#### VI. Acknowledgement

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TABLE I. Comparison of initial methanation TN for CO and CO<sub>2</sub> hydrogenation in a batch reactor at 300°C over Rh and Fe catalysts. Methane TN in molec•site<sup>-1</sup>•sec<sup>-1</sup>.

Catalyst	Reaction Conditions	Surface Pretreatment	Initial CH <sub>4</sub> TN at 300°C	Ref.
Rh foil	3H <sub>2</sub> :1CO 0.92 atm	Clean Preoxidized <sup>a</sup>	0.13	5
			0.33	5
Rh foil	3H <sub>2</sub> :1CO <sub>2</sub> 0.92 atm	Clean Preoxidized <sup>a</sup>	0.33 1.7	5 5
Rh foil	3H <sub>2</sub> :1CO 6 atm	Clean Preoxidized <sup>b</sup>	0.15 1.7	This paper.
Rh(111)	3H <sub>2</sub> :1CO 6 atm	Clean Preoxidized <sup>b</sup>	0.15 4.6	This paper.
Fe foil	3H <sub>2</sub> :1CO 6 atm	Clean Preoxidized <sup>c</sup>	1.9	12
			18.7	12
Fe foil	3H <sub>2</sub> :1CO <sub>2</sub> 6 atm	Clean	10.9	12

a. 15 min. at 300°C in 700 torr O<sub>2</sub>, then heated to 1000°C in vacuum.

b. 30 min. at 600°C in 800 torr O<sub>2</sub>.

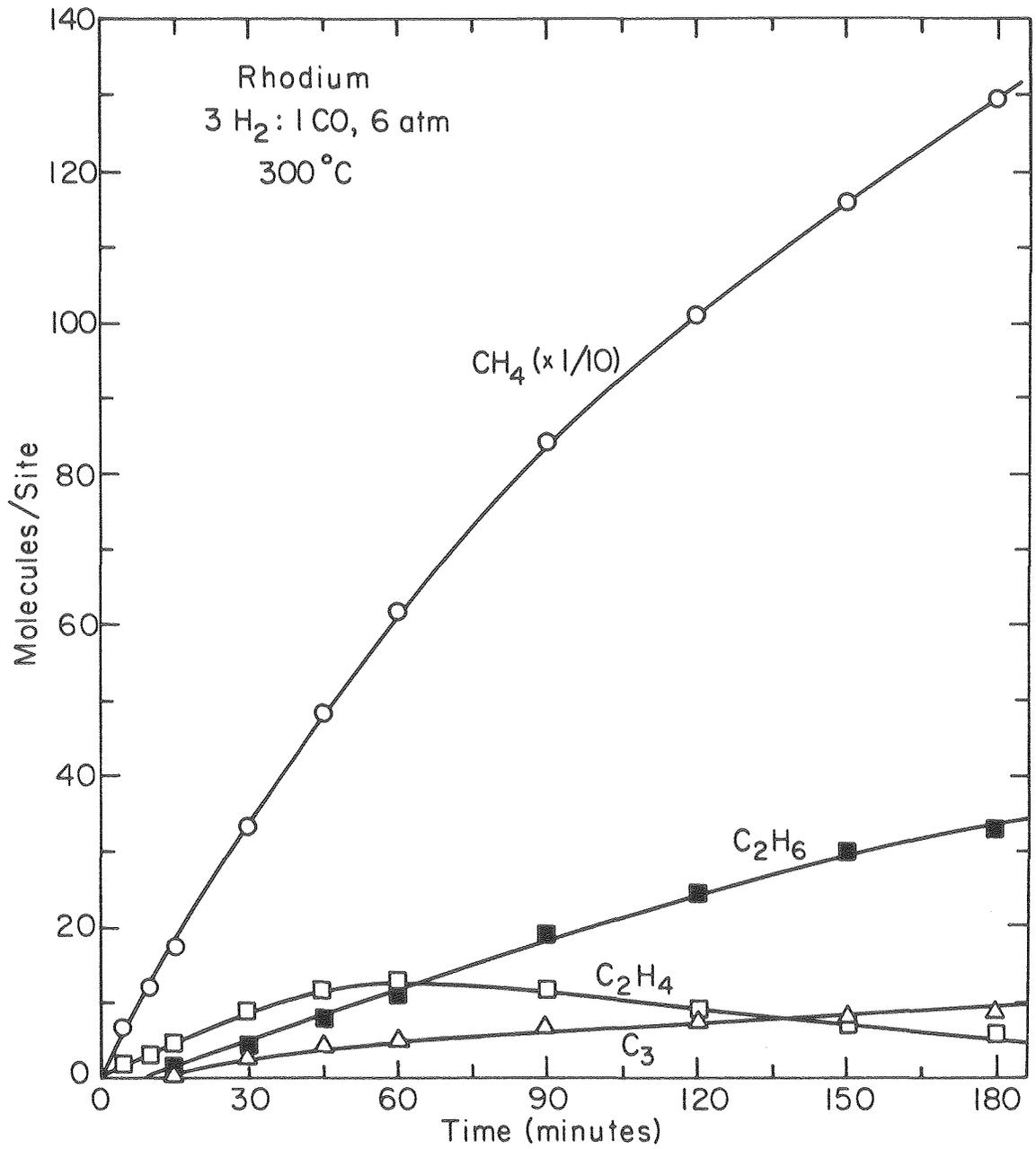
c. 20 min at 300°C in 4 atm O<sub>2</sub>.

TABLE II. Comparison of the Arrhenius Methanation Parameters ( $TN=Ae^{-E_a/RT}$ )  
for CO and CO<sub>2</sub> Hydrogenation over Polycrystalline Rh Foils.

Reaction Conditions	Surface Pretreatment	Ch <sub>4</sub> TN at 300°C (molec•site <sup>-1</sup> •sec <sup>-1</sup> )	A (molec•site <sup>-1</sup> •sec <sup>-1</sup> )	E <sub>a</sub> (kcal/mole)	Ref.
0.92 atm, 3H <sub>2</sub> :1CO	Clean	0.13±0.03	10 <sup>8</sup>	24±3	5
0.92 atm, 3H <sub>2</sub> :1CO <sub>2</sub>	Clean	0.33±0.05	10 <sup>5</sup>	16±2	5
6 atm, 3H <sub>2</sub> :1CO	Preoxidized	1.7 ± 0.4	10 <sup>5</sup>	12±3	This paper.

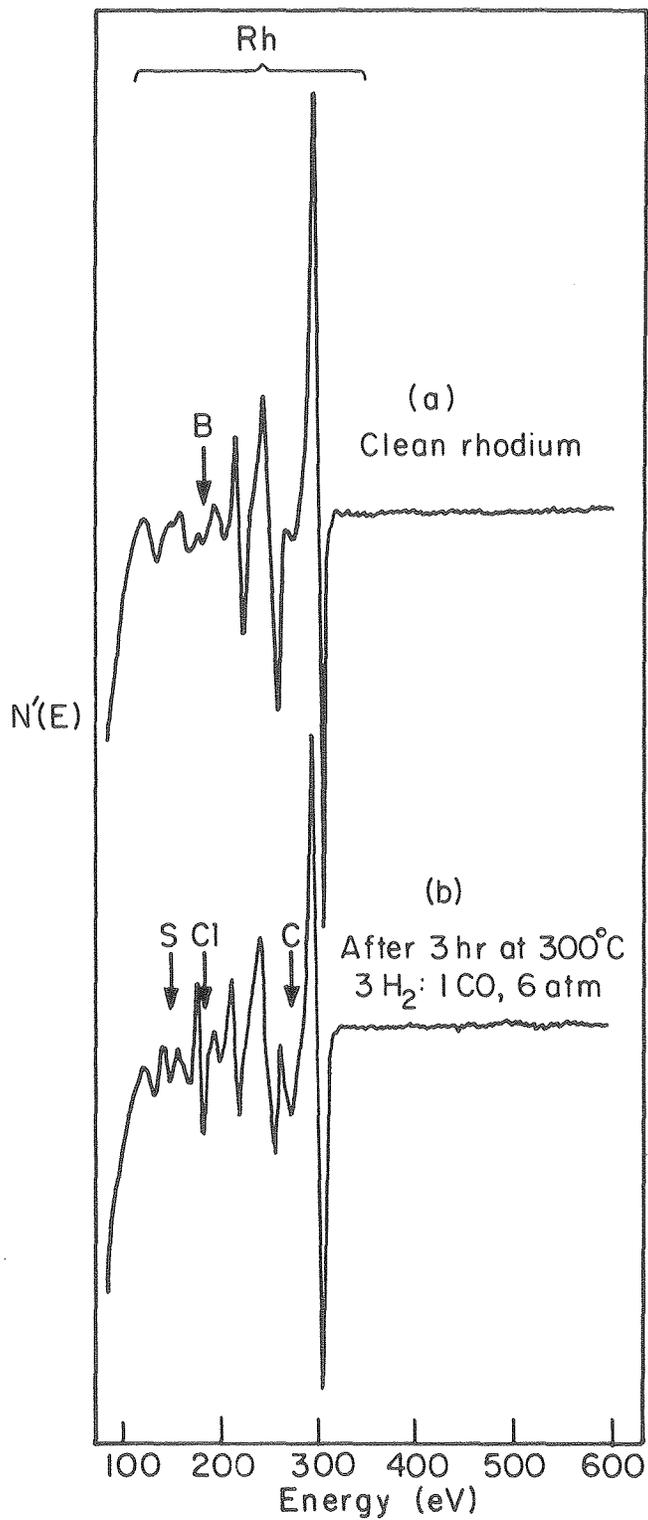
FIGURE CAPTIONS

- Fig.1 Buildup of the C<sub>1</sub> to C<sub>3</sub> hydrocarbon products during CO hydrogenation over initially clean Rh foil or (111) catalysts at 6 atm, 300°C and 3H<sub>2</sub>:1CO.
- Fig.2 AES spectra of the initially clean Rh catalyst (a) before and (b) after three hours of CO hydrogenation at 6 atm, 300°C and 3H<sub>2</sub>:1CO.
- Fig.3 Buildup of the C<sub>1</sub> to C<sub>3</sub> hydrocarbon products during CO hydrogenation over a preoxidized Rh(111) catalyst at 6 atm, 300°C and 3H<sub>2</sub>:1CO.
- Fig.4 The product distributions in weight percent after two hours of CO hydrogenation over pretreated Rh(111) catalysts at 6 atm, 300°C and 3H<sub>2</sub>:1CO. Oxy HC is the sum of the CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>CHO fractions. In C<sub>2</sub> fraction the areas above and below the dotted line represent the C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> fractions.
- Fig.5 AES spectra of the preoxidized Rh(111) catalyst (a) before, and (b) after three hours of CO hydrogenation at 6 atm, 300°C, 3H<sub>2</sub>:1CO, or (c) three hours of CO hydrogenation at 6 atm, 300°C, 1H<sub>2</sub>:3CO,
- Fig.6 Buildup of C<sub>1</sub> to C<sub>4</sub> hydrocarbon products during CO hydrogenation over a preoxidized Rh(111) catalyst at 6 atm, 300°C and 1H<sub>2</sub>:3CO.
- Fig.7 The product distributions in weight percent after two hours of CO hydrogenation over pretreated Rh(111) catalysts at various reaction conditions. (See Fig.4 for explanation of symbols).
- Fig.8 Buildup of the C<sub>1</sub> to C<sub>3</sub> hydrocarbon products during CO hydrogenation over a preoxidized Rh foil at 6 atm, 300°C and 3H<sub>2</sub>:1CO.
- Fig.9 The product distributions in weight percent after two hours of CO hydrogenation over preoxidized Rh foil at 6 atm, and 3H<sub>2</sub>:1CO for various reaction temperatures (See Fig.4 for explanation of symbols.)
- Fig.10 The product distributions in weight percent after two hours of CO hydrogenation over preoxidized Rh(111) catalysts at 6 atm, 250°C and 3H<sub>2</sub>:1CO with 1 mole percent of CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH or C<sub>2</sub>H<sub>4</sub> in the initial reaction mixture. (See Fig.4 for explanation of symbols.)



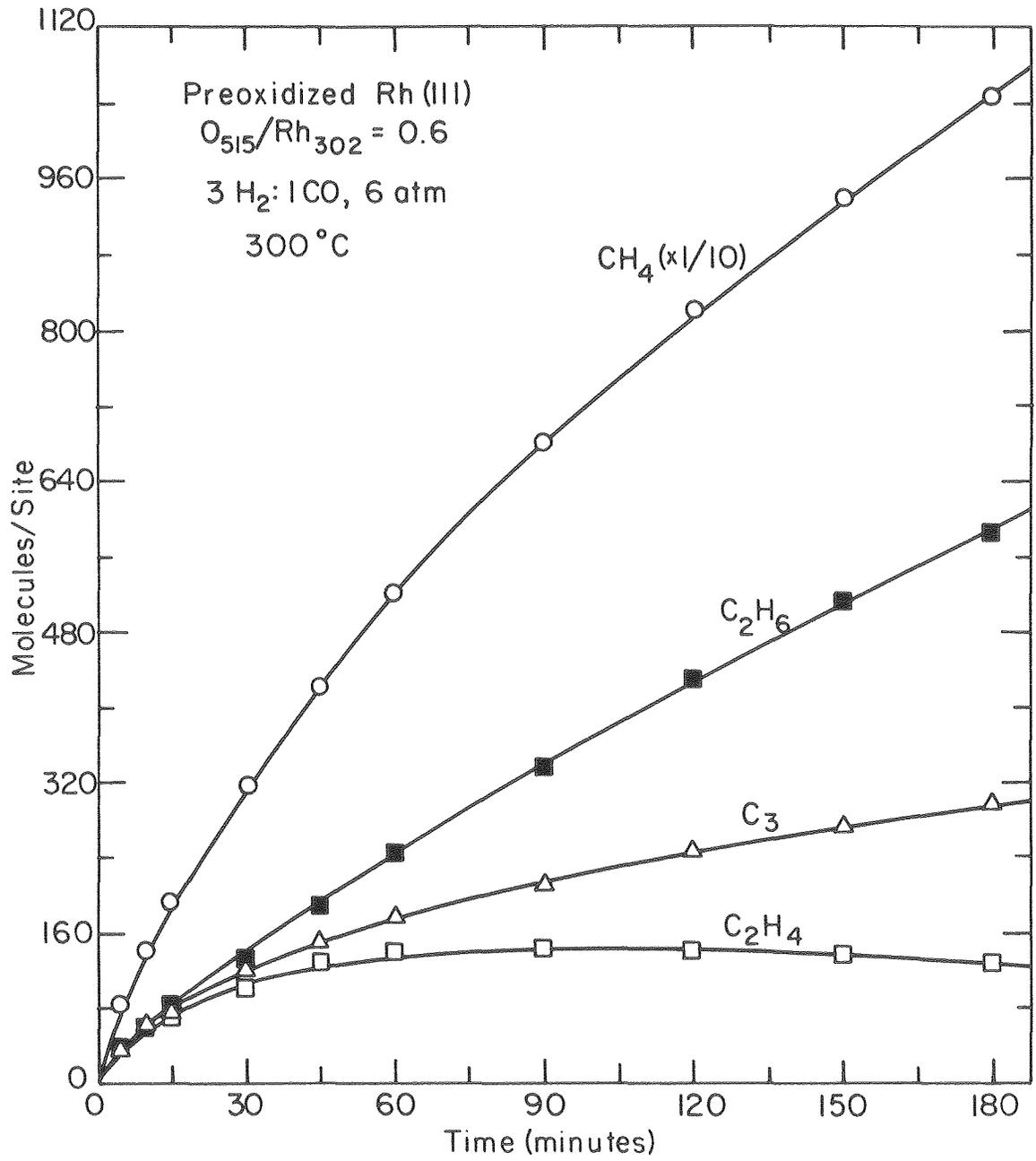
XBL 794-6130

Fig.1



XBL 797-6655

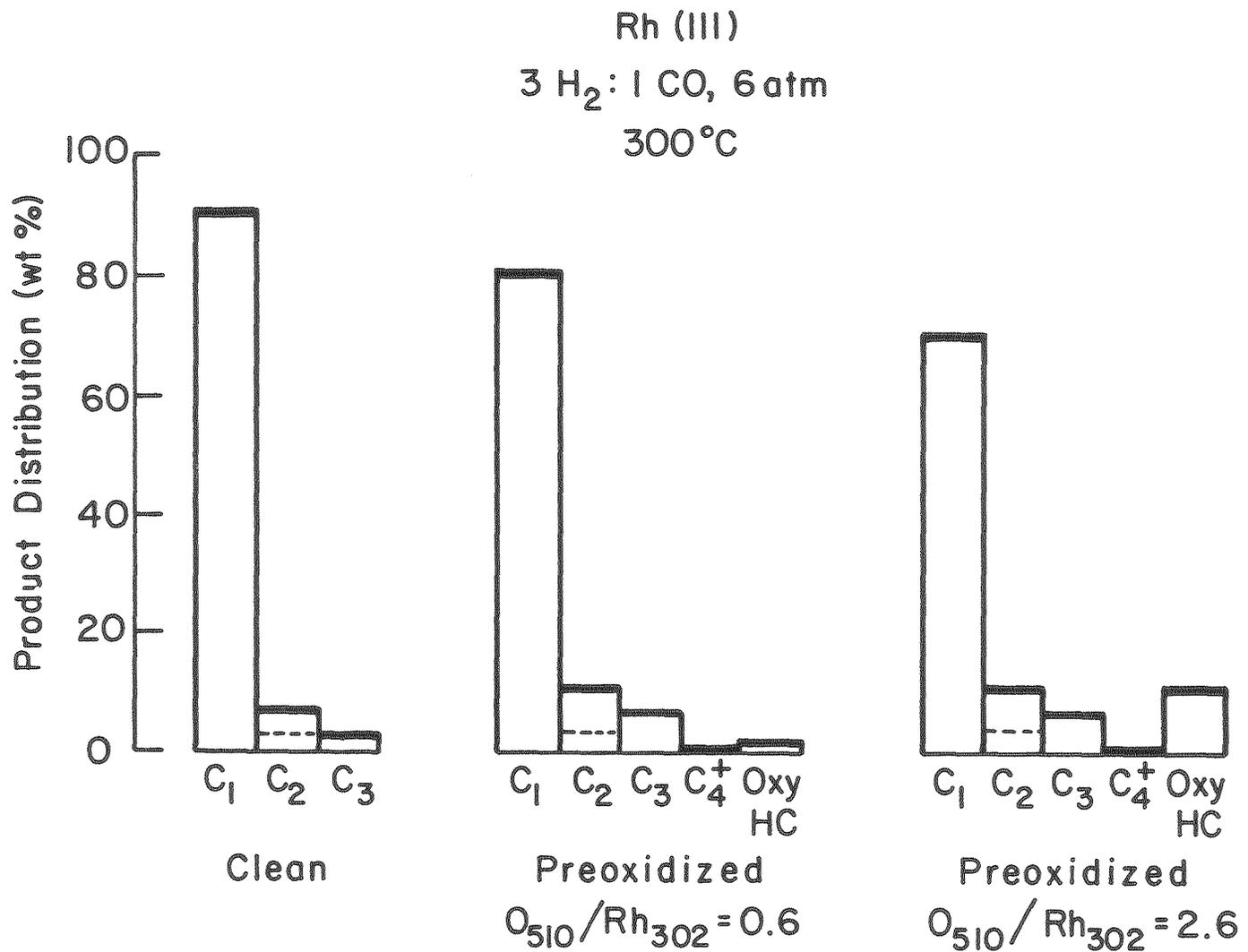
Fig.2



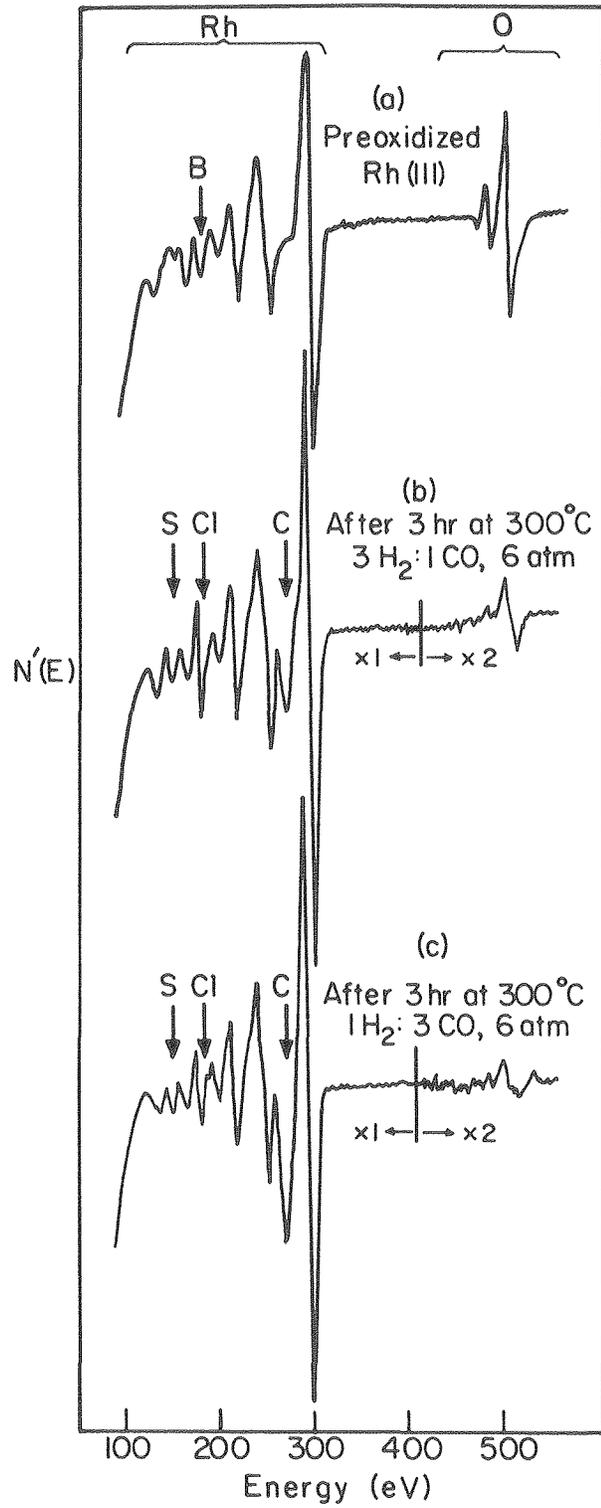
XBL 794-6136

Fig. 3

Fig. 4

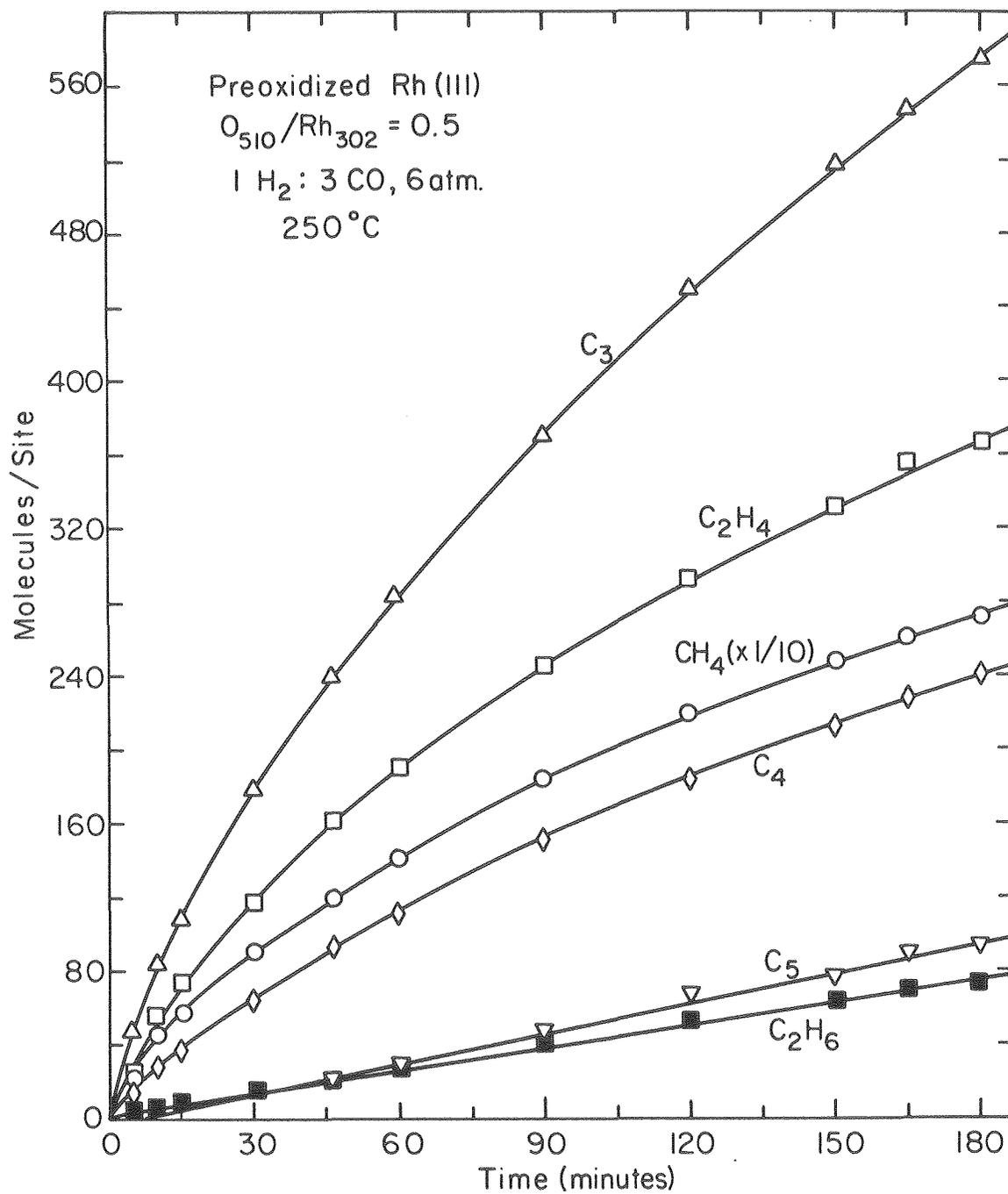


XBL 794-6137



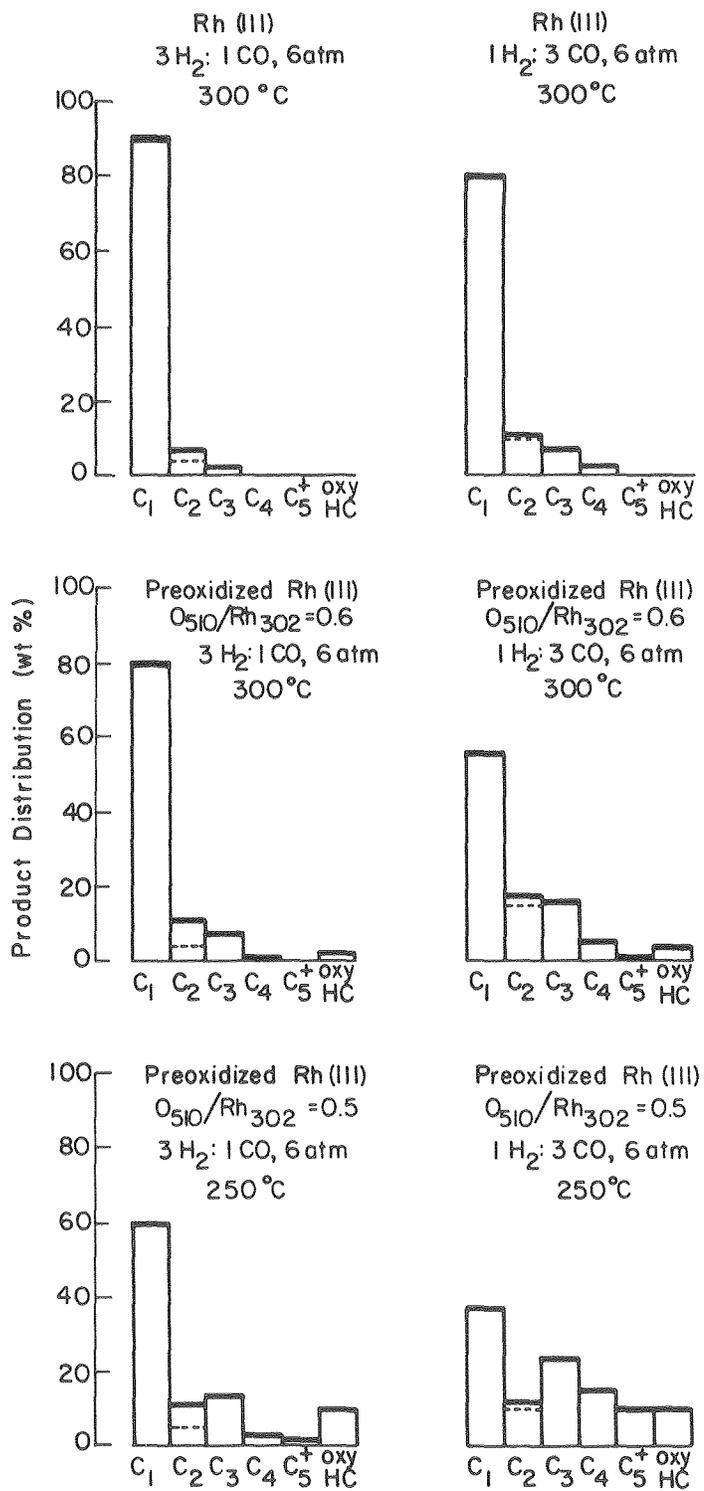
XBL797-6654

Fig. 5



XBL794-6129

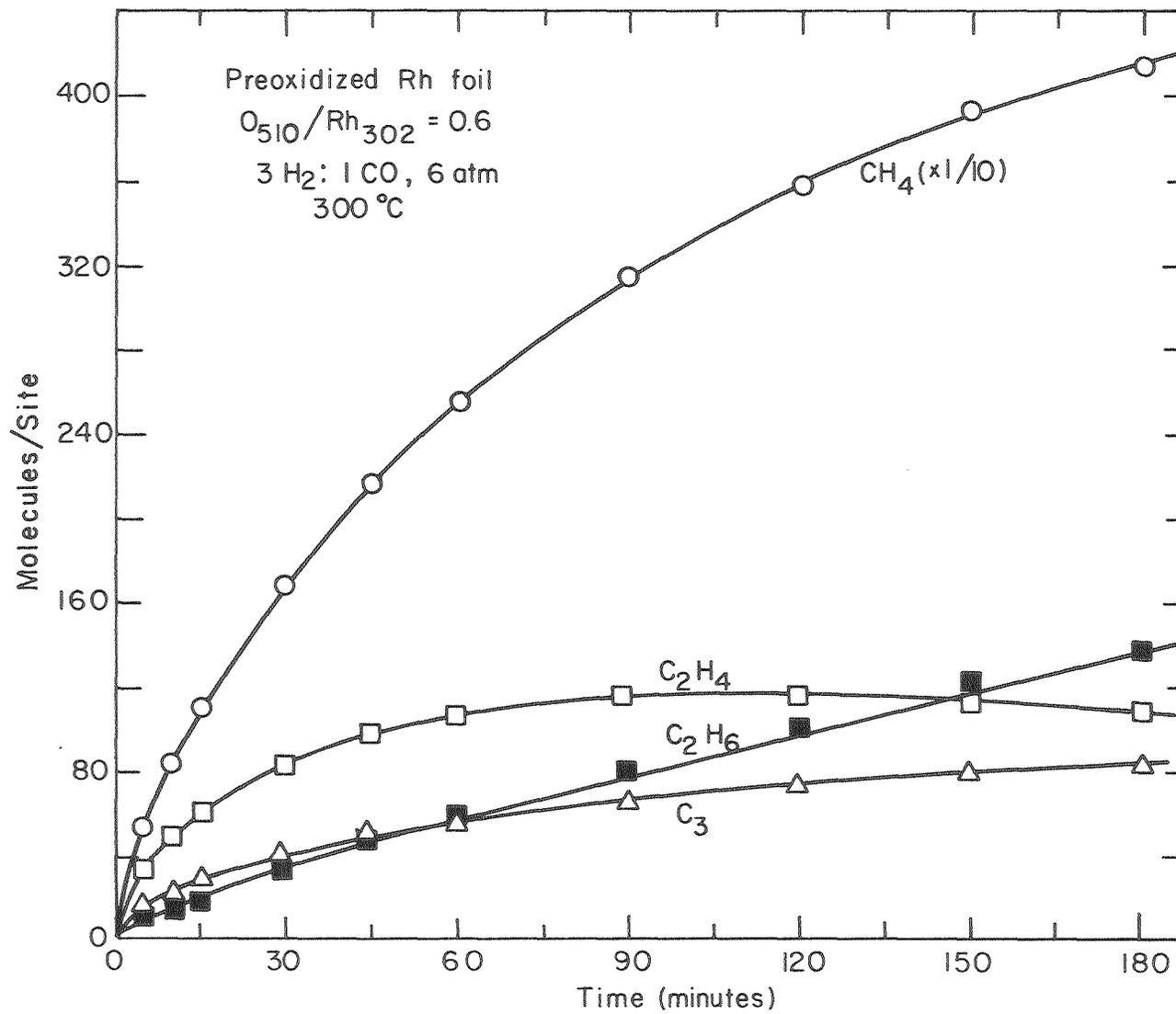
Fig. 6



XBL 797-6653

Fig. 7

Fig. 8



XBL 793-5955

Fig. 9

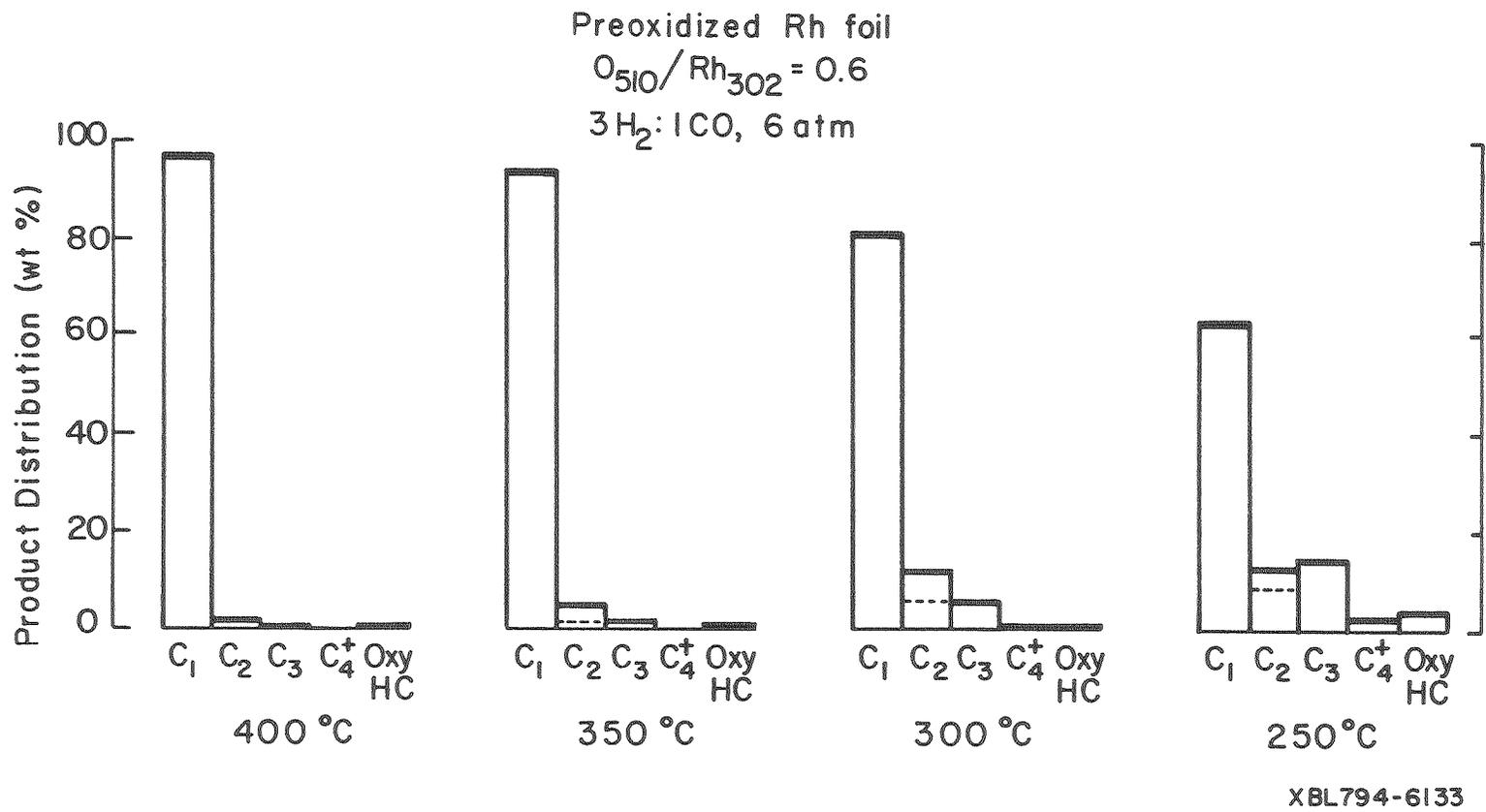
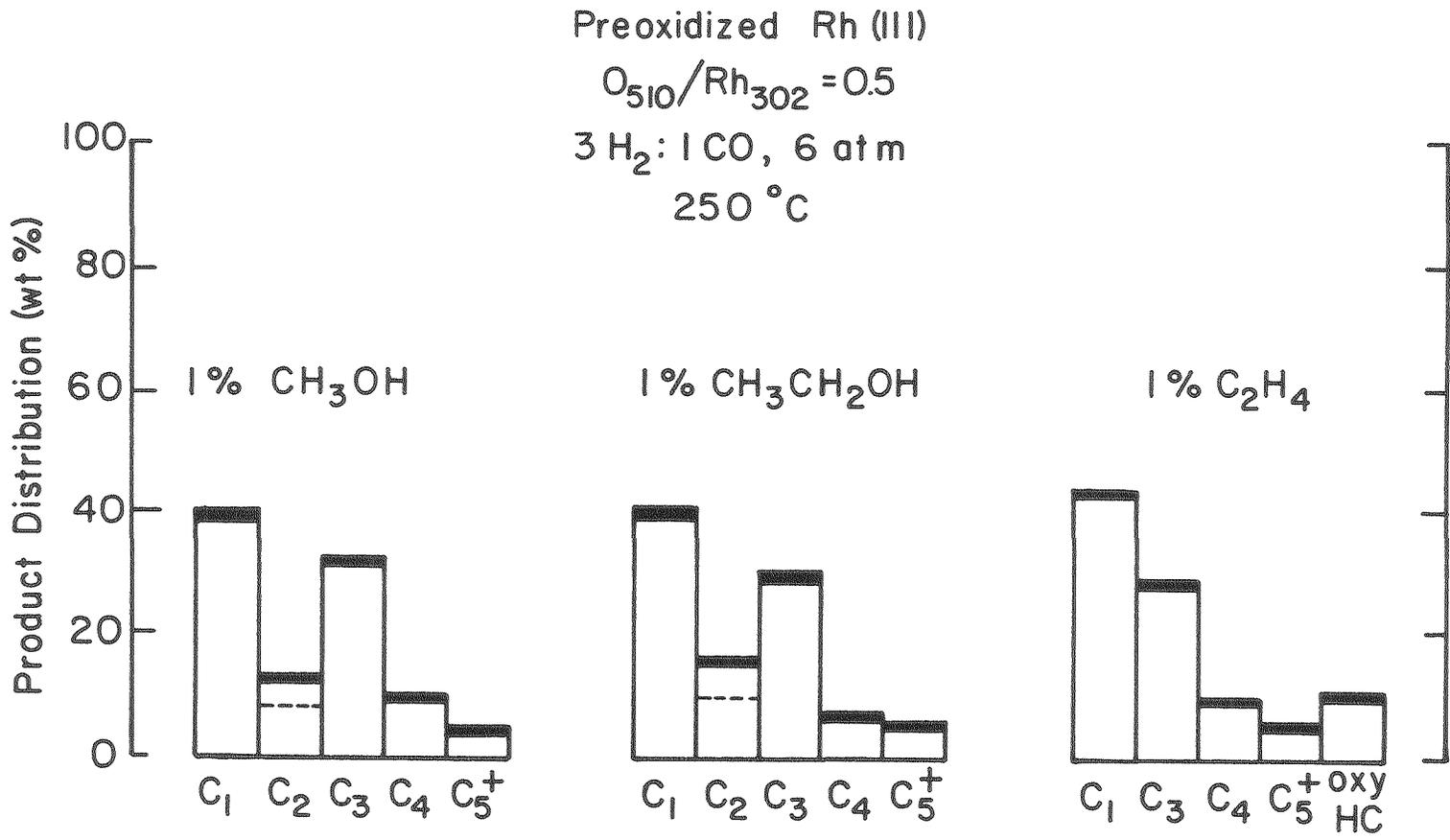


FIG. 10



XBL797-6652