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The Kinetics and Mechanism of Carbon Monoxide Methanation over Silica-Supported Nickel Catalysts

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The rate, r, of CO hydrogenation into methane over Ni/SiO_2 catalysts is shown to vary in a complex way with temperature and pressure. The true activation energy, E_0, calculated from the Temkin relation (apparent activation energy against the order to CO and extrapolation to zero order), corresponds to that of the hydrogenation of carbon deposited on the surface from the CO dissociation reaction. It is deduced that the active intermediate is the surface carbon, and the rate-determining step the hydrogenation of this intermediate. Kinetic data are qualitatively accounted for assuming the following equation

$$r = ke^{-E_0/RT}P_{H_2}(1 - \theta_{CO})^W$$

θ_{CO} is the surface coverage in nondissociated inactive adsorbed CO molecules which are considered as the most abundant species present on the surface. The parameter W is probably very large (W = 13 on the basis of data of CO + H_2 over $Ni–Cu/SiO_2$). In this equation, the term $(1 - \theta_{CO})^W$ represents the probability of having W adjacent Ni atoms free from inactive adsorbed CO. This ensemble should be considered as the active site and is covered with one active monocarbon adspecies.

INTRODUCTION

The methanation reaction, discovered in 1902 by Sabatier and Senderens (*1*), still remains a subject of intense interest. It is used in industrial processes to remove CO traces in hydrogen-rich gases of ammonia plants. Moreover, there has recently been a renewed interest in this reaction since it is an important step in the transformation of coal into substitute natural gas, an industrial process planned for the future.

Various models have been proposed to account for the kinetic data on methanation (*2–8*). Most of them are based on the Langmuir approximation, which considers the surface as energetically homogeneous. The first question which arises is the extent to which this crude approximation, which leads to equations which fit experimental data already available in the literature, is capable also of representing the kinetic behavior of this reaction over a larger range of experimental conditions. There is a second question which concerns the reaction intermediate. In a series of kinetic treatments (*2–4*), intermediates such as CHOH bonded to one metallic atom were first considered. After it was established in 1974 that CO can be dissociated into surface carbon and oxygen (*9*), the previous model was thought to be groundless and it was proposed that the surface carbon, C_s, could be the intermediate. In the corresponding kinetic treatment, however, C_s was considered as adsorbed on one site, while it is known from magnetic measurements (*10*) that it is bonded to three nickel atoms. Moreover, it has been proposed that it is probably interacting with a larger number of metallic surface atoms, as suggested by recent data on CO hydrogenation over Ni–Cu alloys (*11*). So far, the concept of an intermediate requiring ensembles composed of a large number of metallic atoms has not been applied to the kinetic treatment of methanation. Thus, it seemed to us of interest to examine to what extent such a

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standpoint can help us in the understanding of the kinetic behavior of the methanation reaction. The purpose of this paper is to present new kinetic data obtained over a large range of experimental conditions and to offer a new model of the methanation reaction.

EXPERIMENTAL

The morphological characteristics (*12*) of Ni/SiO_2 catalysts used in this work are summarized in Table 1. Let us briefly recall that they were prepared by reduction for 15 h of precursors obtained by reacting the support (SiO_2, Aerosil Degussa, 200 m^2/g) with a solution of nickel nitrate hexammine. Magnetic measurements showed that reduction of the samples was almost complete and also allowed us to calculate the surface average diameter D_s (*12*). Concerning the porosity of the samples (used as powders) no pores with diameter under 15 nm were observed.

Kinetic experiments were carried out in a flow system with a fixed-bed reactor at atmospheric pressure. The microreactor consisted of a quartz tube with a porous disk and samples were held in place by quartz wool. The total flow at room temperature was 35 ml/min. Carbon monoxide, hydrogen and helium (used as a diluent) had a purity better than 99.99%. Gas analyses were performed on line by gas chromatography with thermal conductivity and flame-ionization detectors. Conversion yields were generally kept smaller than a few percent (for these conditions no significant aging phenomena were observed) and various masses of catalyst (3 to 300 mg) were used in order to measure kinetic parameters (orders with respect to reactants n, apparent activation energy E_a) over a large range of experimental conditions.

TABLE 1

Morphological Characteristics of Ni/SiO_2 Catalysts

Sample	Ni loading (% wt)	Reducing Temperature (°K)	Degree of reduction	D_S (nm)
1	4.5	800	0.95	2.5
2	11.0	920	1	5.7
3	23.0	920	1	6.3
4	23.0	1000	1	7.5
5	23.0	1200	1	14.0

Temperature was varied over the range 140–400°C; CO partial pressure was varied from 1 to 180 Torr, and H_2 partial pressure from 150 to 630 Torr. The order with respect to reactant 1 was obtained in the usual way by changing the partial pressure of 1, keeping the partial pressure of reactant 2 constant (the partial pressure of He was adjusted in order to balance the change in pressure of reactant 1 and to keep the total flow constant).

No carbonyl formation was detected, even at low temperature where the CO pressure was kept low (for instance, at 140°C, $p_{CO} < 25$ Torr).

RESULTS

Figure 1 shows the influence of the partial pressure of CO on the CO conversion. The drastic decrease of conversion observed when decreasing the CO pressure, P_{CO}, is due neither to aging phenomena arising from the reversibility of the curve nor to thermodynamic limitations (it seems, moreover, to be temperature independent). Figure 2 illustrates the influence of the reaction temperature on the orders with respect to H_2 (n_H) and to CO (n_{CO}). Whereas n_H appears temperature independent and close to unity, in rather good agreement with results from the literature (2,5,13), n_{CO} is negative, increases with temperature and tends to zero at high temperature. The observed values are in quite good agreement with data from the literature on the CO + H_2 reaction over various Ni catalysts; particularly, values of n_{CO} against temperature (*2, 13–15*) fit well with our own results. Figure 3 shows the variation of n_{CO} with respect to the partial pressure of CO, P_{CO}.

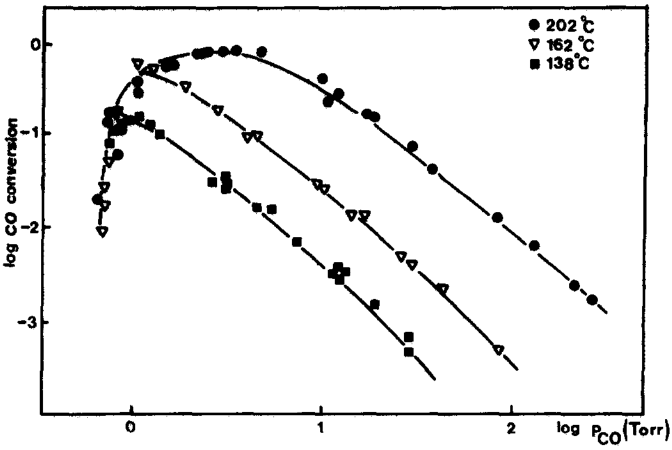

FIG. 1. Plots of log[CO conversion] versus log [partial pressure of CO (Torr)]. Sample 2. P_{H_2} = 500 Torr.

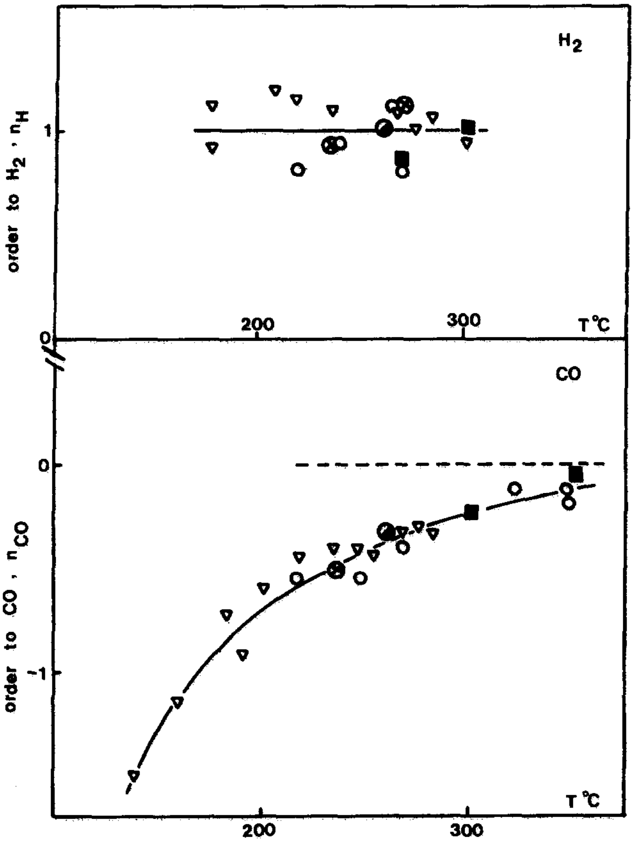

FIG. 2. Orders with respect to H$_2$, n_H, and to CO, n_{CO}, against temperature of reaction T. Samples: ■, 1; ◕, 2; ▽, 3; ⊗, 4; ○, 5.

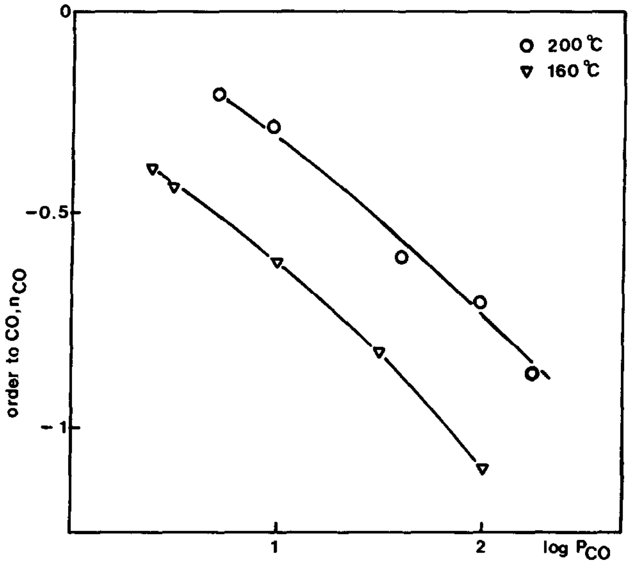

FIG. 3. Order with respect to CO as a function of partial pressure of CO. Sample 2. P_{H_2} = 500 Torr.

The higher P_{CO} the lower n_{CO}, suggesting an inhibiting effect of CO adsorbed species; values for very low P_{CO} are not reported owing to the drastic change observed when decreasing CO pressure (see Fig. 1). Figure 4 gives a typical Arrhenius plot showing that the apparent activation energy, E_a, depends on the temperature and decreases when the temperature of reaction T increases. The variations of E_a against T are reported in Fig. 5 for various Ni/SiO$_2$ samples; the observed values are in good agree-

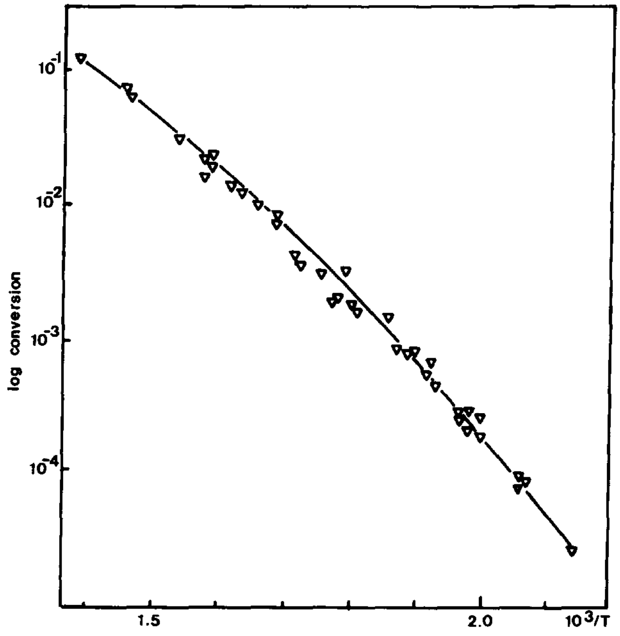

FIG. 4. Arrhenius plot (log conversion against $1/T$). Sample 2. P_{H_2} = 500 Torr; P_{CO} = 120 Torr.

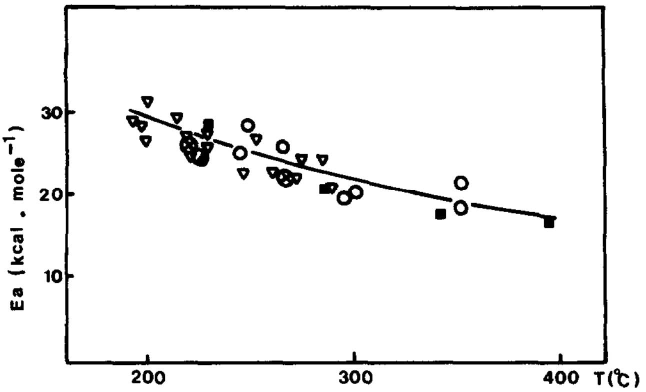

FIG. 5. Apparent activation energy, E_a versus temperature of reaction T. Samples: ■, 1; ◐, 2; ▽, 3; ⊗, 4; ○, 5.

ment with results from the literature (*2, 13–17*) when measured over the same range of temperature.

DISCUSSION

Review of the Previous Models

As a first step the validity of the models already proposed will be discussed in the light of the experimental data reported in this paper and in other works. Three points will be examined in turn.

(i) Most of the kinetic models so far proposed predict a maximum in the rate variation with CO pressure, and this behavior has actually been observed by van Herwijnen *et al.* (*18*). The order in CO at low CO pressure calculated from the kinetic equations (*2–6, 8, 18*), however, cannot be larger than +1. It does not fit our experimental data since orders as large as 20 are measured at low CO pressures (Fig. 1). This points to the first limitation of the models based on the Langmuir approximation which does not consider the surface heterogeneities and the interactions between adspecies. The low CO pressure experiments reported in this paper probably reveal a dramatic change in the nature of the most abundant species present on the surface. It can be assumed that at low CO pressures, CO is replaced by adsorbed hydrogen in a sudden and reversible way, in good agreement with the hypothesis of Van Ho and Harriott (*5*). This intriguing phenomenon, which occurs at a given pressure and which seems to be temperature independent, deserves further experiments.

(ii) Several models (*2–4, 6*) predict that $n_H - n_{CO} = \frac{x}{2}$, where x is the number of H atoms (or adsorbed H$_2$ molecule halves) which are involved in the rate-determining step:

$$\mathrm{CHOH} + \frac{x}{2}\mathrm{H_2} \rightarrow \mathrm{CH}_x + \mathrm{H_2O}$$

$$\mathrm{C_s} + x\mathrm{H} \rightarrow \mathrm{CH}_x$$

In our experimental conditions, where n_H remains nearly constant (Fig. 2), the variations of n_{CO} with T and P_{CO} reported in Figs. 2 and 3 would reflect parallel variations of x. It is hard to comprehend why x would vary with T and P_{CO} and why its variation would be continuous. Moreover, these models do not allow a correct prediction of the n_{CO} values at low temperatures. As a matter of fact, x should lie between 1 and 4; if one takes $n_H = 1$, as observed in this work, n_{CO} should vary over the range -1 to $+0.5$. This does not fit our observations since orders in CO as low as -1.5 are measured at low temperature. The model proposed by Van Ho and Harriott (*5*) exhibits the same drawback, since it does not allow the order to CO to be smaller than -1 (*5*).

(iii) In some works, the hypotheses dealing with the hydrogen adsorption do not seem realistic. In two cases (*2, 3*), adsorbed H_2 molecules rather than H are considered and one-half or three-halves of a H_2 molecule are assumed to react with the carbon-containing intermediate. These concepts are difficult to understand and have been criticized by Bond and Turnham (*4*). In the model of Van Ho and Harriott (*5*), the H_2 hydrogen adsorption is assumed to require only one site, a point which is debatable if one considers that the surface stoichiometry H/Ni_s is unity at saturation (*19*). In another work (*7*), the hydrogen coverage, θ_H, is taken proportional to the square root of the hydrogen pressure, according to the Langmuir approximation. Experiments on hydrogen adsorption (*19, 20*) show that θ_H is proportional to $P_{H_2}{}^a$ with $a \simeq 0.15$ in the experimental conditions where the CO hydrogenation is usually performed. It cannot be predicted how the exponent a varies in the presence of CO; there are no reasons, however, to believe that the exponent a would tend toward 0.5 for these conditions.

It can therefore be concluded that most of the kinetic models so far proposed present some drawbacks and that an improved treatment of the mechanism seems to be desirable.

Nature of the Intermediate

Surface carbon is generally considered as a key intermediate in the methanation process. There is, however, an interesting question about its exact nature and that of the rate-determining step which has been raised by Van Ho and Harriott (*5*): the activation energy of the hydrogenation of carbon deposited from the reaction of CO into $C + CO_2$ (17 or 15 kcal/mol (*21, 5*)) differs from that of the methanation reaction (20–25 kcal/mol). It is concluded by these authors that the surface carbon hydrogenation does not seem to be rate controlling. This assertion, however, can be criticized on the basis that the activation energies are not measured in the same conditions; for the first case, the surface is mainly covered with C, while in methanation conditions the surface is probably mostly covered with CO and the coverage of CO is expected to vary with temperature. As pointed out by Temkin (*22*), differences in experimental conditions can give rise to differences in activation energies. To be precise, Temkin (*22*) states that "the apparent activation energy, E_a, of a reaction which takes place in an adsorbed layer differs generally speaking from the true activation energy, E_0, on account of the change in surface concentration with a change in temperature." Temkin has shown that apparent and true activation energies are related by the following equation:

$$E_a = E_0 - \Sigma n_i Q_i$$

where n_i is the order with respect to the partial pressure of the reactant i, and Q_i is the isosteric heat of adsorption of the reactant i. A demonstration of this equation, slightly different from that proposed by Temkin, and an application to the ethane hydrogenolysis reaction has been given elsewhere (*19*). For the case of the methanation reaction, where the surface can be considered as covered mainly with CO, the relation becomes:

$$E_a = E_0 - n_{CO}Q_{CO} \qquad (1)$$

If it is assumed that, as a first approximation, Q_{CO}, the isosteric heat of adsorption of CO, in the reaction conditions, is more or less constant, one should observe a straight line by plotting E_a (Fig. 5) against n_{CO} (Fig. 2). This is indeed observed in Fig. 6. The true activation energy thus obtained by extrapolation to $n_{CO} = 0$ is $E_0 = 17$ kcal/mol, a figure which is in excellent agreement with the activation energy of the hydrogenation of surface carbon deposited from the CO disproportionation reaction on the metal surface (*16, 5*). This means that the true activation energy of the methanation reaction is the same as the activation energy of surface carbon hydrogenation. Thus it can be

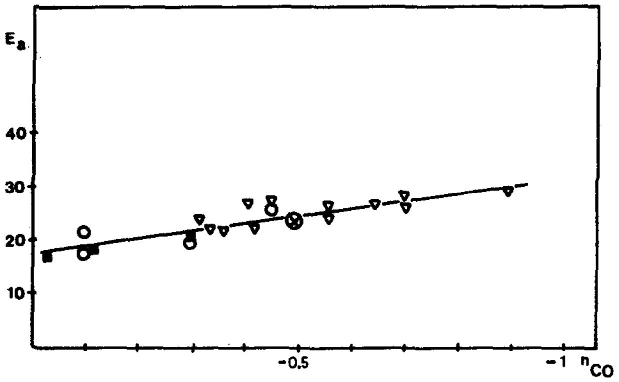

FIG. 6. Apparent activation energy, E_a versus order with respect to CO, n_{CO}. Samples: ■, 1; ▽, 3; ⊗, 4; ○, 5.

concluded that the rate-determining step of the methanation reaction is probably the hydrogenation of surface carbon.

If that is the case, how is it possible to explain that the methanation of surface carbon is much faster than that of CO (*23, 24*)? This is likely to be due to the fact that during the CO + H_2 reaction, only a part of the Ni surface is covered with the active surface carbon, and the observed rate is probably directly connected with the concentration of this active species. We have indeed observed (*10*) that different adsorbed species can be present at the surface in the conditions of the reaction. The so-called Ni_4CO (adsorbed CO bound to 4 Ni surface atoms) is in equilibrium with dissociated species, surface carbon Ni_3C_{surf} (the active species), and adsorbed oxygen. Moreover, other inactive species, the linear and bridged adsorbed CO (NiCO and Ni_2CO, respectively) which are observed under static conditions only below 100°C (*12*), could be present on the surface at higher temperatures in dynamic conditions. In the stationary state, the surface of the catalyst is probably mainly covered with *inactive* adsorbed CO species (NiCO, Ni_2CO, Ni_4CO . . .). This is justified by the fact that dissociated species which are probably more energetic, are more encumbering (*11*) and hence less numerous, so that the energetic balance is more favorable to the coverage of inactive nondissociated CO adspecies. This picture of the surface, covered with *inactive* CO species besides the active surface carbon, appears to be in good agreement with the negative value of the order with respect to CO.

Kinetic Equation

The data of Fig. 6 show that the Temkin relation, Eq. (1), is obeyed. It implies that the rate, r, depends on the CO coverage and that for a given P_{H_2} it can be written as:

$$r = Ke^{-E_0/RT}f(\theta_{CO}) \qquad (2)$$

where K is a constant independent of T and θ_{CO}, E_0 is the true activation energy, and $f(\theta_{CO})$ is a function of the CO coverage.

The kinetic treatment of ethane hydrogenolysis (*19*) can help us in the determination of $f(\theta_{CO})$. The behavior of CO adsorbed species in CO methanation is similar to that of adsorbed H_2 in C_2H_6 hydrogenolysis: both orders are negative, they increase with the temperature (with zero as a limit) and decrease when increasing the partial pressure. Moreover, both reactions present other similar features: the apparent activation energies decrease when increasing the temperature of reaction, the orders with respect to the other reactant (H_2 in the CO + H_2 reaction, C_2H_6 in the hydrogenolysis) are near 1 and roughly partial pressure independent over a large domain of variation.

The rate of C_2H_6 hydrogenolysis was shown (*19*) to obey the following kinetic law:

$$r = k'e^{-E_0'/RT}P_{C_2H_6}(1 - \theta_H)^X \qquad (3)$$

where θ_H is the H_2 coverage, $E_0' \sim 15$ kcal/mol, $X \sim 15$. Equation (3) suggested that the rate-determining step involved the collision of a C_2H_6 molecule with an ensemble of about 15 neighboring surface Ni atoms, free from adsorbed inactive hydrogen which is expected to play a diluting role.

The above analogies between CO methanation and C_2H_6 hydrogenolysis suggest developing relation (*2*) analogously to Eq. (3) according to:

$$r = ke^{-E_0/RT}P_{H_2}(1 - \theta_{CO})^W \qquad (4)$$

with $E_0 = 17$ kcal/mol. In this equation the term $(1 - \theta_{CO})^W$ reflects the negative order with respect to CO, and includes two unknown parameters, namely CO coverage, θ_{CO}, and W. An experimental determination of θ_{CO} at the temperature of reaction by means of volumetric measurements seems rather difficult, due to the various adsorbed species present on the surface and to CO dismutation. According to our hypothesis θ_{CO} is the coverage of the different inactive CO adspecies (i.e., NiCO, Ni_2CO, and Ni_4CO). This equation accounts qualitatively for observed data. As P_{CO} increases, θ_{CO} increases and $(1 - \theta_{CO})^W$ decreases, accounting for negative orders in CO. Moreover, one can easily demonstrate that when $r = k'(1 - \theta_{CO})^W$, then $n_{CO}/a = - W\theta_{CO}/(1 - \theta_{CO})$, where $a = (\partial \log \theta_{CO}/\partial \log P)_T$ is the slope of the log–log transform of the CO isotherm and is also the exponent of the relation $v_{CO} = kP_{CO}{}^a$, where v_{CO} is the volume of adsorbed CO. When θ_{CO} increases (T decrease or P_{CO} increase), one observes that the order in CO, n_{CO}, is more negative, assuming that the exponent a does not vary over the range of θ_{CO} considered. In the same way, when θ_{CO} tends to zero then n_{CO} tends to zero.

It should be emphasized that Eq. (4) cannot account for data obtained at very low CO pressure (Fig. 1) and that a complete quantitative treatment of the methanation reaction would require further kinetic studies in the low CO pressure region. As proposed above, the drastic change in the order in CO at very low CO pressure reveals a dramatic change in the nature of the adsorbed phase (hydrogen becomes the most abundant adspecies). This could induce a drastic change in the mechanism of CO hydrogenation. Hence a general equation accounting for both mechanisms (low and high CO pressure) appears difficult to imagine without including many adjustable parameters, whose physical meaning would be hard to apprehend.

Physical Significance of the Proposed Kinetic Equation

Let us now consider the $(1 - \theta_{CO})^W$ term. If a random distribution of CO adsorbed species is assumed, $(1 - \theta_{CO})^W$ represents the probability of finding an ensemble of W neighboring nickel surface atoms, free from adsorbed, inactive CO. We have recently shown (*11*) in the course of a study dealing with the CO + H_2 reaction over silica-supported Ni–Cu catalysts that the area activity A_x (expressed in transformed CO molecules per second and per metallic unit area) of an alloy of copper content x was connected to the activity of pure nickel A_0 by:

$$A_x = A_0(1 - x)^N \qquad (5)$$

with $N = 13 \pm 2$. This result is consistent with the idea that the active site is an ensemble of $N \sim 13$ adjacent Ni atoms. In Eq. (5) the activity of pure nickel A_0 includes the rate expression (Eq. (4)). Equation (5) can therefore be written as:

$$A_x = ke^{-E_0/RT}P_{H_2}(1 - \theta_{CO})^W(1 - x)^N \qquad (6)$$

where θ_{CO} is independent of x (in good agreement with a volumetric study of CO adsorption at 20°C on these alloys (*25*); it has indeed been shown that the metallic area of the alloys as deduced from CO uptake decreases linearly when x increases, suggesting a constant value for the CO coverage). Equation (6) therefore includes a term of combined probability, indicating that the activity decreases with the decreasing probability of finding at the surface of the alloy an ensemble of adjacent Ni atoms, free from inactive CO species. Then one can propose $W \equiv N$. This hypothesis is supported by the rather good agreement between the values of the exponents N (alloying effect) and X (H_2 coverage effect) as observed in hydrogenolysis reactions (*26*).

Equation (4) suggests that the rate-determining step of the CO methanation includes the collision of an H_2 molecule with a site S composed of an ensemble of approximately 13 adjacent Ni atoms, free from inactive adsorbed CO species. As E_0 is very close to the activation energy of the surface carbon hydrogenation, the above site S is probably occupied by one active surface monocarbon species derived from the dissociative adsorption of CO. The S site should be considered as rapidly saturated with the active surface carbon, since at high temperatures, where θ_{CO} is low and hence the inhibiting role of CO inactive adspecies is disappearing, the limit of the order to CO seems to be zero, as illustrated in Fig. 2.

To summarize our hypothesis the surface of the catalyst can be represented by the following picture. The inactive adsorbed CO molecules are randomly distributed on the surface, jumping from Ni atoms to others before desorbing. The concentration of S sites composed of W adjacent Ni atoms free from inactive CO adspecies is $(1 - \theta_{CO})^W$. They can be considered as having a certain lifetime directly correlated with the time of sojourn of adsorbed CO on Ni atoms. These ensembles should be considered as rapidly saturated, by an active surface carbon via dissociative adsorption of CO. The rate-determining step is linked to the hydrogenation of this surface carbon; the probability of existence of this step, and hence the activity, depends on the probability of collision between gaseous hydrogen [term P_{H_2}, Eq. (4)] and the active surface carbon [term $(1 - \theta_{CO})^W$]. Let us underline that it does not mean that the active hydrogenating species is molecular gaseous H_2 but that the probability of hydrogenation is governed by the number of the above-described collisions and then that the real active hydrogenating species could be dissociated adsorbed hydrogen. Therefore we do not propose a Rideal mechanism, in the strict sense of the term, for the CO methanation. The problem of the exact nature of the active hydrogenating species still remains open and further experiments are now in progress to try to elucidate this question.

CONCLUSION

The activity in CO methanation over Ni/SiO$_2$ catalysts appears to depend on the probability of collision between two species: (i) molecular hydrogen and (ii) a surface compound formed by an active surface carbon bound to an ensemble of a large number of adjacent nickel atoms, free from inactive molecular adsorbed CO. The proposed kinetic equation includes terms whose physical meanings account for this model.

An ensuing work is now in process of completion to extend the model to the formation of C–C bonds during CO + H_2 reaction, in the light of a previous study (*11*) on Ni–Cu/SiO$_2$ catalysts.

As a general conclusion, we point out that, at least on Ni/SiO$_2$ catalysts, the surface active site could be composed of a large number of adjacent Ni atoms particularly when the reaction involves atomic bond rupture as in alkane hydrogenolysis (*19, 27*) or CO hydrogenation ((*11*), this work). On the contrary, when no rupture is necessary, as in C_6H_6 hydrogenation, only a few surface atoms form the active site (*28*).

REFERENCES

1. Sabatier, P., and Senderens, J. B., *J. Soc. Chim. Ind.* **21,** 504 (1902).
2. Vannice, M. A., *J. Catal.* **37,** 449 (1975).
3. Ollis, D. F., and Vannice, M. A., *J. Catal.* **38,** 514 (1975).

4. Bond, G. C., and Turnham, B. D., *J. Catal.* **45,** 128 (1975).
5. Van Ho, S., and Harriott, P., *J. Catal.* **64,** 272 (1980).
6. Ross, J. R. H., *J. Catal.* **71,** 205 (1981).
7. Rautovuoma, A. O. I., and van der Baan, H. S., *J. Catal.* **71,** 423 (1981).
8. Liu Dan Chu, Bakhshi, N. N., and Mathews, J. F., *J. Catal.* **71,** 443 (1981).
9. Joyner, R. W., and Roberts, M. W., *J. Chem. Soc. Faraday Trans. 1* **70,** 1819 (1974).
10. Martin, G. A., Primet, M., and Dalmon, J. A., *J. Catal.* **53,** 321 (1978).
11. Dalmon, J. A. and Martin, G. A., "Proceedings, International Congress on Catalysis, 7th (Tokyo 1980)," p. 402, Kodansha/Elsevier, Tokyo/Amsterdam, 1981.
12. Primet, M., Dalmon, J. A., and Martin, G. A., *J. Catal.* **46,** 25 (1977).
13. Vannice, M. A., *Catal. Rev. Sci. Eng.* **14,** 153 (1976).
14. Palmer, R. L., and Vroom, D., *J. Catal.* **50,** 244 (1977).
15. Kelley, R. D., Madey, T. E., Revesz, K., and Yates, J. T., *Appl. Surf. Sci.* **1,** 266 (1978).
16. Schoubye, P., *J. Catal.* **14,** 238 (1969).
17. Bousquet, J. L., and Teichner, S. J., *Bull. Soc. Chim. Fr.* **10,** 3687 (1972).
18. van Herwijnen, T., van Doesburg, H., and de Jong, W. A., *J. Catal.* **28,** 391 (1973).
19. Martin, G. A., *J. Catal.* **60,** 345 (1979).
20. Schuit, G. C. A., and de Boer, N. H., *Rec. Trav. Chim. Pays-Bas* **70,** 1067 (1951).
21. McCarty, J. G., Wentrcek, P. R., and Wise, H., "Symposium on Catalyst degradation, Poisoning, Sintering, and Restructuring, Petroleum Chemistry Division, American Chemical Society." Chicago, August 1977.
22. Temkin, M., *Acta Physicochim. URSS* **2,** 313 (1935).
23. Araki, M., and Ponec, V., *J. Catal.* **44,** 439 (1979).
24. Dalmon, J. A., and Martin, G. A., *J. Chem. Soc.* **75,** 1011 (1979).
25. Dalmon, J. A., *J. Catal.* **60,** 325 (1979).
26. Guilleux, M. F., Dalmon, J. A., and Martin, G. A., *J. Catal.* **62,** 235 (1980).
27. Dalmon, J. A. and Martin, G. A., *J. Catal.* **66,** 214 (1980).
28. Martin, G. A., and Dalmon, J. A., *J. Catal.* **75,** 233 (1982).