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CO Hydrogenation over Clean and Oxidized Rhodium Foil and Single Crystal Catalysts. Correlations of Catalyst Activity, Selectivity, and Surface Composition[1]

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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 ($H_2:CO$ ratio, reaction temperature, surface pretreatment, and gas phase additives) were systematically varied to determine the conditions necessary 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^{-1} sec^{-1} at 300°C, and did not produce detectable amounts of oxygenated hydrocarbons. Preoxidation of the Rh (800 Torr O_2, 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 preexponential 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 $H_2:CO$ ratio increased the C_2H_4 to C_2H_6 ratio and shifted the product distribution toward the higher molecular weight hydrocarbons. The addition of 1 mole% of CH_3OH, CH_3CH_2OH, or C_2H_4 to the $H_2:CO$ reaction mixture caused 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 (*1–4*) 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 reaction pressure, the catalyst support, and method of depositing the rhodium on the support. These results are in contrast to earlier results over Rh foils (*5*) and supported Rh on Al_2O_3 (*6*) 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 for 1 mole% of CH_3OH, CH_3CH_2OH, and C_2H_4 added to the H_2–CO reaction mixture. The surface structure and composition of the catalysts

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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 (*5, 7*). 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 ($\sim 1\ cm^2$) were characterized by LEED and AES, and cleaned by Ar ion bombardment and annealing, as described previously (*8, 9*). After extended cleaning, the only impurity detected on the Rh surfaces was a small amount of boron (<10% of a monolayer). When the cell was closed, the apparatus could be operated as a stirred batch reactor (160 cm^3 volume) or a catalyst pretreatment chamber.

In the batch reactor mode, the cell was closed and first the H_2, then the CO was admitted to the cell loop. The CO (Matheson, 99.95%) was passed through a dry ice–ethanol trap to remove carbonyls; the 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 H_2 and CO. Once the reaction mixture was placed in the cell it was circulated for several minutes to ensure 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 (FID), Chromasorb 102 column, and peak area integrator (Spectra-Physics Minigrator 23000). An FID was needed to detect the low concentration levels of the hydrocarbon products during reaction since our reaction conditions resulted in low conversion of the CO (<1%) to products. Thus, possible reaction products such as H_2O or CO_2 could not be detected. 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 3 hr, 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 min in 800 Torr of O_2. This caused the formation of an epitaxial oxide layer on the Rh crystals and the dissolution of oxygen into the Rh lattice (*10*). The oxide layer produced under these conditions was amorphous and generally had an O_{510}/Rh_{302} peak-to-peak ratio of 0.5 to 0.6. Considerably higher O_{510}/Rh_{302} 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 (molecules $site^{-1}$) the atom density of the Rh(111) surface (1.6×10^{15} atoms cm^{-2}) 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 density on the oxide surface.

III. RESULTS

A. CO Hydrogenation over Clean Rh Catalysts

The buildup of reaction products during a typical 3-hr CO hydrogenation experiment at 300°C, 6 atm, and $3H_2 : 1CO$ 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^{-1} sec^{-1}. Small amounts of C_2 and C_3 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.

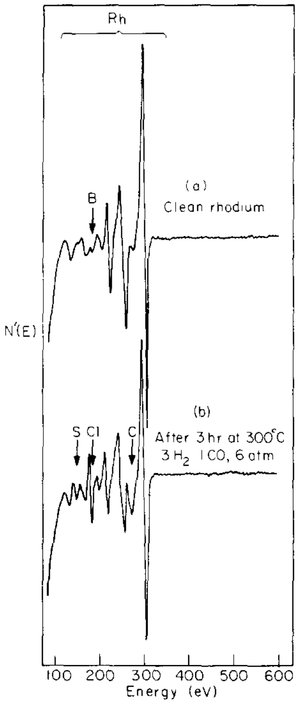

FIG. 2. AES spectra of the initially clean Rh catalyst (a) before and (b) after 3 hr of CO hydrogenation at 6 atm, 300°C, and $3H_2 : 1CO$.

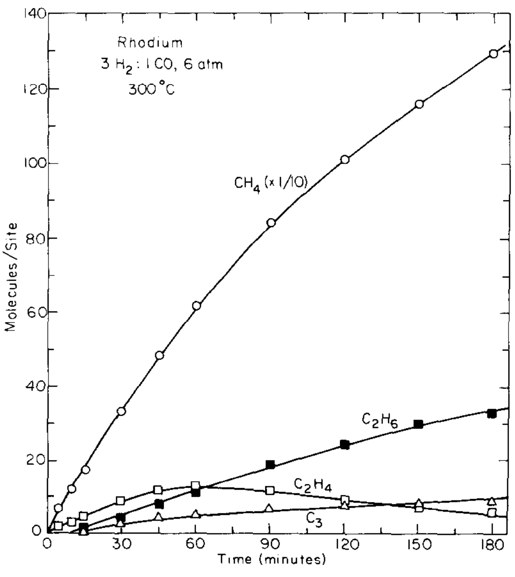

FIG. 1. Buildup of the C_1–C_3 hydrocarbon products during CO hydrogenation over initially clean Rh foil or (111) catalysts at 6 atm, 300°C, and $3H_2 : 1CO$.

Changes in both catalyst activity and selectivity are occurring during the reaction. The CH_4 TN was constant over the first 30 min but then began decreasing and by 2 to 3 hr had reached a value that was about half of the initial TN. In the first hour, C_2H_4 was the major C_2 product, but after 1 hr C_2H_6 was the major C_2 product and the C_2H_4 TN was negative. This C_2 selectivity change probably results from the hydrogenation of C_2H_4 to C_2H_6 because of the high H_2 partial pressure (4.5 atm) in the reactor. When the H_2 partial pressure was reduced to 1.5 atm by changing the $H_2 : CO$ ratio from 3 : 1 to 1 : 3 C_2H_4 remained the dominant C_2 product during the entire reaction. The fall off in the CH_4 TN after 30 min is probably due to catalyst poisoning. The AES spectra in Fig. 2 show that ~5% of a monolayer of S, ~10% of a monolayer of Cl, and ~1 monolayer of carbon are present on the Rh catalysts after a 3-hr reaction. The majority of the increase in the S AES signal occurred during the first 30 min, but it did continue to increase slowly during the remainder of the reaction. Sulfur can be segregated to surface of these catalysts by annealing them in vacuum, thus it is likely that S is diffusing from the bulk to surface and eventually to the active methanation sites on these catalysts resulting in the observed decrease in the CH_4 TN. The Cl and C AES signals increased to their maximum valves before 30 min and did not change during the remainder of the reaction, thus the methanation poisoning is not due to an increase in the amount of Cl or C on the catalyst. A change in the chemical state of C (such as carbide to graphite) could be causing the CH_4 TN decrease but the close proximity of the Rh 256 and 302 AES peaks to the C 272 AES peak prevented analyzing the lineshape of the C peak in order to determine if this was the case. Cl was never detected during any of the low-pressure treatments of the Rh catalysts and probably originates from somewhere in the reactor.

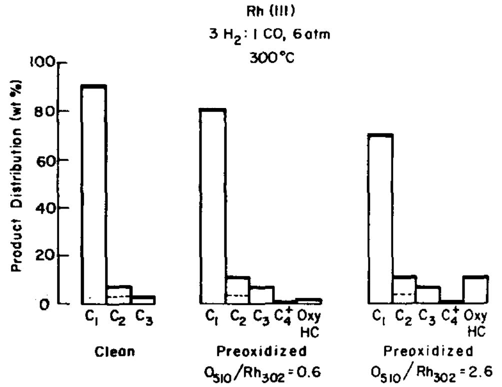

FIG. 4. The product distributions in weight percent after 2 hr of CO hydrogenation over pretreated Rh(111) catalysts at 6 atm, 300°C, and $3H_2 : 1CO$. Oxy HC is the sum of the CH_3OH, CH_3CH_2OH, and CH_3CHO fractions. In the C_2 fraction the areas above and below the dotted line represent the C_2H_6 and C_2H_4 fractions.

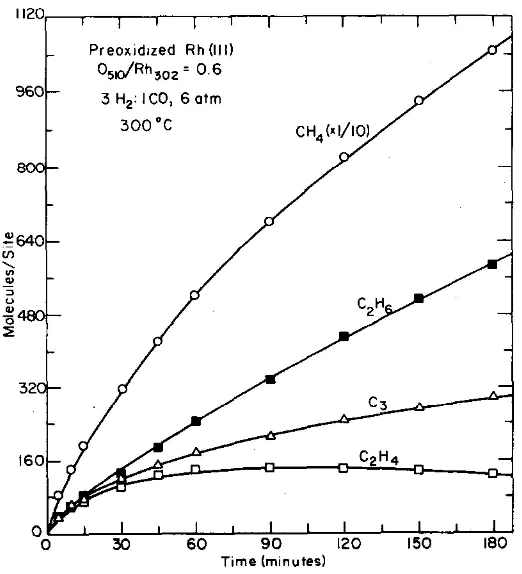

FIG. 3. Buildup of C_1–C_3 hydrocarbon products during CO hydrogenation over a preoxidized Rh(111) catalyst at 6 atm, 300°C, and $3H_2 : 1CO$.

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°C, $3H_2 : 1CO$, and 6 atm are shown in Figs. 3 and 4. The TNs decreased markedly during the first 30 mins, then slowly decreased until they reached a fairly constant value by 3 hr. The initial CH_4 TN was 4.6 molecules $site^{-1}$ sec^{-1}, but unlike over the clean surfaces where it remained constant over the first 30 min, by 15 min, the CH_4 TN over the preoxidized Rh(111) catalyst had fallen off by almost 50%. After 3 hr the CH_4 TN was 20% of the initial rate. The TN decrease could be correlated with the oxygen concentration in the near surface region. During the first 30 min of CO hydrogenation, the oxygen AES signal decreased rapidly to the steady state level shown in Fig. 5b. Thus, the highest activity was observed at the highest oxygen concentration and after the steady-state concentration of oxygen was reached, the catalyst activity decreased to a constant value. Oxygenated hydrocarbons were produced during the entire 3 hr of CO hydrogenation. The S, Cl, and C AES signals behaved in the same manner on the preoxidized Rh(111)

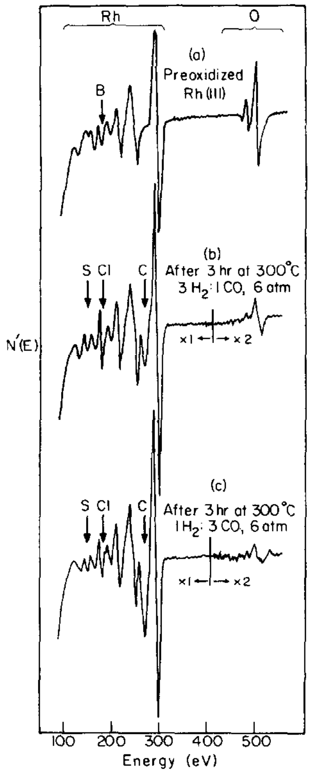

FIG. 5. AES spectra of the preoxidized Rh(111) catalyst (a) before, (b) after 3 hr of CO hydrogenation at 6 atm, 300°C, $3H_2$: 1CO, or (c) after 3 hr of CO hydrogenation at 6 atm, 300°C, $1H_2$: 3CO.

catalyst that was observed on the clean Rh catalysts.

The selectivity changes caused by preoxidation resulted from different degrees of enhancement of the TN. Initially increasing the oxygen concentration to $O_{510}/Rh_{302} = 0.6$ resulted in larger increases in the C_2H_6 and C_3 TN than in the CH_4 and C_2H_4 TN. This yielded the lower CH_4 percentage and C_2H_4 to C_2H_6 ratio. Further increase of the O_{510}/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 CH_4 in the products.

Decreasing the H_2 : CO ratio and reaction temperature shifted the product distribution toward the higher molecular weight hydrocarbons and increased the C_2H_4 to C_2H_6 ratio (Figs. 6 and 7). These changes are due to a decrease in the CH_4 and C_2H_6 TN, while the C_2H_4 and C_3 TN remained relatively constant. During the CO-rich reactions, the only oxygenated hydrocarbon produced was acetaldehyde and two to four monolayers of carbon were deposited on the Rh surface (Fig. 5c).

C. CO Hydrogenation over Preoxidized Rh Foils

Preoxidation of the Rh foil resulted in a large increase in the initial TNs, 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. Figure 8 shows the CO hydrogenation results over a preoxidized Rh foil at 300°C, $3H_2$: 1CO, 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 CH_4 and C_2H_6 TN were smaller, the C_2H_4 to C_2H_6 ratio was larger, and a lower percent-

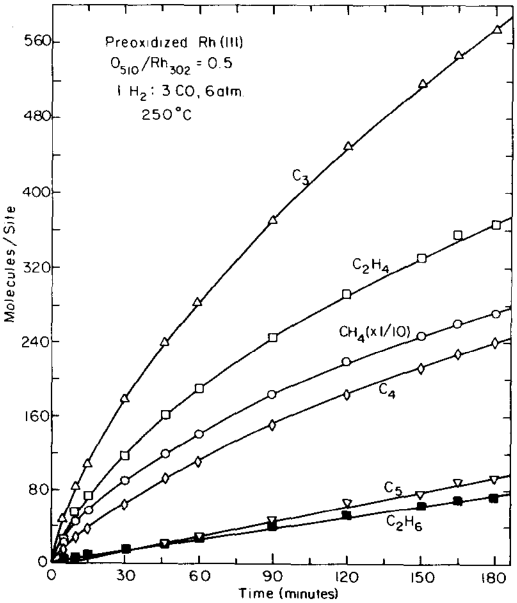

FIG. 6. Buildup of C_1–C_5 hydrocarbon products during CO hydrogenation over a preoxidized Rh(111) catalyst at 6 atm, 300°C, $1H_2$: 3CO.

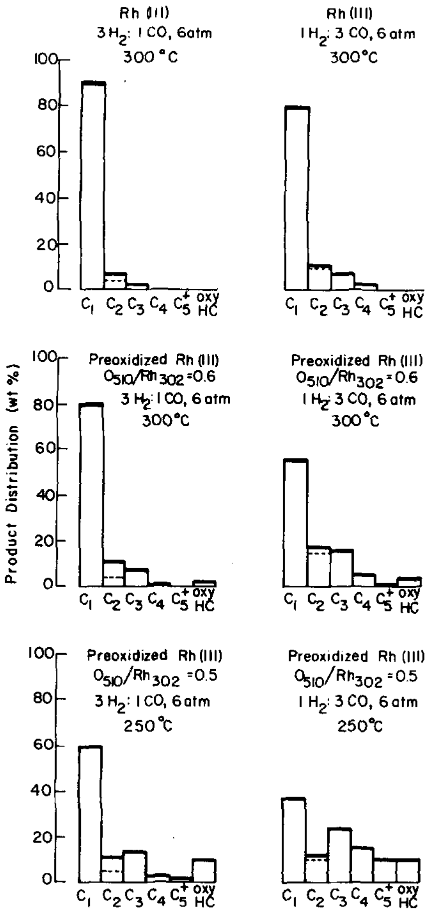

FIG. 7. The product distributions in weight percent after 2 hr of CO hydrogenation over pretreated Rh(111) catalysts at various reaction conditions. (See Fig. 4 for explanation of symbols.)

age 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 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 b). 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 preoxidized Rh(111), i.e., increased C_2H_4 to C_2H_6 ratio and percentage of higher weight products as the temperature was decreased. From a plot of the initial CH_4 TN in Table 1 versus $1/T$, the Arrhenius activation energy (E_a) for methane formation over the preoxidized Rh foil was determined to be 12 ± 3 kcal/mole. Since the initial 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 (*5*) (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 preexponential factor which decreases by $\sim 10^3$ upon preoxidation of the Rh foil. Decreasing the $H_2 : CO$ ratio over the preoxidized Rh foil resulted in an increase in the C_2H_4 to C_2H_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 causing a larger decrease in the reaction rates.

D. CO Hydrogenation with Gas Phase Additives

The selectivity change resulting from

TABLE 1

The Initial Methanation Turnover Numbers (TN) for CO Hydrogenation over Preoxidized Rh Foils at 6 atm $3H_2 : 1CO$ and Temperatures between 250°C and 400°C

Reaction temperature (°C)	CH_4 TN
250	0.74
300	1.7
350	3.5
400	12.7

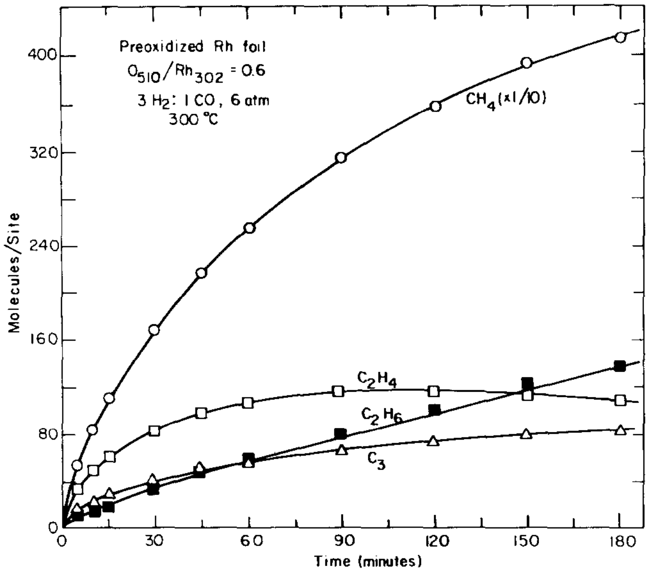

FIG. 8. Buildup of the C_1–C_3 hydrocarbon products during CO hydrogenation over a preoxidized Rh foil at 6 atm, 300°C, and $3H_2$: 1CO.

addition of ~1 mole% of CH_3OH, CH_3CH_2OH, and C_2H_4 to a $3H_2$: 1CO reaction mixture at 250°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 formed by the Rh catalyst, oxygenated hydrocarbons or 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 C_3. The absolute amount of methane produced and the initial CH_4 TN were not significantly affected by the presence of the gas phase additives, thus the decrease in the 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

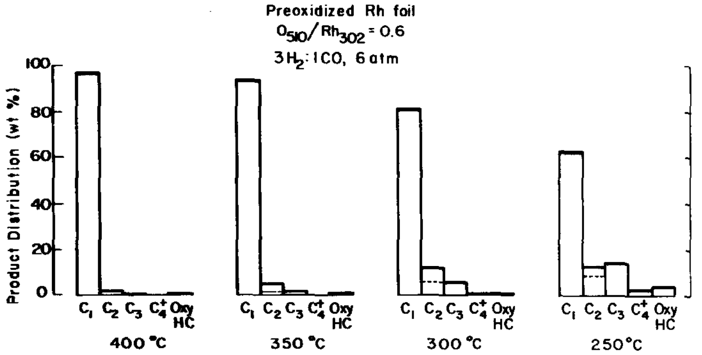

FIG. 9. The product distributions in weight percent after 2 hr of CO hydrogenation over preoxidized Rh foil at 6 atm and $3H_2$: 1CO for various reaction temperatures. (See Fig. 4 for explanation of symbols.)

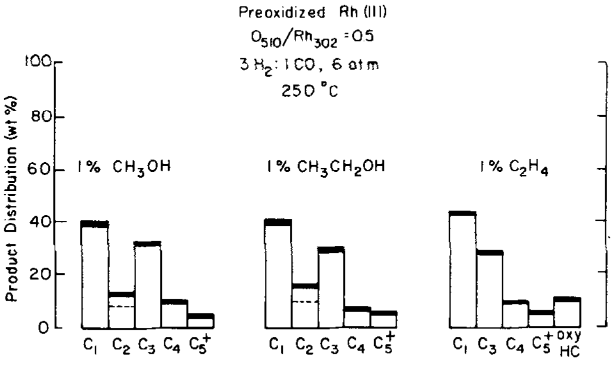

FIG. 10. The product distributions in weight percent after 2 hr of CO hydrogenation over preoxidized Rh(111) catalysts at 6 atm, 250°C, and $3H_2$: 1CO with 1 mole% of CH_3OH, CH_3CH_2OH, or C_2H_4 in the initial reaction mixture. (See Fig. 4 for explanation of symbols.)

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 (*1*) and primarily ethanol on La_2O_3, TiO_2, ThO_2, ZrO_2, and CeO_2 supports (*2*). CO hydrogenation over supported Rh catalysts formed from $RhCl_3$ impregnation on La_2O_3 and Al_2O_3 supports (*3*, *6*) and Rh carbonyl decomposition on SiO_2, SnO_2, WO_3, V_2O_5, and Al_2O_3 supports (*1*) produce 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 CH_4 TN over the unsupported Rh catalysts depends directly on the oxygen concentration in the near surface region as shown in Table 2. The lowest initial 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 (*5*), resulting in a low near-surface oxygen concentration (*10*). The fact that CO_2 hydrogenation gives a higher CH_4 TN than CO hydrogenation under the same reaction conditions suggests that CO_2 is oxidizing the catalysts during hydrogenation. CO_2 has been shown to dissociatively adsorb on Rh surfaces (*8*, *9*, *11*) and an oxygen AES signal was detected in the early stages of CO_2 hydrogenation over the Fe catalysts (*12*).

The dramatic changes in the Arrhenius

TABLE 2

Comparison of Initial Methanation TN for CO and CO_2 Hydrogenation in a Batch Reactor at 300°C over Rh and Fe Catalysts (Methane TN in Molec $Site^{-1}$ Sec^{-1})

Catalyst	Reaction conditions	Surface pretreatment	Initial CH_4 TN at 300°C	Reference
Rh foil	$3H_2$: 1CO	Clean	0.13	*5*
	0.92 atm	Preoxidized[a]	0.33	*5*
Rh foil	$3H_2$: $1CO_2$	Clean	0.33	*5*
	0.92 atm	Preoxidized[a]	1.7	*5*
Rh foil	$3H_2$: 1CO	Clean	0.15	This paper
	6 atm	Preoxidized[b]	1.7	
Rh(111)	$3H_2$: 1CO	Clean	0.15	This paper
	6 atm	Preoxidized[b]	4.6	
Fe foil	$3H_2$: 1CO	Clean	1.9	*12*
	6 atm	Preoxidized[c]	18.7	*12*
Fe foil	$3H_2$: $1CO_2$ 6 atm	Clean	10.9	*12*

[a] Fifteen minutes at 300°C in 700 Torr O_2, then heated to 1000°C in vacuum.
[b] Thirty minutes at 600°C in 800 Torr O_2.
[c] Twenty minutes at 300°C in 4 atm O_2.

preexponential factor and activation energy, shown in Table 3, strongly indicate that a change in mechanism is the cause of the increased CH_4 TN on preoxidized surfaces. 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 CO_2 hydrogenation on clean Rh, again suggesting oxidation by CO_2. Preexponential factors show a similar trend.

Our results for 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 (*1, 2, 6*) and Rh foils (*5*) at 1 atm. This agreement indicates that Rh foils and single crystals are good model catalysts for nonoxygenated 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 (*1, 2*).

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. In the pressure range of 25 to 200 atm oxygenated products have been observed over Rh/SiO_2 catalysts (*3, 4*). 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 (*5*) 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.

The selectivity changes observed from variation of the reaction temperature and $H_2:CO$ ratio were reasonable. The free energies of formation, ΔG_f, of the higher molecular weight hydrocarbons decrease more rapidly than those of the lower molecular weight hydrocarbons as the temperature is decreased (*13*). Also, at the lower temperatures, the olefin ΔG_f's approach the paraffin ΔG_f's (*13*). 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 (*12–14*) reveals

TABLE 3

Comparison of the Arrhenius Methanation Parameters (TN = $Ae^{-E_a/RT}$) for CO and CO_2 Hydrogenation over Polycrystalline Rh Foils

Reaction conditions	Surface pretreatment	CH_4 TN at 300°C (molec site^{-1} sec^{-1})	A (molec site^{-1} sec^{-1})	E_a (kcal/mole)	Reference
0.92 atm, $3H_2:1CO$	Clean	0.13 ± 0.03	$\sim10^8$	24 ± 3	*5*
0.92 atm, $3H_2:1CO_2$	Clean	0.33 ± 0.05	$\sim10^5$	16 ± 2	*5*
6 atm, $3H_2:1CO$	Preoxidized	1.7 ± 0.4	$\sim10^5$	12 ± 3	This paper

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. 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 (*14*), 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.

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