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Catalytic Methanation

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I. INTRODUCTION

Methanation, the hydrogenation of carbon oxides to methane, has been the subject of a large number of catalytic studies during the past 70 years. In the earliest work, that of Sabatier and Senderens [1], nickel was found to be a very efficient catalyst. Nickel is still the material of choice in most investigations of methanation, although ruthenium, cobalt, and iron are also active.

Nickel catalysts used commercially for methanation are usually in supported form, generally on acid-washed kieselguhr or on alumina. In terms of applied catalysis, there are three main reasons for concern with methanation: (1) to form a methane-rich fuel having high Btu value and low CO content, (2) to eliminate carbon monoxide present in small amounts in hydrogen-rich gases by conversion into methane to prevent catalyst poisoning, and (3) to avoid methane formation in the manufacture from synthesis gas of either (a) alcohols or (b) higher hydrocarbons by the Fischer-Tropsch reaction.

This article reviews the catalytic methanation of carbon monoxide and, to a lesser extent, carbon dioxide. Most of the literature cited was published within the past 20 years. Methanation to remove traces of carbon oxide from hydrogen-rich gases, such as those used in ammonia plants, has been considered as well as methanation to produce a methane-rich gas, such as SNG (substitute natural gas). Special catalytic problems related to the latter application of methanation are discussed in an additional section on equipment and heat-removal techniques.

Because good reviews of methanation [2] and Fischer-Tropsch synthesis [3, 4] were made in the 1950s, there seems to be no point of reviewing the early history of methanation. Readers wanting more than the historical high points given in this article should consult Greyson's chapter on methanation [2].

II. NEW IMPORTANCE OF SYNTHETIC METHANE

The manufacture of methane from coal has suddenly become recognized as having enormous potential for meeting the needs in the United States for a clean energy fuel from abundant coal resources secure within national borders [5]. Also, as an immediate, partial measure, plants are being installed to manufacture methane from petroleum naphtha, even though naphtha is in limited supply.

The overall energy needs of the United States are projected to continue to grow exponentially. Even at the 3.5% annual increase which is projected by the Department of the Interior [6], energy requirements will double by 1985 and nearly triple by the year 2000. Moreover, the use of pipeline gas—23 trillion cubic feet per year in 1972 and accounting for 33% of all United States energy needs—is growing even more rapidly, namely at nearly 6% per year. However, for the past 5 years less gas has been discovered in the United States than is being used. Consequently, the annual gas reserve/production ratio has been decreasing, declining from 16.1 in 1967 to 12.3 in 1971 [7]. Furthermore, the ultimate gas resources, including reserves as yet undiscovered, are finite (estimated to be 1500 to 2400 trillion cubic feet) and, it is believed, these will be depleted in the next few decades. Accordingly, as is projected in Fig. 1, the demand for gas will exceed supply significantly. Already gas shortages are being experienced in many parts of the country. One consequence of this shortfall is the initiation of importation of liquid natural gas (LNG) from abroad and the manufacture of gas from naphtha. The cost of such gas is in the $1.15-1.75/thousand cubic foot range compared to about 20¢ for natural gas at the wellhead in recent years. The large expected demand for gas, the shortage of natural gas, and the high price of gas by other alternatives have made the manufacture of SNG from coal attractive.

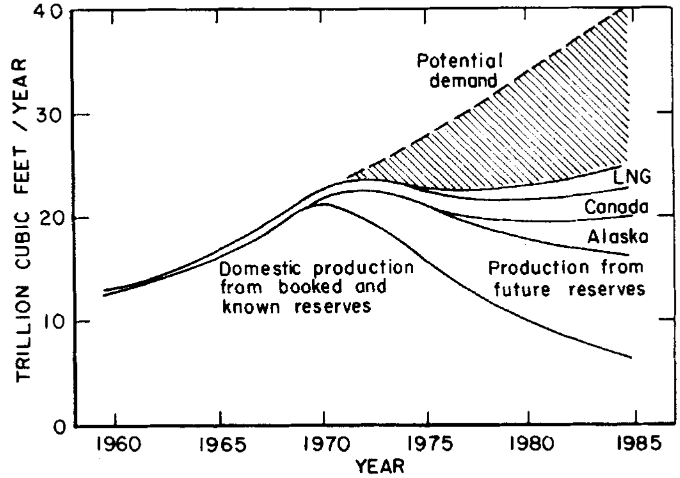


FIG. 1. United States gas supply (Humble Oil and Refining Co.).

Both the number and timing of installation of coal gasification plants have been described in a Federal Power Commission report [8] summarized in Fig. 2. In a separate study, a National Petroleum Council Task Force concluded that even more rapid plant installations would be possible, with a maximum of 36 plants by 1985. The manufacture of methane from coal promises to become an enormous new industry in the United States with a capital investment of over 8 billion dollars in the next 20 years.

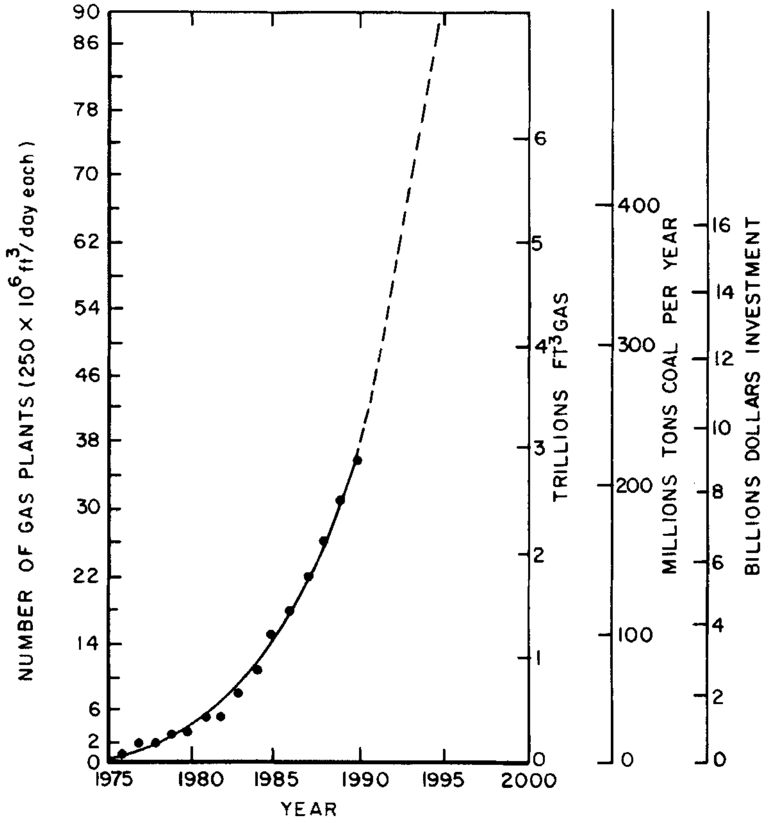


FIG. 2. Projected United States coal gasification plants (Federal Power Commission).

The future supply of fuels must also take into account various consumer groups or use sectors of energy [9]. The four sectors, home and commercial, industrial, transportation, and generation of electricity now are fairly evenly divided in their fuel consumption. Each is expected to grow, although fuels for generating electricity, including nuclear, will assume much greater importance. Fortunately, synthetic fuels can provide in the future for each of the energy use sectors as summarized below:

1. Home, commercial, some industrial.
   High-Btu gas (essentially methane, 1000 Btu/ft^3).
2. Generation of electricity, some industrial.
   (a) Low-sulfur, low-ash oil.
   (b) Low-Btu gas (CH_4, H_2, CO mixture, 150-400 Btu/ft^3).

3. Transportation.
   (a) Gasoline or methanol.
   (b) Gaseous fuel such as methane and/or hydrogen.

In the manufacture of methane, a mixture containing hydrogen and carbon oxides as well as methane is first produced in a "gasification" process step in which coal is reacted with oxygen and steam. Following adjustment of the H_2/CO to a 3/1 mole ratio by the shift reaction, and removal of CO_2 and sulfur compounds, catalytic methanation is carried out to provide a product which is essentially methane plus a small amount of hydrogen and practically no carbon monoxide. (In Europe, town gas currently does not include a methanation step and hence it contains carbon monoxide and hydrogen, and has a lower volumetric heating value).

By way of example, in one of the fluid bed gasification processes being developed in the United States, product gas from SYNTHANE coal gasification process step [10], after removal of carbon dioxide and water vapor, typically has a heating value of 475 Btu/ft^3. The gas consists largely of H_2, CO, and CH_4 in approximately a 4:3:2 mole ratio. This mixture cannot be methanated directly because of sulfur compounds present which would poison the methanation catalyst and because the ratio of hydrogen to carbon monoxide is below 3:1. However, by means of the shift reaction, the hydrogen to carbon monoxide ratio may be adjusted to the desired ratio, usually slightly greater than 3:1. The shifted gas, after thorough sulfur removal, may then be methanated. The product gas from this reaction will contain some excess hydrogen (5-10%) but must contain no more than 0.1% carbon monoxide to meet today's pipeline gas standards. Its heating value will be 900 to 950 Btu/ft^3, which is acceptable for use as pipeline gas.

III. CHEMISTRY AND THERMODYNAMICS

When the hydrogen to carbon monoxide ratio in synthesis gas is equal to or greater than 3, the conversion of carbon monoxide and hydrogen to methane can be described by the reaction:

$$3H_2 + CO \longrightarrow CH_4 + H_2O \qquad (1)$$

Methane is also formed by hydrogenation of carbon oxides in two other reactions:

$$2H_2 + 2CO \longrightarrow CH_4 + CO_2 \qquad (2)$$

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O \qquad (3)$$

However, hydrogenation of carbon dioxide, Reaction (3), does not occur in the presence of carbon monoxide. Also, Reaction (2) can be considered to be a combination of Reaction (1) and the water gas shift Reaction (4):

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (4)$$

Although the water gas shift reaction does not produce methane, it is an important reaction in methanation chemistry, altering the H_2/CO ratio with far-reaching effects on reaction products.

The free energy values of all the above reactions have large negative values for a wide temperature range. However, the reactions are relatively slow and catalysts are needed to accelerate the reactions to acceptable commercial rates. In this connection a further reaction is important, since it can lead to a deposition of carbon on the catalyst with eventual resultant fouling of the catalyst:

$$2CO \longrightarrow C + CO_2 \qquad (5)$$

At temperatures used in coal gasification (900°C), methane formation by hydrogenation of carbon occurs:

$$2H_2 + C \longrightarrow CH_4 \qquad (6)$$

However, this and related reactions, such as the steam-carbon reaction, do not occur significantly at temperatures used in catalytic methanation (250-450°C) and are outside the scope of this article.

Thermodynamic values [11] for Reactions (1)-(5) are given in Table 1 from which Figs. 3, 4, and 5 have been drawn. From the enthalpy values illustrated in Fig. 3 it is observed that all the reactions are exothermic and, indeed, all except Reaction (4) are highly exothermic. This high heat release makes it difficult to prevent overheating and inactivation of the catalyst and also it can make temperatures rise to such a degree that methanation becomes limited due to thermodynamic equilibrium. It is further noted from Fig. 3 that heats of reactions are not greatly influenced by temperature. In contrast, changes in free energy and equilibrium constants for methanation reactions are quite dependent on temperature (Figs. 4 and 5). For the reactions under discussion, ΔF is zero at about 625°C.

Equilibrium methane yields are affected critically by temperature and by synthesis gas H_2/CO ratios, theoretical methane yields being highest at lower temperatures and higher ratios. The effect of temperature on individual reaction equilibria is given in Fig. 5. Pressures do not appreciably affect methane yield until a temperature of about 425°C is exceeded.

TABLE 1

Temperature		Reaction				
°K	°C	1	2	3	4	5
Heat of Reaction, ΔH_f°, kcal						
300	27	−49.298	−59.136	−39.460	−9.838	−41.227
400	127	−50.360	−60.070	−40.650	−9.710	−41.434
500	227	−51.297	−60.815	−41.779	−9.518	−41.499
600	317	−52.084	−61.376	−42.792	−9.292	−41.460
700	427	−52.730	−61.780	−43.680	−9.050	−41.350
800	527	−53.248	−62.047	−44.449	−8.799	−41.190
900	627	−53.654	−62.203	−45.105	−8.549	−40.996
1000	727	−53.957	−62.261	−45.653	−8.304	−40.729
Free Energy of Reaction, ΔF°, kcal						
300	27	−33.904	−40.731	−27.077	−6.827	−28.621
400	127	−28.610	−34.451	−22.769	−5.841	−24.385
500	227	−23.062	−27.956	−18.168	−4.894	−20.111
600	327	−17.338	−21.329	−13.347	−3.991	−15.836
700	427	−11.493	−14.620	−8.366	−3.127	−11.574
800	527	−5.567	−7.865	−3.269	−2.298	−7.332
900	627	+0.594	−1.079	+1.921	−1.500	−3.108
1000	727	+6.444	+5.715	+7.173	−0.729	+1.090
Equilibrium Constant, Log K_p						
300	27	24.698	29.670	19.724	4.973	20.849
400	127	15.630	18.822	12.44	3.191	13.322
500	227	10.080	12.219	7.940	2.139	8.790
600	327	6.314	7.768	4.861	1.453	5.768
700	427	3.588	4.564	2.611	0.976	3.613
800	527	1.521	2.148	0.893	0.628	2.003
900	627	−0.144	0.261	−0.466	0.364	0.755
1000	727	−1.408	−1.248	−1.568	0.159	−0.238

Calculations of the theoretical equilibrium compositions of gas mixtures starting with various hydrogen/carbon monoxide ratios have been presented in graphical form [12] as a function of temperature and pressure.

The effects of temperature, pressure and synthesis gas ratios on the degree of carbon deposition have also been calculated. Whether carbon deposition occurs or not is primarily a function of the synthesis-gas ratio. The carbon deposition boundaries, or limiting H_2/CO ratios above which carbon will not deposit, are shown in Fig. 6 for the temperature range 500-1400°K and for pressures of 1, 10, and 25 atm. Increasing pressure tends to decrease the mini-

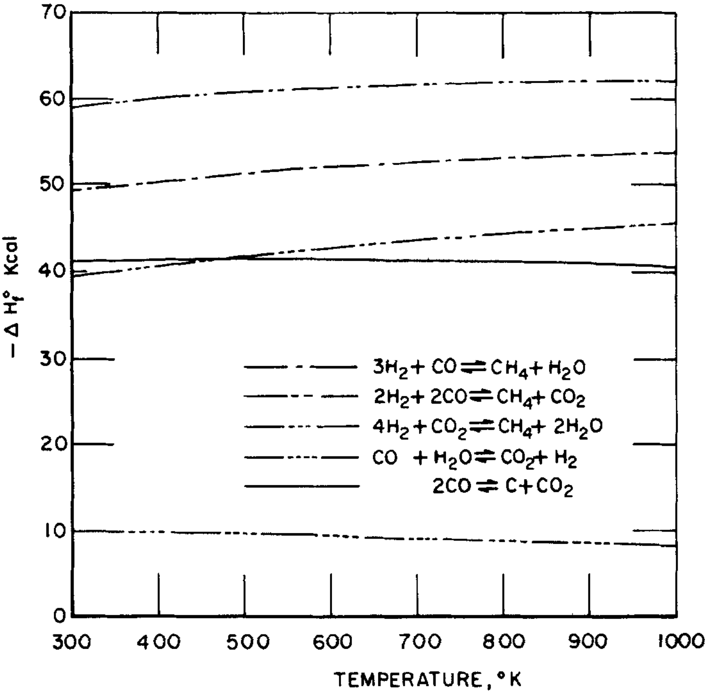


FIG. 3. Heats of reactions as functions of temperature.

mum ratio required for the prevention of carbon deposition.

It can be concluded that catalyst beds should be operated at the lowest temperatures that are consistent with acceptable catalyst activity, and with H_2/CO ratios at or above the limiting boundary ratios. Operation at high pressure tends to permit the use of lower H_2/CO ratios without the deposition of carbon on the catalyst. Unfortunately, operation at elevated pressures produces release of a large quantity of heat per unit volume which, unless adequate means of removal are available, increases catalyst-bed temperatures and decreases methane yield.

IV. MECHANISM OF CO METHANATION

A. Mechanisms Proposed

The mechanism of hydrogenation of carbon monoxide to higher hydrocarbons has been the subject of an intensive study for many

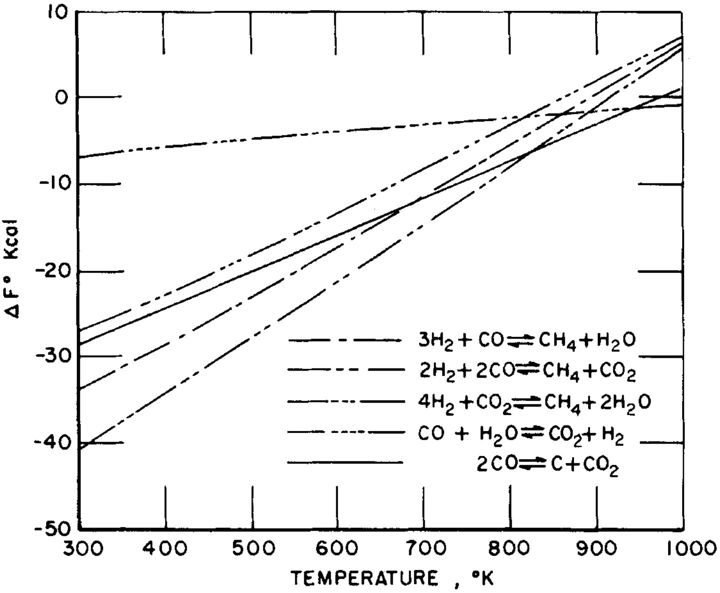


FIG. 4. Free energy changes as functions of temperature.

years. Somewhat surprisingly, relatively little work has been done on the methanation reaction. As Vlasenko and Yuzefovich point out in their excellent review [13], the methanation reaction offers special opportunities for study since it is the simplest reaction of the series. The mechanism of hydrogenation of CO has been examined particularly under conditions of the Fischer-Tropsch reaction in which hydrocarbons higher than methane are formed. Here, in contrast to methane synthesis, the mechanism of chain growth is of great importance. However, despite this consideration and the fact that somewhat different catalysts are used to optimize higher hydrocarbon formation, many considerations in Fischer-Tropsch synthesis are believed applicable to the mechanism of methane synthesis.

One of the earliest proposals for hydrocarbon synthesis was the carbide theory proposed by Fischer and Tropsch [14]. The carbide theory in its simplest form postulates that adsorbed carbon monoxide is reduced to surface carbide. The surface carbide was believed to be hydrogenated and the adsorbed methylene radicals polymerize and desorb as olefinic and paraffinic hydrocarbons. Craxford and Rideal [15, 16] gave a more detailed version of the carbide hypothesis, especially with respect to chain growth.

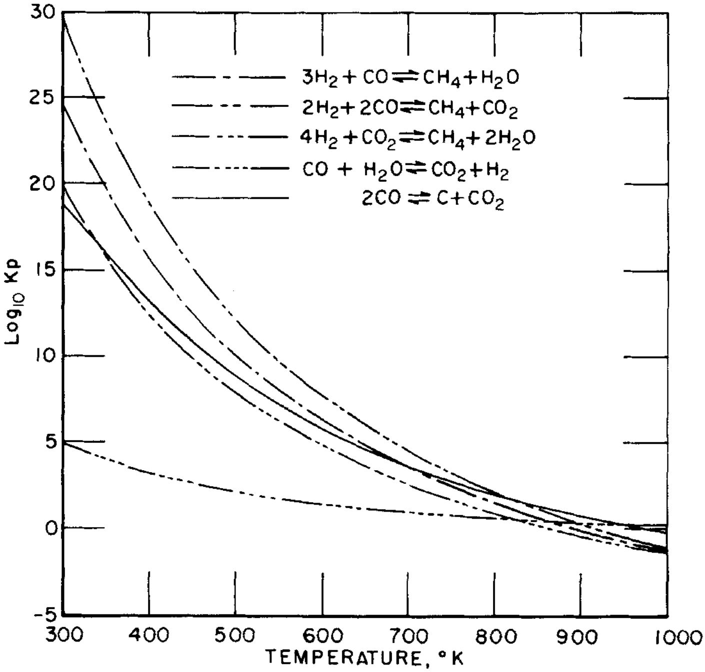


FIG. 5. Equilibrium constants as functions of temperature.

The carbide hypothesis was originally based on the observation that the chief Fischer-Tropsch catalysts—iron, cobalt, and nickel—react with carbon monoxide to form bulk carbides and that these carbides can react with hydrogen to form hydrocarbons. The carbide theory was subsequently found to be inadequate to explain hydrocarbon synthesis by metals of the iron group [17-19].

Other theories of methanation, in addition to the carbide theory, have included schemes in which oxygenated compounds such as methanol [20] or formaldehyde are intermediates. But attempts to detect formaldehyde or methanol in the synthesis of methane on a nickel catalyst were unsuccesful [21]. Moreover, when methanol is used as a starting material over a cobalt catalyst, it was shown that the yield of hydrocarbons is less than that obtained when a mixture of carbon monoxide and hydrogen is used.

An early suggestion put forward [22] was that a metal carbonyl is first formed which is then reduced with the formation of methane. A similar explanation for the synthesis of higher hydrocarbons has been proposed [23].

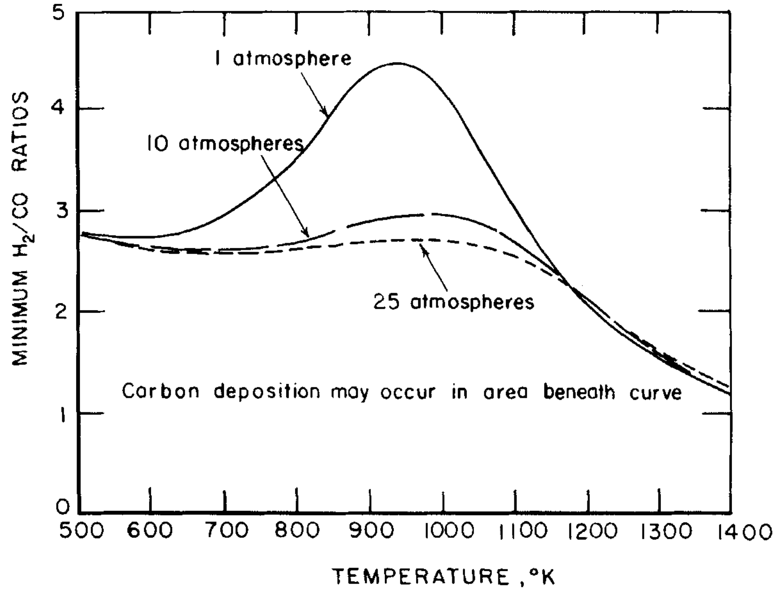


FIG. 6. Carbon deposition boundaries [2].

Several workers have concluded that synthesis based on CO and H_2 involves the production of an unstable intermediate complex, containing C, H, and O atoms, which is the precursor of both hydrocarbons and alcohols. Such a proposal [24] was made as early as the carbide hypothesis.

At present, two related mechanisms deserve special consideration. Both involve the concept of initial formation of a HCOH surface complex, but differ in subsequent steps. One mechanism involves methylene radical intermediates and emphasizes electronic charge or polarization factors.

Vlasenko and Yuzefovich [13] conclude that the most probable scheme for the mechanism of the reduction of carbon monoxide to methane on nickel, cobalt, and possibly iron catalysts is

$$[\ ] + e + H_2 \longrightarrow [H_2]^- \qquad (7)$$

$$[\ ] + CO \longrightarrow [CO]^+ + e \qquad (8)$$

$$[CO]^+ + [H_2]^- \longrightarrow [HCOH]^+ + e \text{ (slow stage)} + [\ ] \qquad (9)$$

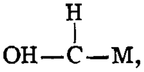
$$[HCOH]^+ + [H_2]^- \longrightarrow [CH_2] + H_2O + [\ ] \qquad (10)$$

$$[CH_2] + [H_2]^- \longrightarrow CH_4 + e + 2[\ ] \qquad (11)$$

The symbol [ ] denotes a vacant active center on the catalyst surface. The symbols in square brackets represent adsorbed species.

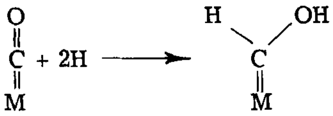
For the synthesis of higher hydrocarbons, the fifth stage of this scheme is not the reaction of methylene radicals with hydrogen, but their polymerization.

Orlov's suggestions [25] that methylene radicals are formed in the primary stages of the hydrogenation of carbon monoxide was believed verified experimentally by the existence of CH_2 radicals in the methylation of benzene to toluene [26]. Evidence was obtained that CH_2 species are formed from carbon monoxide and hydrogen [27]. On the basis of the results obtained, Eidus [17] concluded that on cobalt and nickel catalysts the primary stages of the process involve the successive hydrogenation of carbon monoxide, first to an unstable oxygen-containing group, and then to a methylene radical. Eidus [28] has provided a recent review of his views on the mechanism of the Fischer-Tropsch reaction.

Hamai [29] proposed a similar mechanism having an intermediate oxygenated complex,  $OH—\overset{\overset{\displaystyle H}{|}}{C}—M$, which is reduced to M—$CH_2$ groups. The M—CH_2 groups, in the adsorbed state, polymerize to long-chain hydrocarbons on the surface. Hamai concluded that, except at the highest temperatures, methane formation did not occur at the catalyst surface.

Storch, Golumbic, and Anderson [18, 30] have proposed a different mechanism for the Fischer-Tropsch reaction based on oxygenated intermediates as shown below. They assumed that: (1) hydrogen is adsorbed as atoms on the surface of the metal, (2) chemisorption of carbon monoxide occurs on metal atoms with bonding similar to that in metal carbonyls, and (3) adsorbed carbon monoxide is partly hydrogenated according to Eq. (12):

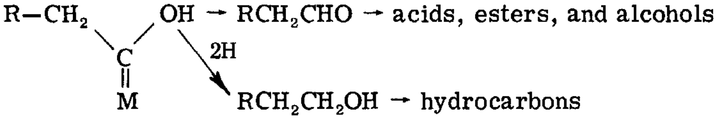
Initiation of chain:



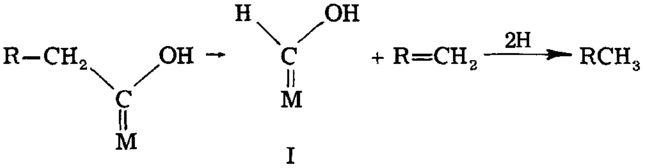
(12)

I

Termination of chain:

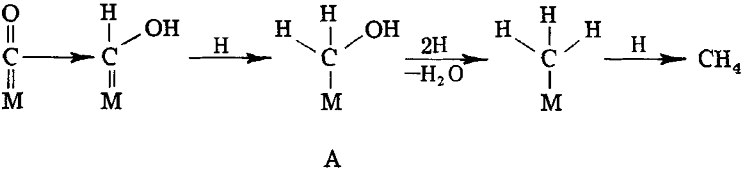


(13)



(14)

While the overall scheme proposed describes details of chain growth not applicable to methane synthesis, the initiation and termination steps are pertinent for the mechanism of the hydrogenation of carbon monoxide to methane. As shown in Reactions (13) and (14), termination products are aldehydes, alcohols, and olefins but not paraffins. The Complex I has been questioned [31] since IR spectra do not indicate a M=C bond but this does not fundamentally change the picture. For methane synthesis it is proposed that this reaction scheme may be modified to become:



(15)

In this scheme Intermediate A would form alcohol under certain circumstances and under other conditions would produce methane. The reversible dissociative sorption of methane on nickel (the reverse of the last step) was demonstrated many years ago [32]. Evidence for this mechanism and the nature of the complexes follows.

B. Evidence from Infrared Spectra

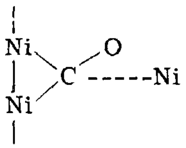
Infrared spectra of carbon monoxide and hydrogen chemisorbed on nickel, iron, and cobalt have provided important evidence as to the existence and nature of surface complexes of possible importance in catalytic methanation. Spectra of carbon monoxide on nickel and other metals were first described in 1954 [33]. Bands attributed to

CO bonded to a single nickel metal atom were found at 4.92 and 5.24 μ. The admission of H_2 to a sample with chemisorbed CO was reported to shift the major bands towards longer wavelengths by about 0.05 μ and broaden the bands. The spectra were interpreted to show that there are two types of bonds to single metal atoms when CO is sorbed on nickel and on palladium. Moreover, the broadness of these bands was taken as evidence that there are greater differences among the bonds contributing to each band than there are in the case of CO on Pt. The theory that carbon monoxide is chemisorbed as a molecule and bonded to the metal through the carbon appears to be confirmed by the IR spectra.

More detailed studies [34, 35] were made with emphasis on the effect of varying the surface coverage. It was found that the spectra of CO on Ni and on Pd showed a number of bands with increasing surface coverage, indicating a heterogeneity of surface. The 5.0-μ region was regarded as a dividing line between bands due to linear and bridged CO. The longer wavelength bridged CO is the most strongly held. The results were interpreted as a measure of the relative importance of surface heterogeneity, interaction between adjacent molecules, and changes in work function of the surface.

The IR spectra of CO chemisorbed on nickel were further studied with emphasis on the effect of nickel concentration [36]. An assignment of IR bands to surface species for CO chemisorbed on nickel samples at room temperature was made as shown in Table 2.

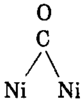
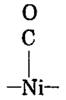
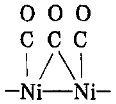
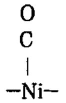
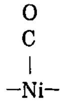
A new technique was reported [37] for the preparation of porous, high area, unsupported metal films which are suitable for IR absorption studies of chemisorbed CO. Reduction was accomplished by CO instead of H_2 so as to preclude the influence of sorbed H_2. A further structure was proposed from these studies:



The presence of adsorbed and dissolved hydrogen influences the properties of nickel toward the sorption of carbon monoxide. The dissolved hydrogen is believed to alter the electronic properties of the metal, and the view was expressed [38] that electrons are transferred to the nickel. Treatment of samples of CO chemisorbed on Ni with H_2 at room temperature shifts the band due to linear carbon monoxide to a lower frequency and increases the relative amount of bridged CO. Removal of H_2 from nickel at 350°C resulted in spectra, when CO was subsequently sorbed, with most of the CO appearing as

TABLE 2

Assignment of Infrared Bands to Surface Species for CO Chemisorbed on Supported Ni Samples at Room Temperature

Band	Frequency cm^{-1}	Species	Site	Strength of adsorption
A	1915		Crystalline Ni	Very strong
C	2035		Crystalline Ni	Very strong
B	1963		Crystalline Ni	Moderately strong
D	2057		Semi-crystalline Ni	Moderately strong
E	2082		Dispersed Ni	Weak

a linear structure. The significance was believed related to the observation that metals which chemisorb CO in the bridged form (Ni and Pd) are better catalysts for hydrogenation to methane than are metals (Cu and Pt) which chemisorb CO in linear form.

There has been some doubt expressed as to the existence of bridged bonds. Calculation [39] by the molecular orbital method showed that all available data on the IR spectra of chemisorbed CO can be explained by assuming only a linear form of bonding. Likewise, from considerations distinguishing between surface sites and surface atoms, the spectra of CO on various nickel catalysts can be described (with reference to the relative number of various types of nearest neighbor surface atoms) on the assumption that only linearly bonded CO is present [40].

The questions of linear and bridged bonds have also been discussed when carbon monoxide is adsorbed on iron [41, 42].

Blyholder and Neff reported [31] IR spectra of surface complexes when silica-supported iron samples were exposed to CO and H_2 at temperatures ranging up to 180°C. A number of workers have found that, in experiments from −80 to 97°C on various iron, nickel, and cobalt catalysts, preadsorption of a small amount of CO enhances the quantity of H_2 subsequently adsorbed, while a large CO preadsorption inhibits H_2 adsorption. The enhancement effect has led to the proposal that complexes such as $M{-}\overset{\overset{H_2}{|}}{C}OH$ are formed on the surface. Eischens [35] in an investigation of the effect of hydrogen on CO chemisorbed on silica-supported iron, found no IR bands in the 2 to 7.5-μ range which could be attributed to such complexes.

In agreement with Eischens, Blyholder and Neff [31] found no interactions between CO and H_2 to the extent of C—H or O—H band formation at or near room temperature. In fact, no interaction was found until the iron surface was hot enough to desorb chemisorbed CO rapidly.

However, IR spectra were obtained at 180°C which can be interpreted as giving evidence for the existence of oxygenated complexes on the surface. This arises from the fact that bands are observed indicating the presence of C—H and O—H bonds in species on the surface. Previously they found [43] that water or mixtures of water and hydrogen do not give O—H bands on silica-supported iron at 20 or 180°C. Therefore, they presumed the O—H groups to be attached to carbon atoms. More work is desirable to establish the nature of the surface complexes in this system.

In contrast to the situation with iron, surface complexes formed by the interaction of H_2 and CO on nickel at temperatures up to 180°C were not found [44] even though products of the reaction of H_2 and CO were readily detected. It was speculated that in order to build up a moderately long hydrocarbon chain it is necessary that the reacting species be firmly enough anchored to the surface that a number of chain-building steps can occur before desorption. It was suggested that the reaction species are much less firmly bonded to the nickel than to the iron catalyst, and this is why the former is better for methanation and the latter for Fischer-Tropsch synthesis.

One of the most important chemical features of chemisorbed CO is its lack of reactivity at room temperature. In fact, experiments showed no reaction of CO with hydrogen until temperatures high enough to desorb chemisorbed CO were reached.

C. Sorption Measurements

The study of adsorption of reactant components may give important information on the formation and composition of reactive surface complexes. In spite of the extensive literature devoted to the adsorption of hydrogen and carbon monoxide on metal-containing catalysts, comparatively few studies have been made under conditions close to those of catalysis.

The effect of a chemisorbed layer of one gas on the chemisorption of another was first studied by Griffin [45], who found that the adsorption of hydrogen on copper and nickel catalysts was increased by the presence of previously adsorbed carbon monoxide.

Studies have been carried out on the adsorption of H_2 and CO in the range 25 to 97°C [46-48] on cobalt-containing Fischer-Tropsch catalysts. For a catalyst containing Co-Cu-ThO_2-CeO_2-Cr_2O_3-kieselguhr, the chemisorption of hydrogen was found to be independent of temperature [47]. The sorption of hydrogen from H_2 + CO mixtures at 50°C was lower than from pure H_2 but increased with temperature so that at 97°C the volume of H_2 sorbed equaled or exceeded the sorption from pure H_2. At constant pressure the chemisorption of H_2 was greater from a gas mixture containing $1H_2$ to 1CO than from a mixture containing $2H_2$:1CO. The chemisorption of CO decreased with increasing temperature and passed through a minimum at about 120°C. From a H_2 + CO mixture the volume of CO sorbed was greater than from pure CO. In the opinion of the authors [47], this may indicate the formation on the catalyst surface of chemisorbed complexes which are possible intermediates in the Fischer-Tropsch synthesis. Since the ratio of H_2/CO adsorbed reached 1:1 at 97°C, it was thought that this may indicate the formation of a complex with the composition HCOH. In other work, however, the value of this ratio at 97°C was 1:2 and it was noted that this ratio corresponds to an enolic surface complex-COH. Mutual intensification was also observed with consecutive adsorption of H_2 and CO, which also indicates strong chemical interaction in the adsorption layer.

In order to establish better the composition of the active complex, adsorption and desorption of carbon monoxide and hydrogen were studied on an iron catalyst at 50°C [49]. As with cobalt catalysts, the adsorption measurements could not prove the formation of reactive complexes since part of the gas was irreversibly adsorbed and this fraction did not participate in the formation of catalytic intermediates. To eliminate the contribution from the irreversible adsorption, the authors used a method involving desorption with decrease in pressure. It was established that, irrespective of the H_2:CO ratio in the original mixture, a gas mixture with an almost constant ratio of 1:1 is desorbed from the catalyst surface after 38 hr. This indicates the existence of a weakly-bound chemisorbed complex which decomposes on desorption.

From adsorption measurements it is not possible to establish the structure of chemisorbed complexes, or indeed to be certain of their composition, nor of their reactivities.

It should be noted that while extensive chemisorption studies on complex Fischer-Tropsch compositions have been reported, information on simple metals active in methanation is meager [50].

D. Kinetic Studies

The rate of methane formation must depend on the concentration of an appropriate complex of the sorbed CO and H_2. Using the static method at about 300°C over nickel catalysts, the rate of formation of methane was found to be approximately proportional to the pressure of hydrogen but retarded by carbon monoxide [51, 52]. The heat of activation was found to be 27 kcal/mole. Using a flow method, an extensive study [53] was made of the kinetics of methane formation at atmospheric pressure over an industrial nickel-kieselguhr catalyst in the range 300-350°C at H_2/CO ratios of 1.2 to 4. The rate of methane formation is expressed by the equation:

$$r = \frac{p_{CO} p_{H_2}{}^3}{(A + Bp_{CO} + Dp_{CO_2} + Ep_{CH_4})^4}$$

where A, B, D, and E are constants.

Additional kinetic expressions for nickel catalysts which reflect the inhibiting influence of CO are discussed in connection with catalyst compositions. One exception to this has been noted [54]. The retarding influence of carbon monoxide at high concentrations is apparently due to the fact that the CO covers the catalyst surface to a considerable extent, leading to a corresponding decrease in the degree of covering with hydrogen. Similarly, the empirical rate of methane formation over a ruthenium catalyst was found to be

$$r = kp_{H_2}{}^{1.33}\, p_{CO}{}^{-0.13}$$

indicating that here also high CO pressure inhibits catalyst activity.

This situation can be changed by the use of a low concentration of CO in a large excess of hydrogen. The kinetic relationship obtained in this way by a flow-circulation method with a nickel-chromium catalyst at 135-175°C and a concentration of CO in H_2 equal to 0.3 vol% has the form [55, 56]

$$w = kp_{CO}{}^{\circ}\, p_{H_2}{}^{\circ}$$

The zero-order of the reaction with respect to both components was attributed to the nonuniformity of the nickel surface with respect to the adsorption of CO and H_2 under the given conditions. Thermogravimetric catalyst measurements during reaction established that at

160°C the degree of coverage of the nickel surface by CO amounted to about 1/3 and 2/3 of the surface being covered with hydrogen. This was taken as an explanation that the heat of activiation observed, 16.2 kcal/mole, was lower than for experiments in which the degree of coverage of the surface by CO was higher.

A recent critical review concluded that the rate expression $r = kp_{CO}p_{H_2}{}^{0.5}$ correlates most of the experimental data except when excess H_2 and/or CH_4 are present [57]. To cover the entire range of gas compositions, this equation was modified to

$$r = \frac{kp_{CO}p_{H_2}{}^{0.5}}{1 + K_2p_{H_2} + K_3p_{CH_4}}$$

Note that this expression does not include a term in the denominator for the inhibiting effect of CO.

The extensive kinetic studies of hydrogenation of CO to higher hydrocarbons have been reviewed [3]. It has been established that carbon dioxide is a secondary product and results from the water-gas shift reaction. For formation of Fischer-Tropsch products, activation energies of about 20 kcal/mole were measured. Empirical rate equations have been established for various catalysts; for example, that with an iron catalyst and $1H_2 + 1CO$ being:

$$-\log(1 - x) = \frac{A}{S} e^{-E/RT}$$

where S represents space rate and A is a constant.

E. Mechanism Evidence from Related Reactions

Other catalytic reactions involving CO and H_2 may be examined for the light they shed on the mechanism of methanation. The synthesis of methanol offers an interesting comparison. Natta [58] has reviewed the catalytic chemistry of methanol synthesis and concluded that the process which determines the rate of reaction is that of reaction among the adsorbed molecules. Kinetic measurements were used principally to distinguish between a bimolecular and trimolecular scheme with the conclusion that the rate-controlling process is the trimolecular reaction

$$CO^* + 2H_2^* \longrightarrow CH_3OH^*$$

Methanol synthesis catalysts are based on zinc oxide. These catalysts behave differently from methanation catalysts both from catalytic and sorption viewpoints. It is not possible at present to make a significant comparison of the structural nature of the complexes and key catalyst properties which distinguish methanation and methanol synthesis catalysis. This should be an objective of future research.

In methanol synthesis, care is taken to exclude iron group metals (which cause unwanted methane formation) which, according to Natta [58], should not be classified as "poisons" but rather as "antiselectivity agents."

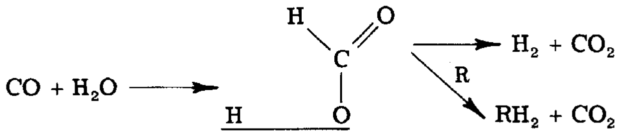
The formation of methane from carbohydrates by biological catalysts occurs with a very high degree of selectivity. Although this has great practical significance, the mechanism requires further elucidation [59].

In the OXO reaction, CO and H_2 add to olefins under the influence of a homogeneous catalyst, cobalt carbonyl. The mechanism has been established [60] and involves the insertion of CO at the end of a carbon chain attached to cobalt. Utilizing its coordinatively unsaturated properties, the catalyst forms complexes with CO, H_2, and olefin. The OXO reaction emphasizes addition of CO and H_2 to the olefin, and although it represents intersecting related chemistry, it is not closely related to methanation.

The water-gas shift reaction also involves CO and H_2 but in a reactant-product relationship:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

A recent significant result [61] is the detection by IR spectroscopy of formate ion on the catalyst surface. It will be recalled that sodium hydroxide adds CO to form sodium formate. In base catalysis the formate ion may be an important intermediate from which H_2 can be evolved or hydrogen transferred to a suitable acceptor molecule [62].



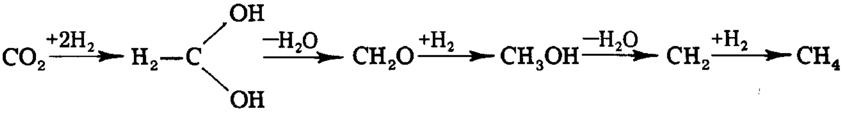
V. MECHANISM OF CO_2 METHANATION

The hydrogenation of CO_2 to methane has not been investigated extensively. Catalyst which bring about methanation of CO_2 are in general those active in methanation of CO and are described in a later section of this paper. It has been noted that CO_2 is not hydrogenated so long as a significant amount of CO is present. It should also be remarked that unlike CO, CO_2 is hydrogenated to methane with a high degree of selectivity.

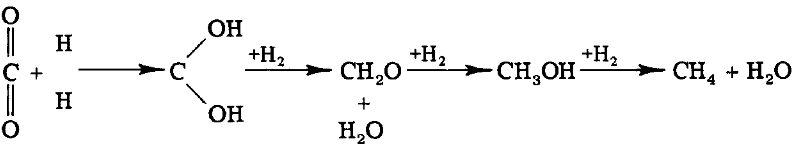
Two proposed schemes for the mechanism of synthesis of methane from carbon dioxide and hydrogen have been discussed in the literature. One of these was proposed by Bahr [63], who considers that the reduction of CO_2 to CH_4 occurs with the intermediate formation of CO. This view is supported in studies of ruthenium [64] and iron group catalysts [65].

However, other evidence strongly indicates that the mechanism does not proceed through intermediate CO formation. Thus it has been shown [66, 67] that in the presence of nickel and cobalt catalysts, CO_2 is converted only into CH_4, and the formation of small quantities of higher hydrocarbons was detected only in some instances when iron-cobalt and copper-cobalt [4] catalysts were used. It has also been shown [68] that CO_2 is not hydrogenated in the presence of CO and does not influence the transformation of the latter. A further fact is that hydrogenation of CO_2 occurs at a lower temperature than for CO.

The idea that CO_2 reacts by a mechanism not involving intermediate CO formation was proposed by Medsford [69].



This mechanism was further developed by Pichler [70] who proposed the following sequence:

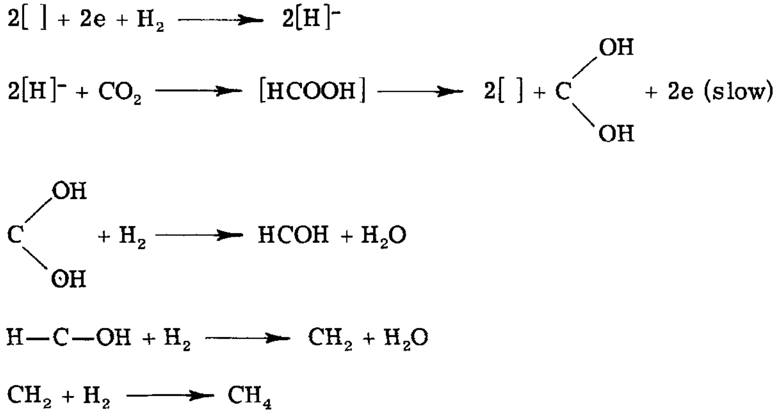


The kinetics of hydrogenation of CO_2 have been reviewed by Vlasenko and Yuzefovich [13] in detail. They conclude that kinetic data cannot confirm a particular mechanism directly, and that evidence by independent methods is required.

They found [71] from weighing experiments that there is no significant adsorption of CO_2 and the products of its transformation. Further, when a mixture of H_2 and CO_2 was introduced to the untreated catalyst, the work function remained unchanged relative to that in an atmosphere of hydrogen [72]. This was taken to indicate that adsorption of CO_2 and the formation of complexes influencing the electronic structure of the catalyst does not take place on the surface of the catalyst containing dissolved hydrogen. They conclude that recent experimental results refute the suggestion that the start of formation of CH_4 from CO_2 on nickel catalysts is preceded by the adsorption of both components of the reaction, and indicate that hydrogen adsorbed on the catalyst surface reacts with molecules of carbon dioxide in the gas phase.

From such considerations, Vlasenko and Yuzefovich conclude [13] that the most probable scheme for the formation of CH_4 from CO_2 and H_2 appears to be one in which the formation of complexes of a type corresponding to the enol form of formaldehyde takes place initially, and in which the subsequent transformations are analogous to the stages in the hydrogenation of CO, but with the significant difference that in the reduction of CO_2 these changes take place not on the catalyst surface, but in the volume of the gas.

The mechanism proposed [13] is:



$$2[\;] + 2e + H_2 \longrightarrow 2[H]^-$$

$$2[H]^- + CO_2 \longrightarrow [HCOOH] \longrightarrow 2[\;] + C(OH)_2 + 2e \text{ (slow)}$$

$$C(OH)_2 + H_2 \longrightarrow HCOH + H_2O$$

$$H{-}C{-}OH + H_2 \longrightarrow CH_2 + H_2O$$

$$CH_2 + H_2 \longrightarrow CH_4$$

According to this scheme, the process is initiated by the activation of only the hydrogen on the catalyst surface, after which the reaction takes place in the gas volume.

This mechanism is certainly controversial. It is possible, of course, that H_2 and CO_2 react on the catalyst surface with a very low concentration of intermediate complexes; that is, with a very low lifetime for these compounds in the adsorbed state. It can only be concluded that the mechanism of methanation of CO_2 is uncertain and is a fruitful field for investigation.

VI. CATALYSTS

A. Overview

After their classic report of the formation of methane by the hydrogenation of both carbon monoxide and carbon dioxide over nickel [1], Sabatier and Senderens extended this study to other metals. They soon showed that cobalt also promoted the reaction [73] but that copper, iron, platinum, and palladium did not form active catalysts [74]. In fact, for the next 20 years most successful methanation investigations employed nickel catalysts, such as the work of Jochum [75], who examined the effect of varying hydrogen to carbon monoxide ratios and of Medsford [69] who discovered the beneficial effect that dehydrating agents, like alumina, used as catalyst supports, had on methanation activity.

Early in the 1920s Fischer, Tropsch, and Dilthey [76] compared the methanation properties of various metals at temperatures up to 800°C. The decreasing order of methanation activity was Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Mo, Pd, Ag. Thus by 1925 all of the metals now considered active for methanation of carbon oxides had been identified. In terms of metals important for methanation, the list could now be shortened to Ru, Ni, Co, Fe, and Mo.

Further progress over the past 50 years has had to do with preferred promoters, supports, and preparation conditions to obtain high selectivity and to maintain catalytic activity. Also important, where methane-enriched fuels were desired, were advances in operating conditions, reactor design, and removal of catalyst poisons, especially sulfur compounds, from the feed stream. The literature recounts advances from many countries. The British Gas Research Board deserves special mention because of their pioneering work to reduce the carbon monoxide content of hydrogen-enriched blue water gas while upgrading its fuel value [77, 78]. Early United States contributions of note include Sabastian's work with molybdenum sulfide [79], the only methanation catalyst unaffected by sulfur impurities; reaction kinetic studies at the University of Michigan by White and Akers [53] followed by other students of White; and, since 1951, the U.S. Bureau of Mines investigations seeking useful methanation catalyst and reactor systems.

The history of these developments is given in more detail in Greyson's chapter on methanation [2]. A description of pertinent literature since the mid-50s follows in which the catalysts are grouped according to their most active constituent.

B. Ruthenium

As mentioned before, ruthenium was early recognized as a very active methanation catalyst; however, the high cost of this metal, no doubt, mitigated against its wide use. In the interim, the adoption of platinum for catalytic reforming of naphthas, on the other hand, has proven that initial high cost need not prevent widespread usage of precious metals if the material can compete favorably with cheaper catalysts. Long catalytic life and high activity and selectivity for the precious metal are essential to meet these requirements.

In recent years the price of ruthenium has been about $50/oz troy for large quantities, 5000 troy oz or more. Consequently, 1 lb of 0.5 wt% ruthenium catalyst contains about $3.65 worth of the metal. A methanation reactor operating at 10,000 GHSV would require $750 to $1000 worth of ruthenium for each million cubic feet of daily gas capacity. The fact that 20 to 30 United States units for gas purification by methanation are now using ruthenium catalyst attests to the potential for this efficient and durable metal. At the present time, however, most hydrogen clean-up methanators in United States plants use nickel catalyst.

Pichler's review of Fischer-Tropsch synthesis summarizes his experience with ruthenium catalysts over a wide range of synthesis pressures [4]. Atmospheric pressure reactions at 300°C gave only methane. At higher pressures the reaction initiated at lower temperature but higher molecular weight products formed with increasing pressure as shown in Table 3. This work had originally been intended as a possible route to carbohydrates but no oxygenated products were found.

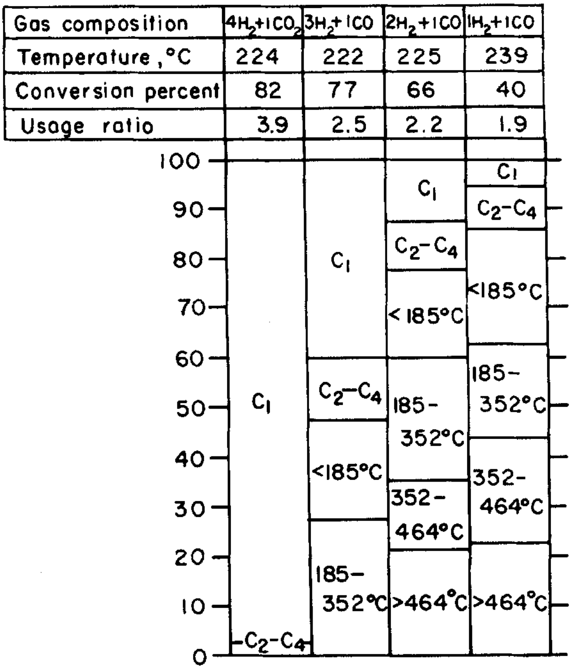
TABLE 3

Synthesis of Hydrocarbons on Ruthenium Catalyst at 180°C [4]

Pressure, atm	CO conversion, %	Hydrocarbon product, wt%		
		Solid	Liquid	Gas
1	0	-	-	-
50	48	46	33	21
100	68	53	31	16
1000	92	59	26	15

Catalytic activity remained unchanged over a period of six months for an experiment conducted at 100 atm and 195°C. However, traces of sulfur compounds rapidly deactivated the ruthenium catalyst.

The U.S. Bureau of Mines, in its search for catalysts capable of producing liquid and gaseous fuels, examined ruthenium catalyst using hydrogen-carbon monoxide and hydrogen-carbon dioxide feedstocks [80]. A catalyst containing 0.5 wt% ruthenium on alumina, obtained from Engelhard Industries [81], was tested over the range of 1 to 21.4 atm at about 225°C using various H_2/CO and H_2/CO_2 ratios. The H_2/CO ratio profoundly influenced the product distribution (Fig. 7); low ratios invariably gave large amounts of high molecular weight products while relatively more methane formed using a higher H_2/CO ratio. Also, as Pichler had found, lower pressures favored methane production. Using CO_2 at a ratio of 4 to 1 H_2/CO_2, a much more selective conversion to methane was obtained than with CO, even at 21.4 atm.



Gas composition	$4H_2+1CO_2$	$3H_2+1CO$	$2H_2+1CO$	$1H_2+1CO$
Temperature, °C	224	222	225	239
Conversion percent	82	77	66	40
Usage ratio	3.9	2.5	2.2	1.9

FIG. 7. Operating conditions and selectivity with 0.5% ruthenium on alumina. At 21.4 atm, 300 hourly space velocity.

Kinetic data from experiments using the 3 to 1 H_2/CO synthesis gas at a pressure of 21.4 atm are given in Fig. 8. Conversion of the synthesis gas, of course, increased with reciprocal space velocity. However, space-time yield, which shows a similar increase at this

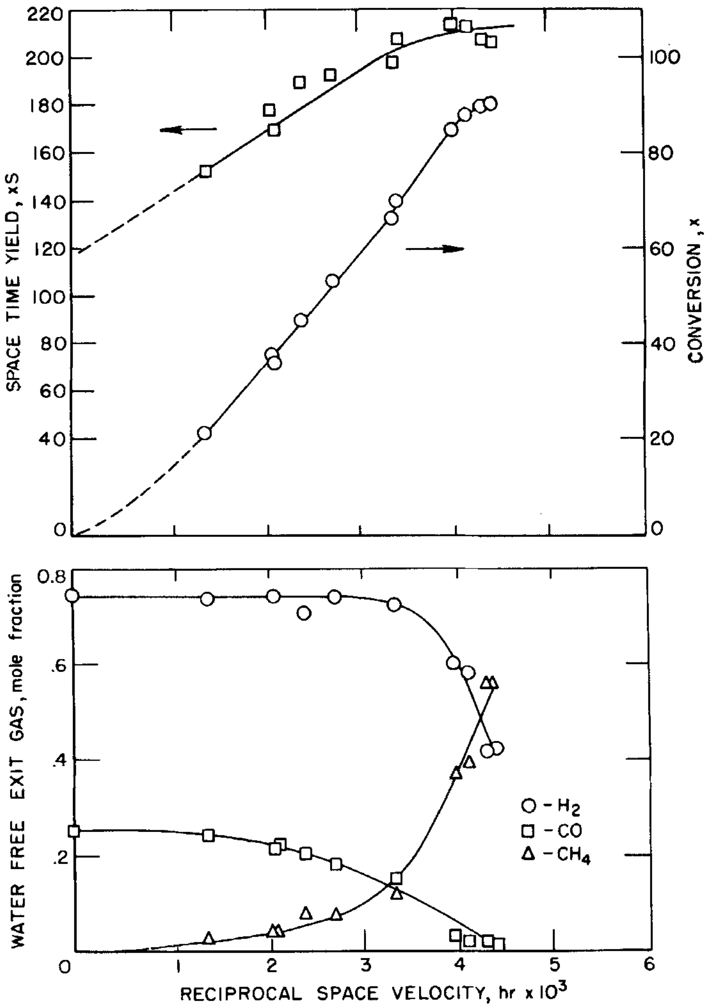


FIG. 8. Rate data for $3H_2$ + CO over a ruthenium catalyst at 222°C and 21.4 atm.

pressure, leveled off at decreasing pressures and showed no change with space velocity at 7.8 atm.

A log-log plot of gaseous hourly space velocity vs absolute pressure gave a family of parallel, constant-conversion lines between 10 and 60% (H_2 + CO) conversion, Fig. 9. The slope of these lines, $d \ln r / d \ln P$, equaled 1.2. A rate equation of the type $r = k p_{H_2}^{1.2+n} p_{CO}^{-n}$ was then fitted to the data; a satisfactory fit was obtained when $n = 0.13$.

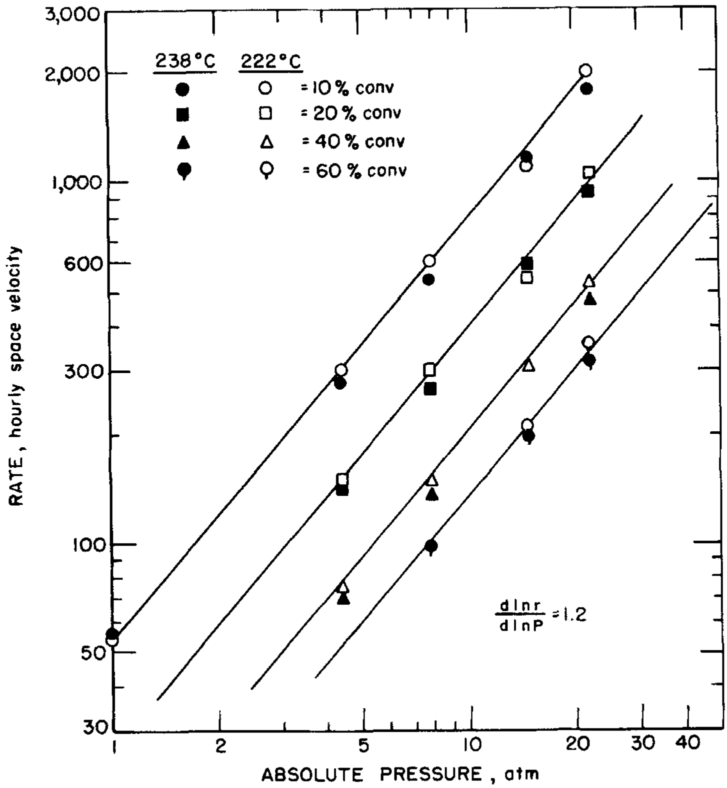


FIG. 9. Pressure dependence for $3H_2 + CO$ over a ruthenium catalyst at 222 and 238°C.

Thus the empirical methanation rate for 0.5% ruthenium on alumina catalyst at these conditions is $r = kp_{H_2}^{1.33} p_{CO}^{-0.13}$. The negative power term for CO partial pressure is in agreement with the experimental findings [80] that high CO pressures inhibit catalyst activity. For example, the use of 1 to 1 synthesis gas always caused a temporary activity loss, but activity was soon regained upon return to higher H_2/CO ratios.

In a study of the interaction of H_2 and CO on various Group VIII metals, McKee has shown the unique behavior of ruthenium in the adsorption of these two gases [50]. Carbon monoxide was much more strongly chemisorbed on platinum, rhodium, and iridium than on ruthenium, and the adsorption of hydrogen on ruthenium was enhanced by the presence of CO.

He also found that, on ruthenium, at temperatures above 100°C methane was produced at a total pressure of less than 100 Torrs whereas only trace amounts were found with rhodium or iridium and none with platinum. Three alloys of ruthenium-palladium (14.3, 21, and 62% Ru) showed that the initial rate of methane formation decreased regularly with decreasing ruthenium content. Based on Arrhenius plots for methanation, using either H_2 or D_2, the apparent activation energy on ruthenium is 9 ± 1 kcal/mole. McKee speculated that the high methanation activity of this metal was probably due to a lower affinity for CO than with other noble metals.

The ruthenium-catalyzed methanation of low concentrations of CO in H_2 has been studied at the Institute of Gas Technology in Chicago [82]. A sample of Engelhard Industries, Inc., 0.5% ruthenium on alumina catalyst in an atmospheric pressure, fixed-bed, flow reactor was tested using 505, 1090, and 3450 ppm CO in H_2. Over the range of temperature employed, 150 to 275°C, the reaction followed pseudo-first-order kinetics for CO conversion (see Fig. 10). An Arrhenius

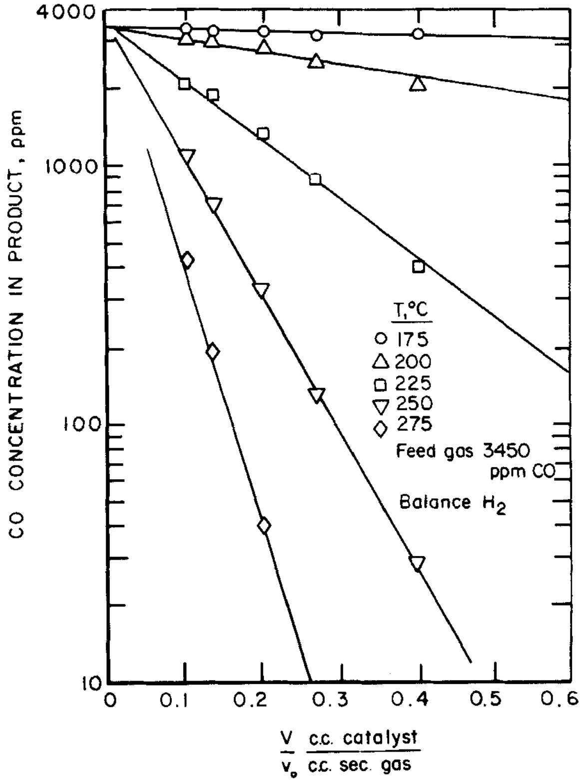


FIG. 10. CO concentration as a function of space time with 3450 ppm gas feed.

plot, shown in Fig. 11, is a straight line for the lower temperatures used but bows at higher temperatures. This is interpreted as a kinetically controlled reaction below 200°C with the effects of diffusion becoming apparent at higher temperatures. The apparent activation energy E of the reaction on this catalyst was calculated to be 37.2 kcal/mole, and the frequency factor k_0 was calculated to be 1.25×10^{17} cc gas/cc catalyst/sec for the equation $k + k_0e^{-E/RT}$.

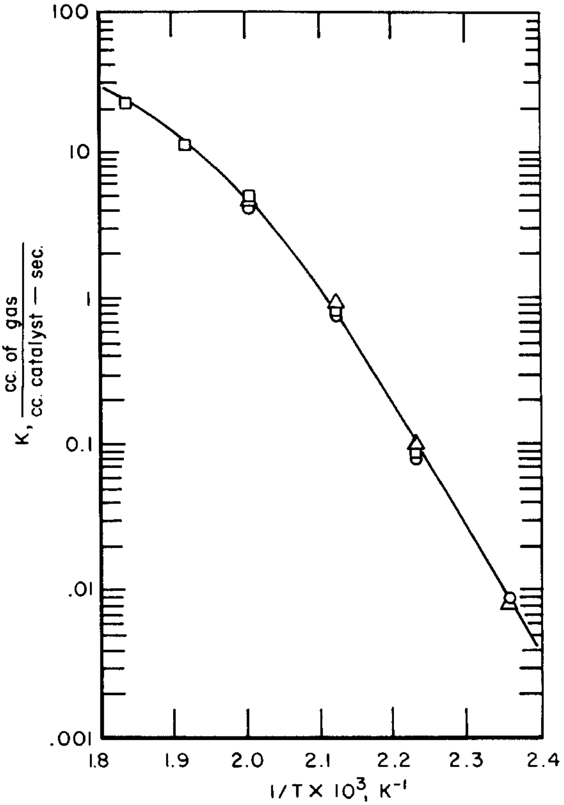


FIG. 11. Arrhenius plot for methanation of CO.

In another IGT paper the selective methanation of CO in the presence of CO_2 was investigated using several catalysts [83]. The catalysts included three commercially available nickel catalysts, one ruthenium-alumina and two leached, IGT Raney nickel catalysts whose descriptions are given in Table 4. A typical gas mixture, containing 0.3% CO, 80% H_2, and 20% CO_2, was passed over each test catalyst at atmospheric pressure and space velocities of 9000 to 36,000 GHSV

TABLE 4

Composition of Catalysts [83]

Catalyst	Identification	Composition
A	Ruthenium	0.5% Ru on α-Al_2O_3
B	IGT Raney nickel (NaOH leached twice)	35% Ni, 5% Al, and 60% $Al_2O_3.3H_2O$
C	IGT Raney nickel (NaOH leached)	30% Ni, 18% Al, 52% $Al_2O_3.3H_2O$
D	Harshaw nickel	58% Ni on kieselguhr
E	CCI nickel	47% NiO on Al_2O_3
F	Girdler G-65	32% Ni on Al_2O_3

and at temperatures of from 125 to 300°C. Each catalyst showed a maximum conversion between 200 and 250°C; with further increase of temperature a reverse shift reaction occurred such that CO was produced from CO_2 faster than it was consumed to form methane. This is shown for the two most active ruthenium and nickel catalysts, A and B, in Figs. 12 and 13. With nickel catalysts B, E, and F, the product CO level at 300°C exceeded the amount originally present in the feed. Based on this study the catalysts could be ranked in descend-

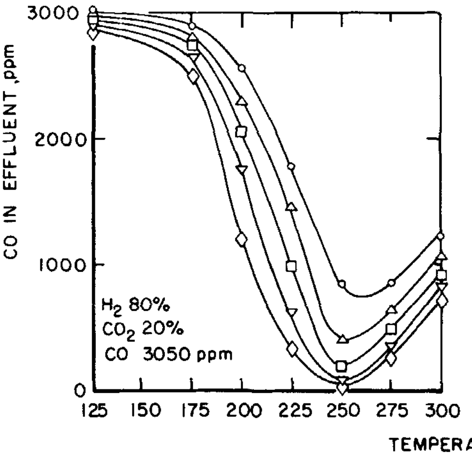


FIG. 12. Selective methanation of CO using ruthenium catalyst A.

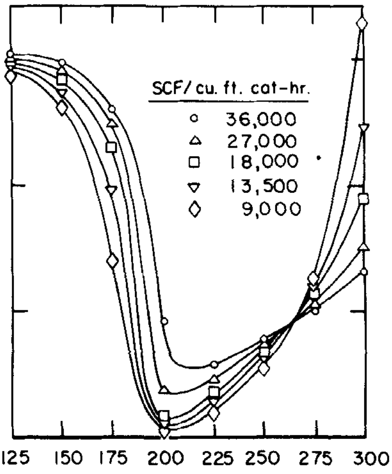


FIG. 13. Selective methanation of CO using IGT Raney nickel catalyst B.

ing order of activity as B, C, A, D, E, and F. However, considering the very small amount of ruthenium present in A, if they were ranked according to the efficiency of the active constituent, A would definitely lead all others.

The IGT work shows that selective methanation of CO in the presence of CO_2 is quite possible at atmospheric pressure but that very low space velocities and moderate temperatures, probably below 225°C for ruthenium, would be required to achieve low ppm values of CO.

Pichler [4] revealed that CO_2 in the absence of CO is rapidly methanated even at 100°C. The Bureau of Mines work [80] indicated that the methanation of CO_2 (in the absence of CO) is faster than that of CO alone. It is impossible to completely eliminate CO without some conversion of CO_2 also.

C. Nickel

As a methanation catalyst, nickel is preeminent; the metal is relatively cheap, it is very active when present in a form having high surface area, and it is the most selective to methane of all materials. Its main drawback is that it is easily poisoned by sulfur compounds, a fault common to all of the more active methanation catalysts. It is also true that nickel can react with carbon monoxide to form a carbonyl, $Ni(CO)_4$, a carbide, Ni_3C, or even free carbon, but these are easily avoided through the proper selection of reaction temperature and use of an excess of H_2 over the stoichometric H_2/CO 3/1 ratio.

Although less active than ruthenium, nickel has been by far the preferred active constituent in commercial catalysts for methanation of traces of carbon monoxide in hydrogen streams. The commercial catalysts consist of rather high concentrations, 25-77 wt%, of nickel dispersed on a high surface area, refractory support, such as alumina or kieselguhr. Chromia-supported nickel has been used primarily by Czechoslovakian and Russian investigators.

Over the past 15 or 20 years many nickel catalyst compositions have been reported to have good methanation activity. Table 5 lists the most noteworthy of these. Besides the supported nickel catalysts, alloys, particularly Raney nickel, and a few nickel compounds were active.

The Russians Gudkov and Chernyshev reported using partially leached nickel-aluminum alloy in a fluidized bed [84, 85]. This catalyst had exceptional activity, and reaction rates of up to 60,000 liters of synthesis gas per liter of catalyst were found possible. This form of catalyst was also used by the U.S. Bureau of Mines with a fresh synthesis gas [86] and to complete the methanation of a synthesis gas which had first been partially (85 to 90%) methanated over an iron

TABLE 5

Composition of Nickel Methanation Catalysts

Type	Composition	Proportions	Comments	Refs.
Alloy	Ni-Al		Fluid bed, fused	84
	Ni-Al (Raney)	42:58	Caustic leached	85, 86, 89
	Ni-Al-Al_2O_3	30-35% Ni 5-18% Al 52-60% Al_2O_3. $3H_2O$	Leached Raney Ni	83
	Ni-Cu	<4% Cu	>4% Cu reduces CH_4 yield	90
	Ni-Mn-Al	10:2:1		91, 92
Ni compound	2NiO.Al_2O_3.4.$7H_2O$		Dehydrated in vacuo at 500°C, then H_2 treated at 500°C; 203 m^2/g	54
	Ni_2B		Pptd on silica gel from $NiCl_2$ using $NaBH_4$	93
Alumina-supported	Ni-Al_2O_3 and	23% Ni		94, 95
	Ni-η-Al_2O_3	12% Ni	Reduced at 420°C	96
	Ni-Ca aluminate on β-Al_2O_3 hydrate	27:25:48	High activity, CCI catalyst ($K_w \sim 30{,}000$)	97
	Ni-K_2O-η-Al_2O_3	11.5:2.5:86	Reduced at 450°C	96
	NiO-MgO-Al_2O_3	20:55:25	Reduced > 600°C	96
	Ni-Mn on Al_2O_3 and diatomaceous earth	100:20:350:100	Nitrates coprecipitated	98
Spinel-supported	NiO-$MgAl_2O_4$	9-10% Ni	Reduced at 420°C	96
	NiO-K_2O-$MgAl_2O_4$	9-10% Ni and 2-3% K_2O	Reduced at 570°C	96

TABLE 5 (continued)

Type	Composition	Proportions	Comments	Refs.
Chromia-supported	$NiO\text{-}Cr_2O_3$	4.2:1 M	Reduced at 300°C	99
	$Ni\text{-}Cr_2O_3$		Use Fe catalyst in first stage	100, 101
	$Ni\text{-}Cr_2O_3$	50:50	Reduced at 350°C	96
	$NiO\text{-}Cr_2O_3$	1:0, 1.8:1, and 9:1	Optimum reduction temperatures differ	102, 103
	$Ni\text{-}Cr_2O_3$	23% Ni	Less active than kieselguhr based catalyst	95
Kieselguhr-supported	Ni-Kslgr	59% Ni	CH_4 and CO from CO_2	104
	Ni-Kslgr		Comparison with Raney nickel	89
	Ni-Kslgr	58% Ni	Harshaw catalyst used	105
	Ni-Kslgr	23% Ni	Compares favorably with other compositions	95
	$Ni\text{-}C4_2O_3$-Kslgr	29.2:4.1:66.7		106
	Ni-MgO-Kslgr		Organic S compounds removed first using sulfurized Ni	107
	Ni-MgO-Kslgr	60:5:35	Methanates at 165-205°C	108
	Ni-MgO-Kslgr	60:10:30	Methanates > 15% CO_2 at 180-250°C in two stages in 98-99% yield	109

catalyst [87]. The object of the Bureau's work was to demonstrate that a high Btu gas product could be produced from coal by gasification and methanation. The gas product after the first stage of methanation had a heating value of about 850 Btu/CF and after the second stage of methanation a heating value of 980+ Btu/CF. In a subsequent article the use of a tube wall reactor which had been sprayed with the Raney alloy and then leached was shown to be very effective for temperature control [88].

Dirksen and Linden at the Institute of Gas Technology also found that partially leached Raney nickel was much more active than nickel on kieselguhr but showed a tendency toward carbon deposition, especially with feed gas having low H_2/CO ratio [89]. Laboratory tests with 3:1 synthesis gas conducted at 75 to 150 psig, 315+°C and 10,000 GHSV indicated a useful life of 20,000 to 40,000 CF methane/lb of Raney alloy used. In later work from IGT, Rehmat and Randhava showed that specially leached Raney nickel was decidedly more effective than three commercial nickel catalysts for methanating low levels of carbon monoxide [83].

Alloys of nickel with different proportions of copper were found to vary in their selectivity when methanating carbon dioxide [90]. Good selectivity to methane was achieved only with pure nickel, and selectivity to CO was very pronounced with less than 4% copper in the alloy; with more than 50% copper, CO was obtained but no methane. The conversion of CO_2 remained virtually unchanged for alloys ranging from 4 to 100% copper as shown in Fig. 14.

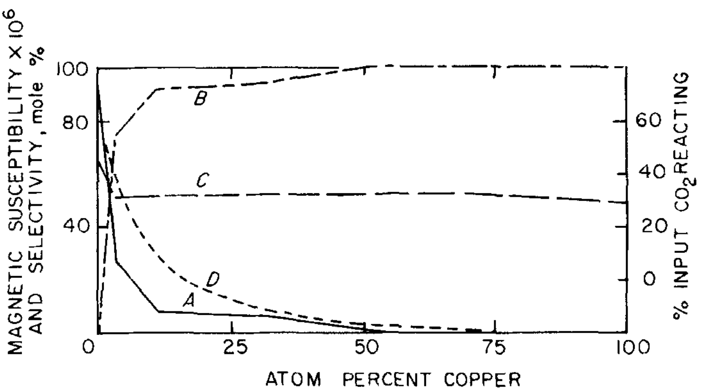


FIG. 14. Hydrogenation of CO_2 over nickel-copper catalysts at 420°C. Curve A: Selectivity to CH_4. Curve B: Selectivity to CO. Curve C: Percent of input CO_2 which reacted. Curve D: Mass magnetic susceptibility per gram of catalyst.

The authors, Cratty and Russell, were interested in the electronic structure of these catalysts, particularly holes or unpaired electron spins in nickel's 3d-band. Magnetic measurements were made to learn more about the 3d-band electrons in the alloys since these would be involved in any chemisorption on nickel. A linear relationship between ferromagnetic Curie temperature and the atom percent of copper present was established. Based on specific magnetization and magnetic susceptibility measurements, the number of spins per nickel atom may be estimated. In this case, magnetic susceptibility at reaction temperature proved to be a better measure of pertinent electronic factors. In the region of 0 to 50+% alloyed copper, a decreasing number of holes in the catalyst d-band caused a corresponding decrease in the chemisorption of hydrogen and the production of methane. The relatively constant conversion of CO_2 over most of the alloy composition range, however, suggests these electronic factors had little influence on the reverse shift reaction to produce CO.

Bousquet and Teichner [54] prepared a nickel hydroaluminate $2NiO.\,Al_2O_3.4.7H_2O$, which upon dehydration of 500°C in vacuum followed by hydrogen reduction at the same temperature produced an active nickel-alumina composition. This material, which had a BET surface area of 203 m^2/g, and a nickel grain size averaging 57 Å, was used in low pressure (most at < 60 Torrs) kinetic studies at 270 to 320°C. Under these conditions, the initial rate, $r_1 = kp_{H_2}{}^{1.4}p_{CO}{}^{-0.9}$, was found to change with time and in the presence of methane to $r = k''p_{H_2}{}^{0.5}p_{CO}{}^{1.5}p_{CH_4}{}^{-0.5}$, showing some autoinhibitory effect of methane. The apparent activation energy was found to be 20 kcal/mole at the initial reaction time.

Variations in the preparation of nickel-alumina catalysts can greatly affect the activity and stability of these contacts. Vahala [95] reports that catalyst prepared by impregnation of alumina with nickel nitrate had low activity and stability compared to a coprecipitated catalyst from nickel nitrate and sodium aluminate. Catalyst and Chemicals, Inc., in a German patent [97], blend a powder mixture of nickel oxide, calcium aluminate, and alumina hydrate, roll and water spray this to form pellets, and then calcine these to give a highly active methanation catalyst. Catalytic activity is sensitive to the amount of nickel oxide used, the catalyst surface area, and the macroporosity of the composition.

Schoubye at Haldor Topsoe Research Laboratories has compared six nickel catalysts in a fluid bed differential reactor and developed an empirical general rate equation [96]:

$$r = \frac{Z_1{}^{-E_1/RT}p_{H_2}{}^{n}}{[1 + Z_2{}^{E_2/RT}(p_{CO}/p_{H_2})]^{0.5}}$$

Methanation rates were calculated for 250°C and 1 atm pressure to give data, as shown in Table 6, from which the following points can be made regarding these catalyst compositions:

1. There was an effect of carrier on methanation rate in which η-Al_2O_3, $Cr_2O_3 > MgAlO_4$.
2. Apparent activation energies varied from 18 to 28 kcal/mole with the lowest value assigned to η-Al_2O_3.
3. Both K_2O and MgO promoters had an adverse effect on methanation activity; K_2O was particularly harmful.
4. K_2O had little influence on the catalyst's capacity for adsorption of H_2S.

TABLE 6

Effects of Carrier and Promoter on Nickel Methanation Kinetics

Catalyst	1	2[a]	3	4[b]	5	6
Nickel, %	9-10	9-10	12	12	20[c]	50
Promoter, %	-	K_2O[a]	-	K_2O, 2.5	MgO, 55	-
Carrier	$MgAlO_4$	$MgAlO_4$	η-Al_2O_3	η-Al_2O_3	Al_2O_3	Cr_2O_3
Z_1, Nl CO/hr g $\times 10^8$	4.7	14	0.45	8.5	17.5	68
E_1, kcal/mole	23.36	28	18	24	25	23
$r_{250°}$, Nl CO/hr g	0.081	0.0028	1.35	0.080	0.063	10
S capacity, ppm	1000	850	5450	5400	2300	-

[a] Catalyst #1 with a few percent K_2O added.
[b] Catalyst #3 with 2.5% K_2O added.
[c] 20% NiO.

A preferred catalyst, described by Novohradsky, contains nickel, alumina, manganese, and Borovanska diatomaceous earth in a 100:350:20:100 weight ratio [98]. It was prepared by coprecipitation of the metal nitrates with alkali in the presence of diatomaceous earth, filtering, and washing the filter cake. This was extruded, dried, and activated in flowing hydrogen for 2 hr at 340°C or for a shorter time at 400°C. The promotional effects of several stable oxides on nickel were compared by Novohradsky on the basis of activity-time above 95% CO reduction activity. The results, presented in Table 7, showed alumina, alumina and silica, and thoria to be preferred over others tested.

Solc prepared a NiO-Cr_2O_3 catalyst (4.2:1 molar ratio) from basic nickel carbonate and chromic acid with which the methanation of CO_2 had an apparent activation energy of 20.5 kcal/mole [99]. Vahala et al. recently published three papers concerning the preparation and properties of Ni-Cr_2O_3 compositions in which he concludes that it is

TABLE 7

Effective of Promotors on Nickel Methanation Catalyst During Lowering of Activity to 95%

Catalyst	Hours	Average CO Reduction	Moles CO reduced per mole Ni	Relative effectiveness, Ni = 1
Ni	5	98.7	8.49	1.0
Ni + 10% SiO_2 gel	10	97.5	16.93	2.0
Ni + 10% BaO	140	97.5	223.5	26.3
Ni + 10% SrO	10	97.5	18.66	2.2
Ni + 10% CaO	1	95.0	1.76	0.2
Ni + 10% Al_2O_3	250	99.0	405.2	47.7
Ni + 10% Al_2O_3 + 10% SiO_2	250	99.4	386.7	45.4
Ni + 10% ThO_2	250	99.4	364.6	43.9

less active than nickel on kieselguhr or a coprecipitated catalyst from water glass and nickel nitrate [95, 102, 103]. A Russian patent [100] and a Czechoslovakian article [101] describe the use of Ni-Cr_2O_3 catalyst in the second stage of a methanator but employ a cheap iron catalyst to remove sulfur poisons and partially methanate the gas in the first stage.

Nickel supported on kieselguhr has been widely used for a long time and was the composition selected by White el al. upon which to determine kinetics of methanation of CO [53] and CO_2 [104]. Ruhrchemie patents [107-109] describe a 60% nickel, 5-10% MgO, 30-35% kieselguhr catalyst for methanation to produce high Btu gas. Sulfur removal was required to protect the active methanation catalyst. For this purpose it was necessary first to desulfurize organic sulfur compounds to H_2S and then adsorb the H_2S in a mixture of $CaCO_3$, SiO_2, Fe_2O_3, and Al_2O_3. The methanation reactors were maintained at 165 to 205°C and gas rates up to 5000 GHSV at 15 atm were processed.

D. Cobalt and Iron

In 1956 the Bureau of Mines was investigating catalysts derived from Raney alloys as a means of synthesis of high Btu fuel gas [86]. Raney cobalt, when extracted with alkali to remove only a portion of aluminum, was found to be very active for CO methanation, producing gas with a CO_2-free heating value over 950 Btu/CF at high space velocity. However, this catalyst tended to deposit carbon more than nickel catalysts under the same operating conditions.

Kurita and Tsutsumi prepared the borides of nickel, cobalt, and iron from their chlorides using an excess of sodium borohydride [93]. These catalysts, supported on silica gel, were tested with 2:1 synthesis gas at 1 liter/hr/g over a range of temperatures. The conversion of CO was nearly complete at 280°C for Ni and 340°C for Co; the iron catalyst converted no more than 20% CO even at 340°C. The nickel catalyst was not only more active, but at high conversions was more selective toward methane than the cobalt catalyst which produced much C_{2+} product.

An unusual iron catalyst, carbon-expanded iron, was discovered by the Bureau of Mines to have activity as a Fischer-Tropsch and a methanation catalyst [110]. In one example, a small amount (1.73 g) of finely divided electrolytic iron was dispersed on glass wool in a 50-ml reactor, contacted with hydrogen at 400°C, and then simply allowed to react with 1:1 synthesis gas at 209-232°C before heating to an operating temperature of 336°C. A voluminous carbon deposit developed which contained finely dispersed iron. This catalyst produced about 20% methane and 80% Fischer-Tropsch products from 1:1 synthesis gas. Another expanded iron catalyst, from steel turnings that were first oxidized 20% in steam and then reduced, was used to methanate a 3:1 synthesis gas at 400 psig and 320°C using hot gas recycle [111]. Even at the higher H_2/CO ratio the product gas contained 10.6% C_2-C_5, and oils accounted for 3.2% of the hydrocarbons produced. It is a very active form of iron and maintains its activity well, but ultimately carbon deposition leads to bridging and plugging of the reactor.

E. Molybdenum and Tungsten

Molybdenum and tungsten methanation catalysts stand out because they are sulfur resistant and, in fact, are commonly sulfided before use. Wencke, in a well-documented paper [112], demonstrated the benefits of high molybdenum compositions, 50-70% Mo-Al_2O_3. Before use, MoO_3 was reduced in hydrogen at 600°C and the resultant Mo then sulfided with H_2S. A loss in methanation activity due to sulfiding was made up for by using higher pressures (see Fig. 15). The 70% Mo catalyst, in a fluid bed at 40 atm and temperatures under 400°C, raised the heating value of 2:1 synthesis gas by a factor of 1.61 (CO_2-free basis).

A variety of molybdenum catalysts were prepared and tested for methanation activity by the Bureau of Mines at 21 atm and about 300 GHSV [113]. Only moderately active catalysts were formed at best, as shown in Table 8, and relatively high temperature was required

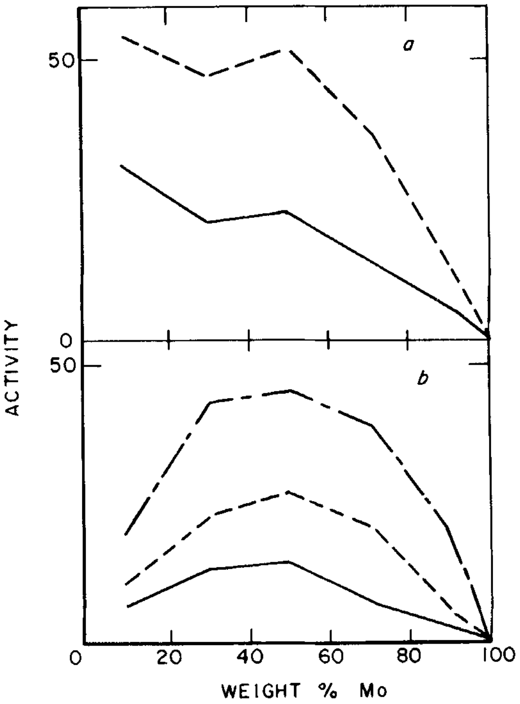


FIG. 15. Acitivity of unsulfided and sulfided catalysts at different pressures as a function of their composition. (a) Unsulfided catalysts: (—) 20 atm, (- -) 30 atm. (b) Sulfided catalysts: (—) 20 atm, (- -) 30 atm, (— -) 40 atm.

TABLE 8

Methanation over Molybdenum Catalysts[a]

Mo, %	11.2	38.5	40.6	11.0
Type	Impregnated	Impregnated	Coppt.	Coppt.-H_2S
Support	Cracking catalyst	Active carbon	Al_2O_3	Al_2O_3
Temperature, °C	401	401	400	400
H_2/CO conversion, %	41.1	67.9	37.5	47.6
Hydrocarbon distribution, wt%				
C_1	79.7	83.6	84.1	93.7
C_2	16.0	13.0	15.6	5.9
$C_3 + C_4$	4.3	4.4	0.3	0.4
C_5+	-	-	-	0.0

[a] 21 atm, ~300 GHSV, using 3:1 H^2/CO.

for these conversions. The selectivity to methane was 79 to 94% in the examples shown; a coprecipitated and sulfided catalyst gave the highest selectivity. In terms of high Btu gas, a small amount of ethane in methane is acceptable, and therefore the 99+ selectivity to

$C_1 + C_2$ hydrocarbon product from the alumina-based catalysts would be satisfactory.

Molybdenum catalysts showed an unexpected methanation response to sulfur in synthesis gas. The coprecipitated and sulfided catalyst, when fed a synthesis gas containing a low level of H_2S, deactivated slightly and, as it accumulated more sulfur, its selectivity declined as evidenced by higher C_3-C_5 make (see Table 9). Similarly, the unsulfided MoO_3-Al_2O_3 shown in Table 9 declined in activity when methanating 3:1 synthesis gas containing low levels of H_2S. However, this time the selectivity approached that of the coprecipitated and sulfided catalyst. Upon using H_2S-free synthesis gas again, both compositions returned to their original activity and selectivity.

TABLE 9

Effect of Sulfur on MoS-Al_2O_3 Catalyst[a]

H_2S added, via gas	None	0.087 g	0.325 g
GHSV	295	297	320
H_2/CO conversion, %	47.6	41.3	37.3
Hydrocarbon distribution, wt%			
C_1	93.7	93.1	64.6
C_2	5.9	6.7	4.1
$C_3 + C_4$	0.4	0.2	29.4
C_5	0.0	0.0	1.9

[a] 11.0% Mo-3.6% S-Al_2O_3 coprecipitated, 21 atm, 3:1 H_2/CO, 400°C.

Unsupported nickel, molybdate, and cobalt molybdate compositions were also prepared [113]. These were more active at lower temperatures than the molybdena catalysts cited above. Selectivities to C_1, C_2, $C_3 + C_4$, and C_5+ were 84.4, 11.5, 4.1, and 0.0 for nickel molybdate and 76.8, 10.2, 10.3, and 2.7 for cobalt molybdate, respectively. Carbon dioxide was methanated over nickel molybdate at 350°C to give 97+% methane.

A tungsten-alumina catalyst prepared by coprecipitation was quite inactive, requiring 599°C for 43.6% conversion of 1:1 synthesis gas; its selectivity to methane, ~90%, was good considering the feed gas was far from the desired H_2/CO ratio [113]. Tungsten sulfide, WS_2, was claimed as a catalyst active in the direct methanation of CO or CO_2 present in the gasification product from coal to obtain a higher Btu fuel gas [114].

Preferred conditions for methanation were 475°C and 1,000 psig at space velocities about 1000 GHSV. Heating values in excess of 900 Btu/CF on a CO_2-free basis were obtained. The catalyst was found to be unaffected by sulfur.

F. Noble Metals

The effectiveness of a few platinum metal catalysts for methanation was commented on earlier. However, in recent years, except for ruthenium, little attention has been paid to these metals. McKee showed that rhodium and iridium, at reduced pressure and 200°C, had only slight methanating activity, while platinum had none [50]. Ruthenium, as discussed earlier, has outstanding activity even under such mild conditions.

In a survey of noble metals, the Bureau of Mines has published comparative methanation data [113]. The catalysts were each tested as 0.5% metal on alumina (except for charcoal-supported oxmium) using 3:1 synthesis gas at 21 atm and about 300 GHSV. Based on temperature-conversion data, these metals can be arranged in order of decreasing activity as Ru $\gg$ Rh $\gg$ Re $>$ Pt, Pd $>$ Os. Their selectivity to methane, however, would be quite a different arrangement: Pd $>$ Re $>$ Os, RH $\gg$ Pt $\gg$ Ru. The data are summarized in Fig. 16. For ruthenium the temperatures shown represent the boiling point of hydrocarbon fractions.

The 40.6% molybdena-alumina catalyst, shown for comparison, would, on the basis of cost vs effectiveness, appear to be a reasonable alternate to the very expensive noble metal compositions. Also, for the production of high Btu gas, its product distribution and sulfur tolerance would be advantageous.

VII. INDUSTRIAL APPLICATIONS

At present, methanation is used to convert relatively small amounts of harmful carbon oxides to methane where, as in ammonia synthesis, carbon monoxide especially would interfere with catalytic utilization of gas mixtures. However, it now appears that methanation will be used on a large scale in the manufacture of "high Btu" or pipeline gas, which is essentially methane.

From an industrial viewpoint, high selectivity to methane is not difficult to achieve. Rather the problems are prevention of catalyst inactivation by sulfur compounds or carbon deposition and also those arising from the highly exothermic nature of methanation.

With nickel catalysts it is usual to limit sulfur in the gas to less than 1 ppm by providing rigorous purification. Carbon deposition on the catalyst can be avoided by operation with a sufficiently high H_2/CO mole ratio under the conditions indicated in Fig. 6.

Excessive temperatures in methanation are avoided by either limiting the carbon monoxide content of reactant gases or providing apparatus to permit rapid heat removal. For every 1% CO, the tem-

Catalyst	Pt	Pd	Ru	Rh	Os	Re	Mo
Cat No	L1138	L1140	L1141	L1139	L1163	L1154	L6137
Run No	Z360	Z362	Z363	Z361	Z408	Z394	Z353
Temp °C	513	499	222	441	600	451	420
SVH	297	318	303	302	295	281	288
CO_2 – free contraction, %	38.2	24.8	67.1	64.8	57.5	64.4	44.2
Conversion %	56.4	35.5	79.7	86.7	70.0	85.5	56.4
Usage ratio H_2/CO	1.8	2.2	2.4	2.4	2.3	2.4	1.8

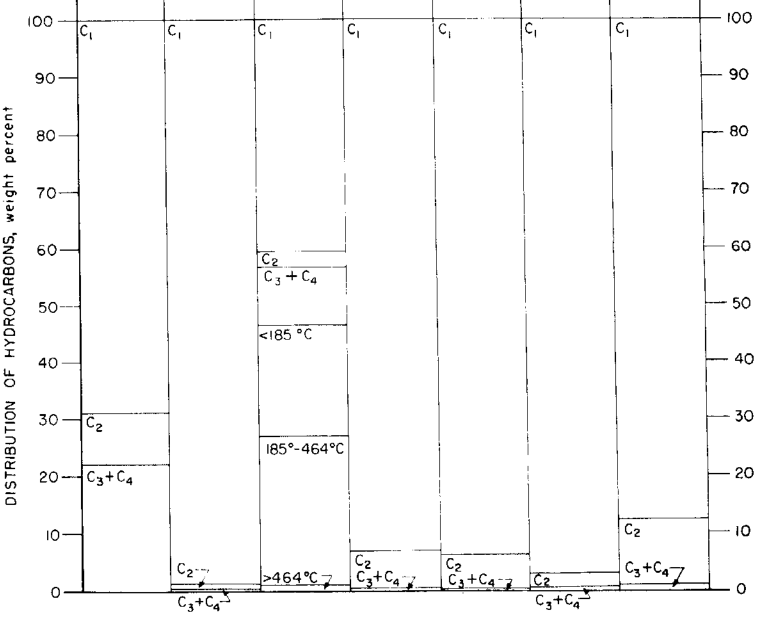


FIG. 16. Comparison of operating conditions and selectivity using $3H_2 + CO$.

perature rise due to the methanation reaction is over 100°F. High temperatures can not only cause decomposition of methane, but methanation catalysts can also be rendered inactive due to sintering.

Numerous catalysts have been prepared and tested, particularly by the British Gas Research Board and the U.S. Bureau of Mines, as described in the catalyst section of this paper.

In gas purification applications by methanation it is usual to limit treatment to gas streams containing not over about 2 mole % oxides of carbon [115]. Under proper operating conditions the reaction goes almost to completion and exit gases contain only a few ppm of carbon oxides. The catalyst does not require regeneration and has an expected service life of several years. A diagrammatic flow sheet typical of final purification of the hydrogen used for ammonia synthesis is shown in Fig. 17. Inlet gas temperatures may vary from 350 to 750°F; however, because of unfavorable equilibrium at elevated temperatures, the exit-gas temperatures should not exceed 825°F. The pressure range over which the process can be operated extends from atmospheric to 12,000 psi. Space velocities of 1000 to 2000 vol/(vol)(hour) are typical for operation at atmospheric pressure, and space velocities are 3 to 5 times larger at 20-30 atm. Typical operating conditions of commercial operations are shown in Table 10.

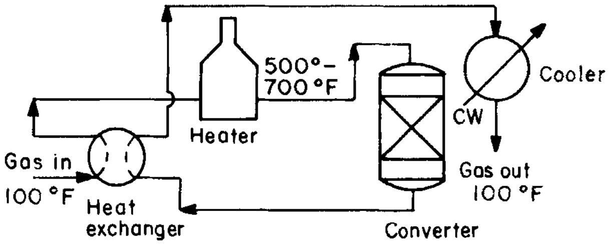


FIG. 17. Schematic flow diagram of methantor.

TABLE 10

Typical Operating Conditions for Methanation of Oxides of Carbon[a]

Design variables	Plant A	Plant B	Plant C
Inlet temperature, °F	520	500	500-600
Outlet temperature, °F	550	550	500-600
Pressure, psig	10	750	3,600
Space-velocity, vol/(vol) (hr)	1,000	7,500	10,000
Inlet gas, ppm:			
CO	2,300	6,000	1,000
CO_2	500	200	50
O_2	-	-	1,000
Outlet gas, ppm:			
CO	0.7	10	1
CO_2	1.5	10	1
O_2	-	-	5

[a] Courtesy Chemetron Corporation.

For manufacture of methane, gas streams of much higher concentrations of carbon monoxide must be converted. For example, the H_2, CO, and CH_4 relative percentages from the Synthane gasifier are 40, 24, and 36; after shift reaction they are 48, 16, and 36. The composition of gases entering the methanator are shown in Table 11, where CO content is lowered significantly by gas recycle.

TABLE 11

Composition of Gas Being Methanated

	Synthane				
Mole %	TWR	Hot gas recycle	HyGas [116]	Hydrane [117]	Naphtha
H_2	20.3	5.8	14-35	26	17
CO	5.7	1.1	2-10	3	1
CO_2	3.0	3.7	2	1	21
CH_4	68.7	78.9	53-87	70	61
C_2H_6	0.4	0.2			
N_2	1.8	1.7			
H_2O	0.1	8.6			

Reactor designs capable of providing for removal of heat of hydrogenation have been discussed [118] based on the extensive experience with the Fischer-Tropsch process. Temperature control can be achieved by fixed bed, gas recycle, fluid bed, or slurry catalyst systems or by combinations of these.

In one design the fixed bed reactor (Lurgi-Ruhrchemie) [119] is a vertical tube heat exchanger, the catalyst being placed inside the tubes with water on the outside. The heat released is absorbed by boiling the water in the shell. The reaction temperature is controlled by controlling the pressure of the boiling water. The reactor contains approximately 2000 tubes holding about 40 m^3 of catalyst. The catalyst tubes are about 40 ft long and 1.8 in i.d.

For the circulating fluid bed system designed by Kellogg and operating at Sasol, about 7000 tons of catalyst per hour are circulated through a 120-ft high reactor (Fig. 18). Heat removal is accomplished in two ways. First, the combined feed-gas entering the system at 150° and leaving at 330°C removes the main part of the heat; and second, the residual heat is extracted through two oil-cooled coolers built in the reactor. The Hydrocol Process unit at Brownsville, Texas, was a fixed, fluidized bed system.

Reactor systems specifically designed for methanation have also been reviewed [85, 120]. By use of hot gas recycle it is possible to control reaction temperatures [121, 122] although high recycle rates are required (Fig. 19).

Oil circulation has also been investigated over a fixed catalyst bed to control temperatures [123].

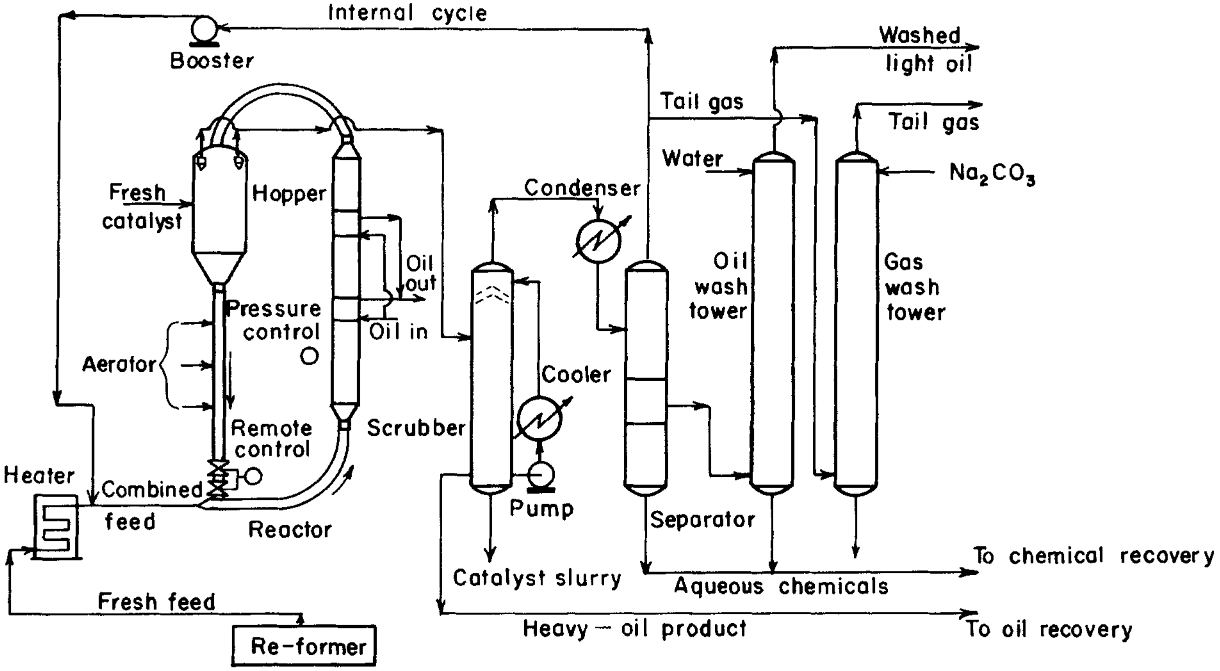


FIG. 18. Flowsheet of medium-pressure synthesis on iron catalyst with entrained, fluid-bed reactor (Sasol-Kellogg).

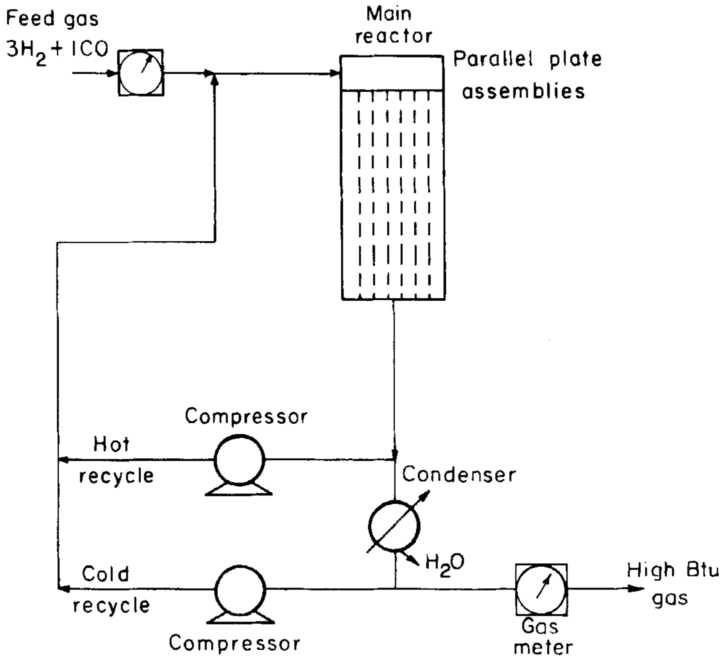


FIG. 19. Flowsheet of hot-gas recycle process.

Recently, Forney and associates [124-126] have described a very interesting catalyst system called the tube wall reactor (TWR) (Fig. 20). The catalyst is prepared by flame spraying a nickel aluminum alloy on tubes of 2 in. diameter so as to form a bonded layer. The coating is then partially leached with caustic to form a Raney-type catalyst adherent to the tube wall. By having a heat transfer medium such as Dowtherm on one side of the tube, catalyst temperature can be closely controlled. The Synthane pilot plant under construction will use the tube wall reactor system as one methanation system.

The engineering basis for designing methanators has been discussed [127] covering a wide range of catalyst particle sizes, pressures, temperatures, and kinetic effects.

A recent article by Allen and Yen [128] gives general startup, operating, and shutdown procedures for a methanation reactor and a method for sizing a methanator using Girdler G-65 catalyst. The potential health hazard of nickel carbonyl is presented, and conditions are suggested to avoid its formation; namely, to maintain the temperature above 260°C until all CO has been purged from the

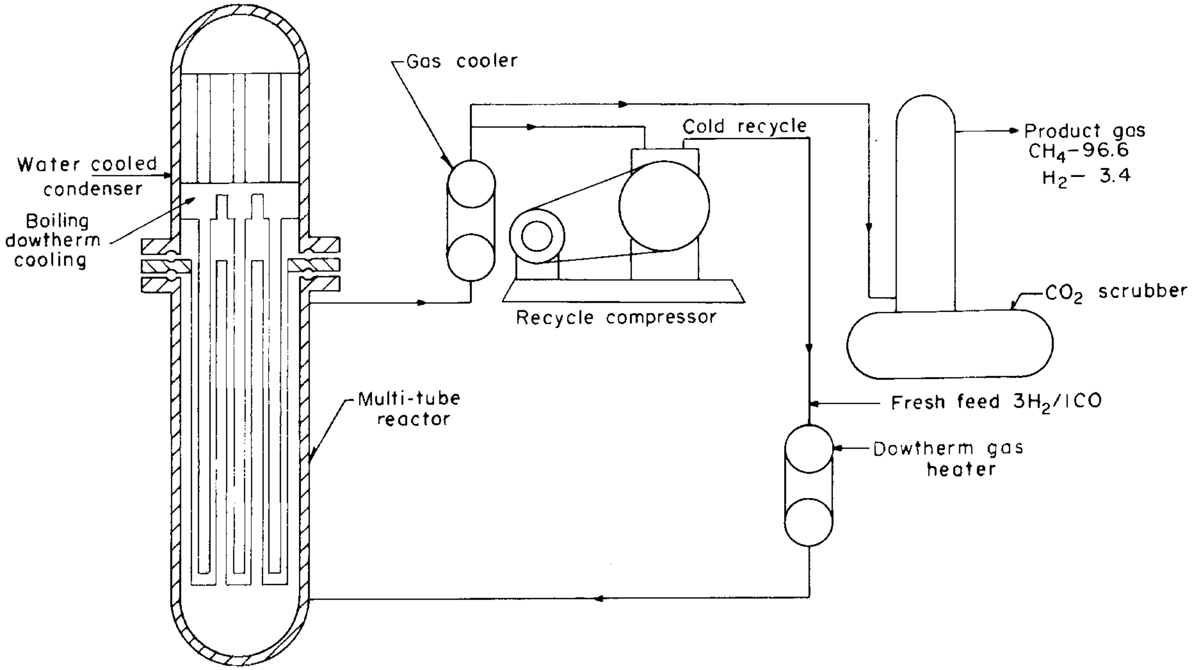


FIG. 20. Tube wall reactor methanator.

reactor. Methanators producing SNG from synthesis gas would be especially vulnerable since $Ni(CO)_4$ formation varies with the fourth power of the CO partial pressure.

At present, about 25 naphtha gasification plants are being constructed in the United States. In contrast to European practice, these will include a methanation process step. Because of the relatively low CO content from the reforming unit (Table 11), essentially the same methanation technology can be used as in gas cleanup by CO methanation.

The amount of catalyst needed for methanation in a naphtha gasification plant has been estimated [129]. Assuming 12 plants are built, each capable of producing 250 million ft^3/day of SNG, an estimated charge of 500 tons of catalyst would be required.

For production of pipeline gas by coal gasification, there is an intensive research and development program underway to establish suitable catalysts and apparatus to provide for methanation of the high CO gas content. Methanation is required for either fixed bed or for fluid bed processes. Four large pilot plants are under construction in the United States and different methanation process technology is being installed at each—cold gas recycle (HYGAS), tube wall reactor, hot gas recycle (SYNTHANE), and fluid bed (BI-GAS). In some instances an additional "trim" reactor is being installed to ensure complete methanation.

Further improvement in methanation catalysis constitutes one of the most fertile fields for research [130]. Catalysts are needed which are much less sensitive to sulfur and are able to withstand higher temperatures without sintering and loss of activity. Also needed are catalytic reactor systems capable of removing heat without costly equipment or high gas recycle rates. While at present high selectivity to methane is desired, future catalysts may require a selectivity that provides for some C_2 and higher hydrocarbons.

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