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Methanation of Carbon Monoxide on Nickel and Nickel–Copper Alloys

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Methanation of CO and CO_2, disproportionation of CO, and hydrogenation of carbon deposited on the surface of catalysts have been studied on Ni and Ni–Cu alloy films at low pressures, at temperatures of 250–350°C. Under these reaction conditions, two steps of the overall mechanism have been identified; namely, dissociation of CO and hydrogenation of deposited carbon by adsorbed hydrogen. CO can be dissociated only on places where carbon atoms can be bound to several Ni atoms simultaneously; therefore addition of Cu to Ni strongly reduces the rate of methanation.

INTRODUCTION

Because of the great practical importance of its reaction, methanation has been a subject of many studies and extended reviews (*1*, *2*) are available on this subject. The main concern with this reaction was usually the removal of CO from various synthesis mixtures (e.g., ammonia), but recently the reaction assumed a new importance as an attractive way of producing clean fuels from coals (natural gas substitute). The chemistry of the reaction is apparently simple,

$$CO + 3H_2 \rightarrow CH_4 + H_2O,$$

and almost all thermodynamic data on this and related reactions are available. However, much less is known for sure on the detailed mechanism of this reaction. A recent review (*2*) summarizes all suggestions in the literature into essentially three different mechanisms:

(i) the reaction proceeds via formation of surface carbides;
(ii) the essential intermediate contains oxygen (e.g., HCOH);
(iii) the reaction has carbonyls as important intermediates.

It seems (*2*) that most authors reject (i) because carbides have been disproved as intermediates for the related Fischer–Tropsch hydrocarbon synthesis, and (iii) because carbonyls are unstable at the temperature usually used. However, it is known that when Fischer–Tropsch synthesis is performed on surfaces carbided by radioactive-labeled carbon, not the higher hydrocarbons but methane contained much of the radioactivity (*3*), which indicates that the formation of CH_4 and higher hydrocarbons may be running via different intermediates. There is also no principal reason why the formation of methane and of higher hydrocarbons should have to proceed by a mechanism identical in all details.

Another interesting question was the influence of Cu in alloys on the activity of Ni. It was known (*4*) that Cu changes drastically the activity of Ni in CO_2 hydrogenation, but no information was

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available on the behavior of the CO/H_2 mixture. Neither was it known in which step of the overall methanation reaction Cu actually affects the process: in CO adsorption, a possible CO dissociation, CO hydrogenation into an oxygen containing complex, hydrogen adsorption, etc. These were the questions which have led us to perform the research reported below.

EXPERIMENTAL

All measurements were performed in a static closed apparatus which allowed us to prepare the films under ultrahigh vacuum conditions. The apparatus, materials and the experimental procedure were all essentially the same as in the previous papers (see, e.g., Ref. *5*). Because of the low total pressure and the wide connecting tubes (16-mm diameter) no circulation pump was used in this experiment. The absence of complications due to diffusion was checked experimentally.

Alloy films were annealed at 350°C at which temperature Ni and Cu are completely miscible. In spite of that, the X-ray diffraction peaks of the samples (subject to the same operations as the whole film withdrawn from the system after catalytic measurements) were sometimes broad and with an indication of two maxima showing the films were not completely homogenized. However, no special measures were taken to achieve a true equilibrium because from the photoemission measurements (*6*, *7*) we knew that the surface composition of all films *in vacuo* is the same for bulk compositions varying between about 10 and 80% Cu.

When the film had been evaporated and annealed, hydrogen (0.48 Torr) was admitted to the film at 300°C. This step has been introduced for two reasons. First, it allowed us to set up the leak to the mass spectrometer formed by a Granville–Phillips bakable valve. Second, it reduced a possible background reaction with the carbon present in the system. For instance, it has been observed that in spite of a careful preparation (filaments were outgassed and the cell baked out for several days) of the films and ultrahigh vacuum condition throughout (p of the order 10^{-9} Torr or lower during the preparation and annealing), there was always a certain background reaction with the carbide present in the system, in the filament, W-leads, and also in the film. However, the first hydrogenation step removed the background reaction up to a negligible extent. After about 1 hr, hydrogen and products were pumped off and the reaction mixture was admitted.

Analysis of the reaction mixtures has been performed by a small bakable MS 10 (AEI, England) calibrated (relative sensitivities) by a membrane manometer (Varian, MAT). Calibrations were repeated several times during the experiments. The following m/e peaks were used to determine the partial pressures: $2(H_2)$, $15(CH_4)$ (not disturbed by fragmentation peaks of water and CO_2), and $44(CO_2)$. In the experiments with ^{13}CO the amounts of $^{12}CH_4$ and $^{13}CH_4$ were determined from two peaks, 14 and 15, solving a simple system of two linear equations. Water could not be followed accurately because of the irreproducible way in which water formed in the source of the mass spectrometer, and adsorption of water on the walls of the apparatus which had been baked out before the experiment, etc. However, in a semiquantitative way, water production showed the same behavior as the formation of methane.

Reacting gases were premixed in a reservoir and then admitted to the film. After admitting the reaction mixture to the film, the total pressure was 0.58 Torr, the initial H_2 to CO ratio was kept around 5 in all experiments. Disproportionation of CO was followed with an initial pressure of 0.48 Torr of CO. These conditions were kept constant in all experiments.

RESULTS

General Features of Methanation

If the mixture of hydrogen and CO was admitted to a clean Ni film at, e.g., 250°C, methane was formed. However, the formation of methane revealed an induction period; i.e., the rate of methane formation was very low at an early stage of the first run but increased rapidly with the reaction time (Fig. 1). In the repeated runs on the same film, the rate of methane formation was always higher until it reached a certain, more or less, steady value after about five runs (Fig. 2).

Quite opposite effects were observed in the CO_2 production. Thus, CO_2 was always produced from the mixture in spite of the presence of hydrogen. However, it appeared in the first run without any induction period and the rate of its formation decreased with repeated runs. In repeated runs (with the same film) also, an induction period was observed and the rate of CO_2 formation decreased with repeated runs.

The changes in rate and selectivity of the reaction indicate the influence of the modification of the surface by the reaction mixture itself.

Disproportionation of CO

Because disproportionation appeared to be a reaction which, under the conditions used, accompanied the methane reaction, the formation of CO_2 from CO has been followed in separate experiments in the absence of hydrogen. Disproportionation takes place according to the equation:

$$2CO \rightarrow C_s + CO_2, \qquad (1)$$

where C_s stands for carbon deposited on the surface. The pressure of CO_2 increased according to the equation:

$$CO_2(t) = CO_2(\infty)[1 - \exp(-k_1t)], \qquad (2)$$

where $CO_2(t)$ is the number of molecules at the time t, $CO_2(\infty)$ is the number of molecules after a sufficiently long time $(t \rightarrow \infty)$, and k_1 is the reaction rate constant (sec^{-1}). Some of the linear plots of Eq. 2 are shown in Fig. 3.

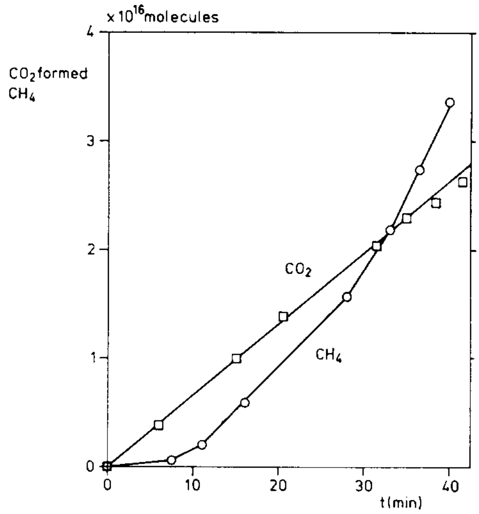

FIG. 1. Number of molecules formed of CO_2 (disproportionation in presence of H_2) and CH_4 (methanation) from the reaction mixture H_2/CO as a function of time. Standard conditions, T = 250°C, virgin film, first run.

Hydrogenation of the Deposited Carbon

The amount of carbon deposited, C_s, is equal to the number of CO_2 molecules in the gas phase. The number of all carbon atoms deposited on the surface can be also determined by a quantitative hydrogenation of the deposited carbon. Indeed, it has been found that after a sufficiently long time (2 ~ 3 hr at 250°C), these two values are of the same order of magnitude on Ni. The number of methane molecules found at time t from the deposited carbon C_s can be expressed again by an empirical equation:

$$CH_4(t) = C_s(\infty)[1-\exp(-k_2t)], \qquad (3)$$

where $C_s(\infty)$ stands for the number of deposited carbon atoms. The initial rate of methane formation can be determined when the constants $C_s(\infty)$ and k_2 are known from the linear plot of the integral Eq. 3:

$$\left(\frac{dCH_4(t)}{dt}\right)_{t\rightarrow 0} = k_2C_s(\infty). \qquad (4)$$

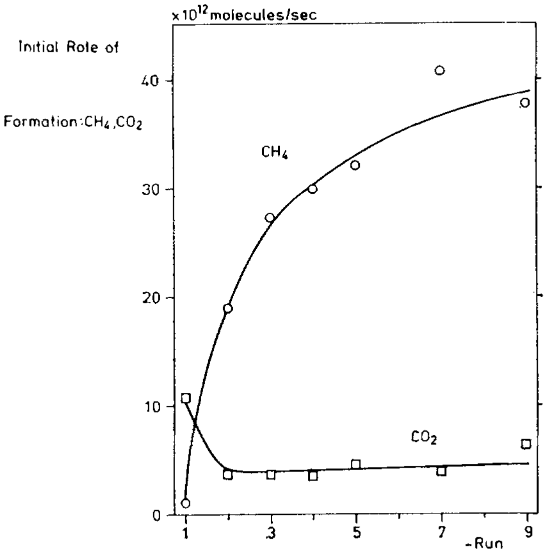

FIG. 2. Initial rate of formation of CO_2 and CH_4 from the reaction mixture H_2/CO in subsequent runs when reaction is repeated with a new mixture on the same film. Standard conditions, $T = 250°C$.

The initial rates of CO formation from the H_2/CO_2 mixtures and the initial rate of CO_2 formation from the H_2/CO mixtures and CO alone were determined using formally the same equation and procedure.

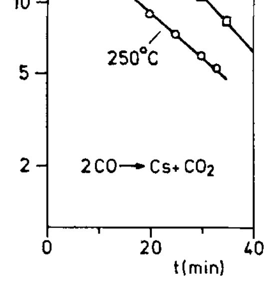

FIG. 3. Formation of CO_2 from CO (disproportionation in absence of H_2) at two different temperatures. C(t), CO_2 formed at time t, $C(\infty)$, at $t \rightarrow \infty$. Arbitrary units, semilogarithmic plot.

As already mentioned, if hydrogen alone was admitted to the film covered by the deposited carbon (C_s), methane was formed. It is interesting to note that this methane formation is then faster than when a mixture of H_2/CO is admitted to such a film. Evidently, the presence of CO suppresses the rate of hydrogenation of the deposited carbon. It should be mentioned in this regard that various papers report that the order of the methanation reaction is usually negative with regard to the CO pressure (*2*, *8*). Evidently, CO and hydrogen compete for the same sites and hydrogen must be adsorbed before it can enter the reaction with deposited carbon (C_s).

The Mechanism of Methane Formation (Methanation of CO)

The results mentioned above led to the suspicion that also methanation from H_2/CO mixtures is running via a dissociative chemisorption of CO, that is, with formation of C_s and O_s as intermediates. Therefore, experiments were carried out in which the amount of carbon deposited was

TABLE 1

Influence of the Amount of Deposited C_s on the Rate of Methane Formation

Amount of C_s ($\times 10^{16}$ atoms)	Pumping condition after deposition of C_s		Initial rate of methane formation upon hydrogenation of Ni film covered by C_s at 250°C ($\times 10^{14}$ mol/sec)
	Time (hr)	Temp. (°C)[a]	
22.0	22	250	2.2
23.6	1	250	2.5
60.6	1	300	3.6

[a] Also the temperature of C-deposition by disproportionation of CO.

varied. By changing the pumping conditions as specified in Table 1, we hoped to vary the amount of strongly bound CO, if present.

The finding that the extent of surface carburization influenced the rate of the subsequent methanation more than pumping strengthened our suspicion with regard to the role of C_s as an intermediate of methanation. However, a conclusive proof could only be obtained by using isotopically labeled molecules. Therefore, the following experiment has been performed.

A dose of ^{13}CO ($p = 0.48$ Torr) was admitted at 300°C to a clean Ni film and the disproportionation was allowed to proceed for 30 min. The apparatus was then evacuated at 300°C for 60 min by the Vacion pump. According to the thermal desorption data (*9*), irreversibly bound ^{13}Co is almost completely removed under such conditions. After the pumping period, a reaction mixture of hydrogen and ^{12}CO (5/1) has been admitted at 250°C. The production of various products as registered by the mass spectrometer in the gas phase is shown in Fig. 4.

As can be seen immediately, the first product appearing from this mixture is $^{13}CH_4$. The formation of $^{12}CH_4$ and $^{12}CO_2$ is accompanied by an induction period of 20 ~ 25 min. Even after 60 min, no $^{13}CO_2$ could be detected. No exchange between $^{13}C_s$ and CO was detected either. These facts demonstrate clearly that C_s (in this case, $^{13}C_s$) is used for methanation rather than CO coming from the gas phase, and C_s does not recombine easily with O into CO and CO_2 molecules.

Reactions of CO_2

In addition to the experiments already mentioned, some measurements were also performed with CO_2-hydrogenation from H_2/CO_2 mixtures. Also in the reaction mixture of H_2/CO_2 the methane formation reveals an induction period during the first run on a clean surface. All this suggests that the first step of CO_2-methanation is the reduction to CO, and the second step is the dissociation of it into C_s and O_s:

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (5)$$

$$CO \rightarrow C_s + O_s \quad (6)$$

$$C_s + H_s \rightarrow (CH)_s \ldots, \text{ etc.} \quad (7)$$

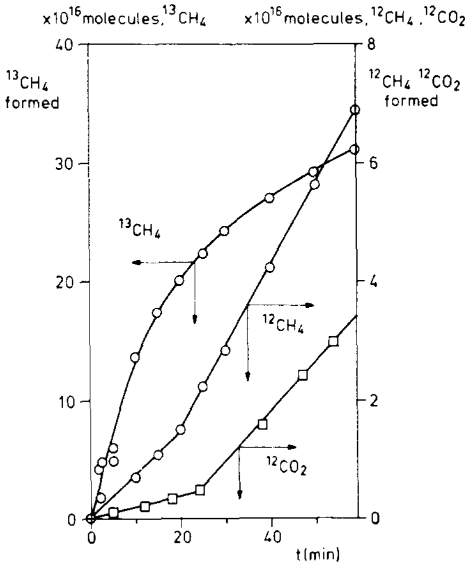

FIG. 4. Number of molecules formed of compounds with indicated composition as a function of time. $T = 250°C$, standard conditions. Ni film had been saturated by $^{13}C_s$ formed by disproportionation of ^{13}CO; then the reaction of ^{12}CO and H_2 on the same film was followed. The time course of the CO_2 formation with an induction period is typical for the CO_2 formation on all runs with H_2/CO mixtures repeated on the same films.

The Influence of Alloying on the Hydrogenation of CO, CO_2, and C_s

On clean Cu film no methane formation from CO, CO_2, or C_s was detected up to 350°C. Addition of Cu to Ni decreases the rate of all reactions followed: hydrogenation of CO, CO_2, and C_s as well as disproportionation of CO. This can be seen in Figs. 5 and 6.

In order to see the influence of alloying on the individual steps of methanation, the two relevant reactions were performed separately on the clean alloy film, i.e., disproportionation of CO and hydrogenation of C_s. The data were again evaluated using formally the first-order equation. In terms of this equation, Cu has some small influence on k_1 and k_2 constants, but it affects in a much more pronounced way the constants $CO_2(\infty)$ and $C_s(\infty)$, respectively (Table 2). In other words, by diluting Ni with Cu we drastically reduce the number of places where C_s can be formed and held. How can such an effect be achieved? For Ni/Cu alloys, it is known that the electronic structure of Ni atoms varies only marginally by alloying. Both components also preserve their individuality in alloys (see, e.g., Ref. *13*). Chemically, Cu is almost inactive in disproportionation (dissociation) and methanation, so that the main effect of alloying is dilution of active Ni in an inactive matrix. This diminishes the number and size of Ni clusters (always present in Ni–Cu alloys) (*13*). Such clusters exposing ensembles of several active sites to the gas phase are evidently necessary for dissociation of CO and deposition of C_s on the surface, and most likely for this reason the constants $CO_2(\infty)$ and $C_s(\infty)$ (as well as the rate of methanation) are so strongly decreased when Ni is diluted in Cu.

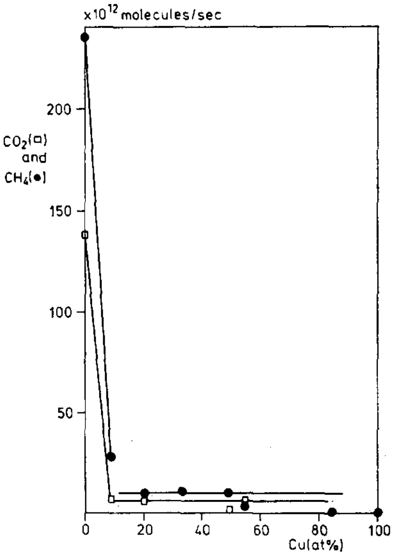

FIG. 5. Ni–Cu alloy films. The influence of alloying on the initial rate of CH_4 and CO_2 formation from H_2/CO mixtures, at 300°C. Standard conditions, steady state in repeated runs achieved.

DISCUSSION

The results obtained show that at low pressures an unpromoted Ni-film is a catalyst for methanation. In the low pressure region methanation is accompanied by CO_2 formation. How can CO_2 be formed? One possibility can be a water/gas-shift reaction:

$$CO + H_2O = CO_2 + H_2 \qquad (8)$$

For this reaction, water must be formed first by the methanation reaction:

$$CO + 3H_2 = CH_4 + H_2O \qquad (9)$$

However, Ni is a bad catalyst for this reaction and, moreover, we see from Fig. 1 that CO_2 is formed on a virgin film faster and at an earlier stage of the reaction than CH_4. Therefore, CO_2 must be formed by other reactions, namely:

$$CO\ (\text{gas}) \rightarrow C_s + O_s \qquad (10)$$

$$O_s + CO\ (\text{gas, or adsorbed}) \rightarrow CO_2\ (\text{gas}). \qquad (11)$$

The experiment with isotopic labeling showed that the recombination reactions $C_s + O_s$ and $C_s + 2O_s$ contribute less to the overall reaction than the reaction (11). Figure 1 also shows that reaction (10) takes

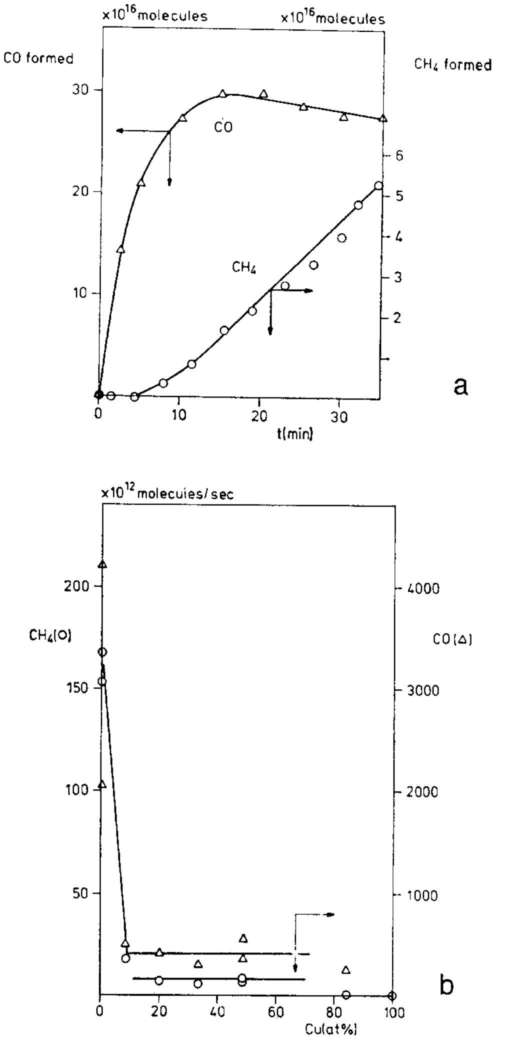

FIG. 6. (a) Formation of CO and CH_4 from H_2/CO_2 mixtures at 250°C, standard conditions, virgin Ni film. (b) Ni–Cu alloy films. The influence of alloying on the initial rates of CH_4 and CO formation from the H_2/CO_2 mixtures at 300°C. Standard conditions, steady state in repeated runs achieved.

place even in the presence of hydrogen. However, under the reaction conditions when hydrogen is also present and particularly at higher hydrogen pressure, a part of the oxygen atoms, O_s is certainly taken away from the surface by the reaction with hydrogen.

By reaction (10) carbon is deposited on the surface, and when we consider the discussion on the role of C_s in methanation (see below), the most likely explanation of Fig. 2 is that the amount of the carbon deposited increases with repeated runs and C_s modifies the selectivity of the surface towards various reactions.

When a reaction mixture ($CO + H_2$) is admitted to a film which is covered by C_s to a high extent, the behavior is different from that of a fresh film; CO_2 is now produced after an induction period but CH_4 is formed immediately with a maximum rate. This shows that first a part of C_s must be removed from the surface and only then may CO_2 be formed, most likely by reactions (10) and (11) as with the fresh film.

Let us now summarize the most essential results with regard to the mechanism and rate of the methanation: (i) hydrogenation of carbon atoms deposited on the surface is an easy reaction, faster than the methanation in the reaction mixture under the same temperature and hydrogen pressure; (ii) on increasing the amount of carbon C_s deposited on the surface before the reaction has been started, there is an increase in methanation rate (Fig. 1; Table 1); (iii) dissociation of CO (and at low hydrogen pressure also the production of CO_2) can also proceed in the presence of hydrogen (Fig. 1); (iv) as the experiment with isotopic labeling revealed (Fig. 4), hydrogen from a mixture of CO and H_2 prefers to react with carbon already present on the surface from the preceding disproportionation (dissociation) rather than to react with CO from the gas phase and subsequently adsorbed on the surface.

These facts (i–iv) have led us to the following conclusions:

1. At the reaction temperatures the primary processes are dissociative:

$$H_2 \rightarrow 2H_s \qquad (12)$$

$$CO \rightarrow C_s + O_s. \qquad (13)$$

Because CO hinders methanation from C_s

TABLE 2

Rate Constants k_1, k_2, and Maximum Amounts of Deposited C_s on Ni and Ni–Cu Alloys

	Disproportionation of CO		Hydrogenation of C_s	
	k_1 ($\times 10^{-3}$ sec^{-1})	$CO_2(\infty)$ ($\times 10^{16}$ atoms)	k_2 ($\times 10^{-3}$ sec^{-1})	$C_s(\infty)$ ($\times 10^{16}$ atoms)
Ni				
Range	0.80 ~ 1.10	52.1 ~ 92.1	1.21 ~ 2.96	29.5 ~ 56.4
Average	0.95	66.0	2.1	43.0
Alloys				
Range	0.87 ~ 2.99	0.32 ~ 11.5	0.49 ~ 0.65	0.18 ~ 0.72
Average	1.45	3.6	0.57	0.42

(see (i) above) and because we know that adsorption of CO is stronger than adsorption of hydrogen, we can combine these pieces of information and say that hydrogen reacts with C_s in an adsorbed state:

$$C_s + H_s \rightarrow (CH)_s. \quad (14)$$

From earlier work we know that also upon interaction with oxygen, hydrogen is in an adsorbed state (*14*):

$$O_s + H_s \rightarrow (OH)_s$$
$$(OH)_s + H_s \rightarrow H_2O. \quad (15)$$

Therefore, we conclude that the products of dissociation (Eq. (12), (13)) recombine with CO and with each other into the final reaction products (CH_4, H_2O, and CO_2) and the product pattern is dependent on the reaction conditions (temperature of reaction, pressure of gases, the state of the surface).

2. Formation of methane via dissociation is in our opinion the main route of this reaction. We derive this from the fact that this is a possible route [see (i)–(iii)] and a preferential route (iv) under the reaction conditions used. In contrast to it, the insertion of CO into a metal–hydrogen bond is known to be a difficult process, and the existence of oxygen-containing intermediates which would arise by insertion is only supported by the kinetics (see Ref. *8* for review, and Refs. *12*, *14*, and *24* therein).

3. The facts [(i)–(iv)] and their explanation (1. and 2., above) contradict the mechanism which was a basis for various derivations of kinetics, viz., the addition of hydrogen to the undissociated CO molecule as the essential step towards CH_4 formation. The present results do not bring any evidence for complexes like "HCOH" (associative mechanism), but point to the importance of "C_s" as an intermediate (dissociative mechanism). However, the kinetics derived from the various associative mechanisms describe the macroscopic kinetic data very well (Refs. *1*, *2*, *8*, and *12*), so that any alternative mechanism should lead to the same equations. Indeed, this can be done. Assuming that the hydrogenation of carbon C_s (or of CH, CH_2, CH_3) species is the rate determining step, the rate of methanation r is:

$$r = k\theta_C\theta^{(m)}{}_H. \quad (16)$$

When θ_C, the coverage by C_s or by other carbonaceous species relevant in this respect, is approximately independent of the CO-pressure (p_{CO}) and if CO and H_2 compete for the same sites and CO adsorption is much stronger than that of hydrogen, then $\theta_H \sim p_{H_2}{}^{\alpha} p_{CO}{}^{\beta}$ with $\alpha > 0$ and $\beta < 0$. With this expression, Eq. 16 reads:

$$r = kp_{H_2}{}^{(m\alpha)}p_{CO}{}^{(m\beta)}. \quad (17)$$

An equation of this type is in agreement with the experiments (*8*, *12*), so that the suggestions made above with regard to the mechanism (point 2) are not controversial with the kinetics determined at higher pressures of gases.

One more point deserves a comment. It is known (*1*, *2*) that Ni methanation catalysts are very sensitive to poisoning by sulphur. Further, UPS spectroscopy revealed (*11*) that sulphur depresses dissociation of CO. These facts can be easily understood on the basis of the mechanism suggested in this paper.

CO_2 can also be converted into methane. As could be expected, on a fresh surface CO_2 reduction is a faster reaction than methanation.

The net production of CO_2 in mixtures of CO and H_2 (see Figs. 1 and 2) which, under the given reaction conditions, reaches a certain steady state in repeated runs, can be kept on this level by simultaneously running reactions (10)–(15). It seems most likely, but it has not been proved here, that the reverse of reaction (11) is mechanistically the first step of CO_2 reduction (reaction (5)).

All reactions studied were affected by alloying. It was important to learn what is the effect of Cu (separately) on the disproportionation of CO and hydrogenation of C_s.

The results showed that the rate constant of hydrogenation of C_s did not vary by alloying more than by a factor of about 4 (Table 2). However, a much more pronounced effect is observed on the maximum number of deposited carbon atoms $C_s(\infty)$ (Table 2). This strongly suggests that for the deposition of C_s only those places on the surface of alloys are suitable where several Ni atoms are joined together; that is, an ensemble of several sites is required to bear a C_s atom.

Because the rate of methanation is reduced more strongly than the constants k_1 and k_2, we deduce that the mechanism of Cu influence on methanation is that the number of places (ensembles) on which CO can dissociate and yield C_s is reduced by diluting active Ni sites in a matrix, itself inactive for this reaction. The values of apparent activation energy of methanation on various films are scattered but they show no distinct difference between alloys on one side and Ni on the other (Table 3). This strengthens the belief that the influence of Cu is correctly explained *in terms of the number of available Ni ensembles.*

TABLE 3

Apparent Activation Energy of Methanation[a]

Cu, bulk concentration	$E_{\mathrm{kcal/mol}}$
0	22.3; 24.7
8.7	18.4
15.9	19.7
20.0	24.6
33.0	20
54.5	23.2

[a] Activation energy determined as in Ref. *5*.

Parallel to this kinetic research, experiments have been performed on infrared spectra of adsorbed CO (*10*). They revealed that C_s atoms are predominantly deposited on those places where CO is adsorbed with a stronger back-donation (that is giving rise to the infrared absorption band at 1950 cm^{-1}). These places are most probably the surface holes among several Ni atoms; the same valley sites are probably required for the deposition of C_s atoms as well.

According to the earlier study (*15*) of the infrared spectra of CO adsorbed on Ni and Ni–Cu alloys, Cu eliminates most of the adsorption in the form with strong back-donation, i.e., the adsorption most likely in the valleys among surface atoms (surface holes). As mentioned above, Cu reduces the rate of disproportionation and methanation of CO by almost the same factor. From these facts we conclude that a valley position with one or more Cu atoms around is no more able to adsorb and dissociate the CO molecules and catalyze methanation.

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