INTRODUCTION

Processes which involve the conversion of relatively low Btu substances to useful fuels and chemical feedstocks are assuming ever increasing roles as potential substitutes for those that involve the conversion of petroleum. One such process which has been in commercial operation for many years is the Fischer-Tropsch synthesis involving the reduction of carbon monoxide by hydrogen. The Fischer-Tropsch synthesis yields a wide variety of saturated and unsaturated hydrocarbons and oxygen-containing compounds. A judicious choice of reaction conditions and catalyst will generally result in the selective production of the desired product distribution. The special case of the Fischer-Tropsch synthesis in which methane is the only carbon-containing product is referred to as methanation. Both the Fischer-Tropsch synthesis and methanation are heterogeneous catalytic processes which are known to occur on certain group VIII metals and their oxides. Although a fairly large number of studies have been performed in an effort to understand the reaction mechanisms of the Fischer-Tropsch and methanation processes, no thorough understanding of either process has been developed. The purpose of this study is to seek a mechanistic understanding of the methanation reaction on unsupported ruthenium. Since the Fischer-Tropsch and methanation processes are so directly related, a brief discussion of the Fischer-Tropsch synthesis will precede a more detailed discussion of the methanation process. Excellent reviews of both the Fischer-Tropsch and methanation processes have been published [1-7].

The general reactions for the hydrogenation of carbon monoxide to paraffins, olefins and alcohols are as follows:

$$(2n+1)H_2 + nCO \rightleftarrows C_nH_{2n+2} + nH_2O \qquad (1)$$

$$2nH_2 + nCO \rightleftarrows C_nH_{2n} + nH_2O \qquad (2)$$

$$2nH_2 + nCO \rightleftarrows C_nH_{2n+1}OH + (n-1)H_2O \qquad (3)$$

The special case of reaction (1) in which n = 1 is the methanation reaction:

$$3H_2 + CO \rightleftarrows CH_4 + H_2O \qquad (4)$$

Other reactions which are thermodynamically favored include the formation of aldehydes, ketones, aromatics and organic acids. It should be noted that when feedstocks rich in hydrogen are used, paraffins are produced, whereas low hydrogen content feedstocks are required for the production of olefins and alcohols.

A number of potentially complicating reactions can occur under the same conditions as the Fischer-Tropsch and methanation syntheses. The water-gas shift reaction (5) has the rather insignificant effect

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (5)$$

of converting the water by-product to carbon dioxide. However, the undesirable effect of the water-gas shift reaction is to change the hydrogen to carbon monoxide ratio during the reaction process. This could alter the product distribution in some cases. Both the Boudouard reaction (6) and coke deposition (7) can occur on most of these catalyst surfaces. Both reactions have the effect of producing a carbon

$$2CO \rightleftarrows C + CO_2 \qquad (6)$$

$$H_2 + CO \rightleftarrows C + H_2O \qquad (7)$$

overlayer on the surface. This frequently leads to catalyst fouling and often decreases the lifetime of the catalyst significantly. These reactions are generally reversible and the catalyst activity can be regenerated by high temperature reduction. Metal carbide formation (8)

$$xM + C \rightarrow M_xC \tag{8}$$

is generally irreversible and leads to permanent deactivation of the catalyst.

A summary of the significant discoveries in Fischer-Tropsch chemistry is shown in Appendix I. The first catalytic hydrogenation of carbon monoxide was reported in 1902 [8,9] and involved the production of methane at atmospheric pressure over supported nickel and cobalt catalysts. Although these scientists observed carbon monoxide conversion, they were quite disappointed that methane was the sole carbon containing product. Until about the middle of this century, cheap natural gas was readily available in most parts of the world and alternate methane sources were neither being looked for nor were they being commercialized when discovered. The real hope among scientists was that carbon monoxide could be hydrogenated to produce higher molecular weight hydrocarbons and oxygenated compounds--especially gasoline and alcohols. The Badische Anilin-und-Soda-Fabrik A. G. was successful in producing a fairly wide range of hydrocarbons and chemicals at high pressure over a range of catalysts. In 1913 they were granted a German patent [10] for this process and in 1923 they received two French patents [11,12] for a similar high pressure process which produced only methanol from carbon monoxide and hydrogen.

The fundamental understanding of the carbon monoxide-hydrogen interaction and the early commercialization of the process came about as a result of Franz Fischer and the members of his group at the Kaiser Wilhelm Institut für Kohlenforschung at Mülheim Ruhr. Fischer worked with Hans Tropsch during the period from 1922 until 1928, conducting basic research into the carbon monoxide-hydrogen interaction at atmospheric pressure. Their first publications on the conversion at atmospheric pressure were in 1926 [13-15] and contained the fundamental observations that became the basis for the early understanding of the process:

1) Iron, cobalt and nickel are active catalysts for the reaction. Cobalt tends to produce higher hydrocarbons and nickel tends to favor methane production.
2) Oxides that are difficult to reduce, such as ZnO and Cr_2O_3, have increased catalytic activity and are more resistant to sintering than the metals.
3) Small doses of alkali favor the formation of larger hydrocarbon molecules.
4) Copper-iron mixtures are more active than iron alone.
5) Sulfur poisons the catalysts.

It was as a result of this work that the reaction became known as the Fischer-Tropsch synthesis. In general, all the studies made during this period were at atmospheric pressure with a few at 15 atmospheres. The catalysts were generally some form of cobalt or iron and the temperatures fell in the 523-673K range.

Tropsch left Mülheim in 1928 to become director of a coal research institute in Czechoslovakia. From 1928 until 1934 Fischer, Meyer, Koch and Roelen continued to study the Fischer-Tropsch synthesis with emphasis on catalyst preparation and its effect upon product distribution. They worked primarily with kieselguhr-supported nickel and cobalt catalysts. The development of more active catalysts made it possible to run the reaction at 450K. This resulted in a substantial lowering of the amount of methane formed (30 per cent of the synthetic hydrocarbons consisted of methane at 450K compared to 90 per cent at 525K). The cobalt catalyst led to lower conversion to methane and became known as the "standard cobalt catalyst". The findings of the catalyst development work with cobalt may be summarized as follows [16]:

1) Increasing catalyst age and increasing temperatures cause lower molecular weight products.

2) Increasing amounts of ThO_2, increasing amounts of unreduced cobalt and traces of alkali increase the yield of higher hydrocarbons.

3) Higher carbon monoxide to hydrogen ratios increase the yield of olefins.

4) The percentage of olefins decreases with increasing molecular weight of the hydrocarbon products.

5) The reaction products are mainly straight chain hydrocarbons with small amounts of oxygenated products.

During the period 1935 to 1937, Fischer and Pichler continued the research on the Fischer-Tropsch synthesis. They modified the atmospheric pressure process to consist of several steps with immediate removal of liquid reaction products [17]. This increased the product yield by 10-20 per cent without modifying the catalyst or the reaction temperature. Although most of the early work from Fischer's group was carried out at atmospheric pressure producing primarily hydrocarbons, it was known that by increasing the pressure a larger yield of oxygenated products could be achieved. Fisher and Pichler developed a "medium pressure" process which operated at 5 to 20 atmospheres and used the same cobalt-thorium-kieselguhr catalyst as in the atmospheric pressure process. The medium pressure process had these advantages:

1) The yield of solid paraffins increased tenfold.
2) The yield of C_3+ hydrocarbons (those with more than three carbons per molecule) increased by 20 per cent.
3) Catalyst regeneration, required in the atmospheric pressure process, was not needed.
4) The reaction products were in general more saturated. This is an advantage for production of paraffins and diesel oil, but a disadvantage for gasoline production.

Until early 1935, iron had not been used in the Fischer-Tropsch synthesis because the yields of C_5+ hydrocarbons had been too low. Fischer and Meyer in [2] and Meyer and Bahr in [2] made some studies to improve the yields of higher hydrocarbons on iron, but the results had not been promising. However, with the development of the medium pressure process, the yield of these higher molecular weight hydrocarbons over iron catalysts was significantly increased. During the period from 1938 to 1945, Fischer and Pichler developed iron catalysts which had 1.0 per cent copper and 0.25 per cent alkali and were quite satisfactory Fischer-Tropsch catalysts. Their work involved the development of precipitated iron catalysts (which generally contained both copper and alkali), decomposition iron catalysts, fused iron catalysts and pretreated iron ores. Unlike cobalt, iron catalysts are useful under a wide range of synthesis conditions. Different preparation techniques were found to yield catalysts with different properties.

Pichler [18] obtained some very interesting results using a ruthenium catalyst at 413K and very high pressure (~150 atmospheres). He observed the formation of paraffins with molecular weights and melting points higher than were known before. Indeed, compounds with molecular weights as high as 400,000 can be produced over ruthenium. Pichler's ruthenium catalyst was found to be very stable for long periods of time. Pichler extended the Fischer-Tropsch work to high pressures using thoria and other catalysts and found that branched hydrocarbons were produced [19].

Since the late forties there has been little change in the fundamental understanding of the Fischer-Tropsch synthesis and of the fundamental processes to produce hydrocarbons from carbon monoxide and hydrogen. Research has continued and has resulted primarily in the improvement of already existing catalysts and processes. One significant contribution has recently come from Pruett and Walker [20] who have developed a homogeneous rhodium catalyst that catalyzes the conversion of carbon monoxide and hydrogen to ethylene glycol at 523K and 1360 to 3400 atmospheres total pressure. This discovery has opened a new frontier of Fischer-Tropsch research involving the novel approach of homogeneous catalysis instead of the traditional heterogeneous catalytic approach. Table 1 lists the catalysts, along with their applications, that have been found to be most useful in Fischer-Tropsch synthetic processes. In general metal catalysts favor the production of normal paraffins and olefins whereas metal oxides such as ThO_2/Al_2O_3 can produce isomerized hydrocarbons. Metal oxides and doped metal

Table 1. Catalysts frequently used in the Fischer-Tropsch synthesis

Nickel	Used primarily in methanation
Cobalt	Promoted with ThO_2/MgO and supported on kieselguhr Used primarily in the atmospheric pressure process for making higher hydrocarbons and in the medium pressure process for synthesizing paraffins
Iron	Most important medium pressure catalyst in use today--generally promoted by alkali
Ruthenium	Unique for the production of high molecular weight hydrocarbons
Metal Oxides	Used in the production of oxygenated products

oxides are generally required for the production of alcohols from carbon monoxide and hydrogen.

In order to use the Fischer-Tropsch synthesis to produce chemicals and fuels, large quantities of carbon monoxide and hydrogen must be available relatively cheaply. One process which involves the gasification of coal to supply the carbon monoxide and hydrogen is shown in Figure 1. Coal plus either steam or oxygen is introduced into a gasification chamber where the coal is oxidized yielding primarily carbon monoxide and hydrogen, with slight amounts of carbon dioxide, methane and sulfur-containing compounds. The methane is removed at this stage and the remaining feedstream is passed into a desulfurization-purification chamber to remove the carbon dioxide and sulfur-containing compounds which would foul the catalysts downstream. The remaining feedstream is passed into the water-gas shift reactor to catalytically adjust the hydrogen to carbon monoxide ratio to the desired value (usually between 2 and 3). Finally, the feedstream passes over the

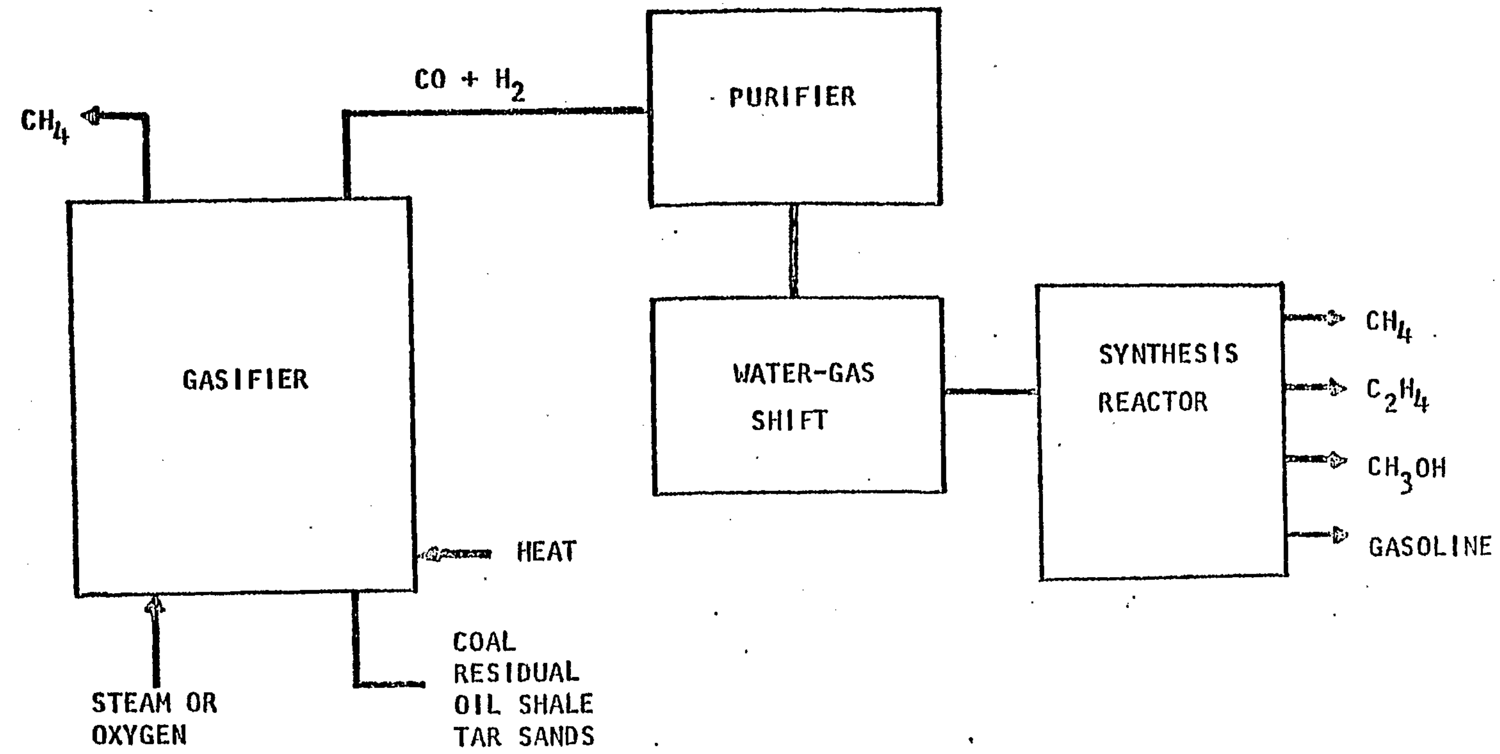


Figure 1. Schematic of process for the conversion of hydrogen deficient materials to useful chemicals and fuels

Fischer-Tropsch catalyst and the products are produced. Only one commercial plant utilizing this technology is in operation today. This is SASOL in South Africa where large coal reserves combined with essentially no petroleum reserves led to an early development of such a process.

The mechanism for the Fischer-Tropsch synthesis is obviously dependent upon the choice of products. Many scientists believe, however, that most, if not all, of the products have identical reaction intermediates. In 1926, Fischer and Tropsch proposed the "carbide theory" [21] in which a reactive metal carbide intermediate exists on the surface. This theory was refined by Craxford and Rideal [22,23] but was subsequently rejected as a result of work discussed by Pichler [2] and Kini and Lahiri [24].

The first proposal that oxygen containing surface intermediates are involved came from Elvins and Nash [25], also in 1926. Today, two forms of this proposal are believed most likely to describe the reaction sequence. A theory proposed by Storch and co-workers [26] postulates that carbon monoxide and hydrogen interact on a metal surface to produce an intermediate of the type $M\text{-}CH_2O$. They propose that chain growth occurs *via* the interaction of these intermediates to form longer chain oxygen containing complexes of the general form $M\text{-}CH_2(CH_2)_xOH$. A theory by Pichler and Schulz [27] postulates the same $M\text{-}CH_2O$ intermediate but requires that chain growth occur *via* the interaction of this intermediate with an adsorbed carbon monoxide molecule. Recently, tracer studies by Emmett, *et al*. [28], Sanstri, *et al*. [29] and Kölbel and Hanus [30] tend to support the Anderson model. whereas work by Blyholder and Goodsel [31] tends to support Pichler's model. Although there seems to be agreement as to the structure of one of the reaction intermediates, the details of the mechanism are still not understood.

The methanation reaction has, over the past 70 years, received quite a bit of attention, although not nearly so much as the more industrially significant Fischer-Tropsch synthesis. There are essentially three reasons for studying the methanation reaction:

1) to form a high Btu methane rich fuel with low carbon monoxide content
2) to eliminate carbon monoxide present in small amounts in hydrogen rich gases by conversion to methane
3) to avoid methane formation in the manufacture of higher hydrocarbons and oxygenated chemicals from synthesis gas <u>via</u> the Fischer-Tropsch reaction

Early research was concerned primarily with learning enough about the methanation process to avoid methane formation in manufacturing higher hydrocarbons and alcohols <u>via</u> the Fischer-Tropsch synthesis. Later work has been concerned with the conversion of the small carbon monoxide impurity present in a lot of natural gas so that it will meet federal requirements for introduction into transcontinental pipelines (0.1 ppm max.). Also, with the growing world shortage of petroleum and natural gas supplies, the formation of large quantities of methane from alternate fuel sources is becoming increasingly feasible.

The thermodynamics of the methanation reaction are summarized in Table 2. The free energy values indicate that the reaction is thermodynamically favored at lower temperatures. This requires the operation

Table 2. Methanation Thermodynamics[a] [32]

T (K)	ΔG^o (kcal/mole)	ΔH^o (kcal/mole)
300	-33.9	-49.3
400	-28.6	-50.4
500	-23.0	-51.3
600	-17.3	-52.1
700	-11.4	-53.2
800	- 5.5	-52.7
900	0.5	-53.6
1000	6.5	-53.9

[a] All reactants and products have a gaseous standard state.

of the reaction process at the lowest possible temperature in order to increase the thermodynamic yield. As is the case with all activated processes, lower temperatures reduce the kinetic rate of the overall process. Therefore, a situation exists in which two opposing factors must be simultaneously satisfied--the temperature must be kept low enough for a favorable thermodynamic equilibrium and to prevent sintering of the catalyst, but high enough to achieve an appreciable rate of conversion to products. Generally the methanation reaction is run at a temperature of 525 to 725K. Fairly high reactant pressures are used to achieve rapid conversion and higher product yields. Once a reaction temperature is chosen for a process, special precautions must be taken to prevent the highly exothermic reaction from causing catalyst overheating.

Wide varieties of catalysts and conditions have been used to study the methanation reaction. The work reported has included studies that measured the kinetics of the reaction process as well as spectroscopic and thermal desorption studies designed to yield information about the bonding and interaction of the carbon monoxide and hydrogen to the surface.

During the past few decades many studies have been made to determine the kinetics of the methanation reaction on a variety of catalysts. Because of its economic availability as well as its high reactivity and selectivity toward methane formation, nickel has been used in most of these studies. Work by Vannice [33] in 1975 produced a turning point in the reporting of methanation kinetic results. The vast majority of the kinetic data taken prior to 1975 did not include measurement of the surface areas of the catalysts used. Although the information obtained from each of these early studies was useful, comparisons between laboratories or even between studies with a given lab were impossible since the rates were dependent upon catalyst surface areas. Vannice introduced the specific activity (molecules of methane produced per site per second) which is generally independent of the catalyst surface area. Most of the data since Vannice's work have been in the form of specific activities and comparisons are much more informative. Subsequent studies by Vannice [34-36] have demonstrated that, because of catalyst support interactions, the specific activities of metals supported on different materials are not necessarily the same.

Several reviews have discussed the kinetics of the methanation reaction, therefore, no detailed comparison of kinetic results will be presented here. Instead, a brief summary of these results on the group VIII metals will be followed by a more detailed discussion of the mechanisms that have been proposed for the methanation process in recent years.

One fact that is immediately evident from the earlier methanation studies is that great diversity exists among the results. Much of the variation is likely due to differences in reaction parameters as well as differences in catalyst support materials and methods of pretreatment. If one choses to compare results with similar hydrogen to carbon monoxide ratios, say between 1 and 3, then some useful generalizations can be made. Usually the data are fit to a rate law of the form:

$$r_{CH_4} = k\, P_{H_2}^{m}\, P_{CO}^{n} \tag{9}$$

The kinetic order in hydrogen, m, is usually between 0.5 and 1.5 and the order in carbon monoxide, n, falls in the 0 to -1.0 range. The interaction of the products with the catalyst is usually quite weak and yields a zero order dependence in the rate law. The kinetic studies have led to a general belief that under the conditions of the methanation reaction, the surface is nearly completely covered with strongly adsorbed carbon monoxide with the more weakly bound hydrogen competing for the remaining sites.

Vannice was the first to determine the specific activities of all the group VIII metals, except osmium, toward the methanation reaction [33]. His experiments were conducted at atmospheric pressure and 558K on alumina supported catalysts. The specific activities of these metals toward the methanation reaction are as follows:

$$\mathrm{Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir}$$

It is quite surprising that only two orders of magnitude separare the specific activities of ruthenium and iridium. Sinfelt's work with the hydrogenation of ethane demonstrated a difference of eight orders of magnitude between the specific activities of the most active and least active metals [37]. Vannice fit the kinetic data from his study to the same rate expression used in earlier studies (9). He found that for all the metals studied the kinetic order in hydrogen was between 0.77 and 1.6 and that for carbon monoxide was between 0.10 and -0.60, in general agreement with earlier results.

In a subsequent paper [38] Vannice demonstrated that there is an inverse trend between the heat of adsorption of carbon monoxide on a group VIII metal and the methanation activity of that metal. An opposite trend exists when the rates are compared to the heats of adsorption of hydrogen on the metals studied. A fairly large compensation effect exists for the methanation reaction on these metals.

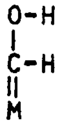
Spectroscopic studies have generally led to the conclusion that carbon monoxide adsorbs on the group VIII metals in such a fashion that one of the following structures is an intermediate in the methanation reaction:

$$\begin{array}{c} O \\ \| \\ C \\ \| \\ M \end{array}$$

$$\begin{array}{cc} C & - O \\ ||| & | \\ M & M \end{array}$$

Another intermediate in the methanation reaction is believed to be identical to one of the ones postulated for the Fischer-Tropsch synthesis, $M-CH_2O$. This results from studies that establish a carbon monoxide to hydrogen ratio of 1:1 in this surface intermediate.

Although the structure of this surface complex is the subject of ongoing investigations, many believe that it can be adequately represented as follows:



$$\begin{array}{l} \mathrm{O{-}H} \\ | \\ \mathrm{C{-}H} \\ \| \\ \mathrm{M} \end{array}$$

Several mechanisms have been postulated to describe the methanation reaction. All except two have been fit to data taken over nickel catalysts. The first mechanism for the methanation reaction was reported in 1965 by Kozub, Rosov and Vlasenko [39]. They performed work function measurements on a nickel-chromium catalyst and established that the mechanism should involve the interaction of charged species; adsorbed hydrogen increased the work function whereas adsorbed carbon monoxide decreased the work function. When a carbon monoxide dose was followed by a hydrogen dose the work function dropped, suggesting a positively charged surface complex. The proposed mechanism which is consistent with these work function changes is as follows (M=metal surface site):

$$M + e^- + H_2 \rightarrow MH_2^- \tag{10}$$

$$M + MH_2^- + e^- \rightleftarrows 2MH^- \tag{11}$$

$$M + CO \rightarrow MCO^+ + e^- \tag{12}$$

$$MCO^+ + 2MH^- \rightarrow MHCOH^+ + 2e^- + 2M \tag{13}$$

$$MHCOH^+ + MH_2^- \rightarrow MCH_2 + H_2O + M \tag{14}$$

$$MCH_2 + H_2 \rightarrow CH_4 + M \tag{15}$$

The intermediates in this mechanism seem quite reasonable. The authors did not specify the structure of the adsorbed MH_2^- complex, however it is assumed that the hydrogen is dissociatively adsorbed. The postulation that hydrogen is molecularly adsorbed at the elevated temperatures used in the methanation process is difficult to believe. In a subsequent paper, Vlasenko and Yuzefovich [6] modified the mechanism to involve only one type of adsorbed hydrogen:

$$M + e^- + H_2 \rightarrow MH_2^- \qquad (16)$$

$$M + CO \rightarrow MCO^+ + e^- \qquad (17)$$

$$MCO^+ + MH_2^- \rightarrow MHCOH^+ + e^- + M \qquad (18)$$

$$MHCOH^+ + MH_2^- \rightarrow MCH_2 + H_2O + M \qquad (19)$$

$$MCH_2 + MH_2^- \rightarrow CH_4 + e^- + 2M \qquad (20)$$

It was postulated that the step denoted by (18) is the rate determining step.

The second methanation mechanism was proposed in 1969 by Schoubye [40] who made a kinetic study on several nickel catalysts. Schoubye found that his data, which were collected between 443 and 623K and 1 to 15 atmospheres total pressure, could be fit by a rate law of the following form:

$$r_{CH_4} = \frac{AP_{H_2}^{0.15}}{\left[1+\left(\frac{BP_{CO}}{P_{H_2}}\right)\right]^{0.5}}$$

By assuming that the major surface species were adsorbed carbon monoxide and adsorbed hydrogen, the following simple mechanism was found to fit the data:

$$CO + 2M \rightleftarrows M_2CO \qquad (21)$$

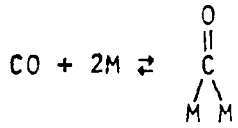
$$H_2 + 2M \rightleftarrows 2MH' \qquad (22)$$

and/or $$H_2 + 2M \rightarrow M_2H_2 \rightleftarrows 2MH \rightarrow 2MH'' \qquad (23)$$

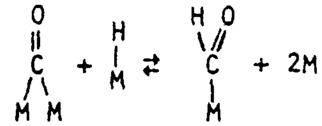
where only MH' and MH'' (which are probably identical) can react with adsorbed carbon monoxide. The author postulates that the dissociation of the hydrogen molecule is the rate limiting step in the methanation reaction and that the dissociation of carbon monoxide is a poisoning side reaction which can occur.

In 1972 Bousquet, Gravelle and Teichner [41] proposed a mechanism to describe the methanation reaction over a nickel-alumina catalyst at 573K and with total pressures between 0.1 and 1 atmosphere. The kinetic results did not allow this group to distinguish between a Langmuir-Hinshelwood model and a Rideal-Eley model (see Appendix II) for those steps leading to the formation of the MH_2CO surface complex. Therefore, the authors developed a Langmuir-Hinshelwood mechanism in which adsorbed carbon monoxide is involved in the reaction:

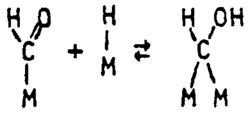
$$H_2 + 2M \rightleftarrows 2MH \qquad (24)$$



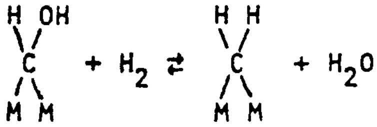
$$\mathrm{CO + 2M \rightleftarrows \underset{M\ \ M}{\overset{O}{\overset{\|}{C}}}} \qquad (25)$$



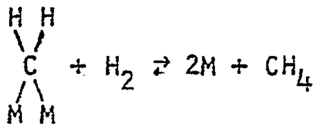
$$\mathrm{\underset{M\ \ M}{\overset{O}{\overset{\|}{C}}} + \underset{M}{\overset{H}{|}} \rightleftarrows \underset{M}{\overset{H\ \ O}{C}} + 2M} \qquad (26)$$



$$\mathrm{\underset{M}{\overset{H\ \ O}{C}} + \underset{M}{\overset{H}{|}} \rightleftarrows \underset{M\ \ M}{\overset{H\ \ OH}{C}}} \qquad (27)$$



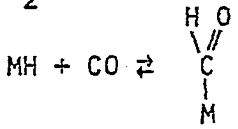
$$\mathrm{\underset{M\ \ M}{\overset{H\ \ OH}{C}} + H_2 \rightleftarrows \underset{M\ \ M}{\overset{H\ \ H}{C}} + H_2O} \qquad (28)$$



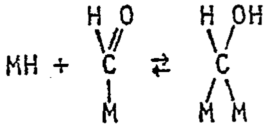
$$\overset{H\ H}{\underset{M\ M}{C}} + H_2 \rightleftarrows 2M + CH_4 \qquad (29)$$

and a Rideal-Eley mechanism in which adsorbed carbon monoxide is an inhibitor:

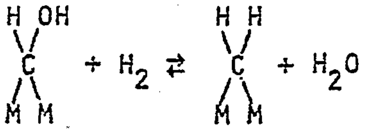
$$H_2 + 2M \rightleftarrows 2MH \qquad (30)$$



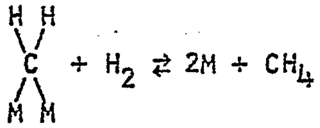
$$MH + CO \rightleftarrows \overset{H\ O}{\underset{M}{C}} \qquad (31)$$



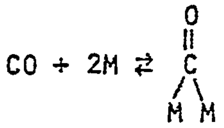
$$MH + \overset{H\ O}{\underset{M}{C}} \rightleftarrows \overset{H\ OH}{\underset{M\ M}{C}} \qquad (32)$$



$$\overset{H\ OH}{\underset{M\ M}{C}} + H_2 \rightleftarrows \overset{H\ H}{\underset{M\ M}{C}} + H_2O \qquad (33)$$



$$\overset{H\ H}{\underset{M\ M}{C}} + H_2 \rightleftarrows 2M + CH_4 \qquad (34)$$



$$CO + 2M \rightleftarrows \overset{O}{\underset{M\ M}{C}} \qquad (35)$$

Both of these mechanisms are quite reasonable. Each involves the reaction of adsorbed hydrogen atoms and hydrogen gas with adsorbed carbonaceous intermediates to produce methane and water. It is interesting to note that, according to these models, the water is at no time bound to the surface of the catalyst.

Van Herwijnen, Van Doesburg and De Jong [42] in 1973 developed a mechanism for the methanation reaction in the 443 to 483K range and at atmospheric pressure. The reaction was found to have a variable CO order from +1.0 to -1.0. No attempt was made to obtain a hydrogen order. The data were fit by the following expression (constant hydrogen pressure):

$$r_{CH_4} = \frac{AP_{CO}}{(1+BP_{CO})^2}$$

It was assumed that the rate determining step involved the interaction of two adsorbed species--one of which is carbon monoxide or a complex formed by carbon monoxide. The authors proposed the following interaction, involving an adsorbed enol complex and adsorbed hydrogen, as the rate determining elementary step:

$$MH_2CO + MH_2 \rightarrow MH_2O + MCH_2 \qquad (36)$$

This is a fairly incomplete description of the methanation process since it does not specify the steps preceding the rate determining step, nor does it specify the modes of bonding of any of the intermediates to the surface.

At about the same time as Van Herwijnen's model was proposed, Fontaine [43] developed a different model of the methanation process, once again on nickel. For pressures greater than 0.1 atmospheres, the following four steps were proposed:

$$CO + M \rightleftarrows M\text{-}CO \qquad (37)$$

$$H_2 + 2M \rightleftarrows 2M\text{-}H \qquad (38)$$

$$M\text{-}H + M\text{-}CO \rightleftarrows MHCO + M \qquad (39)$$

$$M\text{-}H + MHCO \rightleftarrows MH_2CO + M \qquad (40)$$

The last step was found to be the rate determining process. For pressures less than 0.1 atmosphere, it was determined that two more reaction steps were needed to describe completely the methanation process:

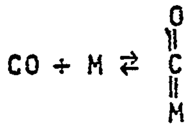
$$M\text{-}H + MH_2CO \rightleftarrows MH_3CO + M \tag{41}$$

$$MH_3CO + M\text{-}H \rightarrow \text{Products} \tag{42}$$

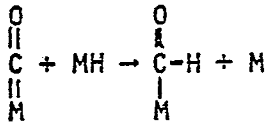
As in the case of Van Herwijnen's model, Fontaine proposed that the H_2CO surface complex was formed <u>via</u> an irreversible reaction step. In the low pressure case, the last step (producing products) would be rate determining. The relative rates of these two irreversible steps would govern the concentration of the adsorbed H_2CO intermediate.

In 1975 McGill and Richardson [44] proposed a mechanism to describe their data taken between 423 and 673K over a commercial nickel-kieselguhr catalyst. The total pressure was 1 atmosphere. The mechanism that was proposed is as follows:

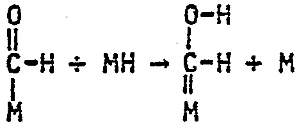
$$H_2 + 2M \rightleftarrows 2MH \tag{43}$$



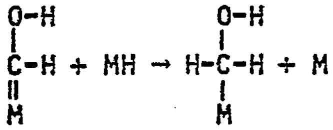
$$CO + M \rightleftarrows \begin{array}{c} O \\ \| \\ C \\ \| \\ M \end{array} \tag{44}$$



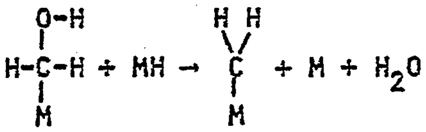
$$\begin{array}{l} O \\ \| \\ C \\ \| \\ M \end{array} + MH \rightarrow \begin{array}{l} O \\ \| \\ C\text{-}H \\ | \\ M \end{array} + M \tag{45}$$



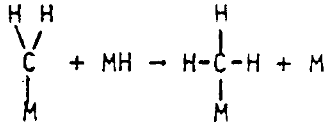
$$\begin{array}{l} O \\ \| \\ C\text{-}H \\ | \\ M \end{array} + MH \rightarrow \begin{array}{l} O\text{-}H \\ | \\ C\text{-}H \\ \| \\ M \end{array} + M \tag{46}$$



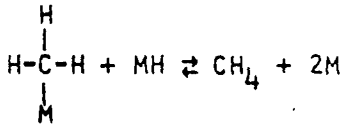
$$\begin{array}{l} O\text{-}H \\ | \\ C\text{-}H \\ \| \\ M \end{array} + MH \rightarrow \begin{array}{c} O\text{-}H \\ | \\ H\text{-}C\text{-}H \\ | \\ M \end{array} + M \tag{47}$$



$$\begin{array}{c} O\text{-}H \\ | \\ H\text{-}C\text{-}H \\ | \\ M \end{array} + MH \rightarrow \begin{array}{c} H\ H \\ \backslash / \\ C \\ | \\ M \end{array} + M + H_2O \tag{48}$$



$$\overset{H\ \ H}{\underset{M}{C}} + MH \rightarrow H-\underset{M}{\overset{H}{C}}-H + M \qquad (49)$$



$$H-\underset{M}{\overset{H}{C}}-H + MH \rightleftarrows CH_4 + 2M \qquad (50)$$

This mechanism proposes that atomic hydrogen is the adsorbed form of hydrogen. The atomic hydrogen in a stepwise fashion attacks the carbon-containing intermediate. McGill and Richardson found that at temperatures below 473K the step designated by (48) is rate determining. Between 473 and 573K step (45) is rate determining and at temperatures above 573K it was found that the adsorption of carbon monoxide (44) is the rate determining step.

In the same year Vannice [33] reported the results of a study that established an order for methanation activity of the group VIII metals based upon their specific activities. In a subsequent study [38] the kinetics of the methanation reaction were measured over the same metals. The studies were performed at atmospheric pressure and 548K on supported catalysts. Two mechanisms were proposed to describe the methanation process. The first was postulated for uniform surfaces:

$$CO + M \rightleftarrows MCO \qquad (51)$$

$$H_2 + M \rightleftarrows MH_2 \qquad (52)$$

$$MCO + MH_2 \rightleftarrows MCHOH \qquad (53)$$

$$MCHOH + \frac{y}{2}MH_2 \rightarrow MCH_y + H_2O \qquad (54)$$

$$MCH_y + \left(\frac{4-y}{2}\right)MH_2 \rightarrow CH_4 \qquad (55)$$

In this mechanism the step designated by (54) is the rate determining process and the surface is believed to be predominantly covered with the MCHOH complex. For non-uniform surfaces with two types of sites, the following mechanism was proposed:

$$H_2 + * \rightleftarrows *H_2 \quad (56)$$

$$M + CO + H_2 \rightarrow MCHOH \quad (57)$$

$$MCHOH + (\tfrac{y}{2})*H_2 \rightarrow MCH_y + * + H_2O \quad (58)$$

$$MCH_y + (\tfrac{4-y}{2})H_2 \rightarrow CH_4 + M \quad (59)$$

The two non-equivalent surface sites are represented by M and *. In order to obtain a fit with this mechanism it was assumed that the step designated by (58) is the rate determining step. Sites designated by M adsorb only carbon monoxide and cover the greater portion of the surface. Sites designated by * adsorb only hydrogen. The intermediates in both mechanisms are reasonable, however the suggestion that one half (y=1) or three halves (y=3) of an adsorbed molecule could be involved in the reaction is unacceptable. This is the only mechanism known that attempts to describe the methanation process on all metals studied (the value of y depends upon the metal) and it is one of only two mechanisms that have been proposed to describe the reaction on ruthenium catalysts.

About a year later, Vannice's mechanism was modified by Bond and Turnham [45] to involve a different form of hydrogen bonding to the catalyst. A Ru-Cu supported bimetallic catalyst was used to collect kinetic data between 533 and 673K at pressures of about 0.1 atmosphere. The modified mechanism for uniform surfaces is as follows:

$$H_2 + 2M \rightleftarrows 2MH \quad (60)$$

$$CO + M \rightleftarrows MCO \tag{61}$$

$$2MH + MCO \rightleftarrows MCHOH + 2M \tag{62}$$

$$MCHOH + aMH \rightarrow MCH_a + H_2O \tag{63}$$

$$MCH_a + (4-a)MH \xrightarrow{rapid} CH_4 + (5-a)M \tag{64}$$

The step designated as (63) is the rate determining step, as in Vannice's proposal. This mechanism, although it only describes work on the Ru-Cu alloy, is more acceptable than Vannice's proposal because the hydrogen is explicitly adsorbed in the atomic form and the problem concerning fractional adsorbed molecules is eliminated. This, of course, assumes that Vannice intended that $*H_2$ represent an adsorbed hydrogen molecule. His paper did not specify the sort of hydrogen bonding involved.

Also in 1976, Araki and Ponec [46] performed some methanation studies on nickel and nickel-copper alloys. They found that at 573K and 0.48 torr, the carbon monoxide disproportionation reaction (6) occurs. This led to a mechanism involving dissociated carbon monoxide:

$$H_2 + 2M \rightleftarrows 2MH \tag{65}$$

$$CO + 2M \rightleftarrows MC + MO \tag{66}$$

$$MC + MH \rightarrow MCH + M \tag{67}$$

$$MO + MH \rightarrow MOH + M \tag{68}$$

$$MOH + MH \rightarrow H_2O + 2M \tag{69}$$

The step designated as (67) was postulated as being the rate determining step. One situation not addressed by the authors concerns the observation that nickel catalysts tend to coke quite rapidly in Fischer-Tropsch processes. This coking reduces the catalyst activity tremendously. If surface carbon is the active intermediate then it would seem that coking would not decrease the rate so rapidly and significantly.

Finally, a recent study by Ekerdt and Bell [47] has reported a mechanism for the methanation reaction on silica supported ruthenium catalysts. The study combined infrared and kinetic techniques. A temperature range of 464 to 548K was employed. The pressure was in the 0.1 to 1.0 atmosphere range. The following mechanism was proposed:

$$CO + M \rightleftarrows MCO \tag{70}$$

$$MCO + M \rightleftarrows MC + MO \tag{71}$$

$$MO + H_2 \rightarrow H_2O + M \tag{72}$$

$$H_2 + 2M \rightleftarrows 2MH \tag{73}$$

$$MC + MH \rightleftarrows MCH + M \tag{74}$$

$$MCH + MH \rightleftarrows MCH_2 + M \tag{75}$$

$$MCH_2 + H_2 \rightleftarrows CH_4 + M \tag{76}$$

In order to have this mechanism fit the kinetic data it was assumed that step (76) was the rate limiting step and that the coverage of adsorbed carbon monoxide molecules was much larger than that of any other intermediate.

Although some very significant differences exist among these mechanisms, some general trends seem to be apparent:

1) Each mechanism involves the interaction of one or more forms of adsorbed hydrogen.

2) All involved adsorbed molecular carbon monoxide except that proposed by Araki and Ponec. The mechanism by Ekerdt and Bell involves adsorbed molecular carbon monoxide which dissociates to form adsorbed carbon and adsorbed oxygen atoms.

3) All involve a H_2CO type adsorbed complex except those of Schoubye, Akari and Ponec and Ekerdt and Bell. It is very likely that a H_2CO type complex is involved in Schoubye's mechanism, but he does not explicitly state so.

4) No mechanism except those of Araki and Ponec and Ekerdt and Bell involves the direct bonding of oxygen to the surface.

Work currently in progress will hopefully increase our understanding of the mechanism involved in the methanation reaction on a variety of catalysts.

Ruthenium has been found to be unique among the group VIII metals with respect to the catalysis of the hydrogen-carbon monoxide conversion. While it is the most active catalyst known for the methanation reaction, it is one of the least selective for methane formation, with about 60 per cent methane selectivity under moderate conditions. The remainder of the products are higher hydrocarbons, and it is these higher hydrocarbons that contribute to ruthenium's uniqueness. Ruthenium produces the highest C_5^+ fraction of all group VIII metals even at atmospheric pressure. Under conditions of high pressure and low temperature ruthenium will catalyze the formation of high molecular weight (up to 400,000) paraffinic waxes from carbon monoxide and hydrogen. No other catalyst is known to do this. The products of the reduction of carbon monoxide over ruthenium are generally a wide variety of saturated hydrocarbons. Essentially no oxygen containing compounds are produced (other than H_2O and CO_2). This unique ability to form high molecular weight compounds coupled with the high activity of the catalyst has resulted in several investigations that focused on a fundamental understanding of the reaction processes that occur on ruthenium. One of the major drawbacks to the widespread use of ruthenium catalysts in Fischer-Tropsch/methanation processes has been its relatively rapid deactivation under rigorous industrial conditions. If this lifetime could be improved and the selectivity of product formation adequately controlled, then the use of ruthenium in processes that produce saturated hydrocarbons might be possible.

Although ruthenium primarily catalyzes the production of higher molecular weight paraffins the selective formation of methane can be caused to occur by modifying the reaction conditions. Relatively few kinetic studies of the methanation reaction have been made using ruthenium catalysts. The results of these studies have been fit to the same rate expression as those studies on other group VIII metals (equation (9)). A summary of these results is presented in Table 3.

A wide variety of spectroscopic studies has been performed on carbon monoxide and hydrogen adsorbed on ruthenium. Carbon monoxide is believed to adsorb in the undissociated form at low pressures. Higher pressure pulsed kinetic studies suggest that both undissociated and dissociated carbon monoxide exist in equilibrium at temperatures above 373K. It is generally believed that hydrogen adsorbs in the dissociated form.

If the two mechanisms that have been proposed to describe the methanation reaction on ruthenium are examined closer it is evident that each involves steps that are somewhat difficult to justify. For ruthenium, Vannice found that $y=4$. This leads to the following rate

Table 3. Kinetics of methanation studies on ruthenium

Catalyst	Temperature (K)	Pressures (atm)			Rate expression	Reference
		H_2	CO	Total		
0.5% Ru/Al_2O_3	493-533	16.1	5.3	21.4	$r_{(3H_2+CO)}=kP_{H_2}^{1.33}P_{CO}^{-0.13}$	48
Ru metal	293-433	0.02-0.05	0.013-0.13	0.01-0.16	$r_{CH_4}=kP_{H_2}^{2}$	49
1.5% Ru/Al_2O_3	473-613	0.55	0.18	0.73	$r_{CH_4}=kP_{H_2}^{1.8}P_{CO}^{-1.1}$	50
5% Ru/Al_2O_3	478-503	0.75	0.25	1.0	$r_{CH_4}=kP_{H_2}^{1.6}P_{CO}^{-0.6}$	33
0.5% Ru/Al_2O_3	448-548	1.0	0.0005	1.0	$r_{CH_4}=kP_{CO}$	51

determining step for his mechanism (determined by substituting y=4 into equation (54)):

$$MCHOH + 2MH_2 \rightarrow CH_4 + H_2O \qquad (77)$$

This step involves a three body collision which simultaneously adds four hydrogen atoms to the intermediate while the carbon-oxygen bond is being cleaved. So many bonds are being broken and formed during the rate determining step that it does not even resemble an elementary process.

The mechanism by Ekerdt and Bell proposes that the carbon monoxide molecule dissociates prior to being attacked by hydrogen in the methanation process. This is in disagreement with not only Vannice but also a considerable amount of spectroscopic and flash desorption evidence which suggests that carbon monoxide adsorbs on ruthenium in a non-dissociated manner. Also, the authors postulate a rate determining step which involves the attack of an adsorbed methylene group by gas phase hydrogen to form methane. They comment that they have no basis for expecting this to actually occur, but that it does cause the mechanism to fit the kinetic data.

Two recent studies have probed the effects of temperature, pressure and space velocity [52] and catalyst support [53] upon the hydrogenation of carbon monoxide on ruthenium. Catalyst activity and product selectivity were studied as functions of these variables. The results may be summarized as follows:

1) Low temperatures decrease the methane selectivity and increase the olefin to paraffin ratio in the higher hydrocarbons.

2) The tendency to form higher hydrocarbons increases with pressure as does the tendency to produce carbonaceous deposits.

3) Feedstocks with low mole percent carbon monoxide are selective to methanation.

4) Low space velocity increases methane production.

5) Both Fischer-Tropsch and methanation activities vary by an order of magnitude depending upon the catalyst dispersion and support.

6) The fraction of olefins may be increased by having low carbon monoxide conversions or by using Cr_2O_3 or ThO_2 to support the ruthenium.

7) Methane selectivity is independent of support.

8) Isomerization occurs subsequent to and downstream from straight chain production (probably occurs on the support).

These results provide guidelines that may be important in future attempts to produce ruthenium catalysts and processes to selectively convert carbon monoxide and hydrogen to methane and other hydrocarbons. Recent evidence suggests that carbon dioxide may be hydrogenated to methane on ruthenium catalysts [54,55] and that in a mixture of carbon monoxide and carbon dioxide, the carbon monoxide can be selectively hydrogenated [56].

It has been suggested that similar intermediates exist for both the methanation and Fischer-Tropsch reactions. The relative concentrations of these surface complexes likely determine which reaction will occur. The purpose of this study is to develop a mechanistic understanding of the methanation reaction on unsupported ruthenium catalysts. An attempt will be made to correlate these results with other methanation studies as well as with results obtained under conditions that favored the formation of higher hydrocarbons. The role of the carbonaceous overlayer present on most Fischer-Tropsch/methanation catalysts under reaction conditions will also be discussed.