

Interaction of Hydrogen and Carbon Monoxide on Platinum Group Metals

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Received March 3, 1967; revised April 18, 1967

The coadsorption and interaction of carbon monoxide and hydrogen on a series of unsupported noble metal catalysts was studied in the temperature range 100–200°C. In the case of platinum, CO was preferentially adsorbed from mixtures with H₂ and the resulting chemisorbed CO could not be completely removed by reduction and evacuation at 150°C. With rhodium and iridium there was some evidence of interaction between the two gases and small amounts of methane were detected at 200°C. Ruthenium and its alloys showed quite different behavior. Chemisorbed CO could be completely removed by reduction and evacuation at 150°C, the adsorption of H₂ was enhanced by the presence of CO, and methane was formed at an appreciable rate at temperatures above 100°C. On ruthenium, the activation energies for the reactions between CO and H₂ or D₂ were about 9 kcal/mole. The highly specific behavior of ruthenium in the methanation reaction is probably due to a lower affinity for CO than with the other noble metals.

INTRODUCTION

Although the metals of the platinum group are all generally active as hydrogenation-dehydrogenation catalysts, they differ considerably in their ability to catalyze the various reactions between carbon monoxide and hydrogen. Ruthenium has been known for many years to be an effective catalyst in the Fischer-Tropsch synthesis (1) and in the catalytic synthesis of methane from carbon monoxide and hydrogen (2), the reactions producing high molecular weight waxes at high pressures and large quantities of methane at atmospheric pressure. Recently (3), suspensions of ruthenium oxides in a hydrocarbon solvent have been shown to possess exceptionally high activity, the CO-H₂ reaction being measurable at 100°C. By contrast the other platinum metals are much inferior catalysts for these reactions. Rhodium and osmium have been shown to exhibit some activity at elevated temperatures, whereas platinum, palladium, and iridium are generally inert

for both the Fischer-Tropsch synthesis and the methanation reaction (4). Apart from these gross differences in behavior, no detailed study of the interaction and coadsorption of hydrogen and carbon monoxide on the noble metals seems to have been made at pressures below 1 atm, although the kinetics of the methanation reaction over nickel have been investigated repeatedly (5, 6). It seemed likely, therefore, that a study of this type over a series of noble metals under the same conditions would throw some light on the specific behavior of ruthenium in these reactions.

EXPERIMENTAL

Catalyst preparation. Noble metal powders were prepared by a method similar to that originally used by Adams to prepare platinum black (7). Chloroplatinic acid or chlorides of rhodium, iridium, or ruthenium were intimately mixed with a large excess of Reagent Grade sodium nitrate. The mixture was then fused in a silica dish at

500°C for 3 hr. The residue was cooled and washed thoroughly to remove nitrate and chloride and the resulting suspension of the metal oxide was reduced at room temperature by hydrogen bubbling through a fritted disc for 2 hr. Platinum oxide was reduced rapidly under these conditions whereas reduction was not complete with the other metal oxides. The product was allowed to settle, washed again, dried slowly in air under a heat lamp, and then ground and sieved through a 400-mesh nylon screen. Weighed quantities of each catalyst were sealed into the adsorption apparatus, evacuated, and then reduced with hydrogen at 200°C for 4–5 hr. Further evacuation overnight to a residual pressure of 1×10^{-6} torr was carried out before each catalytic run.

Alloy catalysts were similar to those used in previous investigations (8) and were prepared by reduction of mixed halide solutions of the noble metals with 5% sodium borohydride solution. The powders were reduced in flowing hydrogen for 3 hr at 300°C before being sealed into the apparatus. This treatment resulted in residual surface areas of 5–10 m²/g, whereas the pure metal powders made by the Adams method had surface areas in the range 20–50 m²/g.

Apparatus and procedure. The adsorption and catalytic experiments were carried out in a static volumetric apparatus to which was attached a mass spectrometer (Consolidated Electrodynamics Model 21-610) for direct measurement of the composition of the gas phase in contact with the catalyst. Catalyst samples weighing 1.0–1.3 g were sealed into the cylindrical adsorption cell, which had dimensions 25 × 13 mm diameter ID, and a total dead space volume when filled of about 2.2 ml. Attachments to the cell included an array of gas burettes for mixing and measuring the reactant gases, a wide-bore mercury manometer, and palladium diffusers for admitting hydrogen and deuterium to the system. The total volume of the gas space over the catalyst was generally 66.6 ml, excluding the dead space in the reactor. This gas space was connected to a sampler section and mo-

lecular flow leak attached to the ionization chamber of the mass spectrometer. Slugs of gas, amounting to no more than 1% of the total present over the catalyst, were removed from the system and analyzed at regular intervals. Adsorption isotherm measurements and BET surface area determinations were carried out in the usual way by measuring the pressure changes of the adsorbate at constant volume. The temperature of the catalyst, as measured by a thermocouple attached to the reactor, was generally kept constant to within $\pm 0.5^\circ$.

Materials. Metal and alloy powders were prepared from Reagent Grade salts as described above. Deuterium and hydrogen were purified by passage through a heated palladium thimble before being admitted into the vacuum system. The CP carbon monoxide used contained less than 0.2% CO₂ as impurity.

RESULTS

1. Platinum

Curve I in Fig. 1 illustrates the adsorption of carbon monoxide on a platinum sample at 150°C, the sample having been previously reduced and evacuated at this temperature for 16 hr. The surface area of the metal was 5.4 m²/g. The adsorption process was rather slow, although equilibrium was attained within 30 min at each point.

After the adsorption measurements the sample was evacuated at 150°C for 70 hr and the adsorption of carbon monoxide determined again (Curve II, Fig. 1). It is apparent that part (about 25%) of the adsorbed CO in Curve I was weakly bound and could be desorbed by pumping alone. A similar effect has been observed in the case of CO adsorption on Pd dispersed on alumina (9). After measurement of the adsorption isotherm II, the platinum sample was reduced in hydrogen for 5 hr at 150°C and then evacuated at this temperature for a further 16 hr and the adsorption of CO determined again (Curve III). Although the amount of CO adsorbed had been increased somewhat as a result of

the hydrogen treatment, over half the metal surface was still covered by the CO adsorbed initially. Carbon monoxide was thus more strongly chemisorbed on the platinum catalyst than hydrogen. It seems likely that a fraction of the adsorbed CO was more weakly held than the rest and could be slowly removed by hydrogen treatment.

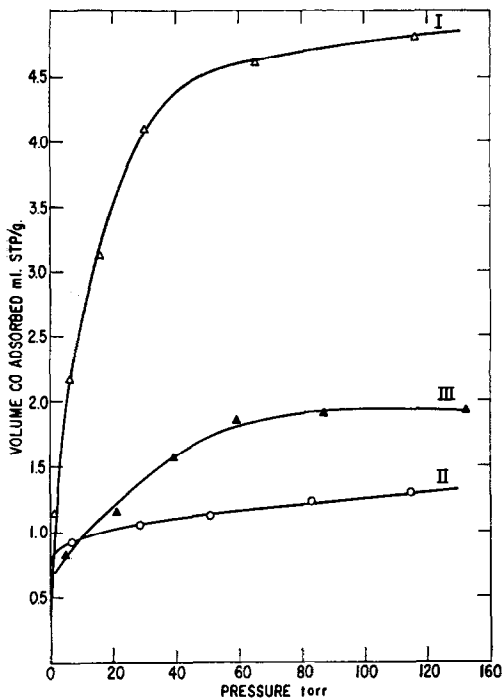


FIG. 1. Adsorption of CO on Pt at 150°C. I. Adsorption of CO on fresh sample. II. Subsequent adsorption of CO after evacuation at 150°C for 70 hr. III. Adsorption of CO after reduction in H₂ for 5 hr at 150°C followed by evacuation for 16 hr at 150°C.

The changes in composition of a H₂-CO mixture in contact with a platinum sample as a function of time are shown in Fig. 2. A fresh platinum sample was reduced in hydrogen at 150°C and then evacuated at this temperature for 3 hr. A mixture of 59 torr H₂ and 55 torr CO was then admitted and the total pressure and composition was followed as a function of time by mass spectrometric analysis. As shown in Fig. 2, although the total pressure fell only slightly, the CO content of the gas de-

creased monotonically while the H₂ pressure increased at first and then remained constant. No methane, CO₂, or water were detected in this case even at temperatures exceeding 200°C. As the surface of the

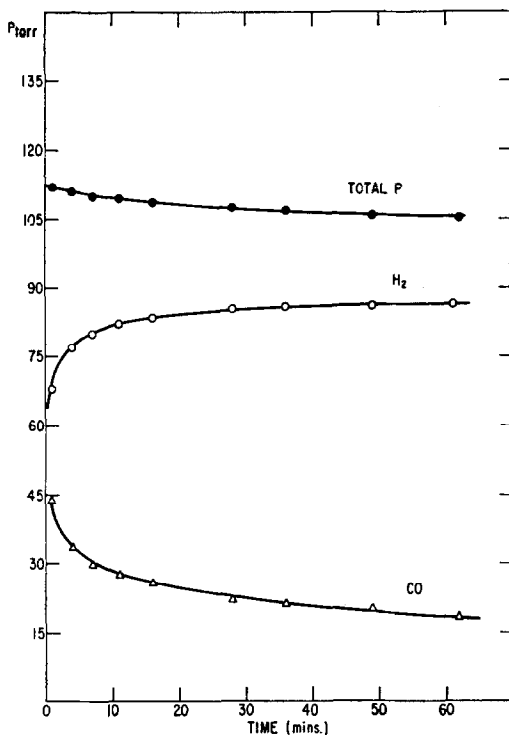


FIG. 2. Interaction of CO and H₂ over Pt at 150°C (1.25 g Pt, 59 torr H₂ + 55 torr CO initially).

metal certainly contained residual hydrogen, the results indicate that as CO was adsorbed hydrogen was displaced from the surface. The resulting chemisorbed CO could not be removed completely by reduction but only by oxidation to CO₂.

2. Rhodium

The behavior of rhodium was similar to that of platinum in that carbon monoxide was generally more strongly adsorbed than hydrogen and tended to displace the latter from the metal. A typical mass spectrometric run on a rhodium sample at 200°C is shown in Fig. 3. Initially CO was rapidly adsorbed and the hydrogen pressure in the gas rose. In this case, however, there was evidence that some interaction of

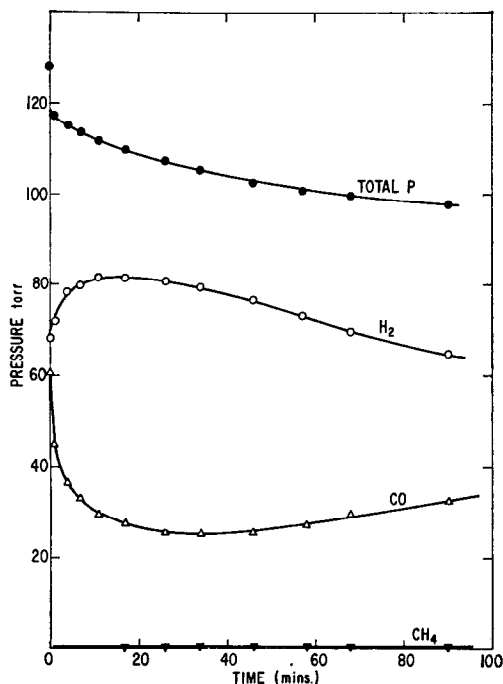


FIG. 3. Interaction of CO and H₂ over Rh at 200°C (1.22 g Rh, 67 torr H₂ + 61 torr CO initially).

the two gases took place as the hydrogen partial pressure increased to a maximum and then decreased slowly and small amounts of methane were detected in the gas phase.

The presence of chemisorbed oxygen or bulk oxide on the rhodium sample was found to give rise to preferential oxidation of carbon monoxide in CO-H₂ mixtures. Figure 4 shows the course of reaction of a CO-H₂ mixture at 150°C on an unreduced rhodium sample. Reduction of the surface was accompanied by a rapid decrease in hydrogen partial pressure and the simultaneous formation of carbon dioxide and small quantities of methane and water. The formation of CO₂ was always absent when the metal had been prereduced to remove oxide.

3. Iridium

Reduced iridium samples behaved in a similar manner to rhodium. Carbon monoxide was strongly adsorbed from CO-H₂ mixtures and small amounts of methane were formed at temperatures above 200°C.

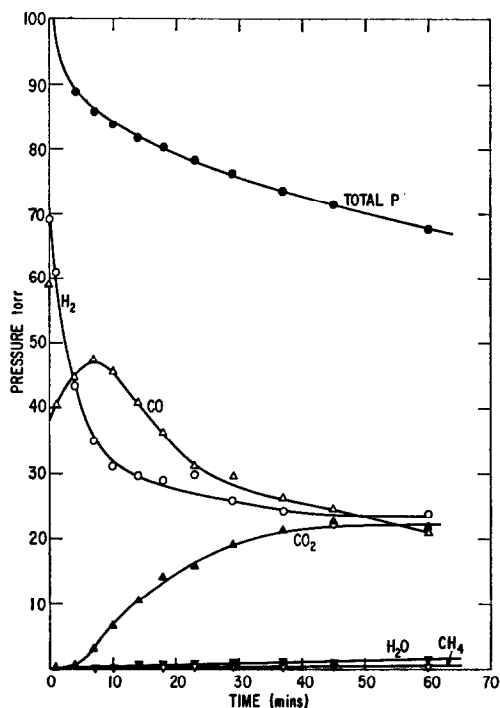


FIG. 4. Interaction of CO and H₂ over unreduced Rh at 150°C (1.22 g Rh, 69 torr H₂ + 43 torr CO initially).

4. Ruthenium

The behavior of ruthenium towards CO-H₂ mixtures was found to be unique among the noble metals. The adsorption isotherms of Fig. 5 were obtained with a metal sample having a surface area of 21.9 m²/g. Adsorption appeared to be more rapid than with platinum and equilibrium was attained within 10 min at each point. About 50% of the total CO adsorbed at 150°C (Curve I) could be desorbed by pumping at this temperature for 16 hr (Curve II). Complete removal of the chemisorbed CO was achieved by treatment with hydrogen followed by further evacuation and the initial adsorption isotherm for CO could then be reproduced very closely. These results suggest that CO is much less strongly chemisorbed on ruthenium than on platinum, rhodium, or iridium.

Carbon monoxide chemisorbed on ruthenium was not only readily desorbed by hydrogen, but this metal catalyzed chemical reaction between these gases at temper-

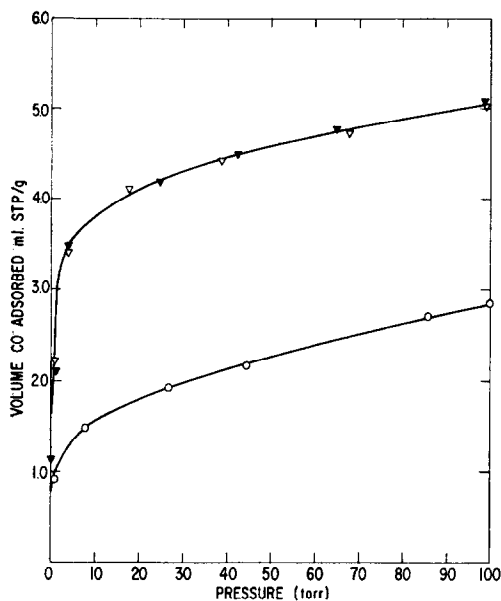


Fig. 5. Adsorption of CO on Ru at 150°C: ∇ , adsorption of CO on fresh sample; \circ , subsequent adsorption of CO after evacuation at 150°C for 16 hr; \blacktriangledown , adsorption of CO after reduction in H_2 for 5 hr at 150°C followed by evacuation for 16 hr at 150°C.

atures above 100°C. The course of this reaction over a ruthenium sample at 150°C is shown in Fig. 6. In contrast to the behavior of the other noble metals, the partial pressures of both reactants in the gas phase decreased rapidly and methane and water appeared as products. No carbon dioxide or other products were observed in this case.

The ability to catalyze the methanation reaction was found also for binary noble metal alloys containing ruthenium. Figure 7 shows the course of the reaction at 150°C for an alloy powder of composition Pt-28.6 wt % Ru. In general the initial rate of methane formation over a noble metal alloy was found to decrease regularly with decreasing ruthenium content of the catalyst. Figure 8 shows changes in the CH_4/CO ratio in the gas phase at 300°C for a series of sintered ruthenium-palladium catalysts of low surface areas. Palladium itself was found to be completely inactive for this reaction.

The conclusion that chemisorbed hydrogen and carbon monoxide interact in the

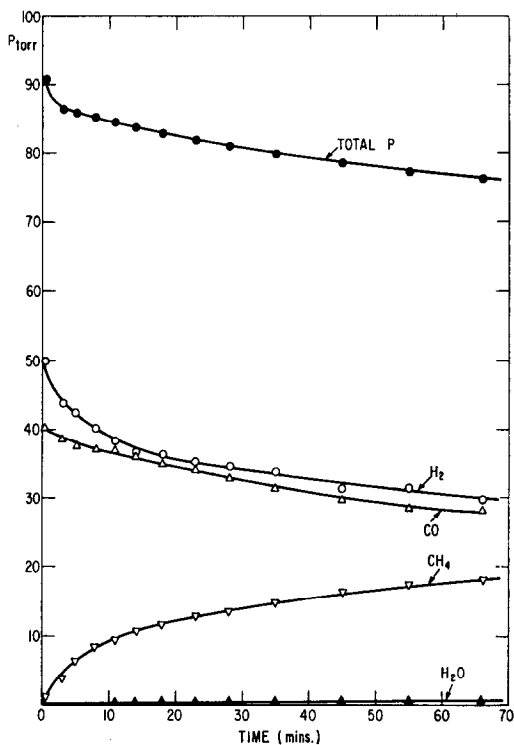


Fig. 6. Interaction of CO and H_2 over Ru at 150°C (1.25 g Ru, 65 torr H_2 + 55 torr CO initially).

adsorbed layer on ruthenium surfaces is reinforced by volumetric measurements of the amounts of the two gases chemisorbed separately and in the presence of each other. Table 1 shows the volume of each gas adsorbed separately on a ruthenium

TABLE I
ADSORPTION OF H_2 AND CO ON RUTHENIUM

Temp. (°C)	Surface area, 24.5 m ² /g		V_{CO}/V_{H_2}
	H_2 adsorbed (ml STP/g)	CO adsorbed (ml STP/g)	
102°	1.185	2.725	2.3
154°	1.119	1.965	1.7

sample at two different temperatures after 5 min contact time. The ratio V_{CO}/V_{H_2} was close to 2, suggesting that most of the CO was present in the linear form on the surface. The volumes of the individual gases adsorbed from a 50:50 mixture on the same catalyst after 5 min at a series of temperatures are shown in Table 2. In this case,

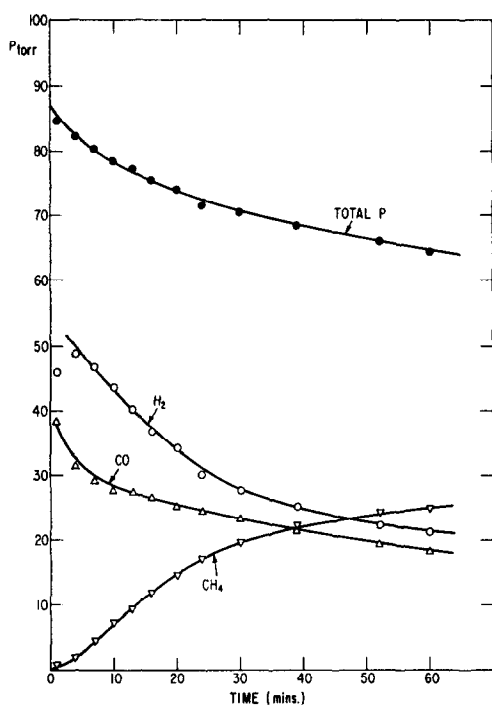


FIG. 7. Interaction of CO and H₂ over a Pt-23.6 wt % Ru alloy at 150°C (1.25 g catalyst, 60 torr H₂ + 52 torr CO initially).

the volume of H₂ adsorbed has been increased, and that of CO decreased, whereas the ratios of the gases in the adsorbed phase is closer to unity. The rate and extent of hydrogen adsorption was thus increased in the presence of CO, suggesting interaction in the surface layer. Such an effect was not found with the other noble metals.

The kinetics of the methanation reaction on ruthenium were studied in more detail by measurements of the effect of changes in reactant mixture composition on reaction rate. Figure 9 is a plot of the log of the

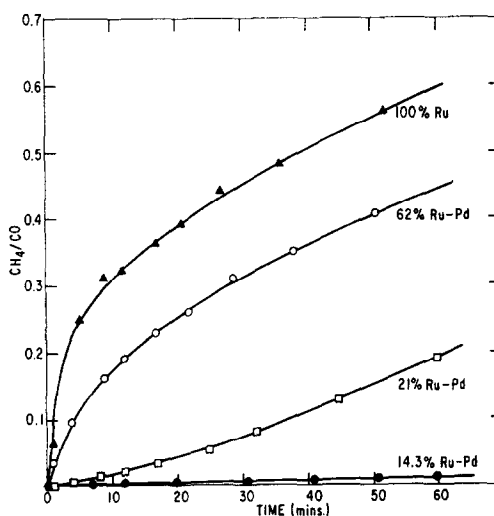


FIG. 8. CO + H₂ reaction on sintered Ru-Pd alloys at 300°C (1 g catalyst, 60 torr CO + 60 torr H₂ initially).

initial rate of formation of methane at 150°C as a function of the log of the hydrogen partial pressure in the original gas mixture, the partial pressure of CO being kept constant. The slope of this plot gives the apparent order with respect to hydrogen concentration, which was found to be 1.94 under the chosen experimental conditions, using the method of least squares. The effect of CO concentration on the initial rate is shown in Fig. 10, at constant hydrogen partial pressure. In spite of the considerable scatter of the data no strong dependence was found and the initial rate was essentially zero order with respect to CO concentration.

Small amounts of carbon dioxide were detected in the reaction products in experiments with high initial carbon monox-

TABLE 2
ADSORPTION OF H₂ AND CO FROM A 50:50 MIXTURE ON RUTHENIUM

Temp. (°C)	Surface area, 24.5 m ² /g			
	H ₂ adsorbed (ml STP/g)	CO adsorbed (ml STP/g)	Total vol. (ml STP/g)	V _{CO} /V _{H₂}
45°	2.302	1.677	3.979	0.73
69°	2.127	1.745	3.872	0.82
80°	1.983	2.005	3.988	1.01
102°	2.166	1.767	3.933	0.82
124°	1.835	1.758	3.593	0.96
154°	2.080	1.495	3.575	0.72

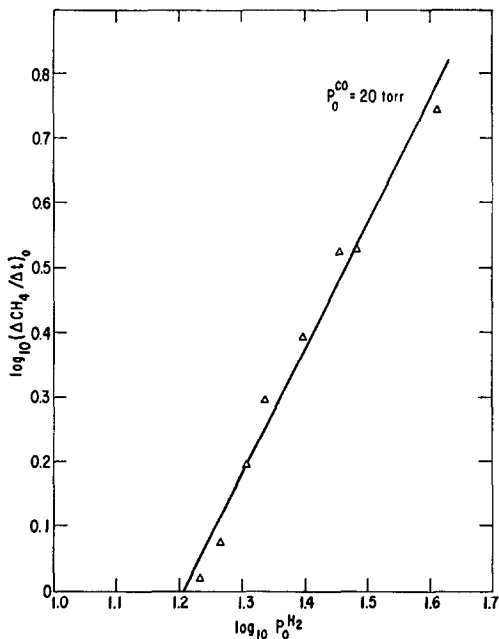


FIG. 9. Initial rate of CH_4 formation on Ru as a function of initial H_2 pressure; 150°C .

ide pressures. This CO_2 , which never amounted to more than 5% of the total gas mixture, was presumably formed as a result of the equilibrium

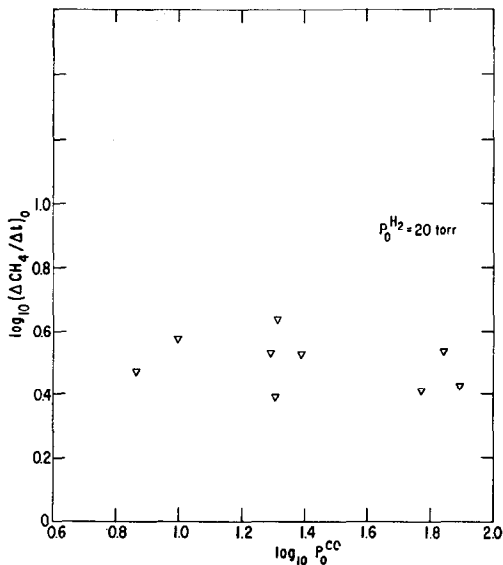
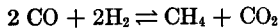


FIG. 10. Initial rate of CH_4 formation on Ru at 150°C as a function of initial CO pressure.

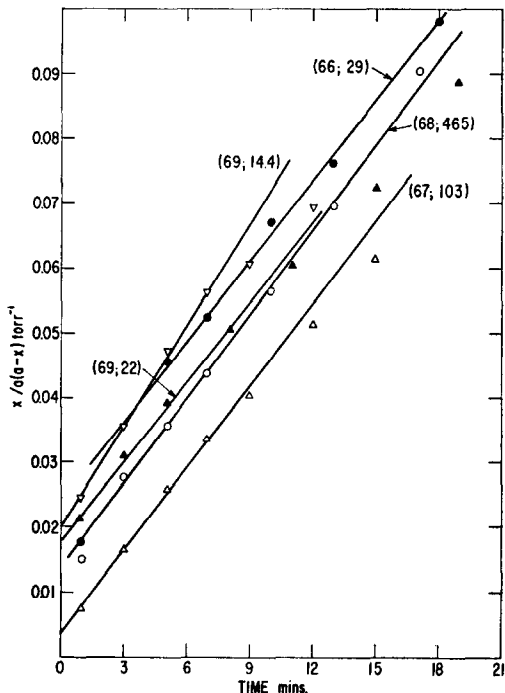


FIG. 11. Kinetic data for $\text{CO} + \text{H}_2$ reaction on Ru at 150°C ; x , decrease in H_2 pressure after time t ; a , initial H_2 pressure. Initial composition of gas mixture ($\text{H}_2:\text{CO}$) shown in parentheses.

If the kinetics of the methanation reaction follow a relation of the type: $d[\text{CH}_4]/dt = k P_{\text{H}_2}^2 P_{\text{CO}}^0$ the rate of decrease in hydrogen partial pressure during the course of the reaction should obey the relation: $dx/dt = k'(a-x)^2$ or, in integrated form, $k't = x/(a-x)a$, where x is the decrease in hydrogen pressure after time t and a is the initial pressure of hydrogen. This simple law was found to fit the experimental results over a wide range of initial gas mixture compositions, the value of the rate constant k' being essentially independent of CO concentration. Typical second order plots of this type are shown in Fig. 11 for a series of runs at 150°C . The initial composition of the gas mixture is indicated in parentheses. On admission of the gas mixture to the evacuated catalyst an initial rapid decrease in pressure of both reactants occurred as a result of chemisorption on the metal surface. The amount of each component initially adsorbed depends on its concentration in the gas phase and hence

the plots of Fig. 11 do not generally pass through the origin. Apart from this initial pressure change, subsequent changes in the partial pressure of hydrogen followed the second order law.

This rate equation is of similar form to that reported recently for 0.5% ruthenium supported on alumina at 220°C and 21.4 atm pressure (10). Under these conditions the differential rate, r , was found empirically to be

$$r = kP_{H_2}^{1.33}P_{CO}^{-0.13}$$

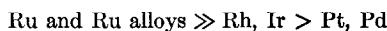
although in this case appreciable amounts of higher molecular weight hydrocarbons were found in the products.

In order to estimate the activation energy of the methanation reaction on ruthenium, measurements of initial rate of methane formation were made at a series of temperatures between 25° and 150°C using a constant initial composition of the reactant mixture. The resulting Arrhenius plot for a typical sample of 24.5 m²/g

surface area is shown in Fig. 12. Also included are measurements of the initial rate of formation of CD₄ from D₂-CO mixtures under the same conditions. The reaction appears to show a kinetic isotope effect, the ratio of the rates CH₄/CD₄ being about 2.2 in this temperature range. Both reactions, however, proceed with similar activation energies of 9 ± 1 kcal/mole. A similar activation energy has been reported for the methanation reaction over supported nickel catalysts (6).

DISCUSSION

The order of activity of the noble metals for the methanation reaction between carbon monoxide and hydrogen has been found to be



This conclusion is confirmed by early work on the related Fischer-Tropsch reaction (4) in which ruthenium was found to be very active, giving rise to high molecular weight waxes at high pressures and mostly methane below atmospheric pressure. By contrast, palladium and platinum were found to have only slight activity both in the Fischer-Tropsch synthesis and in the methanation reaction. It has been found that nickel is also very active as a methanation catalyst (11).

It was suggested by Fischer and Tropsch (12) that the tendency of metals to give methane was related directly to the affinity of the metal for hydrogen. However, recent data on the heats of adsorption of hydrogen on the noble metals (13) does not indicate any significant differences in the affinity of Ru, Pt, and Rh for this gas. In the light of the present results, it seems more likely that the observed differences in the behavior of the platinoid metals is related to the relative coverages of the two adsorbates on the catalysts during the reaction. As we have found, the extent of hydrogen adsorption on ruthenium is increased in the presence of carbon monoxide, suggesting that interaction is taking place on the surface of the metal. On platinum, on the other hand, CO is strongly chemi-

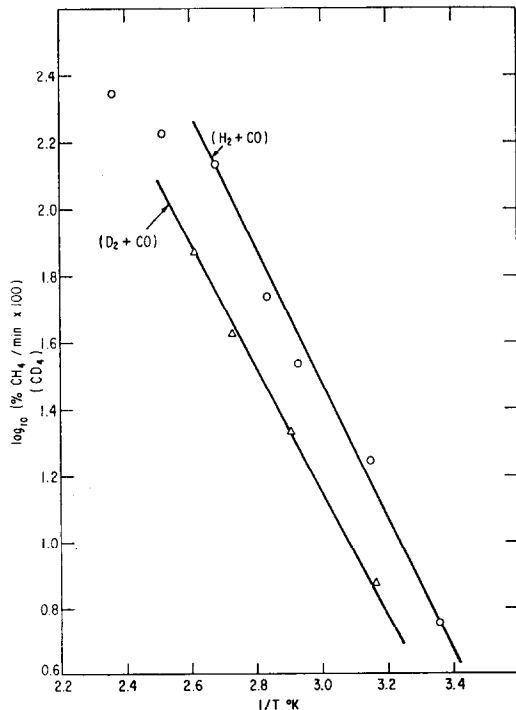
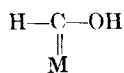


FIG. 12. Arrhenius plots for CO + H₂ and CO + D₂ reactions on Ru (1.25 g Ru, 60 torr H₂ + 60 torr CO initially).

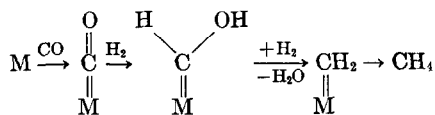
sorbed and displaces hydrogen from the adsorbed layer.

Kemball (14) has recently argued that the methanation reaction is unlikely to be an important step in the synthesis as the formation of ethane from methane is thermodynamically unfavorable at temperatures around 200°C. However, although it is possible that the mechanisms of the two reactions are different, both methanation and synthesis occur readily over ruthenium, the yield of higher molecular weight products increasing with pressure and with decrease in the usage ratio H_2/CO in the feed (10). The fact that methane was the only product detected at the low pressures used in the present work may be a result of a small surface coverage of C_1 intermediates so that chain growth does not occur under these conditions.

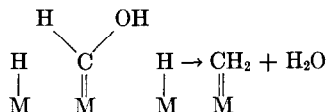
There is still no general agreement on the nature of the intermediates present on the catalyst surface during the methanation reaction and the Fischer-Tropsch synthesis. The early suggestion that surface carbides were formed which hydrogenated to methylene radicals has been discredited as carbided catalysts are not usually very active and this scheme fails to account for the formation of the oxygenated compounds which are typical products of the Fischer-Tropsch synthesis. Craxford and Rideal, however, observed that ortho-para hydrogen conversion does not take place during the Fischer-Tropsch synthesis but it does occur during the formation of methane on cobalt catalysts (15). This result indicates that chemisorbed hydrogen atoms are present on the catalyst surface during reaction. It is now generally believed that an intermediate of the type



is formed between adsorbed CO and H_2 on active catalysts. Such a radical could lose water to give $CH_2=M$ followed by further hydrogenation to methane as envisaged by Hamai (16)



It is possible that the slow step may involve the addition of two hydrogen atoms to the oxygenated intermediate



although this would tend to give a rate proportional to P_{H_2} rather than to $P_{H_2}^2$. Deuterium atoms being more strongly chemisorbed on the metal than hydrogen, the rate of the D_2 -CO would be expected to be slower than the methanation.

It is interesting that from the results of studies on the exchange reaction between methane and deuterium it has been found that ruthenium has a much more pronounced tendency to promote multiple exchange than does platinum (17). As multiple exchange of methane involves the intermediate formation of methylene radicals, $CH_2=M$, on the metal surface, it seems feasible that this tendency is related to the observed activity of ruthenium in the methanation reaction. Nickel also is very active as a methanation catalyst (11) and also promotes the multiple exchange process between methane and deuterium (18). It is to be expected that information on the relative heats of adsorption of H_2 and CO on the noble metals would shed further light on the unique behavior of ruthenium in the methanation reaction.

ACKNOWLEDGMENTS

The author wishes to thank S. Gilman and L. W. Niedrach for many helpful discussions during the course of this investigation.

This work includes parts of the program under contracts DA-44-009-AMC-479(T) and DA-44-009-ENG-4909, ARPA Order No. 247 with the U. S. Army Engineer Research and Development Laboratories, Ft. Belvoir, Virginia, to develop a technology which will facilitate the design and fabrication of practical military fuel cell power plants for operation on ambient air and hydrocarbon fuels.

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