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THE HYDROGENATION OF CO AND CO₂ OVER POLYCRYSTALLINE RHODIUM:
CORRELATION OF SURFACE COMPOSITION, KINETICS AND PRODUCT DISTRIBUTIONS*

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ABSTRACT

Rhodium, in the form of a small surface area (~1 cm²) polycrystalline foil was used to study the CO-H₂ and CO₂-H₂ reactions at low (~10⁻⁴ Torr) and at high (700 Torr) pressures in the same apparatus. Reaction rates and product distributions were monitored with a mass spectrometer and a gas chromatograph, respectively, and the surface composition was determined by Auger Electron Spectroscopy. The various binding states of CO were studied by thermal desorption. Under reaction conditions (250-350°C, 700 Torr) the surface is covered with a catalytically active carbonaceous deposit while some oxygen is located below the surface. No surface oxygen was detectable after reaction as the removal of chemisorbed species by either the CO-O₂ or H₂-O₂ reactions was rapid at low temperatures. Carbon monoxide was found to adsorb in molecular form on clean Rh surfaces, but dissociated on surfaces pretreated in CO, or by heating in the presence of gaseous CO. Co-adsorption of H₂/CO mixtures at low pressures increased the amount of molecular CO but no changes in CO binding energy were observed.

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At low pressures (10⁻⁴ Torr) the reaction probability for both the CO-H₂ and CO₂-H₂ reactions is too low to detect products. At high pressures (700 Torr), the rates, activation energy (24±3 kcals) and product distributions from the small surface area Rh foil is nearly identical to that obtained on a dispersed rhodium catalyst. The CO₂-H₂ reaction produces methane exclusively and with a lower activation energy (16±2 kcals) than for the CO-H₂ reaction. Pretreatment of the clean surface changes the product distribution and the rates in both reactions. Pretreatment with acetylene deposits surface carbon and facilitates chain growth in the CO-H₂ reaction (a higher percentage of C₂ and C₃ products). Pretreating with oxygen dissolves oxygen in the bulk and increases the methanation rate by up to a factor of five over the clean surface. It appears that active rhodium- carbon- oxygen complexes form at the surface and rehydrogenate to yield the various products.
I. INTRODUCTION

The synthesis of organic compounds from carbon monoxide and hydrogen mixtures over transition metal catalysts has been described extensively \(^{(1)}\) in the literature since its discovery in 1902 by Sabatier and Senderens. Most of the chemical studies concentrated on maximizing the yields and optimizing the selectivity for the main reactions; methanation, \(^{(2)}\) the methanol synthesis, \(^{(3)}\) and the synthesis of higher molecular weight hydrocarbons (Fischer-Tropsch reaction \(^{(4)}\)).

The formation of hydrocarbons from CO-H \(_2\) mixtures is thermodynamically favorable, although higher pressures (in excess of one atmosphere) are necessary to facilitate the formation of higher molecular weight products. (The pressure dependence of the thermodynamics of hydrocarbon production is described in the Appendix.)

The rates of formation of products by this reaction are very low as compared to other hydrocarbon reactions (dehydrogenation or hydrogenolysis). Thermodynamic equilibrium between reactants and the many possible products is not established even at the high pressures commonly employed. Thus, surface reactions determine the rate and product distribution, and it is important that we investigate the elementary steps of the surface reactions on the atomic scale to learn how to control the kinetics and the selectivity.

The purpose of our studies is to correlate the reactivity of the catalyst surface with its atomic structure and chemical composition. We have developed new instrumentation that permits the characterization
of the catalyst surface structure and composition in ultra high vacuum by electron scattering techniques (Low energy electron diffraction (LEED) and Auger electron spectroscopy (AES)). Then, using the same apparatus we can carry out chemisorption studies and reaction studies at low pressures (~10^{-4} Torr) and at high pressures (1-100 atm). This instrument will be described in detail.

This paper reports studies of the reaction of CO and H₂, and CO₂ and H₂ to form hydrocarbons, using polycrystalline rhodium as a catalyst. We shall show that the kinetics of methanation on this metal foil of about ~1 cm² area, is in excellent agreement with the results obtained on dispersed and supported rhodium catalysts. Thus, small area metal samples can be used as models of Fischer-Tropsch catalysts. We have determined the specific reaction rates (turnover numbers) and product distributions under a variety of experimental conditions. The surface reaction layer was characterized before and after the high pressure runs by AES and thermal desorption measurements.

We have found evidence for the presence of both molecular and dissociated CO on the surface, during the synthesis. The active rhodium surface develops a carbonaceous deposit, whilst chemisorbed oxygen is rapidly removed from the surface layer by CO and H₂. Oxygen also appears to be located below the metal surface. By changing the composition and/or structure of the rhodium-carbon surface complex by pretreatment (with acetylene or oxygen) both the reaction rate and the product distribution can be markedly altered. The CO₂-H₂ reaction yielded methane predominantly, in contrast with the much broader product
distribution obtained from CO-H₂ reactions under the same conditions.
II. EXPERIMENTAL METHODS

The apparatus used in this study has been described in detail elsewhere\(^{(5)}\) and it is shown schematically in Fig. 1. Essentially, it is an UHV surface analysis instrument incorporating an internal isolation cell, for catalytic studies at pressures from 1-100 atmospheres. In this work, this cell was operated at 700 Torr during the high pressure experiments, and for low pressure studies (10\(^{-8}\)-10\(^{-4}\) Torr), the UHV chamber was used as the reaction vessel.

The rhodium samples were small, rectangular pieces of .005" thick, high purity foil, with surface areas < 1 cm\(^2\), mounted on either a thin tantalum or rhodium holder. For quantitative measurement of reaction rates and thermal desorption on only one side of the foil, tantalum was used as an inert mask to cover unwanted portions. In other experiments, such as measurement of surface composition, a rhodium holder was used. For quantitative measurements of rates, masking of the rhodium foil was necessary, because only one side was accessible to the ion bombardment gun.

The tantalum or rhodium holder was spotwelded to two stainless steel heating rods, which were connected to the copper heating bars of the manipulator. As shown in Fig. 1, the manipulator provided a 180° axial rotation of the sample, and was enclosed in the 0.5" I.D. lower port of the isolation cell. A chromel-alumel thermocouple was spotwelded to the rear of the sample. Rotary movement was achieved via a teflon compression-sealed stainless steel shaft. This seal was
leak-free in the UHV environment, as well as having the capability of operation at high pressures (<5000 psi). It was essential to keep the internal volume of the manipulator assembly to an absolute minimum, as it formed part of the reaction cell at high pressures. Commercial manipulators were rejected on the basis of excessive internal volume, and lack of a high pressure capability (>1 atm internal pressure).

As shown in Fig. 1, the Rh sample was located at the focus of the LEED optics in the centre of the UHV chamber, and a 180° rotation was possible to direct the surface toward the quadrupole mass spectrometer for Thermal Desorption measurements, the sputter ion gun for cleaning, and the Auger gun for surface analysis. In the case of single crystals, LEED observations are also possible using this manipulator, although none are reported in this work.

The UHV chamber was pumped by a fast, (1000 l s⁻¹) 6" diffusion pump, with a 20 hour liquid nitrogen trap, and a titanium sublimation pump. This pumping combination was chosen to handle the large gas loads of CO and H₂ encountered when opening the high pressure cell, and to reduce the pump-down time before analysis of the surface after a high pressure run. After bakeout, the system base pressure was <1×10⁻⁹ Torr, which was adequate for sample cleaning purposes, and low pressure adsorption and catalysis experiments (10⁻⁹-10⁻⁴ Torr).

The high pressure isolation cell, which is shown in Fig. 1 in the closed position, was a stainless steel cylinder with a small (~30 ml) cavity which enclosed the Rh sample, and was sealed by a copper gasket situated below the sample, on the fixed portion of the
cell. This cylinder was attached to a small hydraulic press situated on top of the apparatus, which moved it up and down. The whole assembly had a total travel of about 3 inches, and was bellows sealed, to maintain UHV during movement. The sealing elements of the cell were rounded knife edges, which permitted many seals using the same gasket, and approximately 2000 psi hydraulic pressure was needed to provide a totally leak-free seal. The gasket, which was a commercial "Mini-Conflat" copper type, was softened by annealing before use, and has been in service for over 100 seals without replacement. (At one atmosphere internal operation, with an external vacuum of \( \sim 10^{-9} \) Torr)

Gases were admitted to, and circulated through the isolation cell by means of ports along the axis of the cell. As stated previously, the lower port enclosed the rotary manipulator, and gas could be circulated out through the upper port in the movable piston, and back into the manipulator, via an external metal bellows pump. (Metal Bellows Corporation Model MB10). This external loop also incorporated a small volume (0.1 ml) gas chromatography sampling valve, which extracted samples for analysis into the Gas Chromatograph (Perkin Elmer Model 3920). The isolation cell and external gas circulation route therefore were operated as a small volume (100 mls \( \pm 5 \)) stirred batch reactor.

Admission of a \( \text{H}_2/\text{CO} \) gas mixture to the reactor (cell + loop) was accomplished via a sorption-pumped manifold, which had inlets for \( \text{H}_2, \text{CO}, \text{CO}_2, \text{Ar} \) and calibration gases. This manifold served also to admit gases to the UHV chamber for low pressure experiments. All gases
were high-purity, from Matheson Gas Products, and no further purification was attempted. Gas mixtures were usually prepared in the manifold, then expanded into the reactor, or bled into the UHV system.

For low pressure catalysis studies ($10^{-8}$-$10^{-4}$ Torr), the isolation cell was raised to the open position, and the Rh sample cleaned by $\text{Ar}^+$ ion bombardment (2 keV ions $5\times10^{-5}$ Torr, 20 μA) and annealing at 1000°C in UHV. After AES analysis, gases could be admitted to the chamber via variable leak valves, and adsorption experiments, or catalytic reactions were carried out. For a catalysis experiment, the chamber was operated as a flow system, in which a dynamic pressure was maintained between $10^{-8}$ and $10^{-4}$ Torr by reducing the pumping speed with partial closure of the gate valve, while the sample was heated to a desired reaction temperature. Reaction products were detected with the quadrupole mass spectrometer, and reaction rates and product distributions determined by analysis of the cracking patterns. The maximum pressure ($10^{-4}$ Torr), that could be employed in these experiments is determined by the mass spectrometer detection. One advantage of this method was that in situ AES or LEED analyses of the catalyst surface were possible during the reaction, due to the sufficiently long electron mean free path at these reduced pressures.

For a high pressure (1 atm) catalysis experiment, the sample was usually cleaned by $\text{Ar}^+$ ion bombardment (2000 eV, 20 μA) and annealing, and following surface analysis, the isolation cell was lowered and sealed. [At this point, it was possible to demount the entire manipulator assembly and change samples, without breaking UHV in the
main chamber) Gases were pre-mixed in the manifold, then expanded into the cell and evacuated loop, to a total pressure of 700 Torr as measured on an absolute pressure dial gauge. The circulation pump was started and the loop was isolated from the manifold via a valve. Several preliminary G-C samples were taken, then the sample temperature was adjusted to reaction conditions (200-450°C) by a proportional temperature controller, which compensated for variations in temperature due to resistance changes and gas flow variations. Regulation was possible to within one or two degrees, and the Chromel-Alumel thermocouple output was measured on a Keithley millivoltmeter.

Periodically, samples were extracted into the gas chromatograph for analysis. Negligible change in total pressure occurred due to sample extraction (~0.1%). After reaction, the gases were evacuated from the central cell and loop by the sorption pumps, and the cell was then isolated from the loop, and re-exposed to UHV by raising the upper cell cylinder. The pressure was usually in the low $10^{-8}$ range within 10 minutes and below $1\times10^{-8}$ Torr within 30 mins.

Surface analysis, and thermal desorption measurements were carried out, and the sample could then be re-cleaned for a new run. A series of blank experiments was conducted and it was found that there was negligible hydrocarbon production from CO-H$_2$ mixtures on the tantalum support, thermocouple, or stainless steel walls.

Gas chromatography samples at high pressures (700 Torr) were analysed over Chromosorb 102 columns, which resolved all of the lower molecular weight hydrocarbons adequately. A consequence of the use of
small surface area (< 1 cm²) catalyst samples was that conversions were about 0.1%, and flame ionization detection was necessary to detect the product formation. Product detection and analysis was simplified by the fact that H₂, CO, and CO₂ were not detectable in the hydrogen flame, although regretfully, other products such as H₂O were also not detectable.
III. RESULTS

A. Low Pressure Studies

1. Preparation of clean rhodium surfaces

The Auger spectra of the Rh surface before and after cleaning are shown in Figs. 2(A) and 2(B). The main initial impurities were sulphur and carbon and these were easily removed by ion bombardment (2000 eV, 20 μA) resulting in a clean Rh surface spectrum of Fig. 2(B). To maintain reproducible catalytic and adsorption activity, annealing was necessary, and a short anneal (~5 mins @ 1000°C) was usually done, although this was minimized because of the segregation of an impurity (~180 eV, chlorine) upon cooling the sample. This was presumed to be chlorine and not tantalum as it appeared also on rhodium-supported samples, and no higher energy Ta peaks were observable in the spectrum. Attempts were made to rid the sample of chlorine by repeated ion bombardments and temperature cycling, but a final solution was to ion-clean the sample, and minimize the annealing time to prevent segregation. No segregation was observed in the low temperature catalysis and adsorption experiments. The peak overlap between the Rh(260) peak and the C(270) peak was not reduced by lowering the modulation amplitude below 5V RMS, and was therefore a consequence of the natural peak widths and instrumental broadening. Quantitative analysis of carbon on these surfaces was therefore very difficult and was not attempted.

Removal of carbon by other methods such as high temperature oxygen treatment was tried, and found to be less effective than ion bombardment.
A surprising observation after oxygen treatments was the lack of substantial oxygen Auger signals. The rhodium surfaces did not accumulate oxygen near the surface as easily as carbon. In Fig. 2(c) is shown the Auger spectrum of the clean Rh surface, heated in $O_2$ (1×10⁻⁷ Torr) at 500°C for 10 mins. Only a small oxygen emission is seen.


CO was found to adsorb strongly on the clean Rh surface at low pressures (10⁻⁹-10⁻⁴ Torr) and 300K, but the adsorption behavior was markedly dependent on the surface pretreatment. Molecular, or α-CO desorbed around 250°C from the clean surface, and the thermal desorption spectra, as a function of coverage are shown in Fig. 3. These spectra were taken with a surface heating rate of 25°C/second, and by pre-selecting the mass 28 peak in the quadrupole mass spectrometer. The surface saturated with CO between 10-30L (IL=10⁻⁶ Torr seconds), and all of the CO desorbed as a single peak on the clean surface. This behavior is similar to observations of CO adsorption on other group VIII metals such as Ir(6), where CO also desorbs around 250°C.

It was found, however, that a single thermal desorption peak of the type in Fig. 3 was only obtained after scrupulously cleaning the Rh surface by ion bombardment. In particular, maintaining the surface at 800°C during Ar⁺ ion bombardment was found to be necessary. If this was not done, a second CO thermal desorption peak was also present, around 700°C, as shown in Figs. 4 and 5. As will be discussed later this high temperature CO desorption peak is believed to be a
recombination of adsorbed C and O atoms from dissociated CO, and the dissolution could be induced by adsorbing CO on a surface which was previously contaminated with C or O impurities (from previous experiments), or by pre-heating the surface in CO.

The desorption temperature of ~250°C is similar to the value found for molecular CO on iridium\(^6\) although the heat of adsorption cannot be determined from our data. Independent measurements of the heat of adsorption on rhodium gave the value as 44 kcal/mole\(^\)\((17)\) and this is similar to the value reported for iridium\(^6\). The 250°C peak is therefore certainly molecular, but the 700°C desorption peak is most probably a recombination of adsorbed C and O. This hypothesis is supported by the observation of a similar recombination of C and O atoms to form CO at around 800K on a Ni(110) crystal\(^18\).  

Figure 4(A) shows the desorption of CO around 250°C from the clean surface, prepared by the high temperature ion bombardment, and annealing. Figure 4(B) shows the effect of ion bombarding the surface, without annealing it: the amount of adsorbed CO is increased, but no new peaks appear, implying that this is caused by a surface area increase. In Fig. 4(C) to 4(E), the clean surface was heated in \(10^{-6}\) Torr of CO/H\(_2\) (1:1); CO and CO\(_2\), respectively for 30 mins at 300°C. The scale on these spectra has been reduced by a factor of 4. A new CO thermal desorption peak, around 700°C, has appeared, and there is no significant difference in the spectra of 4(C) to 4(E), indicating similar species on the surface.
Both gas phase CO and CO₂ therefore dissociate on the clean Rh surface upon heating and hydrogen does not seem to be necessary for this process to occur.

After the thermal desorption spectrum of 4(E) was taken, CO was then re-adsorbed on this surface and Fig. 5(F) resulted. Instead of a single peak, both molecular (250°C) and dissociated (700°C) CO desorbed. The presence of the dissociated CO however was related to the rate at which CO was adsorbed on the surface, and this is illustrated in 5(G) and 5(H). Spectrum 5(G) was obtained by saturating the surface from 5(F) with CO at 2x10⁻⁶ Torr, and spectrum 5(H) was obtained by slowly adsorbing CO from the residual vacuum (1x10⁻⁹ Torr) over a period of 2 hours. In the case of the short exposure, the low temperature peak dominates, but for the slow adsorption, the high temperature peak dominates. The high temperature peak could again, be eliminated by Ar⁺ ion bombardment at 800°C, followed by annealing. In spectrum 5(I), a H₂-CO mixture (1:1) was adsorbed on the clean surface to saturation at 1x10⁻⁶ Torr. The amount of low temperature CO on the surface significantly increased, but there were no apparent changes in binding energy of this state. Thus the presence of gas phase hydrogen does not appear to change the binding energy of adsorbed CO on the metal surface.

The Auger spectra of the Rh surface prior to adsorption of CO, when the high temperature peak was present, were identical to the clean surface. Therefore it is proposed that very low concentrations of C and O dissolved in the near-surface layers of rhodium may affect
the CO desorption, by promoting the dissociation of molecular CO. The predominance of dissociated CO upon heating the sample in H\textsubscript{2}-CO, CO, and CO\textsubscript{2}, and the similarity of the thermal desorption spectra suggests that it is a layer of carbon and oxygen atoms, recombining and desorbing as carbon monoxide. No other species were detectable during these desorption experiments. (eg. CO\textsubscript{2})

Hydrogen adsorption was studied, and H\textsubscript{2} was found to desorb around room temperature, so accurate data was not taken. The outgassing of H\textsubscript{2} dissolved in the Ta holder was also a problem. From the previous spectra, hydrogen does not seem to play an important role in the CO dissociation process, although it did increase the amount of α-CO on the surface, during CO-adsorption.

Carbon dioxide was found to adsorb on the clean surface of Rh, although when desorbed, or heated in a pressure of 1×10\textsuperscript{-6} Torr of CO\textsubscript{2}, dissociation occurred and a high temperature CO desorption peak was seen, similar to that from heating in CO.

3. Low Pressure Catalysis Studies

In these experiments, the mass spectrometer was the detector, and a dynamic pressure of the reacting gases was established in the UHV chamber by adjusting the leak rate and the pumping speed. The amplitude of the detected masses is proportional to their rate of production in the chamber under these flow conditions.

In the first experiments, mixtures of H\textsubscript{2} and CO gas varying from 1:1 to 3:1 ratio were established in the chamber at pressures between 1×10\textsuperscript{-4} Torr and 1×10\textsuperscript{-7} Torr. The sample temperature was raised as
high as 600°C, but usually around 300°C, and a search was conducted through the entire mass range (1 to 60) to find new masses or changes in those present. At no time was there any evidence for hydrocarbon product formation under these conditions. In particular, no methane was detectable.

Other mixtures of gases were tried, including H\textsubscript{2}-O\textsubscript{2} and CO-O\textsubscript{2}. H\textsubscript{2}O formation was observed over a short period of time (several minutes) from the H\textsubscript{2}-O\textsubscript{2} mixture (10\textsuperscript{-7} Torr, 1:1, 300°C), but no reliable kinetic data could be taken due to changes in the rate with time. The CO-O\textsubscript{2} reaction, however, was more reproducible and the reaction rate was measured as a function of temperature in Fig. 6. The only product was CO\textsubscript{2}, and the amplitude of the mass 44 peak was measured as a function of temperature from room temperature to 600°C. The reaction rates were quite reproducible, showing no hysteresis as the temperature was cycled, and the surface appeared capable of sustaining the reaction indefinitely. The maximum in the rate vs. temperature curve in Fig. 6 is similar to the curves observed on other transition metals, e.g. Ir\textsuperscript{(6)}.

The mechanism is believed to involve adsorbed oxygen atoms reacting with gas phase CO. Auger analysis during reaction showed that oxygen was present on the surface, but disappeared upon evacuation of the reactant gases. The importance of this mechanism to the understanding of the CO-H\textsubscript{2} reaction at high pressures, and an explanation of the absence of CO-H\textsubscript{2} products at low pressures, will be included in the discussion.
B. Atmospheric Pressure Studies

1. The Product Distribution and Surface Composition on the Clean Rhodium Surface

The CO-H\textsubscript{2} reaction was investigated at 700 Torr total pressure, with the high pressure cell operating as a batch reactor. Prior to isolation of the sample, it was Ar\textsuperscript{+} ion bombarded at 800°C for 20 mins, then annealed at 1000°C for 5 mins in UHV (<1x10\textsuperscript{-8} Torr). The surface was then analysed with AES. The high temperature ion bombardment was necessary to remove near-surface impurities (C, O, and S) introduced from previous experiments. Reproducible catalytic behavior was only possible with the above treatment.

In Fig. 7 we show the results of a 5 hour run at 300°C, 3:1 H\textsubscript{2}/CO ratio and 700 Torr total pressure. The data is plotted as a hydrocarbon concentration in molecules per unit geometrical surface area of catalyst versus time. The slope of the line represents the rate of reaction. Turnover numbers, or molecules per surface site per second, may be calculated from this data if the number of active sites per cm\textsuperscript{2} is known; in the following text, 10\textsuperscript{15} sites per cm\textsuperscript{2} was chosen as a rough value for comparison with other data, since the surface atom density of the polycrystalline rhodium sample cannot be measured accurately.

Under these reaction conditions, CH\textsubscript{4} was the dominant product, with smaller amounts of C\textsubscript{2} and C\textsubscript{3} products also detectable. Very small amount of C\textsubscript{4} products (<1%) were also observed. The product distribution remained constant over the 5 hour period, and the rates
of production essentially constant, which implies that poisoning effects due to product inhibition were not operative. There was no detectable induction period for this reaction, and the rates of formation were reproducible to within 5%, from run to run, provided the sample was cleaned in UHV prior to the experiment.

In Table I we compare this data from polycrystalline Rh at 300°C, and the data reported by Vannice on a supported 1% Rh/Al₂O₃, catalyst adjusted to 300°C. Vannice's product distribution on supported Rh was measured at 265°C, but only a small difference is expected between this and 300°C. The product distributions are very similar, except that ethylene was observed as a product in this work, but not on the supported Rh. The absolute rates of reaction at 300°C agree within a factor of 4, and this is very reasonable considering the different methods of surface area measurement (Hydrogen chemisorption versus geometrical measurement). This good agreement in catalytic behavior suggests that small surface area foils can be readily used as model catalysts for the CO-H₂ reaction.

After this experiment was performed at one atmosphere, the sample was re-exposed to UHV, and analysed with AES to determine the surface composition. The results of these analyses are presented in Fig.8. After reaction, carbon was the dominant surface species, and no oxygen, or only traces, were seen. Occasionally, small amounts of sulphur were observed on the surface. Figure 8 shows analyses after 30 minutes and after five hours of reaction at 300°C. The amount of carbon usually increased with time, and after 5 hours of reaction, the estimated
surface concentration was probably ~1-2 monolayers, based on the attenuation of the rhodium peaks.

This carbon appeared to be in a form other than adsorbed CO, since it was removed only by heating the sample to 1000°C. The mechanism of removal was either by desorption, or diffusion into the bulk metal. The carbonaceous deposit did not appear to inhibit hydrocarbon production as Fig. 7 showed a constant production over a period when the surface changed from clean to one with the carbon layer present. The absence of surface oxygen is apparent, and the small Auger peak in Fig. 8 was the maximum ever observed after reaction. In the majority of runs, no surface oxygen was detectable. One possible reason for its absence, is the reaction of CO or H₂ with chemisorbed oxygen as the sample cooled down from reaction temperatures (250-350°C) to the region where the CO-0₂ and H₂-0₂ reactions were observed to have significant rates at low pressures (~200°C).

2. The Variation in Methanation Rate with Ion Bombardment Pretreatment

To obtain reproducible reaction rates on the foil samples, it was stated previously that a high temperature ion bombardment was needed, to rid the near surface layers of C and O impurities from previous runs. It was found, however, that if the surface was not annealed reproducibly, or if high temperature was not used during bombardment, that large variations in reaction rates (up to a factor of 6) were possible. The first effect (annealing) will be discussed in this section, and the effect of near-surface impurities is discussed later.
Figure 9 summarises the results. Only methane production is shown as the product distribution was the same as that from the annealed surface in all cases. The lower curve shows the rate of methane production at 300°C on a bombarded and annealed surface. The upper curve shows the rate on a bombarded surface only — the rate is a factor of 3 higher. This behavior agrees with the results of thermal desorption at low pressures and reflects the effects of surface roughness. A 5 minute anneal at 1000°C was found to be sufficient for reproducible behavior; shorter anneals resulted in rates lying in between those indicated by the two curves. A standard surface treatment which removes surface damage was therefore essential in preparing ion bombarded samples for reaction.

3. The Variation in Product Distribution and Reaction Rates with Temperature and CO-H₂ Ratio, on the Initially Clean Rh Surface.

The variation of reaction rates and production distributions with CO-H₂ ratios and temperature were studied. For the methanation reaction, the data taken between 250 and 450°C with a 3:1, H₂:CO ratio is shown in Fig. 10. This data was extracted from experiments by increasing the sample temperature sequentially, and taking all the data in a single run. All of the rate curves are linear, and data was taken for a short time only to avoid possible poisoning effects at high temperatures. The Arrhenius plot, shown in Fig. 11 indicates an activation energy of 24±3 kcas which is in excellent agreement with Vannice’s value for the 1% Rh/Al₂O₃ catalyst under the same conditions.
To investigate whether the higher molecular weight hydrocarbons (C₂, C₃) were produced with the same activation energy, the H₂-CO ratio was varied between 0.5 and 9 and the reaction rates and product distributions of the various species followed between 250 and 350°C. Product distributions as a function of temperature and H₂/CO ratios are shown in Table 2. The general trend is that CH₄ is the dominant product under all conditions, that were employed, but the fraction of C₂ and higher molecular weight products increases with decreasing H₂/CO ratio and decreasing temperature. The most favorable conditions for chain growth from Table 2 are a 1:2 H₂/CO mixture at 250°C, and the most favorable methanation conditions are a 9:1 H₂/CO mixture at 350°C.

The product distribution has been truncated at C₃ (propane) because in most cases C₄'s were <1% of the total products, and near the detection limit. Under favorable chain growth conditions, small amounts of C₄'s and C₅'s were seen, but are not listed in Table 2. These results are very similar to those reported by Vannice (7) on supported Rh, with one exception, and that is the type of C₂ product. In our experiments, ethylene (C₂(=)) was found to be the major product, with ethylene/ethane ratios as high as 12:1 under conditions of excess CO. Generally, the C₂H₄/C₂H₆ ratio decreased at high H₂/CO ratios, but had different behavior as a function of temperature, depending on the H₂/CO ratio. At H₂/CO = 0.5, the C₂H₄/C₂H₆ ratio increased considerably with increasing temperature, but at H₂/CO = 9 it decreased dramatically at temperatures in excess of 300°C. In fact the ethylene appeared to be hydrogenating, as the concentration decreased with time...
at 350°C. The presence of ethylene as a major C₂ product contrasts
with Vannice's data on supported Rh, in which he reported ethane as
the dominant product, except at low hydrogen concentrations. This
difference in product distribution may reflect the role of the alumina
support, and will be discussed later.

It was reported earlier that the activation energy for methanation
was 24±3 kcals, at a 3:1 H₂/CO ratio, and 250-450°C. The variation in
reaction rates as a function of temperature, for the C₁-C₃ products,
at the three H₂/CO ratios reported in Table 2, were also studied. The
results are summarized in Fig. 12 (A,B,C) where we show Arrhenius plots
for all products at three H₂/CO ratios. The dashed line corresponds
to an activation energy of 24 kcals per mole of product, and is used
as a reference. In general, detailed comparisons of "activation
energies" will not be made, but several general features will be dis-
cussed. At 3:1 H₂/CO ratio (Fig. 12(B)), CH₄ forms with an activation
energy of 24 kcals ± 2, and this is also the value observed at H₂/CO =
9:1 (Fig. 12(C)). For a 1:2 ratio (Fig. 12(A)), the activation energy
apparently increases at low temperatures (< 300°C), to about 24 kcals
at higher temperatures. The methanation rates at 250°C are therefore
lower than expected. These are also the conditions under which more
chain growth is observed, however. Curvature of the Arrhenius plot
is also observed for the C₂ and C₃ products. In general, the ethane
activation energy apparently increases with temperature, except at
9:1 ratio, and ethylene has an apparent decrease in activation energy
with temperature; in fact in Fig. 12(C) at temperatures in excess of
300°C, gaseous ethylene hydrogenates to ethane, and a negative rate of C₂H₄ production results. For propane, an increase in temperature also produces a curved Arrhenius plot, with a decrease in activation energy, particularly above 300°C.

To summarize these results, a fairly similar temperature dependence of the reaction rate is observed for all products below 300°C, but above this temperature, hydrogenation of ethylene to ethane, and smaller rates of C₃ production are observed. Methane formation, however, proceeds with a constant activation energy even to 450°C, as measured previously in Fig. 11.

The variation of reaction rates with partial pressures of CO and H₂ was not studied. Vannice's data on 1% Rh/Al₂O₃ (7) showed that the methanation rate was proportional to the first power in hydrogen, and a small negative exponent for CO, and these results were similar for most of the other group VIII metals.

4. Reaction Rates and Product Distributions for the CO₂-H₂ Reaction on the Initially Clean Rh Surface

As a parallel study, CO₂-H₂ mixtures were reacted on clean Rh surfaces, prepared in the same way as for the CO-H₂ studies. All reactions were carried out at 700 Torr, and temperatures between 250 and 400°C, with CO₂-H₂ ratios between 1:1 and 1:10. Two specific observations were made, firstly, that the CO₂-H₂ reaction is highly selective for CH₄ formation, with little or no C₂ or higher molecular weight products ever observed. Secondly, the specific reaction rates for the CO₂ reaction were always higher than for CO under the same conditions.
For a 3:1 \( H_2/CO_2 \) mixture, at 700 Torr, the reaction rates (\( CH_4 \) formation) and Arrhenius plot are shown in Figs. 13 and 14 respectively. The activation energy for \( CH_4 \) formation from \( CO_2 \) is 16±2 kcals, which is considerably lower than that measured for methanation from \( CO-H_2 \) under the same conditions. As a direct comparison of the activities of the \( CO-H_2 \) and \( CO_2-H_2 \) reactions on the initially clean Rh surface, Table 3 compares the activation energies, for \( CH_4 \) formation, and specific methanation rates at 250°C and 350°C. The \( CO_2-H_2 \) reaction is more active than the \( CO-H_2 \) reaction at lower temperatures, with the rate approximately seven times that for the \( CO-H_2 \), at 250°C. It can be seen that the \( CO_2-H_2 \) reaction is certainly more active in the lower temperature range. The methanation rates for the two reactions only become comparable around 440°C, due to the large difference in activation energies.

Auger analyses of the Rh surfaces, after treatment with \( CO_2-H_2 \) mixtures, were carried out, and the results were identical to the spectra in Fig. 8. A carbonaceous deposit developed during the reaction, whilst no oxygen was seen near the surface. This carbonaceous deposit did not inhibit the reaction, and \( CO_2-H_2 \) mixtures could be catalysed for several hours without a noticeable decline in the methanation activity. Variations in the \( H_2/CO \) ratio did not produce any detectable changes in the surface analysis after reaction, and methane was almost always the exclusive product formed.
5. Comparison of the CO-H₂ and CO₂-H₂ Product Distributions and Rates on Pre-treated Rhodium Surfaces

In the initial stages of this work it was discovered that the specific reaction rates on the Rh surface were dependent on the pretreatment of the surface with various gases. In certain cases, Auger Spectroscopy revealed no obvious surface impurities as being responsible for these variations, however the effects were quite reproducible, and apparently caused by sub-surface impurities. To quantify these effects, a series of eight experiments was conducted, to measure the specific reaction rates and product distributions, on these pre-treated surfaces, and to compare these results with those obtained on the clean surface.

Each pretreatment consisted of heating the clean Rh surface for 15 minutes at 300°C in one atmosphere of a particular gas (O₂, CO or C₂H₂), then exposing the surface to vacuum and flashing to 1000°C to remove any adsorbed gases. The pre-treated surface was then used to catalyse the CO-H₂ and CO₂-H₂ reaction (1:3, 300°C, 700 Torr) for 30 mins. Auger spectroscopic analyses were carried out before and after reaction to monitor changes in surface composition, and the reaction layer was thermally desorbed in UHV after the high pressure runs. Each pretreatment, however was preceded by a high temperature ion bombardment and anneal to remove surface impurities from the previous run and enable unambiguous interpretation of the data.

The data for the methanation rates, on the various surfaces is shown in Fig. 15, the product distributions in Fig. 16, and the data is tabulated in Table 4. As a first observation, a variation in
methanation activity of a factor of 10 was observed, the most active synthesis occurring for the CO₂-H₂ reaction on an oxygen-treated surface and the least active being the CO-H₂ reaction on an acetylene-treated surface. In general, the CO₂-H₂ reaction was always more active than the CO-H₂ reaction on the same surface, and oxygen pretreatment increased methanation rates, while carbon (from C₂H₂) retarded methanation, relative to the clean surface. The surface pre-treated with CO was identical in methanation activity to the clean surface, for both reactions. Taking a closer look at Table 4, the methanation activity for the CO-H₂ reaction on the O₂-treated surface was the same as CO₂-H₂ on the clean surface. The kinetics for the CO₂-H₂ on the C₂H₂-treated surface were non-linear with time, and the rate after 30 mins was similar to CO-H₂ on this surface.

Auger analyses of the surface composition, after pretreatment and prior to reaction did not reveal significant differences to account for this large variation in catalytic behavior. Surfaces treated with oxygen and CO showed no carbon or oxygen peaks after the pretreatment and after flashing in vacuo to 1000°C. Surfaces treated in acetylene, however, showed significant carbon peaks before and after flashing. After the high pressure synthesis studies were carried out for 30 mins, all surfaces had similar Auger spectra, with carbon being the dominant species. No oxygen was detectable on the surface.

The product distributions from the pretreated surfaces also showed differences, and these are depicted in Fig. 16. Surfaces treated with oxygen or CO showed essentially the same product distributions
as the clean Rh foils, and in all cases, the CO$_2$-H$_2$ reaction was highly selective towards CH$_4$ formation. Figure 16(G) and (H) are the distributions from the acetylene treated surface and here, more C$_2$ and C$_3$ chain growth products were observed for both reactions. Surface carbon, formed by decomposing acetylene, therefore seems to facilitate chain growth.

Each of the eight pretreated rhodium surfaces in Table 4 were studied by thermal desorption into UHV after the high pressure catalysis runs. The mass 28 emission was monitored as a function of temperature, and the resulting desorption spectra are shown in Fig. 17. In all cases, only mass 28(CO) was observed during desorption although H$_2$ desorption was occurring, but was not measured for reasons cited previously. For the reaction of CO-H$_2$ on the clean surface, both the low temperature peak, and the high temperature desorption was observed [Fig. 17(A)], indicating both molecular and dissociated CO present. For the CO$_2$-H$_2$ reaction, a very similar spectrum was seen, with the low temperature and high temperature CO desorbing (Fig. 17(B)). These may be compared with Fig. 17(C), which was obtained after heating the clean surface in pure CO at 1 atmosphere and 300°C for 30 minutes. This spectrum is very similar to the previous two and indicates that the dominant surface species seen after reaction are similar for the CO-H$_2$ and CO$_2$-H$_2$ reactions, and consist of molecular CO and dissociatively adsorbed CO.

The total amount of CO desorbed after these runs was approximately 5-10 times that obtained by adsorbing CO on the clean surface at low pressures, and suggests that some of the C and O atoms are incorporated
into the near-surface layers.

The thermal desorption spectra for the acetylene treated and oxygen treated surfaces are seen in Fig. 17 (D) and (E) respectively. For the C_2H_2 case, molecular CO but no significant high temperature peak is seen, although continuous desorption of CO occurred over the entire temperature range. The total amount of high temperature CO desorbed in this case is much less than from the CO-H_2 reaction on the other pretreated surfaces and this correlates with the lowest methanation activity. Chain growth was enhanced on this surface, however. Rhodium pretreated with oxygen gave both the low and high temperature CO peaks as seen in Fig. 17(E), but a large emission of CO was also observed above 800°C and this is almost certainly due to dissolved oxygen reacting with carbon, and liberating CO. The presence of this large CO desorption was the only evidence obtained which supports the contention that dissolved oxygen is responsible for the increased methanation activity.

To summarize this data, oxygen pretreated rhodium surfaces have an enhanced methanation activity for both the CO-H_2 and CO_2-H_2 reactions, relative to the clean surface. This oxygen is undetectable by Auger spectroscopy, and does not change the product distribution, but becomes apparent when it reacts with carbon at temperatures in excess of 800°C and desorbs as CO. Carbon, introduced onto the surface from acetylene, reduces methanation activity relative to the clean surface, and increases the chain growth probability. Thermal desorption spectra show that a significantly smaller proportion of dissociated CO is present on this surface. The clean surface, and CO treated surfaces, show methanation
activities which are in between these two extremes, and thermal desorption spectra show both molecular and dissociated CO present. The CO$_2$-H$_2$ reaction is consistently faster than the CO-H$_2$ reaction on any of these surfaces, but the thermal desorption spectra after reaction look identical.

6. Reaction of Hydrogen with Clean and Pretreated Rh Surfaces at One Atmosphere

In the course of several experiments, pure hydrogen was reacted with the Rh surface to observe any product formation from the surface carbon layer. The first experiments involved running the CO-H$_2$ reaction on the clean surface for 30 mins under standard conditions (3:1 H$_2$:CO, 300°C 700 Torr) then pumping out the gases and exposing the cell to UHV to remove any adsorbed CO. Pure H$_2$ was then admitted to the central cell and it was flushed several times to purge any remaining CO. The sample was then heated to 300°C in 800 Torr of hydrogen. Methane formation was observed, and curves similar to that shown in Fig. 18 were seen. Methane was evolved, the total quantity being many "monolayers" (~60 in Fig. 18) and this implies a substantial amount of carbon removed from the sample. No other products were seen. If cleaned Rh samples (cleaned by Ar$^+$ ion bombardment) were hydrogenated, no methane was seen up to 450°C or so. It appears, therefore that surface or bulk carbon produced during the CO-H$_2$ reaction may be hydrogenated to form methane on Rhodium as low as 300°C.

Similar experiments were carried out on Rh surfaces pre-treated with acetylene where considerable amounts of carbon as determined by AES (in excess of that produced in the CO-H$_2$ reaction) were deposited.
The hydrogenation at 300°C as shown in Fig. 19, produced only methane, but the rate of production was slower than from the CO-H₂ treated surface, although it did not cease hydrogenating over the 30 minute period. Raising the temperature to 375°C produced a significant increase in methane production, and the activation energy for this process, calculated from Fig. 19 is 21±3 kca1s, which is similar to the value observed for methane production from the CO-H₂ mix.

Hydrogen, therefore, can produce methane from surface, or bulk carbon on rhodium in the temperature range (300°C) that the CO-H₂ reaction is active, although we cannot compare the methanation rates from the two processes easily.
IV. DISCUSSION AND SUMMARY

We shall summarize the experimental findings that are useful to unravel the mechanism of hydrocarbon production from CO-H₂ and CO₂-H₂ mixtures.

(a) There are two binding states of CO on polycrystalline rhodium, with widely differing desorption temperatures (250°C and 700°C). Both states are present after reaction with CO-H₂ and CO₂-H₂ mixtures, but hydrogen is not necessary to produce the high temperature state. The thermal desorption spectra after heating in CO alone look identical to the CO-H₂ and CO₂-H₂ cases. Pretreatment of the surface with acetylene reduces the high temperature state.

(b) The active rhodium surface is covered with a carbonaceous deposit under reaction conditions and both carbon and oxygen are dissolved in the surface, as evidenced by CO desorption at high temperatures. Little or no oxygen is present on the surface after reaction. Interaction of hydrogen with the reaction layer after CO-H₂ catalysis produces only methane.

(c) Any oxygen present in the reaction layer during synthesis must be removed rapidly by CO or H₂ to form CO₂ or H₂O, as these reactions (particularly the CO-O₂ reaction) are rapid at low pressures and temperatures.

(d) The methanation rates, product distribution and activation energy for methanation from CO-H₂ mixtures agrees well with that reported for a supported, dispersed rhodium catalyst. The major difference lies
in the production of ethylene as the major C₂ product on Rh foils at less than 300°C.

(e) The reaction of CO₂-H₂ mixtures on the initially clean Rh surface produces methane only, and at a faster rate, with a lower activation energy (16 kcal). At low temperatures (< 250°C) the CO₂-H₂ methanation rate is an order of magnitude higher than the equivalent CO-H₂ rate.

(f) The pretreatment of the rhodium surface with oxygen or acetylene markedly changes the rate and/or product distribution. Oxygen increases the rate of CH₄ formation by more than a factor of five from CO₂-H₂ mixtures, while acetylene facilitates chain growth, and reduces methanation.

Evidence is presented in this work to show that CO is present in both molecular and dissociated form on rhodium surfaces during the CO-H₂ and CO₂-H₂ syntheses. Furthermore, hydrogen is not a necessary agent for dissociation, as CO and CO₂ alone produced the high temperature peaks during heating in these gases at pressures as low as 10⁻⁷ Torr, and 300°C. The dissociation of CO was also found to occur on surfaces contaminated with trace amounts of carbon and oxygen from previous experiments.

The observation of a high temperature binding state of CO has also been observed on iridium single crystals in this laboratory, after heating in CO to several hundred degrees at low pressures (~ 10⁻⁷ Torr). The formation of this state on rhodium foils may be affected by the polycrystalline nature of the surfaces, and further experiments on single crystals are needed to clarify the mechanism of dissociation.
Hydrogen-carbon monoxide interactions have been investigated recently on metal single crystals and films. Wedler et al\(^{(9)}\) interacted H\(_2\) and CO on nickel films at temperatures as high as 353K. They observed no reaction products desorbed at low pressures, but found a considerable increase in the amount of CO adsorbed in the presence of hydrogen at 353K. Other work on (111) platinum\(^{(10)}\) at low pressures showed slight changes in the thermal desorption spectra of a co-adsorbed CO-H\(_2\) mixture, and EID evidence of a surface "complex" containing carbon, hydrogen and oxygen. On a (100) Tungsten surface\(^{(11)}\) Yates and Madey found evidence for significant interactions between adsorbed H\(_2\) and CO, but could find no methane or any other hydrocarbon products desorbed. In this work, we observed an effect similar to Wedler, namely an increase in the amount of CO adsorbed in the presence of hydrogen at low pressures, but desorption of methane, or any other hydrocarbon products were absent, even in catalysis experiments.

Thermodynamically, the formation of methane and higher molecular weight products from CO-H\(_2\) mixtures at atmospheric pressure is quite favorable in the temperature range of interest (250-350°C).\(^{(12)}\) At low pressures, however, the thermodynamics is quite unfavorable and this is outlined in the Appendix. This is simply a consequence of the pressure dependence of a condensation reaction, which is favored only by an increase in pressure. It is not surprising, therefore, that at low pressure, catalysis products are absent in the CO-H\(_2\) reaction, and the importance and necessity of studying this reaction at atmospheric pressure and above is apparent.
The presence of a carbonaceous deposit on the rhodium surface during the synthesis reactions, and the complete absence of oxygen in the Auger spectra is surprising, as rhodium oxides are thermodynamically stable, whilst the carbides are unstable. The carbonaceous layer must therefore consist of some Rh-C complex which forms in preference to a surface oxide. Oxygen is incorporated into the rhodium surface during reaction, however, as evidenced by desorption of a high temperature form of CO after reaction, although it is not detectable with AES. Even after oxygen treatment at high pressures (1 atm) and heating to 300°C, only small oxygen Auger emissions were seen, indicating sub-monolayer coverage. This oxygen pretreatment does, however, have a marked influence on the rates of methanation on this surface indicating that sub-surface oxygen can influence the reaction. The Auger spectra after reaction showed the same carbonaceous overlayer observed in all experiments. We therefore conclude that oxygen, dissolved in the rhodium lattice below the surface promotes the methanation reaction without significantly influencing the product distribution.

The total absence of oxygen in the surface layer after reaction is easily explained with reference to the low pressure CO-O₂ and H₂-O₂ experiments. Both these reactions proceed at low temperatures and pressures (10⁻⁷ Torr and 100°C) and the removal of surface oxygen to form CO₂ and H₂O at atmospheric pressure is expected to be rapid. In fact experiments on supported rhodium catalysts near atmospheric pressure have shown that the CO-O₂ and H₂-O₂ reactions do proceed.
rapidly. (14) The lifetime of an oxygen atom on the rhodium surface under Fischer-Tropsch conditions is therefore short, as the strongly bound carbon overlayer rapidly forms, preventing surface oxide formation, and oxygen atoms may either dissolve in the sub-surface layers or be hydrogenated. This mechanism is supported by the observation of a complete absence of oxygenated hydrocarbons in the synthesis under our conditions of the experiment.

There is excellent agreement between the methanation rates and activation energies reported here, and by Vannice for supported, dispersed rhodium catalysts (Table 3). This is gratifying as we can now use small surface area rhodium foils as model systems, representative of high surface area rhodium catalysts. The product distribution is somewhat different; more ethylene forms in the absence of the high surface area support. Future studies should verify whether the support is indeed responsible for the hydrogenation of unsaturated hydrocarbons, thereby partly masking the catalytic behavior of rhodium.

One of the significant findings of this study is the marked increase in selectivity to methane when CO$_2$ is used as a reactant instead of CO. The chain growth is arrested completely, although the AES analysis shows a similar carbonaceous deposit after reaction. The methanation rates, however, are more rapid than CO at temperatures $< 440^\circ$C, as the activation energy is 16 kcals as opposed to 24 kcals for the CO-H$_2$ reaction. The excess chemisorbed oxygen that forms as a result of partial dissociation of CO$_2$ therefore has a different effect than pretreating the surface with oxygen. It appears that with
CO$_2$ as a reactant either the nature of the surface intermediates in the reaction is altered significantly, or atomic oxygen disperses the carbon species on the surface, increasing the selectivity to methane formation. Another explanation is that atomic oxygen blocks sites responsible for chain growth, or that the metal-carbon complex that forms is re-hydrogenated rapidly enough to minimize the surface concentration of partially hydrogenated species that could link up to form higher molecular weight products. Clearly, unraveling the nature of the surface intermediates that form during the CO$_2$-H$_2$ reaction should help us control chain termination in the Fischer-Tropsch reaction.

The pretreatments of the surface have marked and controlling effects on both the reaction rates and product distributions. While oxygen pretreatment increases the CO$_2$-H$_2$ rate five-fold, acetylene pretreatment reduces methanation and increases chain growth in both the CO$_2$ and CO-H$_2$ reactions. These observations indicate that the surface composition and perhaps also the surface structure that is pre-determined by the oxygen or acetylene pretreatments control the rate and product distribution in the Fischer-Tropsch reaction. Since the surface is covered with a carbonaceous overlayer during the reaction it is reasonable to conclude that the structure and nature of the rhodium-carbon bonding determines the reaction rate and path. The carbon on the rhodium surface is active; we have shown that it re-hydrogenates readily to form methane. It appears that these rhodium-carbon or rhodium-carbon-oxygen compounds at the surface are those that react with hydrogen to form the products.
The hydrogenation, or gasification of carbon using rhodium as a catalyst has been investigated by Tomita et al.\(^{(15)}\) The conversion of carbon to \(\text{CH}_4\) occurred at temperatures in excess of that in the Fischer-Tropsch reaction, but much lower than that required to directly hydrogenate carbon in the absence of a catalyst. Rhodium was the most efficient gasification catalyst investigated.

We cannot deduce the exact nature of the reaction intermediates in the \(\text{CO-H}_2\) reaction without further experiments. It is significant, however, that both molecular and dissociated carbon monoxide are present under synthesis conditions. It is also significant that large amounts of carbon at the surface (from decomposed acetylene) retarded methanation, but increased chain growth. The high temperature, or dissociated \(\text{CO}\), was much less evident on these surfaces, while molecular \(\text{CO}\) was present. There may in fact be a distinction between the methanation reaction, and the chain growth reaction, as methane can be produced readily, from carbon but chain growth products require the presence of adsorbed molecular \(\text{CO}\).

Future studies will be carried out with single crystals to determine the effect of surface structure on the reactivity, and elevated pressures will be used to increase the chain growth probability and investigate this mechanism further. Since the surface composition of the catalyst appears to be all-important in the Fischer-Tropsch reaction on rhodium, other transition metals should also be scrutinized to explore the presence of similar effects. Electron spectroscopy and ion scattering spectrometry techniques appear promising to identify
the bonding of various metal-carbon surface complexes.

ACKNOWLEDGEMENT

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APPENDIX

The Pressure Dependence of the Free Energy of a Condensation Reaction (16)

For the reaction

\[ aA + bB \rightarrow cC + dD \]  \hspace{1cm} (1)

The equilibrium constant in terms of partial fugacities is

\[ K_f = \frac{(f_C)^c (f_D)^d}{(f_A)^a (f_B)^b} \]  \hspace{1cm} (2)

In terms of partial pressures, this becomes

\[ K_p = \frac{(P_{x_C})^c (P_{x_D})^d}{(P_{x_A})^a (P_{x_B})^b} \]  \hspace{1cm} (3)

where \( p = \) total pressure and \( x_A, x_B \) are mole fractions. It follows that

\[ K_f = K_p \cdot K_\gamma \hspace{1cm} \text{where} \hspace{0.5cm} \gamma = f/p \]  \hspace{1cm} (4)

and

\[ K_\gamma = \frac{(\gamma_C)^c (\gamma_D)^d}{(\gamma_A)^a (\gamma_B)^b} \]  \hspace{1cm} (5)

We approximate \( K_\gamma \approx 1 \) for Fischer-Tropsch reaction conditions (\(< 100 \text{ atm})\). Then

\[ \frac{(x_C)^c (x_D)^d}{(x_A)^a (x_B)^b} \approx K_f \cdot p^{-\Delta n} \]  \hspace{1cm} (6)
Thus condensation reactions, where \( a+b > c+d \) are favored by a pressure increase. For all of the Fischer Tropsch reactions, \( a+b > c+d \) is the general rule.

As an example, for the reaction

\[
3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}.
\]

\( (\Delta G_f) \) 430°C, 1 atm = -11.42 kcaels

\[
\therefore K_f = 3.68 \times 10^3
\]

At \( 10^{-4} \) Torr total pressure,

\[
K_f \cdot p^2 = 3.68 \times 10^3 \times 1.73 \times 10^{-14}
\]

\[
= 6.4 \times 10^{-11}.
\]

The equilibrium methane concentration under these conditions would therefore be very low.
REFERENCES

8. B. E. Nieuwenhuys, unpublished results, this laboratory.
Table 1. Comparison of polycrystalline Rh foil with a 1% Rh/Al₂O₃ catalyst in the CO-H₂ reaction at atmospheric pressure.

<table>
<thead>
<tr>
<th></th>
<th>polycrystalline Rh foil (this work)</th>
<th>supported 1% Rh/Al₂O₃ (Vannice)⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction Conditions</strong></td>
<td>300°C, 3:1 H₂/CO 700 Torr</td>
<td>300°C* 3:1 H₂/CO 760 Torr*</td>
</tr>
<tr>
<td><strong>Type of reactor</strong></td>
<td>batch</td>
<td>flow</td>
</tr>
<tr>
<td><strong>conversion</strong></td>
<td>&lt; 0.1%</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td><strong>Product Distribution</strong></td>
<td>90% CH₄ ±3</td>
<td>90% CH₄</td>
</tr>
<tr>
<td></td>
<td>5% C₂H₆±1</td>
<td>8% C₂H₆</td>
</tr>
<tr>
<td></td>
<td>2% C₃H₆±1</td>
<td>2% C₃</td>
</tr>
<tr>
<td></td>
<td>3% C₃H₈±1</td>
<td>&lt;1% C₄ +</td>
</tr>
<tr>
<td></td>
<td>&lt;1% C₄ +</td>
<td></td>
</tr>
<tr>
<td><strong>Absolute Methanation Rate at 300°C (Turnover No.)</strong></td>
<td>0.13±0.03 molecules site⁻¹ sec⁻¹</td>
<td>.034 molecules site⁻¹ sec⁻¹</td>
</tr>
</tbody>
</table>

* data adjusted from 275°C
Table 2. Variation of reaction product distribution with \( \text{H}_2/\text{CO Ratio} \) and Temperature, over Rh foils.

\[ C_1 = \text{methane} \quad C_2(=) = \text{ethylene} \quad C_2 = \text{ethane} \quad C_3 = \text{propane} \]

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Product</th>
<th>( \text{H}_2/\text{CO} = 1:2 )</th>
<th>( \text{H}_2/\text{CO} = 3:1 )</th>
<th>( \text{H}_2/\text{CO} = 9:1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>250°C</td>
<td>( C_1 )</td>
<td>65%</td>
<td>84%</td>
<td>93%</td>
</tr>
<tr>
<td></td>
<td>( C_2(=) )</td>
<td>16</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>( C_2 )</td>
<td>9.8</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>( C_3 + )</td>
<td>9.2</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>300°C</td>
<td>( C_1 )</td>
<td>77%</td>
<td>89%</td>
<td>95%</td>
</tr>
<tr>
<td></td>
<td>( C_2(=) )</td>
<td>13</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>( C_2 )</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>( C_3 + )</td>
<td>6</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>350°C</td>
<td>( C_1 )</td>
<td>83%</td>
<td>94%</td>
<td>98%</td>
</tr>
<tr>
<td></td>
<td>( C_2(=) )</td>
<td>12</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>( C_2 )</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>( C_3 + )</td>
<td>4</td>
<td>1</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Table 3. Comparison of activities for methanation of the CO-H\textsubscript{2} and CO\textsubscript{2}-H\textsubscript{2} reactions on the initially clean Rh surface (1:3 ratio, 700 Torr).

<table>
<thead>
<tr>
<th></th>
<th>CO-H\textsubscript{2} = 1:3</th>
<th>CO\textsubscript{2}-H\textsubscript{2} = 1:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 250°C (turnover No.)</td>
<td>0.017 CH\textsubscript{4} molecules</td>
<td>0.12</td>
</tr>
<tr>
<td>Specific Rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 300°C</td>
<td>0.13</td>
<td>0.36</td>
</tr>
<tr>
<td>Activation Energy (kcals)</td>
<td>24±2</td>
<td>16±2</td>
</tr>
</tbody>
</table>
Table 4. Variation in methanation activity, and product distributions for the CO-H₂ and CO₂-H₂ reactions on clean and pretreated rhodium surfaces. (Reaction conditions 1:3 ratio, 700 Torr, 300°C)

<table>
<thead>
<tr>
<th>Reaction Gases</th>
<th>Surface Pretreatment</th>
<th>Methanation Rate (300°C) (turnover number)</th>
<th>Product Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-H₂</td>
<td>none</td>
<td>0.15±.05</td>
<td>88% C₁, 9% C₂, 3% C₃</td>
</tr>
<tr>
<td>CO₂-H₂</td>
<td>none</td>
<td>0.33±.05</td>
<td>100% C₁</td>
</tr>
<tr>
<td>CO-H₂</td>
<td>O₂</td>
<td>0.33±.05</td>
<td>87% C₁, 10% C₂, 3% C₃</td>
</tr>
<tr>
<td>CO₂-H₂</td>
<td>O₂</td>
<td>1.7±0.2</td>
<td>98% C₁, 2% C₂</td>
</tr>
<tr>
<td>CO-H₂</td>
<td>CO</td>
<td>0.15±.05</td>
<td>88% C₁, 9% C₂, 3% C₃</td>
</tr>
<tr>
<td>CO₂-H₂</td>
<td>CO</td>
<td>0.33±.05</td>
<td>100% C₁</td>
</tr>
<tr>
<td>CO-H₂</td>
<td>C₂H₂</td>
<td>0.07±.02</td>
<td>78% C₁, 18% C₂, 4% C₃</td>
</tr>
<tr>
<td>CO₂-H₂</td>
<td>C₂H₂</td>
<td>0.07±.04</td>
<td>96% C₁, 3% C₂, 1% C₃</td>
</tr>
</tbody>
</table>

*Heated for 15 mins in 700 Torr of the particular gas, then thermally desorbed to 1000°C in vacuo before reaction.
FIGURE CAPTIONS

Fig. 1. Schematic of UHV surface analysis system equipped with sample isolation cell for catalytic studies at high pressures (1-100 atm) and low pressures (10⁻⁸-10⁻⁴ Torr).

Fig. 2. Auger spectra of rhodium surface (A) Before cleaning (B) After cleaning with 2000 eV Ar⁺ ions and annealing at 1000°C (C) After treatment with oxygen (1×10⁻⁷ Torr, 500°C, 10 mins.)

Fig. 3. Thermal desorption spectra of CO on Rh foils. Heating rate 25°K sec⁻¹, adsorption pressures 10⁻⁹ Torr to 10⁻⁵ Torr CO, at 300K.

Fig. 4. Thermal desorption of CO from Rh after various treatments. (A) Clean surface, 30L (B) Ion Bombarded surface, 30L (C) Heated in CO/H₂ 1:1, 10⁻⁶ Torr, 300°C for 10 mins (D) As in (C), but pure CO. (E) As in (C) but pure CO₂.

Fig. 5. Thermal desorption of CO from Rh after various treatments. (F) CO adsorbed on surface from Fig. 4(E), 30L (G) CO adsorbed on (F) rapidly by 2×10⁻⁶ Torr CO, 15 secs. (H) CO adsorbed slowly from ambient on (H), for 120 mins. (I) H₂/CO co-adsorbed (1:1, 1×10⁻⁶ Torr, 30 secs, 300K) on clean surface.

Fig. 6. Variation in the rate of CO₂ production with temperature, in the CO-O₂ reaction on Rh(10⁻⁷ Torr, 1:1).
Fig. 7. Production of hydrocarbons from a 3:1 H₂/CO mix on rhodium foil (700 Torr, 300°C), with the internal isolation cell operated as a stirred batch reactor.

Fig. 8. (A) Auger analysis of the clean Rh surface, (B) the surface after 30 mins. reaction, (300°C, 700 Torr, 3:1 H₂:CO) (C) The surface after 5 hrs reaction.

Fig. 9. Variation in methanation activity of Rh foil with ion bombardment pretreatment.

Fig. 10. Production of methane on initially clean rhodium foils as a function of temperature.

Fig. 11. Arrhenius plot for methane production on rhodium foils, from 250-450°C.

Fig. 12. Arrhenius plots for formation of hydrocarbons from CO-H₂ mixtures over rhodium foils at atmospheric pressure, and 250-350°C. (A) CO:H₂ = 2:1 (B) CO:H₂ = 1:3, (C) CO:H₂ = 1:9.

Fig. 13. Formation of CH₄ from CO₂-H₂ over Rh foil. (1:3 ratio, 250-400°C, 700 Torr).

Fig. 14. Arrhenius plot for methane production from CO₂-H₂ on Rh (1:3 ratio, 250-400°C, 700 Torr).

Fig. 15. Methanation activity of the CO-H₂ and CO₂-H₂ reactions on clean and pretreated rhodium surfaces. (3:1 H₂:CO, 700 Torr, 300°C. Surfaces pretreated with a particular gas, 700 Torr, 300°C for 15 mins, then flashed to 1000°C in vacuo prior to reaction).
Fig. 16. Product distributions for the CO-H$_2$ and CO$_2$-H$_2$ reactions on clean and pretreated rhodium surfaces (See Fig. 15 and Table IV). (A) CO-H$_2$/clean (B) CO$_2$-H$_2$/clean (C) CO-H$_2$/O$_2$ treated (D) CO$_2$-H$_2$/O$_2$ treated (E) CO-H$_2$/CO treated (F) CO$_2$-H$_2$/CO treated (G) CO-H$_2$/C$_2$H$_2$ treated (H) CO$_2$-H$_2$/C$_2$H$_2$ treated.

Fig. 17. Thermal desorption of pretreated Rh surfaces after CO-H$_2$ and CO$_2$-H$_2$ reactions (1:3 Ratio, 700 Torr, 300°C).

Fig. 18. Hydrogenation of the carbon residues produced in the CO-H$_2$ reaction on Rh (3:1 H$_2$:CO$_2$ 700 Torr, 300°C, 30 mins, then hydrogenated with 800 Torr H$_2$, 300°C).

Fig. 19. Hydrogenation of surface carbon formed by decomposing acetylene on the Rh surface (pretreated with 800 Torr C$_2$H$_2$, 300°C, 15 mins, then hydrogenated with 800 Torr H$_2$, 300°C).
GAS CHROMATOGRAPH

SAMPLING VALVE

METAL BELLOWS

CIRCULATION PUMP

HYDRAULICALLY OPERATED MOVABLE PISTON

S.S. WELDED BELLOWS

LEED OPTICS

LN2 TRAP

SAMPLE

DIFFUSION PUMP

TO MECHANICAL PUMP

ELECTRIC FEED-THROUGHS (SAMPLE TEMP CONTROL)

ROTARY MANIPULATOR

COPPER GASKET

Figure 1
Figure 2
Figure 3

![Graph showing CO pressure vs. temperature for different CO/Rh and gas dosages.]

- CO pressure (arb. units)
- Temperature (°C)
- CO/Rh
- 30 L (10^{-6} TORR SEC)
- 10 L
- 2 L
- 1 L
- 0.5 L
- 0.25 L

XBL 765-6847
Figure 4

A. CLEAN RHODIUM

B. ION BOMBARDED NO ANNEAL

C. HEATED IN CO/H₂ × 0.25

D. HEATED IN CO × 0.25

E. HEATED IN CO₂ × 0.25

CO PRESSURE (ARB. UNITS)

T (°C)
Figure 5

TIME DEPENDENCE OF MOLECULAR-DISSOCIATED PEAKS ON PRETREATED SURFACE

F. CO ADSORBED ON PRETREATED SURFACE FROM E

G. CO/H₂ CO- ADSORBED ON CLEAN Rh

H. CO PRESSURE (ARB. UNITS)

T (°C)

0 200 400 600 800 1000

XBL 765-6860
Rh FOIL
1:1 O₂/CO
1x10⁻⁶ TORR

Fig. 6
Fig. 7

CO-H₂/Rh
300°C
1:3
700 TORR
CLEAN SURFACE

AFTER CO-H\textsubscript{2} REACTION
700 TORR, 30 MIN.
300°C

AFTER 300 MIN.
300°C

Fig. 8
ION BOMBARDED, 20 MIN.
NO ANNEALING

ION BOMBARDED, 20 MIN.
ANNEALED 800°C, 20 MIN.
CO - H₂/Rh
1:3
700 TORR

CH₄ PRODUCTION
E₀ = 24 ± 3 K CALS
Fig. 12
**Fig. 13**

CO₂ - H₂
ON RHODIUM
1:3
700 TORR

METHANE PRODUCED (MOLECULES CM⁻² x 10⁻¹⁷)

TIME (MINS)

XBL 765-6851
**Fig. 14**

**CO$_2$-H$_2$/Rh**

1:3

700 TORR

**CH$_4$ PRODUCTION**

$E_0 = 16 \pm 2$ K CALS

---

**CO$_2$-H$_2$/Rh**

1:3

700 TORR

**CH$_4$ PRODUCTION**

$E_0 = 16 \pm 2$ K CALS

---
A. OXYGEN TREATED - CO\textsubscript{2}/H\textsubscript{2}
B. CO TREATED - CO\textsubscript{2}/H\textsubscript{2}
    CLEAN - CO\textsubscript{2}/H\textsubscript{2}
    OXYGEN TREATED - CO/H\textsubscript{2}
C. ACETYLENE TREATED - CO\textsubscript{2}/H\textsubscript{2}
D. CLEAN - CO/H\textsubscript{2}
    CO TREATED - CO/H\textsubscript{2}
E. ACETYLENE TREATED - CO/H\textsubscript{2}
Fig. 16
Fig. 17
This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.