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The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures over the Group VIII Metals

I. The Specific Activities and Product Distributions of Supported Metals

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Specific activities have been determined in the synthesis of hydrocarbons from $CO-H_2$ mixtures over the Group VIII metals. In the methanation reaction the relative activities of supported metals, based on the number of surface metal atoms, are significantly different than similar comparisons in older studies which did not correct for variations in metal surface area. The methanation reaction was fitted to a power rate law of the form $r_{CH_4} = Ae^{-E_m/RT} P_{H_2}{}^X P_{CO}{}^Y$ over all the Group VIII metals except Os. In addition, accurate product distributions, determined under comparable conditions and at low conversions, are provided. The necessity of catalyst characterization, such as the use of selective chemisorption techniques, is clearly evident in this study.

INTRODUCTION

The catalytic synthesis of hydrocarbons from mixtures of carbon monoxide and hydrogen is a well-studied reaction, with Sabatier first reporting in 1902 the synthesis of methane over a nickel catalyst. Later, through the 1920's and 1930's, Fischer headed a large research effort in Germany which resulted in the development of most of the different synthesis processes known today. During the decade following World War II, a number of laboratories were studying $CO-H_2$ synthesis reactions including a major research effort at the U.S. Bureau of Mines. Many excellent reviews have been written describing and summarizing this past work (1–7).

However, nearly all of this research was done before the advent of sensitive analytical instruments which could determine detailed product distributions, and before the development of gas adsorption techniques which could measure the surface area of metal catalysts. Because of the first limitation, high conversions were necessary for product analyses. Therefore few kinetic studies have been conducted under conditions of low conversion, i.e., using a differential reactor, which is desirable for the measurement of the most accurate and unambiguous kinetic data. In addition, due to the second limitation, *no specific activities*, i.e., rates per unit surface area of metal, have been reported in the literature for the synthesis reaction. Because of this, none of the activities of the catalysts in these earlier studies can be compared directly, since differences in surface area cannot be accounted for.

This study was conducted to fill this void and provide a firm foundation for the comparison of the catalytic behavior of supported Group VIII metals in the $CO-H_2$ synthesis reaction. All the Group VIII metals except Os were studied with each metal being dispersed on alumina, a

typical metal oxide support. Selective chemisorption measurements were made to determine metal surface areas and allow the calculation of specific activities. Detailed product distributions were obtained even though low conversions were maintained in the reactor to provide accurate kinetic data.

The first part of this study describes the catalytic behavior of these metals with regard to their product distributions and their specific activities. Significant differences are found when these results are compared to older studies. A second part of this work discusses the kinetic results, particularly with regard to the methanation reaction (*8*).

EXPERIMENTAL METHODS

The kinetic studies were conducted in a flow microreactor system similar to that used by Dalla Betta and co-workers (*9*) except that Wallace & Tiernan differential gages were used in place of oil-filled U-tube manometers. The unit was operated at a total pressure of 1 atm. The catalyst charges were small, usually 0.5 g or less, and the analyses of the exit gas were conducted using a Hewlett-Packard 7620 gas chromatograph with Chromasorb 102 columns and subambient temperature programming capabilities. Peak areas were determined by an electronic Hewlett-Packard 3370B integrator. High space velocities of 2500–10,000 hr^{-1} were typically used to keep CO conversions around 5% or less. This provided conversion data from a differential reactor thereby: (a) minimizing heat and mass transfer effects, (b) eliminating any significant effects due to product inhibition, and (c) producing initial rates without the complication of secondary reactions. A variety of tests including changes in space velocity and the Koros–Nowak technique (*10*) verified the absence of diffusional limitations.

To achieve steady-state operation in the reactor, the H_2/CO feed stream was normally flowed over the catalyst for 20 min at 20 cc/min before a sample was taken for analysis. Then the CO flow was stopped and H_2 only was flowed for 20 min to help regenerate and maintain a clean metal surface. This procedure is similar to that used by Yates and co-workers (*11*). Reproducible results in nearly all cases indicated this technique was successful in providing a clean metal surface.

A standard catalyst pretreatment was used in the reactor. It consisted of heating the sample in flowing H_2 (~40 cc/min) to 120°C, holding this temperature for 30 min, then heating to 260°C and holding this temperature for 30 min before continuing to heat to 450°C. The catalyst sample was held at 450°C for 1 hr before cooling under flowing H_2 to the chosen reaction temperature range, which was usually 240–280°C.

Hydrogen and carbon monoxide chemisorption measurements, used to determine the metal surface area of each catalyst, were made in a typical glass adsorption system capable of a dynamic vacuum $\leq 10^{-6}$ Torr. Liquid nitrogen traps were placed between the oil diffusion pump and the catalyst chamber. CO chemisorption values were determined by obtaining an isotherm between 50 and 250 Torr over a 15 min period, evacuating for 2 min to remove reversibly held CO, obtaining a second isotherm in the same manner as the first, then taking the difference at 200 Torr as a measure of CO adsorption on the metal surface. The intercept value was used to represent H_2 uptakes. Hydrogen and CO adsorption measurements were always made on the used samples and were frequently conducted on the fresh samples too, prior to their use in the kinetic study. CO chemisorption on the used catalyst was taken as the standard measure of active sites on the metal surface and all specific activity data were based on this uptake value. Complications due to carbonyl formation during CO up-

takes did not appear. At the low CO pressures and short exposure times employed no evidence of noticeable carbonyl formation was observed.

Prior to chemisorption measurements, whether on new or used samples, the catalyst was heated to ~450°C in flowing H_2, held there for 1 hr in H_2, evacuated for 1 hr at this temperature, then cooled *in vacuo* to room temperature where H_2 uptakes were measured. The sample was then heated again to 450°C in H_2, evacuated for 1 hr, then cooled *in vacuo* to room temperature for the CO adsorption measurements.

Most of the supported metal catalysts were prepared by standard incipient-wetness techniques using 0.5 cc solution/g. η-Al_2O_3. The Al_2O_3 had a surface area of 200 m^2/g. Aqueous solutions of the following metal salts were used: $RuCl_3$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $RhCl_3$, $PdCl_2$, H_2PtCl_6, and H_2IrCl_6. However, the Fe catalysts were prepared by heating a mixture of Al_2O_3 and $Fe(NO_3)_3 \cdot 9H_2O$ past the melting point of the latter compound using a technique described elsewhere (*12*). After impregnation, the samples were dried overnight at 120°C then stored in a desiccator.

The hydrogen (Linde, 99.95% purity) was further purified by passage through a Deoxo unit followed by a molecular sieve trap to remove water. The carbon monoxide (Matheson, 99.99% purity) and the helium (U.S. Bureau of Mines, 99.995% purity) were passed through molecular sieve traps before reaching the reactor.

RESULTS

Chemisorption data for the different catalysts are listed in Table 1. Also shown are the calculated metal dispersion values, $D = m_s/m_t$, where m_s is the number of surface metal atoms and m_t is the total number of metal atoms in the sample.

The product distributions obtained over each catalyst are shown in Figs. 1 through 7 as a function of the H_2/CO molar feed ratio. The products are represented as the number of C atoms per molecule and their respective concentrations are listed as mole percent. The C_2 fraction is divided into ethylene and ethane since it has been observed in this study that the ethylene/ethane ratio is usually a good indicator of the overall olefin/paraffin ratio in the products. The hydrocarbon product from the Pd catalyst was essentially all methane regardless of the H_2/CO ratio and

TABLE 1
CHEMISORPTION MEASUREMENTS ON CATALYST SAMPLES

Catalyst	CO uptake (μmole/g)		H_2 uptake (μmole/g)		% Dispersion (used sample)	
	New	Used	New	Used	CO[a]	H_2
5% Ru/Al_2O_3	35	28.5	17.4	14.3	6[b]	6
15% Fe/Al_2O_3	21.5	21.5	—	1	1.6	—
5% Ni/Al_2O_3	—	110	—	48	13[b]	11
2% Co/Al_2O_3	16	14.2	1	0.2	8	—
1% Rh/Al_2O_3	—	47	51	25	48[b]	51
2% Pd/Al_2O_3	—	20.8	—	—	22	—
1.75% Pt/Al_2O_3	71	39.5	68	32.5	88	72
2% Ir/Al_2O_3	—	47	—	46	90	88

[a] Assuming bridged bonding.
[b] Assuming linear bonding.

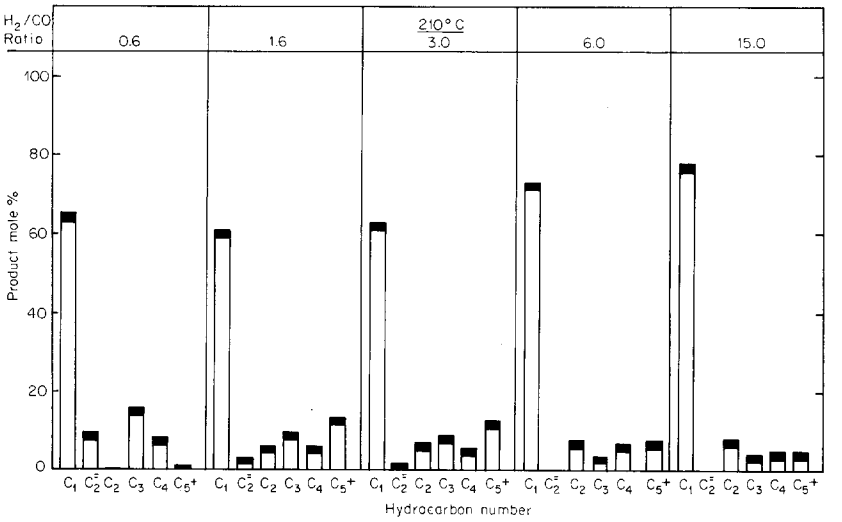

FIG. 1. Product distribution vs H_2/CO feed ratio – Ru/Al_2O_3.

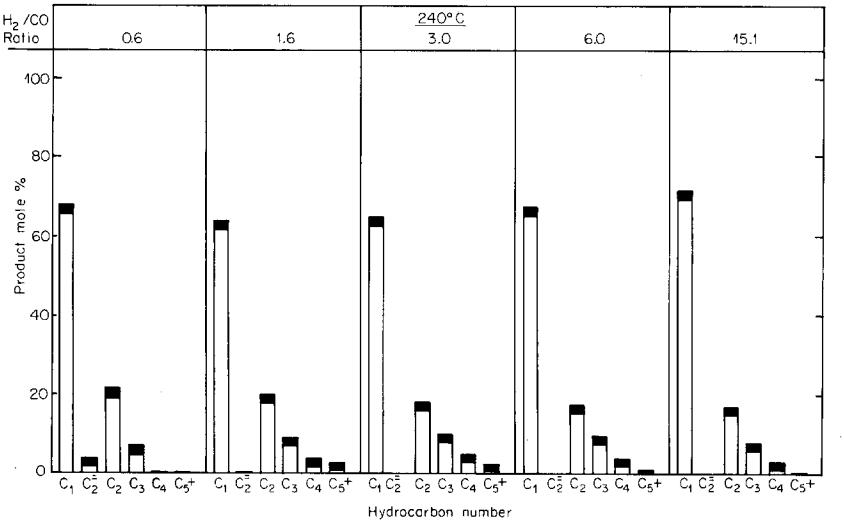

FIG. 2. Product distribution vs H_2/CO feed ratio – Fe/Al_2O_3.

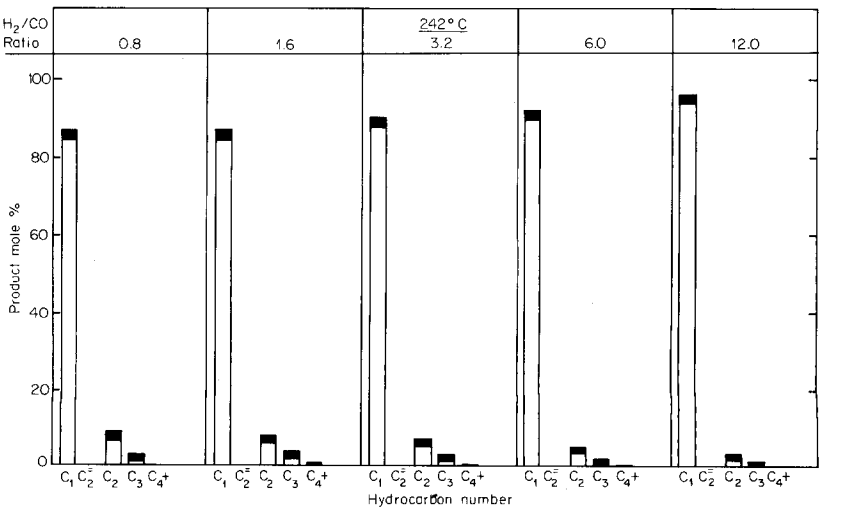

FIG. 3. Product distribution vs H_2/CO feed ratio – Ni/Al_2O_3.

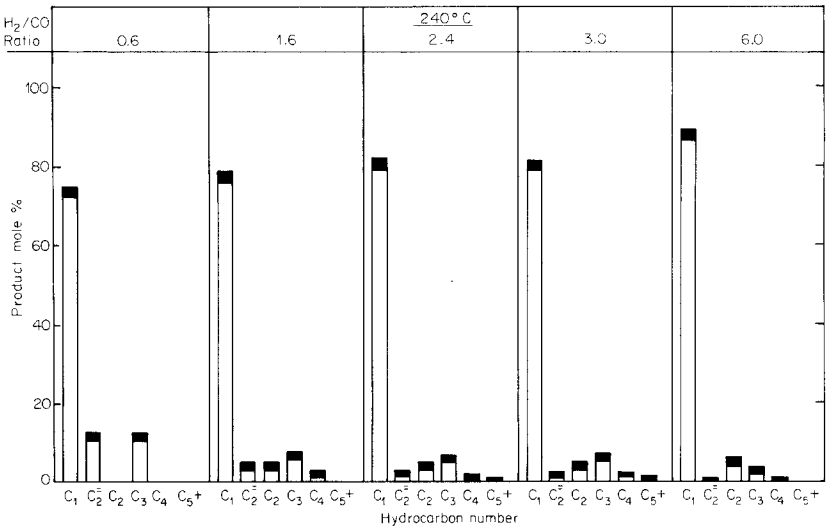

FIG. 4. Product distribution vs H_2/CO feed ratio – Co/Al_2O_3.

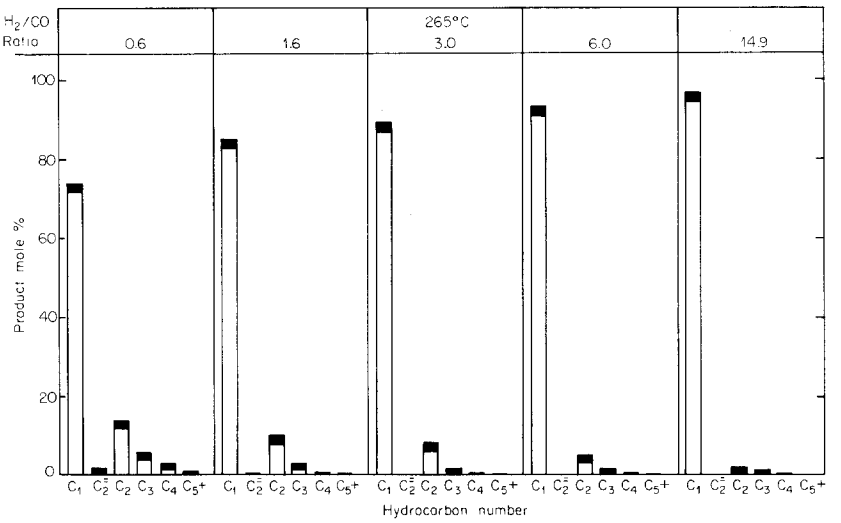

FIG. 5. Product distribution vs H_2/CO feed ratio – Rh/Al_2O_3.

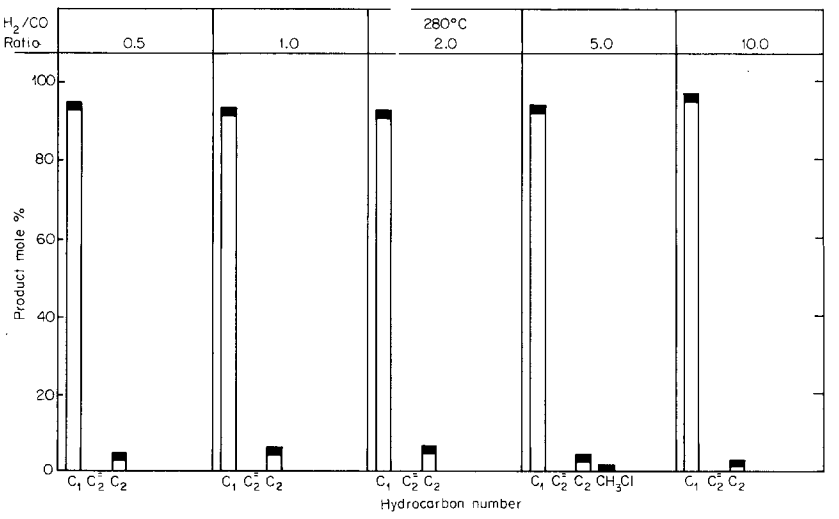

FIG. 6. Product distribution vs H_2/CO feed ratio – Pt/Al_2O_3.

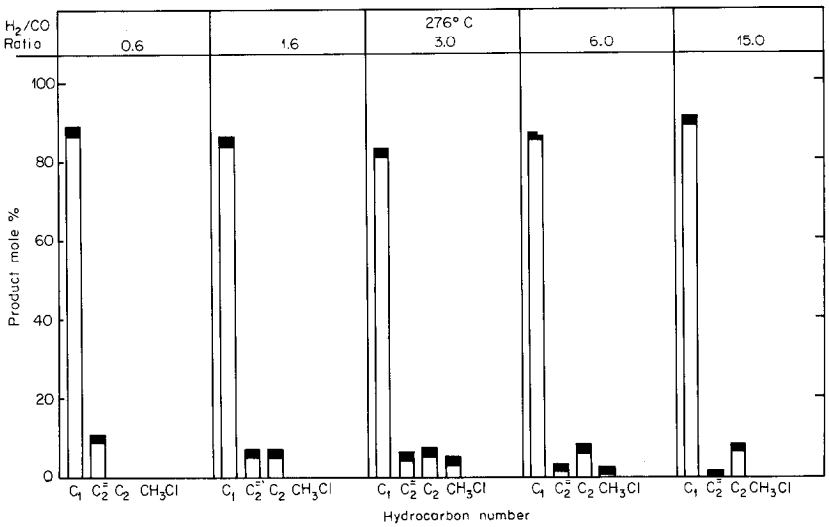

FIG. 7. Product distribution vs H_2/CO feed ratio – Ir/Al_2O_3.

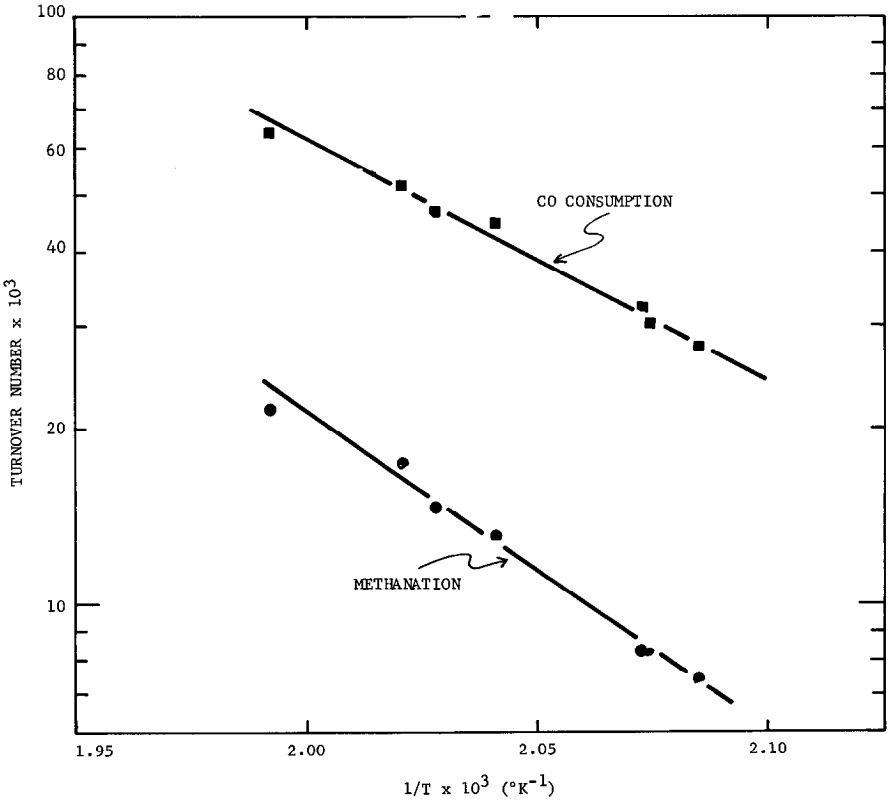

FIG. 8. Arrhenius plots for Ru/Al_2O_3.

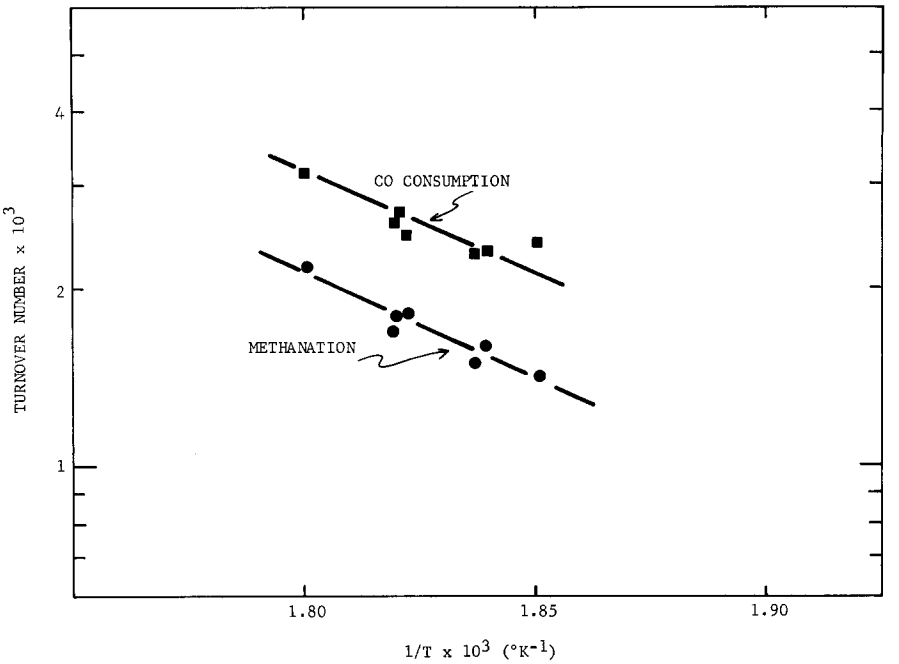

FIG. 9. Arrhenius plots for Ir/Al_2O_3.

therefore no graph is presented. Conversions were lowest at low H_2/CO ratios and the product analyses were least accurate under these conditions since much smaller quantities of higher molecular species were detected.

Shown in Figs. 8 and 9 are data typical of those used in Arrhenius plots to determine the activation energy, E_m, for the methanation reaction and also E_{CO}, which is the apparent activation energy for the conversion of CO into any and all products. The H_2 and CO partial pressures were held constant at a H_2/CO ratio of 3 for these runs. Rates of CH_4 formation and CO conversion to any and all hydrocarbon products are based on accurate CO flow rates coupled with carbon mass balances for the product stream which are determined directly from gc analysis. This technique is accurate because all used samples were analyzed for elemental carbon and no detectable carbon deposits were formed during time on-stream. Either rate is expressed as a turnover number,

$$N_{CH_4} \text{ (or } N_{CO}) = \frac{\text{molecules formed (or reacted)}}{\text{metal site} \cdot \text{sec}}$$

It should be mentioned that conversions can be calculated from turnover numbers in a straightforward way once the number of surface metal atoms is measured. To do this, the following equation is used:

$$\text{conversion} = \left(N, \frac{\text{molecules}}{\text{metal site}\cdot\text{sec}}\right)(m_s) \times \left[\left(\text{Reactant gas flow}, \frac{\text{cc}_{\text{STP}}}{\text{sec}}\right)\left(\frac{44.6\ \mu\text{mole}}{\text{cc gas}}\right)\left(\frac{6.02 \times 10^{17}\ \text{molecules}}{\mu\text{mole}}\right)\right]^{-1}.$$

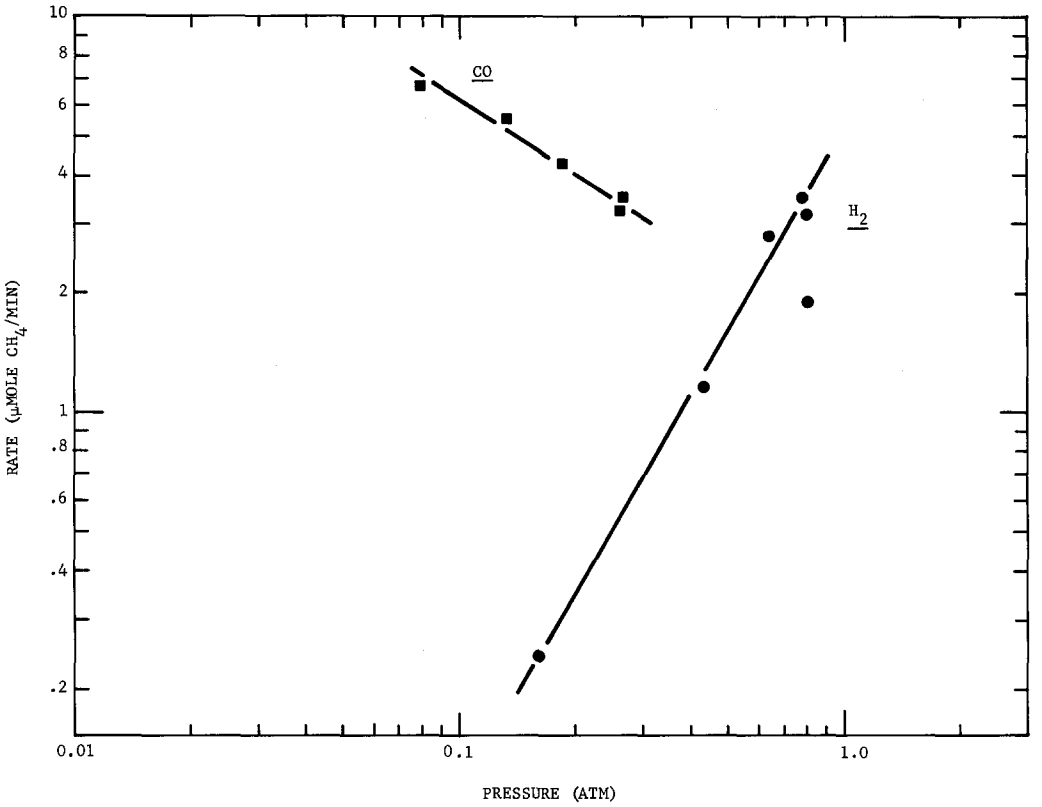

FIG. 10. Partial pressure dependence for Ru/Al_2O_3.

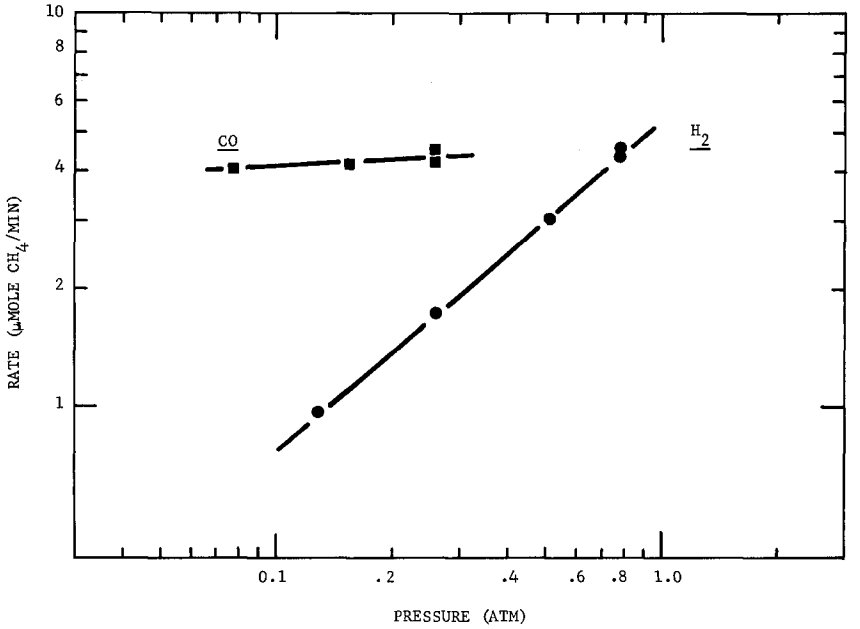

FIG. 11. Partial pressure dependence for Pt/Al_2O_3.

TABLE 2
SYNTHESIS KINETICS OF SUPPORTED METALS[a]

Catalyst	Turnover No. @ 275°C: CH_4 formation $\times 10^3$	Turnover No. @ 275°C: CO reacted $\times 10^3$	E_m (kcal/mole)	X	Y	A (molecules/site · sec)	E_{CO} (kcal/mole)
5% Ru/Al_2O_3	181	325	24.2 ± 1.2	1.6 ± 0.1	−0.6 ± 0.1	5.7×10^8	18.3 ± 1.0
15% Fe/Al_2O_3	57	160	21.3 ± 0.9	1.14 ± 0.10	−0.05 ± 0.07	2.2×10^7	25.9 ± 1.6
5% Ni/Al_2O_3	32	38	25.0 ± 1.2	0.77 ± 0.04	−0.31 ± 0.05	2.3×10^8	23.5 ± 1.1
2% Co/Al_2O_3	20	28	27.0 ± 4.4	1.22 ± 0.18	−0.48 ± 0.28	9.0×10^8	26.7 ± 6.2
1% Rh/Al_2O_3	13	17	24.0 ± 0.4	1.04 ± 0.11	−0.20 ± 0.10	5.2×10^7	24.2 ± 0.4
2% Pd/Al_2O_3	12	13	19.7 ± 1.6	1.03 ± 0.05	0.03 ± 0.09	1.2×10^6	19.7 ± 1.6
1.75% Pt/Al_2O_3	2.7	3.4	16.7 ± 0.8	0.83 ± 0.01	0.04 ± 0.01	1.6×10^4	15.3 ± 0.8
2% Ir/Al_2O_3	1.8	2.6	16.9 ± 1.7	0.96 ± 0.02	0.10 ± 0.08	1.4×10^4	11.7 ± 3.2

[a] $r_{CH_4} = Ae^{-E_m/RT}P_{H_2}{}^X P_{CO}{}^Y$.

The dependence of the rate of methanation on the partial pressures of CO and H_2 was obtained from the slope of log–log plots of the rate versus the reactant partial pressures. Examples of these data are shown in Figs. 10 and 11.

If a power rate law is assumed for the methanation reaction, the rate can be represented by the following equation:

$$\text{rate} = N_{CH_4} = Ae^{-E_m/RT}\, P_{H_2}{}^X\, P_{CO}{}^Y,$$

where A is the preexponential factor and X and Y are the exponential dependencies on H_2 and CO pressures, respectively. All activities are compared at 275°C, either by direct determination from the Arrhenius plot or by extrapolation to this temperature. The kinetic data are tabulated in Table 2. The values along with their standard deviations were obtained by least squares fitting of the experimental points.

In a few cases, such as the Pt catalyst, small amounts of CH_3Cl are produced temporarily. This occurs because of the presence of chloride ions on the Al_2O_3 surface after impregnation by a metal chloride salt. As time on-stream increases, the amount of Cl^- on the Al_2O_3 surface decreases, not only because it reacts to form CH_3Cl but also because it is steam-stripped off as HCl due to the water formed as a product in the synthesis reaction. Experiments showed that the temporary presence of chloride ions does not alter the activity of the metal.

DISCUSSION

The current energy shortage has resulted in renewed interest in the synthesis of organic compounds from CO and H_2, commonly referred to as the Fischer–Tropsch synthesis, because this reaction provides one route to produce clean fuels and chemicals from hydrogen-deficient materials. The overall process includes the steam gasification of heavy materials such as coal or residua to produce a gaseous mixture containing large quantities of CO and H_2 which is purified, then reacted over a solid catalyst to form hydrocarbons. Despite the fact that the synthesis of hydrocarbons from these two gases has been the subject of much research for more than 50 yr, no data existed which gave specific activities for any of the synthesis reactions. Gas chemisorption techniques to measure metal surface areas were not yet commonly used; therefore, specific activities were not determined in these earlier studies. Also, the analytical techniques used for determining conversions and product distributions were not as sensitive and precise as those used today thereby necessitating reactor operation at high conversion, that is, as an integral reactor. This procedure has inherent disadvantages and

kinetic data obtained in such a manner can suffer from heat and mass transfer effects, from product inhibition, and from complications due to secondary reactions. Therefore, accurate kinetic data obtained at low conversions is not plentiful. It was because of this lack of good kinetic data that the Group VIII metals were studied so that a firm foundation of their catalytic behavior would exist. Supported metals were chosen not only because stable, high metal surface areas can be obtained, but also because few studies have been reported on synthesis reactions using supported metals. No H_2/CO synthesis studies have utilized supported metal catalysts characterized by selective chemisorption measurements to determine specific activities in the synthesis reaction. Once these metal catalysts were characterized, meaningful comparisons could finally be made not only between the different metals, but also between different catalyst systems employing the same metal component.

Product Distributions

The product distributions obtained over the various metals in this study are representative of data available from older studies. The characteristics noted by these past studies at higher pressures are also revealed by this study at 1 atm. Co and Fe were the first metals to be used as catalysts to produce hydrocarbon liquids and solids and their larger production of C_4^+ species is apparent. Ni is the commonly used methanation catalyst and its selectivity to CH_4 and other gaseous products is easily seen. Finally, Ru is unique in its ability to form high molecular weight paraffinic waxes at high pressure and low temperature, and even at atmospheric conditions Ru gives the highest average molecular weight distribution and the largest C_5^+ fraction. Therefore it is apparent that studies at atmospheric pressure can reveal differences in the catalytic behavior of these metals which also exist at higher pressures.

The expected behavior occurs for all the catalysts with regard to the H_2/CO feed ratio. As this ratio increases, thereby favoring hydrogenation reactions, the production of higher molecular weight species decreases and methane formation is favored. Also, olefin production decreases as indicated by the reduction in ethylene formation.

It is clear that a wide range of product distributions exist over the different Group VIII metals. Pd is a particularly selective methanation catalyst and both Pt and Ir produce only small amounts of C_2 species in addition to methane, the primary product. The product streams from all three catalysts have an average molecular weight lower than that of the product stream from a Ni catalyst. Ordering these metals according to the average molecular weight of their hydrocarbon products gives the following sequence: Ru > Fe > Co > Rh > Ni > Ir > Pt > Pd.

Specific Activities

The need for characterization of the Group VIII metals in the synthesis reaction according to their specific activities is indicated by Table 3. Fischer *et al.* (*13*) conducted the first study reported in the

TABLE 3
NEW DATA ON GROUP VIII METALS DIFFERS SIGNIFICANTLY FROM OLD LITERATURE

Methanation reaction		
Fischer *et al.* (*13*) (ranked by descending activity)	This study	
	Metal	(turnover no. @ 275°C) × 10^3
Ru	Ru	181
Ir	Fe	57
Rh	Ni	32
Ni	Co	20
Co	Rh	13
Os	Pd	12
Pt	Pt	2.7
Fe	Ir	1.8
Pd		

open literature which examined the catalytic behavior of the Group VIII metals in the methanation reaction. This is also the only other study which compares the behavior of *all* the Group VIII metals in a given synthesis reaction. These results were reported in 1925 (*13*) using unsupported metals and since techniques to measure metal surface areas had not yet been developed, the effect of differences in surface area could not be included in comparing conversion data. Rates were represented by the degree of methane conversion achieved at different temperatures using a given weight of metal catalyst. On this basis, Fischer (*13*) ranked the relative activities of the Group VIII metals as shown in Table 3. Some surprising differences are found when these metals are supported on Al_2O_3 and compared by their *specific activities*. On the right side of Table 3 the metals are ranked according to their turnover number. The order of activity changes significantly with the biggest changes involving the relative positions of Ir and Fe.

The differences in relative activity between this study and that of Fischer *et al.* (*13*) are most likely due to the rate normalization to the number of surface metal atoms in each catalyst. However, with supported metals, one must also be aware of metal particle size effects (*14*) and metal–support interactions that may change the catalytic behavior of the metal component. Some of these supported metals (Ru, Fe, Co, Ni) had average crystallite sizes that were quite large (>100 Å) and their catalytic behavior might be expected to parallel that of the unsupported metal. Other metals (Rh, Pt, Ir, Pd) were more highly dispersed and their average crystallite sizes were very small (≤ 40 Å). In these cases the latter two possibilities mentioned above are more likely to occur and will be discussed in another paper (*15*).

Both the rate of methanation and the rate of CO conversion do not vary widely over the supported Group VIII metals. Only two orders of magnitude separate the most active metal from the least active. By comparison, Sinfelt (*16*) has found activity differences greater than 7 orders of magnitude in the ethane hydrogenolysis reaction over these same metals.

These results are in general agreement with the more recent investigations concerning noble metals in $CO–H_2$ reactions. Karn *et al.* (*17*) found a 0.5% Ru/Al_2O_3 catalyst was quite active in the synthesis reaction and was selective toward methane formation at low pressures. Randhava and co-workers (*18*) also examined a 0.5% Ru/Al_2O_3 catalyst in a $CO–H_2$ reaction at atmospheric pressure where the CO concentration was exceedingly low (505–3450 ppm). Under these conditions only methane was formed. Their apparent activation energy was 37.2 kcal/mole. These authors report diffusion control at high conversions – an example of the problems faced with nondifferential reactors. These are the only two studies involving supported Ru and it is unfortunate that metal surface areas were not measured so that specific activities could be compared with this study. McKee (*19*) examined the behavior of unsupported Ru in the $CO–H_2$ reaction and found it to be more active than Rh, Ir, Pt or Pd. An activation energy of 9 kcal/mole was measured for the methanation reaction catalyzed by Ru. The only other recent study reported for supported Group VIII metals is that of Shultz *et al.* at the U.S. Bureau of Mines (*20*). They studied 0.5 wt% metal loadings on Al_2O_3 at high temperatures and 21.4 atm. They found the relative activities of the metals, based on conversion, decreased in the following order: $Ru > Rh > Os > Pt > Pd$. However, again in this study specific activities are unattainable since metal surface areas were not measured. At this pressure Ru showed the largest production of higher molecular weight hydrocarbons, with the other metals giving smaller amounts of C_2^+ species. The order of C_2^+

hydrocarbon production was Ru > Pt > Rh > Os > Pd.

Large quantities of data exist giving product distributions from Fe and Co although most of these results are reported as distillation fractions and not expressed as mole fractions (*1,2,6*). One of the more recent studies which does give mole fractions using Fe catalysts is that of Bienstock *et al.* (*21*) at the U. S. Bureau of Mines. Unfortunately, no kinetic data are available from which specific activities can be obtained.

The kinetic parameters will be discussed in detail elsewhere along with a kinetic model describing the methanation reaction on supported Group VIII metals (*8*).

CONCLUSIONS

For the first time, kinetic data have been obtained to allow comparison of the *specific activities* of supported Group VIII metals in the synthesis of hydrocarbons from H_2–CO mixtures. The kinetic behavior of these metals has been determined under well-defined experimental conditions and the methanation reaction has been described by a power rate law of the form

$$r_{CH_4} = Ae^{-E_m/RT} P_{H_2}{}^X P_{CO}{}^Y.$$

These data were deliberately obtained at low conversions to minimize heat and mass transfer problems thereby providing accurate rate data without the difficulties encountered at high conversions. When ranked on the basis of *specific activity*, significant changes occur in the ordering of the Group VIII metals for the methanation reaction compared to previous rankings that did not take into account variations in surface areas of different metal catalysts. The methanation reaction occurs readily over these metals and only 2 orders of magnitude separate the rates of the least active metal from the most active.

Product distributions at different H_2/CO feed ratios have been determined which give a good representation of a metal's selectivity toward methane formation. A large range of behavior was observed with Pd and Ru representing extreme examples. Pd gives essentially 100% methane; whereas Ru gives only 60 mole% methane with the balance composed of higher molecular weight hydrocarbons. Even at atmospheric pressure, the Group VIII metals display catalytic characteristics which correspond to their behavior at higher pressures as determined by past studies.

Finally, this study shows the necessity of characterizing metal catalysts so that metal surface areas are known and specific activities can be calculated. Only after rates are corrected for differences in metal surface areas can activities of different catalysts be compared meaningfully. The characterization of kinetic studies in this manner would not only provide more information about the catalyst itself but would allow the comparison of different catalysts reported in the literature.

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