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Mass-Spectrometric Measurements of Enhanced Methanation Activity over Cobalt and Nickel Foils[1]

ROBERT L. PALMER AND DAVID A. VROOM

IRT Corporation, P. O. Box 80817, San Diego, California 92138

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The kinetics of methane synthesis from H_2/CO mixtures has been studied over Ni, Co, and Fe foils. The gas composition of a flowing reaction cell was analyzed using a differentially pumped, modulated mass spectrometer. Ni and Co foils that have been previously oxidized and then reduced in H_2 at 525–600°K show a surprisingly high and specific catalytic activity for methane formation. No unusual activity was observed over iron for any of the surface treatments tried here. Evidence is also presented to support a mechanism for this highly specific reaction involving a labile surface carbon atom intermediate.

INTRODUCTION

Renewed interest in the industrial-scale synthesis of methane and other hydrocarbons has stimulated a number of recent studies of the catalytic conversion of CO/H_2 mixtures (*1–6*). The application of several new experimental methods to this problem promises to expand greatly our knowledge of methanation catalysis and, hopefully, to lead to development of catalyst materials with improved selectivity and poison resistance. We have relied primarily on molecular beam techniques to investigate the mechanisms and kinetics of simple catalytic reactions (*7–9*) and have recently turned our attention to the reaction of CO with H_2 over the group VIII metals.

Using a differentially pumped line-of-sight modulated mass spectrometer system, we have investigated the conditions for maximum catalytic methanation activity over the group VIII metals. This paper describes the surprisingly high activities observed on specially treated high-purity (MRC Marz grade) cobalt and nickel foils, whereas iron and other group VIII metals display much lower activities, in the range usually reported for supported catalysts.

EXPERIMENTAL METHODS

In order to survey more readily the activity of various catalytic materials and operating regimes, we have modified our molecular beam vacuum apparatus slightly as shown in Fig. 1. In this arrangement, a catalytic reaction cell replaces the usual beam source, and the mass spectrometer detector is positioned directly in the line-of-sight path defined by the molecular beam apertures. Thus, we very readily achieve a differentially pumped line-of-sight modulated mass spectrometer system that can be used to sample the composition of the gas which flows through a small orifice (0.010–0.0020 in. in diameter) in the wall

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of the reactor cell. Indeed, accurate kinetic data can be obtained by this arrangement if the conditions within the cell are such that the reaction is kinetically limited and the gas composition is relatively uniform. These requirements are easily satisfied at low total conversions and for pressures within the cell in the 1.0-Torr range or below.

The data reported here were obtained using a reaction cell constructed as shown in exploded view in Fig. 1. The catalyst foil with the dimensions 0.5 × 4.5 × 0.005 in. is formed into a closed sprial and is inserted tightly into a $1\frac{3}{8}$-in.-long inert metal (tantalum) heating tube as indicated in Fig. 1. Tantalum wafers are positioned against the open ends of the catalyst foil spiral, and, finally, machined stainless steel caps are inserted over the ends of the tantalum tube. These end caps fit into water-cooled stainless steel rods that are part of the normal beam source apparatus. The reaction cell is resistively heated by passing current through the cell via the end caps which remain relatively cool by virtue of the water-cooled support rods.

In operation, various gases and gas mixtures can be made to flow through the cell via one of the end caps, through a small hole in the center of the tantalum wafer, and into the catalyst foil region. After flowing around the foil spiral, the gas effuses out a small hole (0.010–0.020 in. in diameter) drilled through the outer tantalum tube and the outer wall of the catalyst foil. The other end cap leads to a capacitance-type manometer (Validyne Model DP7), and normally no gas flows in this section of the line. The temperature of the cell is monitored by means of a thermocouple attached to the outside wall of the cell and, above 1000°K, with an optical pyrometer by looking into the cell via the line-of-sight path through the mass spectrometer. The temperature uniformity of the cell appears to be adequate for the present experiments, although some degree of temperature variation undoubtedly exists within the cell. However, the thermocouple and pyrometer temperatures were within 20°K at 1000°K for various positions of the thermocouple, and the temperature uniformity was undoubtedly enhanced by the high thermal conductivity of the hydrogen inside the cell during the methanation studies.

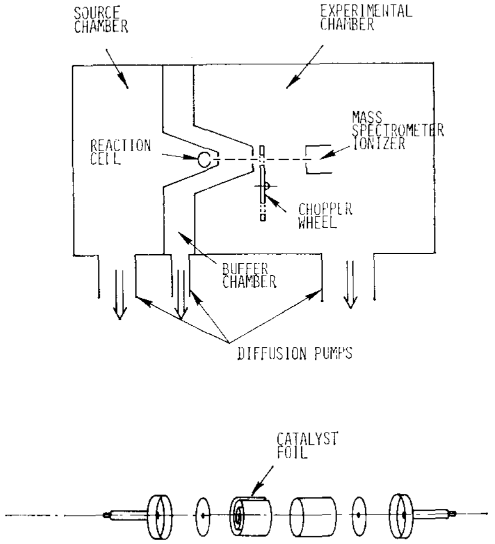

Fig. 1. Schematic of differentially pumped modulated mass spectrometer and exploded view of reaction cell construction.

To clean the foils, the cell was first heated to ~1400°K in hydrogen at a pressure of a few Torr for 15–20 min in order to bring impurities such as carbon and sulfur to the surface. The cell temperature was then lowered to 800–900°K and was exposed alternately to oxygen, then hydrogen. The oxygen exposure was kept brief, about 15 sec at 1–5 Torr. Removal of the surface oxide was observed during hydrogen exposure by monitoring the $m/e = 18$ (H_2O) peak with the mass spectrometer. Exposure to oxygen was repeated after disappearance of the H_2O signal. After four of these cycles the catalyst surface was assumed to have reached some steady-state cleanliness. This reduced foil was very active for H_2/D_2 exchange, being similar in activity to single crystal films that have been studied previously *(10)*.

The gases (H_2 and CO) used in this work were ultrahigh purity (<1 ppm) and were connected by stainless steel lines that were cleaned by baking under vacuum. The impurity level in the gases was immeasurable with the mass spectrometer, indicating less than 10 ppm contamination from species such as H_2O, CO_2, N_2, CH_4, etc. Although the state of the surface could not be monitored *in situ*, the cleaned foils were examined by AES after removal from the reaction cell at the end of the experiments. The only observable contaminants on the catalytically active foils were low levels (1–3%) of carbon and oxygen, presumably resulting from the catalytic decomposition of CO and/or incomplete reduction of the surface oxide.

RESULTS

Using the above experimental arrangement, the catalytic production of methane from H_2/CO mixtures was observed over Ni, Co, and Fe foils. The yields were found to be strongly effected by both the H_2/CO ratio and also the history of the catalyst foils. With Fe, the highest activity was achieved with the cleaning procedure consisting of alternate oxygen/hydrogen exposures as described above and was comparable to the activities of Ni and Co prepared in the same manner. However, it was found that the activities of Ni and Co could be significantly enhanced by doing

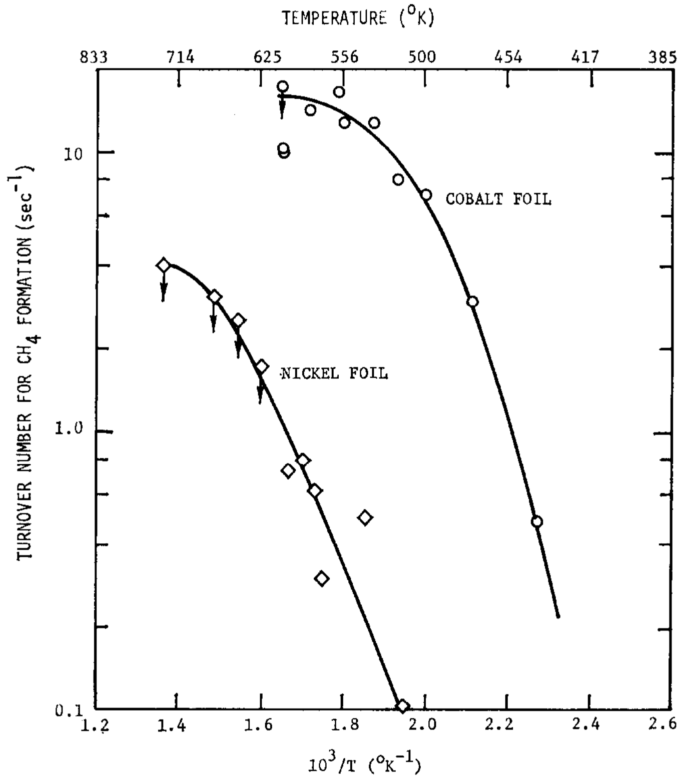

FIG. 2. Arrhenius plots of mass spectrometer (CH_3^+) data over activated Ni and Co foils at an H_2/CO ratio of 40:1 and a total pressure of 2 Torr. Turnover numbers based on geometrical foil area.

the final reduction in hydrogen at 525–600°K rather than at 800–900°K. Ni foils prepared in this manner were more than 10 times as active and Co foils were more than 100 times as active as the higher temperature-reduced foils. No procedure could be found that increased the activity of the fully reduced Fe foils, however.

Because of the much higher activities of the incompletely reduced Ni and Co foils, most of our work was directed toward characterizing and determining the catalytic behavior of these surfaces. All of the results discussed below were obtained on these incompletely reduced foils, i.e., reduced in H_2 at 525–600°K, unless otherwise stated.

Surface contamination does not appear to explain the behavior of these catalytic foils. Sulfur and surface contaminants other than oxygen and carbon were not found in subsequent AES analysis of the surface, and, moreover, the absolute activities of the most active Co and Ni surfaces were unusually high (see Figs. 2 and 3). Turnover numbers calculated for the production of methane, where

$$N = CH_4 \text{ molecules}/(\text{metal site} \cdot \text{sec}),$$

were based on 10^{15} metal sites/cm^2 and the geometrical area of the catalyst foil. Although some roughening of the catalyst foil occurred during oxygen treatment, this probably increases the surface area by about a factor of 2x, not enough to account for the much larger increases in the turnover rates of both Ni and Co.

In addition to CH_4, which was detected as CH_3^+, H_2O was also observed mass-spectrometrically during methanation in quantities comparable with methane. CO_2 in small amounts could also be detected as a reaction product, but its rate was very slight in excess hydrogen where high

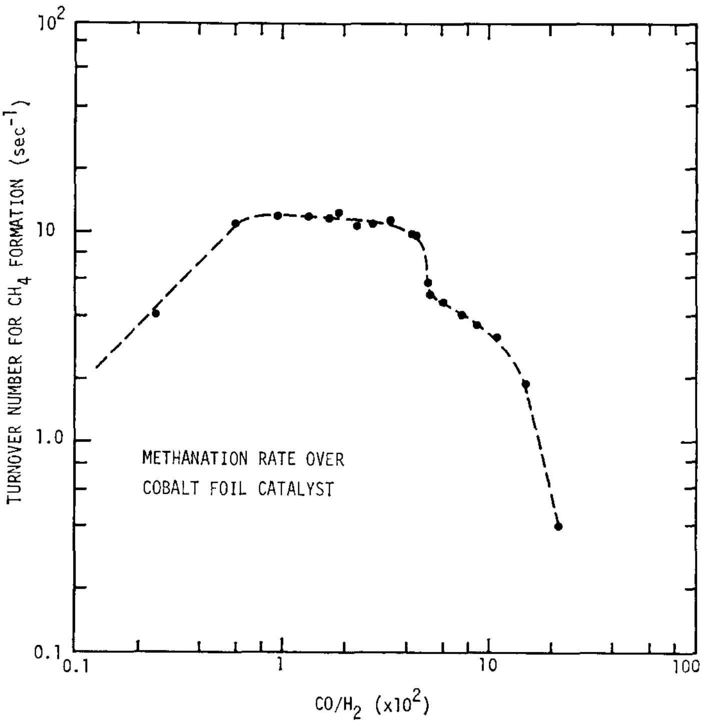

FIG. 3. Methanation rate versus CO/H_2 ratio over activated Co foil at 550°K and total pressure of 3 Torr. Turnover numbers based on geometrical foil area.

methanation rates were observed. Other higher hydrocarbon products such as ethylene, ethane, etc., as well as alcohols, were looked for but not observed. On activated Ni and Co foils under reaction conditions where high methanation rates were observed, hydrocarbons other than methane, if any, must constitute substantially less than 1% of the reaction product.

Temperature Dependence

Data for the temperature dependence of the catalytic activities of Ni and Co foils reduced in hydrogen at 525-600°K after oxygen exposure at 800°K are given in Fig. 2. For these measurements the H_2/CO ratio was maintained at 40:1 at a total pressure inside the cell of 2 Torr. With a 0.020-in. orifice in the cell the flow rate is such that the gas mixture spends, on the average, 3×10^{-2} sec within the catalyst cell volume (2.3 cm^3).

The temperature dependence data were reversible for temperatures below 600°K. At higher temperatures the data points represent initial rates which slowly decayed to much lower steady-state values. This decay was irreversible with temperature, but the initial activities of both Ni and Co foils could be restored by exposure to oxygen, followed by reduction at 525–600°K. At temperatures above 600°K graphite formation becomes rapid on these surfaces, and there is evidence that the surface becomes deactivated at these temperatures as the result of formation of a stable graphite overlayer (*4*, *6*). The slope of the temperature dependence data in Fig. 2 indicates an activation energy of 17 ± 2 kcal/mol for the rate-limiting step on both foils.

H_2/CO Dependence

Figure 3 presents methanation rate data at 550°K over Co foil, prepared as in Fig. 2, as a function of the H_2/CO ratio. The rate is seen to be approximately first order in CO concentration up to 0.6% CO, then approximately zero order to 4% CO. The data below 4% were stable and reversible. Above 4% CO concentration, there was a rapid irreversible decrease in the rate. The data points in Fig. 2 from 4 to 20% CO are final rather than initial values and are quasi-steady-state values obtained after operating for about 1 hr at each point. When all of the CO was removed from the gas flow after the last data point at 20% CO was taken, CH_4 formation still continued at about the same rate, with only H_2 gas flowing through the cell. Replacement of the H_2/CO mixture with O_2 in the cell at 550°K produced strong CO and CO_2 signals in the mass spectrometer that persisted for a long period. These results indicate that the catalyst foil had retained a large amount of carbon in some form during operation at CO concentrations greater than 4%. The full catalytic activity of the Co foil could be restored by repeated oxidation–reduction (O_2–H_2) cycles to remove all carbon, with the final reduction cycle carried out at 525–600°K.

Surface Conditions

Our inability, in this experiment, to investigate directly the catalyst surface composition and structure *in situ*, e.g., via LEED, AES, and photoelectron spectroscopy, leaves us with only indirect inferences regarding the catalyst surface conditions during this experiment. Our best evidence is the absence of sulfur and contaminants other than carbon and oxygen on the foil surface after removal from the reaction cell when examined by AES. The surface layers were sputtered away using 2 keV of Ar^+ while scanning the Auger spectrum. After removal of the initial adlayers, the near-surface composition showed only carbon and oxygen to a depth of ~100 Å. Oxygen exposure at elevated temperatures presumably removed most of the near-surface sulfur, a ubiquitous impurity in transition metals. The oxidation–reduction cycles also increase the surface areas somewhat through roughening, as evidenced by the matte finish the shiny foils acquire during this procedure. Thus, a somewhat higher activity after oxidation–reduction cycles is not surprising. However, the catalytic activity of the Fe foil was not particularly affected by this treatment and was down by more than an order of magnitude from Ni and two orders less than Co. The measured activity of the iron foil is in the range reported by Vannice and Garten (*2*) ($N < 0.1$), so that the activities of Ni and especially Co appear indeed to be anomalously high. The fact that reduction by exposure to hydrogen at higher temperatures, above 800°K, drastically lowers the activities of Co and Ni down to levels comparable to Fe also suggest that oxygen plays an important catalytic function aside from its role in the removal of surface contaminants. Auger analysis of the highly active foils reveals about 2% oxygen, even after removal of the first few surface layers by ion sputtering. Although the presence of low levels of oxygen on these surfaces is not surprising, even without deliberate oxygen exposure, this result is at least suggestive that subsurface oxygen plays a role in enhancing the catalytic activities of Ni and Co. Carbon was the only other detectable surface impurity by Auger analysis.

Boudouard Reaction

Measurements of the kinetics of the related Boudouard (disproportionation reaction),

$$2CO(g) \rightarrow C(s) + CO_2(g),$$

give an additional important clue to the mechanism of the methanation reaction in this work. The rate of the Boudouard reaction was measured with our apparatus in both the presence and absence of H_2. While CO_2 was a minor constituent under conditions of high methanation activity, as in Fig. 2, the removal of H_2 from the gas flow resulted in a high initial rate of CO_2 formation which was, within the limits of experimental uncertainty, equal to the methanation rate in the presence of H_2 over both Ni and Co foils. This result suggests that the direct disproportionation of CO at the surface is the rate-limiting step in the methanation reaction.

DISCUSSION

Several studies of catalytic methanation have recently been reported that give important new information about the mechanism of this reaction (*4–6*). Significantly, these studies are in agreement with regard to most of the salient features, although different catalytic surfaces and somewhat different operating conditions were employed. Sexton and Somorjai have recently reported a study of the hydrogenation of CO and CO_2 over polycrystalline rhodium (*6*). They report that pretreatment of the Rh foils significantly affects the product distributions for both reactions. Pretreatment with C_2H_2 deposits surface carbon and promotes chain growth, whereas pretreatment with oxygen dissolves oxygen in the bulk and increases the methanation rate by a factor of 5x over the clean surface. This last result is analogous to the present results on Co and Ni and suggests that subsurface oxygen may be an important factor in the catalytic activities of other transition metals.

Araki and Ponec have also published the results of a study of methanation on Ni and Ni/Cu alloy films prepared under ultrahigh vacuum conditions (*5*). This careful and thorough investigation also presents significant new data regarding both the kinetics and the catalytic methanation mechanism. Isotopic labeling experiments in their work point convincingly to a surface carbide as the principal intermediate in the methanation reaction. This same conclusion was also reached by Wentrcek *et al.* in their recently published work using alumina-supported Ni (*4*). In both of these studies the rate of dissociative adsorption of CO in the absence of hydrogen is fully rapid enough to account for the observed rate of methanation in the presence of hydrogen.

Most of the results of the present work also support the conclusions of the studies cited above. In particular, the rate of disproportionation of CO matches the methanation rate in the presence of hydrogen in our work as well. Wentrcek *et al.* give an activation energy for the removal of surface carbon from alumina-supported Ni of 17.6 kcal/mol. This result can be compared with the data in Fig. 2 in our work which were obtained in the regime under which the kinetics were zero order in CO pressure, so that removal of surface carbon is rate limiting here also. The present data give an apparent activation energy of 17 ± 2 kcal for this process, excellent agreement that may be coincidental considering the variety of catalytic materials involved. Other values in this range have also been obtained on supported Ni catalysts. Fontaine (11) gives a value of 18 ± 1 kcal/mol with $H_2/CO = 50$. Bousquet and Teichner obtained a value of 20 kcal/mol for the temperature coefficient of the methanation reaction in their study (*12*), and Luengo *et al.* report values of 15.7 and 12.4 kcal/mol over reduced Ni and Co powders, respectively (*13*). These results fall significantly below many published results that are in the 28–31 kcal/mol range (*3*). However, there are two important factors to consider when comparing these temperature kinetic data. First, there are at least two distinct reaction regimes to consider; namely, when CO dissociative adsorption is rate limiting or when removal of surface carbon by hydrogen is limiting. One would expect these two regimes to have distinctly different energies of activation. Second, the buildup of surface carbon significantly lowers the methanation rates on Ni, Co, Rh, and, presumably, on other group VIII transition metal catalysts, so that one would expect concomitant changes in the associated activation energies as well. With the partially reduced foils used in this study, high H_2/CO (>20) was required to prevent the buildup of surface carbon. Although this value may vary from catalyst to catalyst, the conditions in most studies of methanation are such to suggest a significant buildup of carbon in the catalyst. For example, Dalla Betta *et al.* have reported that the activities of Ni and Ru decrease sharply as the result of carbon buildup during reaction with H_2/CO (≤ 6) (*1*).

SUMMARY

Although the present study is somewhat limited in scope, it provides important additional information regarding the kinetics and mechanism of catalytic methanation. The experimental technique is novel and provides fast and reliable kinetic data using line-of-sight mass spectrometry. The experiments have demonstrated dramatic enhancements of the catalytic methanation activities of Ni and Co that appear to be associated with the incorporation of oxygen into the near-surface region of these metals by exposure to the gas at elevated temperatures. Rate enhancements of over 10× and 100×, respectively, are observed with incomplete reduction of the oxidized surfaces compared with the "clean" surface. The results are similar to those obtained by Sexton and Somorjai who obtained a fivefold increase in the activity of Rh with oxygen treatment. Thus, oxygen appears to be a favorable factor in promoting the catalytic activities of certain transition metals and may be of much wider significance. However, with Fe, oxygen lowers the methanation activity. There is also evidence that subsurface oxygen enhances hydrogen chemisorption on Pt surfaces (*14*), a factor that may have been overlooked in previous studies of the chemistry of this material (*7*, *15*, *16*).

The extraordinarily high activity of oxygen-treated Co at high H_2/CO (>20) makes it an attractive catalyst for the removal of CO from ammonia synthesis feed gas. It is also very specific, with higher hydrocarbons being undetectable under the conditions of our experiments.

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