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Kinetics of the Steam Reforming of Methane with Iron, Nickel, and Iron–Nickel Alloys as Catalysts

P. MÜNSTER AND H. J. GRABKE

Max-Planck-Institut für Eisenforschung, Düsseldorf, Federal Republic of Germany

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The steam reforming of methane on iron or nickel, $CH_4 + H_2O \rightarrow CO + 3H_2$, can be regarded as a sequence of two reactions with adsorbed carbon as an intermediate species:

$$CH_4 \rightarrow C(ads) + 2H_2,$$
$$C(ads) + H_2O \rightarrow CO + H_2.$$

As the first reaction is rate limiting, the following rate law can be applied to methane reforming catalysed by iron:

$$v = k_2^{Fe} \cdot a_O^{-n} \cdot p_{CH_4}/p_{H_2}^{1/2},$$
$$0.6 \leqq n \leqq 1.0.$$

The oxygen activity a_O on the catalyst surface is virtually determined by the ratio p_{H_2O}/p_{H_2} in the gas atmosphere. The above rate equation was confirmed by measurements in a flow apparatus for the temperature range 700–900°C. In agreement with the reaction model the steady-state carbon activity on the iron surface and the steady-state carbon concentration in the iron catalyst are very low.

With nickel as catalyst the reaction rate is much higher and independent of the oxygen activity on the catalyst surface. The rate equation reads:

$$v = k_2^{Ni} \cdot p_{CH_4}.$$

Different partial reaction steps of the methane decomposition are rate determining on iron and nickel.

INTRODUCTION

The catalytic reforming of methane is a process of great commercial significance and the understanding of the process mechanism is of particular interest when applied to the direct reduction of iron ore.

The reforming of methane by water vapour,

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad (1)$$

can be considered as a sequence of two partial reactions:

$$CH_4 \rightarrow C(ads) + 2H_2, \quad (2)$$
$$C(ads) + H_2O \rightarrow CO + H_2. \quad (3)$$

The kinetics of these partial reactions are already known from earlier investigations (*1–3*) of the carburization and decarburization of thin iron foils. Since in such experiments equilibrium between adsorbed and dissolved carbon,

$$C(dissolved) \rightleftarrows C(ads), \quad (4)$$

can always be assumed, measurements of the carburization in CH_4–H_2 mixtures (*1, 2*):

$$CH_4 \rightarrow C(dissolved) + 2H_2,$$

and of the decarburization of iron foils in H_2O–H_2 mixtures (*3*),

$$C(dissolved) + H_2O \rightarrow CO + H_2,$$

yield information on Reactions (2) and (3). These investigations have shown that for iron the rate constant of Reaction (2) is smaller by about five orders of magnitude compared with the rate constant of Reaction (3). Therefore, the transfer of carbon from methane to an iron surface is slow,

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whereas the adsorbed carbon is rapidly converted to carbon monoxide. Thus one would expect that the steady-state carbon concentration on and in the iron catalyst is low in a reacting CH_4–H_2–H_2O mixture (*4*).

The rate law for Reaction (2) was determined (*1*, *2*) to be

$$v = k_2^{Fe} p_{CH_4}/p_{H_2}^{1/2} \qquad (5)$$

on iron in the temperature range 700–1100°C. This result indicates that the decomposition of the intermediate CH_3(ads) is rate determining. At very low hydrogen pressure p_{H_2} the rate law becomes

$$v = k_2^{Fe} \cdot p_{CH_4}, \qquad (6)$$

which shows a change in rate control to the decomposition of CH_4(ads). Since Reaction (2) is supposed to be the rate-determining step of Reaction (1) a corresponding rate law is expected for Reaction (1) on iron

$$v = k_2^{Fe} \cdot f(a_O) \cdot p_{CH_4}/p_{H_2}^{1/2}. \qquad (7)$$

In this preliminary rate equation a function $f(a_O)$ of the thermodynamic oxygen activity a_O is introduced that is meant to describe the effect of adsorbed oxygen. Upon Reaction (1) oxygen adsorption can occur according to

$$H_2O \rightleftarrows H_2 + O(ads). \qquad (8)$$

Investigations on the tritium exchange in H_2O–H_2 mixtures (*5*) have shown that Reaction (8) is very fast on iron or nickel catalysts in the temperature range of the present study, 700–900°C. This was further confirmed recently by a study of the water gas-shift reaction on iron (*6*)

$$CO_2 + H_2 \rightleftarrows CO + H_2O,$$

in which Reaction (8) is also a fast reaction step. Therefore it can be assumed that during Reaction (1) the adsorption Reaction (8) is virtually in equilibrium. Thus the thermodynamic oxygen activity on the solid surface a_O can be given by the equilibrium expression

$$a_O = K\, p_{H_2O}/p_{H_2}. \qquad (9)$$

The oxygen activity determines the degree of coverage with adsorbed oxygen and affects the rate of Reaction (1). Therefore some function $f(a_O)$ is expected in the rate law equation (7) for Reaction (1). For very low p_{H_2O}/p_{H_2} ratios a change in rate control to Reaction (3) can be expected. This reaction has been studied on iron (*3*) and can be described at low p_{H_2O}/p_{H_2} by the rate law

$$v = k_3^{Fe} \cdot a_C \cdot p_{H_2O}/p_{H_2}, \qquad (10)$$

where a_C is the steady-state carbon activity, which determines the surface and bulk concentration of carbon.

The rate of carburization of nickel foils according to Reaction (2) is higher by about two orders of magnitude compared to the rate on iron foils (*7*). The rate is proportional to the partial pressure of methane and independent of the hydrogen pressure as given in Eq. (6). Assuming that Reaction

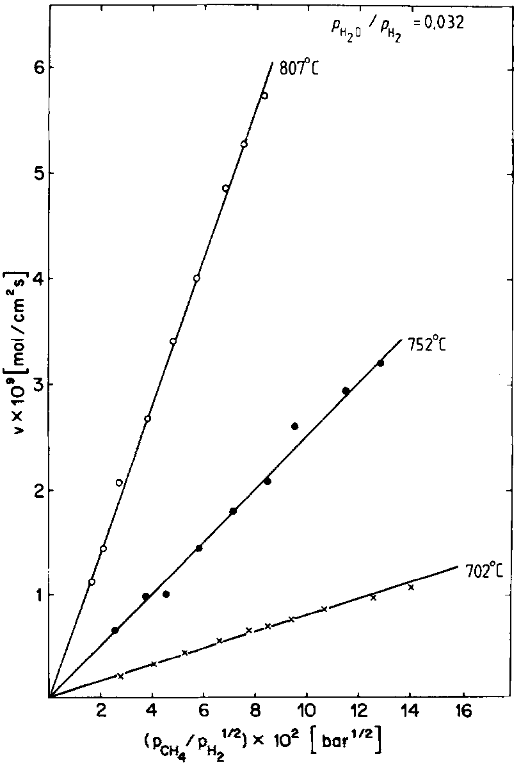

FIG. 1. Dependence of the reaction rate on $p_{CH_4}/p_{H_2}^{1/2}$ at various temperatures and constant ratio $p_{H_2O}/p_{H_2} = 0.032$ (iron catalyst).

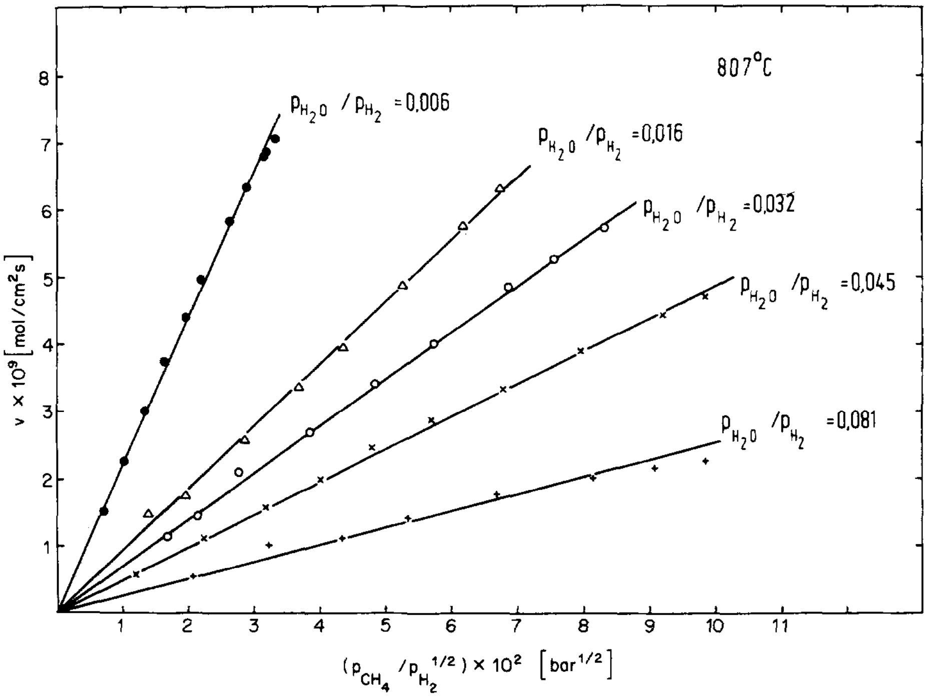

FIG. 2. Dependence of the reaction rate on $p_{CH_4}/p_{H_2}^{1/2}$ at various oxygen activities $a_O = p_{H_2O}/p_{H_2}$ and constant temperature $T = 807°C$ (iron catalyst).

(2) is rate determining for methane reforming also on nickel, the rate equation

$$v = k_2^{Ni} \cdot f(a_O) \cdot p_{CH_4} \tag{11}$$

is expected, and the rate should be much higher on nickel than on iron. As in the case of iron, adsorbed oxygen might affect the rate.

Carburization experiments with iron–nickel alloys showed a steady increase of the reaction rate with increasing nickel con-

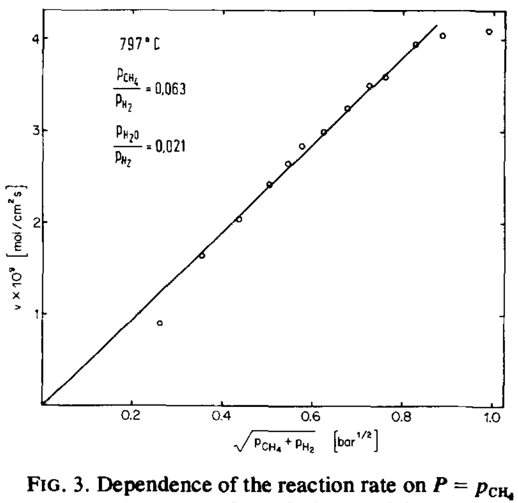

FIG. 3. Dependence of the reaction rate on $P = p_{CH_4} + p_{H_2}$ at constant ratios of the partial pressures p_{CH_4}/p_{H_2} and p_{H_2O}/p_{H_2}, with iron as catalyst.

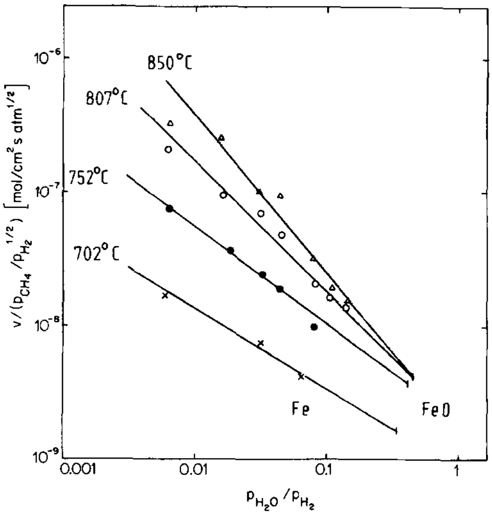

FIG. 4. Dependence of $v/(p_{CH_4}/p_{H_2}^{1/2}) = k_2^{Fe} \cdot f(a_O)$ on p_{H_2O}/p_H [see Eq. (7)].

tent (*8*, *9*). Therefore the rate of methane reforming, too, should increase with increasing nickel content of the catalyst. In this study the aim was to confirm these expected relations by measurements of the methane reforming reaction on iron, nickel and iron–nickel catalysts. The steady-state carbon concentration in the iron catalyst was to be determined in order to verify that the carbon concentration in and on the metal is very low during the reaction in a flowing CH_4–H_2O–H_2 mixture.

EXPERIMENTAL

The experiments were carried out in a flow reactor at a total pressure of ≃1 bar. A detailed description of the experimental apparatus is given in Ref. (*10*). Controlled gas mixtures of CH_4 (99.9995%), H_2 (99.999%), and H_2O were passed through a quartz tube situated in a furnace. The methane content of the gas mixture was varied between 0.5 and 10 vol%. The water vapour content was varied between 0.5 and 8.5 vol% with iron as catalyst and up to 30 vol% with nickel as catalyst. The quartz tube contained a metal foil (iron, nickel, or iron–nickel alloy) as catalyst. Beyond the furnace the gas was dried and then analyzed by infrared gas analyzers (URAS, Hartmann & Braun) for the concentrations of CO, CH_4, and CO_2. The concentration of CO_2 which can possibly be formed in a side reaction,

$$CO + H_2O \rightarrow CO_2 + H_2,$$

can be neglected when considering the equilibrium condition. The concentration of CO was the main measuring parameter.

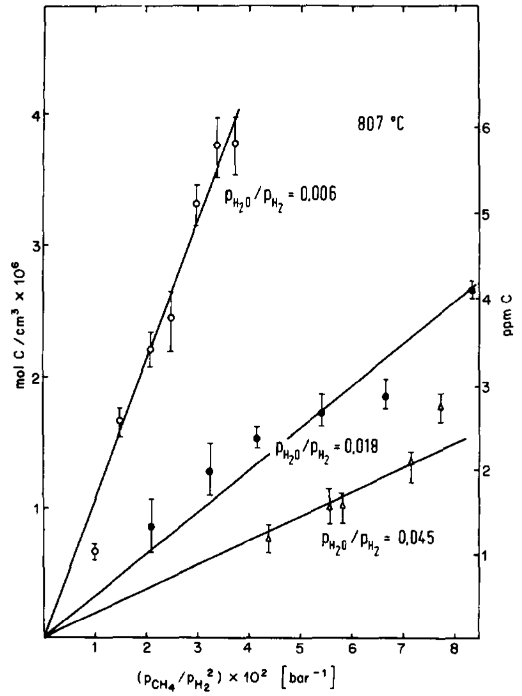

FIG. 5. Steady-state carbon concentrations in the iron catalyst established by a CH_4–H_2–H_2O gas mixture as a function of the ratio $p_{CH_4}/p_{H_2}^2$ at various ratios p_{H_2O}/p_{H_2} and constant temperature T = 807°C.

The rate of reaction v was calculated from the measurements of CO formation for the case of a differential reactor according to

$$v = \frac{dn_{CO}}{A\,dt} = \frac{\dot{V}_{CH_4} + \dot{V}_{H_2}}{ART}\,p_{CO}, \qquad (12)$$

with

$\dot{V}$ = flow rate of the respective gas in cm³/s,
A = geometric surface area of the metal foil,
T = room temperature,
R = gas constant,
p_{CO} = partial pressure of the CO formed.

In order to verify the dependence of the reaction rate on the partial pressures of CH_4 and H_2 (see Eqs. (5) and (8)) the total pressure of the reacting gases was reduced from P = 1 atm to 0.05 atm by adding various amounts of helium to the gas mixture while the ratios of the partial pressures p_{CH_4}/p_{H_2} and p_{H_2O}/p_{H_2} were kept constant. The rate of the reaction on the walls which had been determined separately on the empty reaction vessel was subtracted from the total reaction rate.

The determination of the steady-state carbon activities by measurements of the electrical resistance (4) was carried out in the same flow apparatus with iron foils of 5 μm thickness. The resistance change of the sample caused by carbon uptake was recorded. This resistance change is directly proportional to the carbon concentration. The solubility of oxygen in iron under the reaction conditions of Fig. 5 is negligibly small, about 1 wt ppm O, so that no effect on the electrical resistance was detected. The measurement was calibrated by equilibrating the sample with various flowing CH_4–H_2 mixtures and relating the measured resistance change to the known carbon concentration which is in equilibrium with the given CH_4–H_2 mixture (*11*). From the resistance change by carbon uptake in the flowing and reacting CH_4–H_2O–H_2 mixture the steady-state carbon concentration can be deduced.

RESULTS

With iron as catalyst the reaction rate is proportional to $p_{CH_4}/p_{H_2}{}^{1/2}$. The proportionality to p_{CH_4} is shown in Figs. 1 and 2. At constant ratio p_{CH_4}/p_{H_2} and p_{H_2O}/p_{H_2} the rate is expected to be proportional to the square root of P, i.e., the sum of the partial pressures of CH_4 and H_2. This is in agreement with Eq. (7) according to

$$P = p_{CH_4} + p_{H_2},$$

$$v \sim \frac{p_{CH_4}}{p_{H_2}{}^{1/2}} = \frac{x_{CH_4}}{x_{H_2}{}^{1/2}} \cdot \frac{P}{P^{1/2}} = \frac{x_{CH_4}}{x_{H_2}{}^{1/2}} P^{1/2}, \quad (13)$$

x is the mole fraction of the respective gas in the CH_4–H_2 mixture. The relation in Eq. (13) could be confirmed at 800°C for the range $0.05 \leqq P \leqq 1$ bar, see Fig. 3.

The slope of the linear plots in Figs. 1 and 2 yields the rate coefficient $k_1 \cdot f(a_O)$, which is a function of the oxygen activity. With increasing ratio p_{H_2O}/p_{H_2} the rate coefficient decreases (Fig. 2). This retardation is most probably caused by an increase of coverage with adsorbed oxygen atoms according to the adsorption equilibrium (*8*). A double logarithmic plot of $v/(p_{CH_4}/p_{H_2}{}^{1/2})$ versus

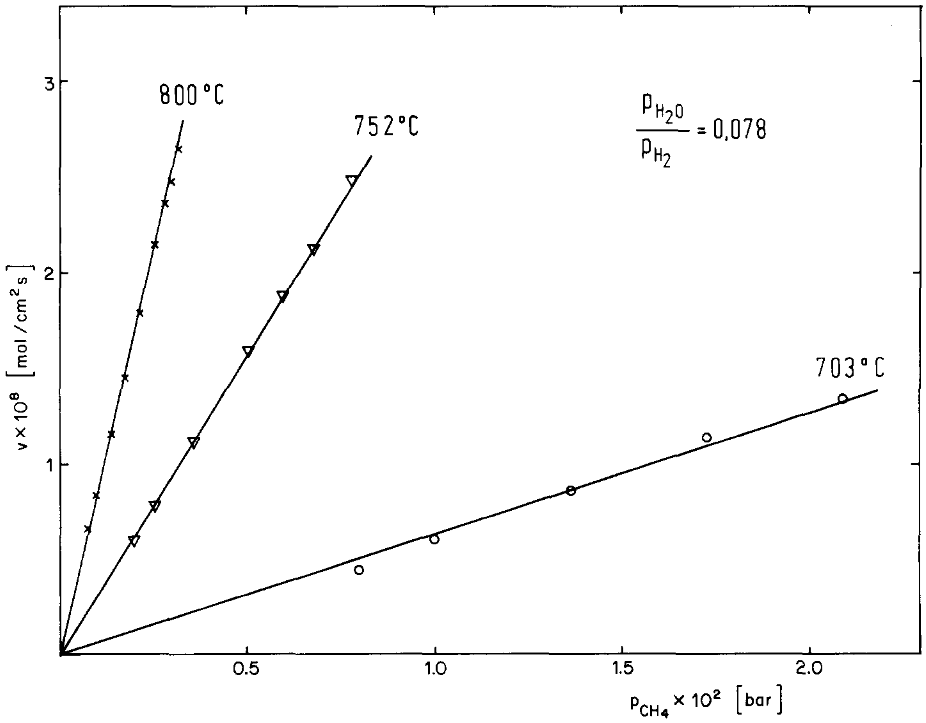

FIG. 6. Dependence of the reaction rate on the partial pressure p_{CH_4} at various temperatures and constant ratio $p_{H_2O}/p_{H_2} = 0.078$ for a nickel catalyst.

p_{H_2O}/p_{H_2} yields straight lines (Fig. 4) up to the value of p_{H_2O}/p_{H_2} where oxidation to FeO occurs. The dependence of the rate coefficient on the oxygen activity can therefore be written as

$$k_2^{Fe} \cdot f(a_O) = k_2^{Fe} \cdot a_O^{-n}. \qquad (14)$$

Accordingly, the rate equation of the steam reforming with iron as catalyst reads:

$$v = k_2^{Fe} \cdot a_O^{-n} \cdot p_{CH_4}/p_{H_2}^{1/2}, \qquad (15)$$
$$0{,}6 < n < 1.$$

Another aim of this study was to confirm that the carbon concentration in and on the iron catalyst is very low in the steady state in a flowing CH_4–H_2–H_2O mixture. As described above, the carbon concentration in the specimen can be detected by measurements of the increase of electrical resistance due to carbon uptake. The results are summed up in Fig. 5, showing that the steady-state carbon concentrations are in the range $\leqq 6$ wt ppm C and decrease with increasing oxygen activity. The measured concentrations are much smaller than the values for the equilibrium carbon concentration in iron in CH_4–H_2 atmospheres with the same carbon activities $a_C \propto p_{CH_4}/p_{H_2}^2$ but in the absence of water vapour. At $p_{CH_4}/p_{H_2}^2 = 0.011$ bar^{-1} in equilibrium with CH_4–H_2 the maximum carbon concentration in α-iron is obtained: 120 wt ppm C. In the presence of water vapour the carbon concentration is much lower, for example at $p_{H_2O}/p_{H_2} = 0.006$ the steady-state carbon concentration is only about 1 ppm C. The carbon activity in the gas phase can even be raised above the value for equilibrium with graphite which is $p_{CH_4}/p_{H_2}^2 = 0.043$ bar^{-1} at 807°C, but in the presence of some H_2O in CH_4–H_2 the steady-state carbon concentration in iron remains far below saturation, and no graphite formation or cementite formation occurs.

With nickel as catalyst the rate of Reaction (1) is proportional to p_{CH_4} (Fig. 6) and to the total pressure $p_{CH_4} + p_{H_2}$ for constant ratios p_{CH_4}/p_{H_2} and p_{H_2O}/p_{H_2} (Fig. 7). These results confirm Eq. (11), which was expected for nickel. The slope of the lines yields the rate coefficient, which is independent of the oxygen activity in a wide range of a_O as can be seen from Fig. 8. Only in the range of $p_{H_2O}/p_{H_2} < 0.1$ does the rate decrease steeply with decreasing oxygen activity. This behaviour is not in agreement with rate control by Reaction (2) but can be correlated with Eq. (10) therefore indicating a change in rate control to Reaction (3).

The temperature dependence of the methane decomposition as a rate-controlling step is seen from an Arrhenius plot of the average values of k_2^{Ni} for $p_{H_2O}/p_{H_2} = 0.1$. This plot yields $k_2^{Ni} = (8.5 \pm 0.6)$ exp $(-182 \pm 7/RT)$ mol/cm^2 s bar (activation energy in kJ/mol). The rate equation for the data obtained with iron–nickel alloys containing up to about 60% nickel is the same as for iron (see Eq. (7)). As shown in Fig. 9a the rate constants increase with increasing nickel content of the catalyst and decrease with increasing oxygen activity. The data obtained with the catalysts containing more than 80% nickel are independent of the oxygen activity in a restricted range (see Fig. 9b).

DISCUSSION

The study has shown how the kinetics of a complex heterogeneous reaction, namely, methane reforming on a metal catalyst, can be derived from a knowledge of simpler reactions, namely, the carburization of the metal in CH_4–H_2 and the decarburization in H_2–H_2O. The results show that with all catalysts used in this study the decomposition of methane, Reaction (2), is rate controlling in a wide range of reaction conditions.

Only for nickel and Fe–Ni alloys containing more than 60% Ni do the data at low p_{H_2O}/p_{H_2} indicate a change in rate control to Reaction (3). Equations (2) and (3) give only a rough model of the atomistic reaction steps. The elementary steps are discussed in more detail in previous papers (*1*, *10*). The dependence of the reaction rate on the

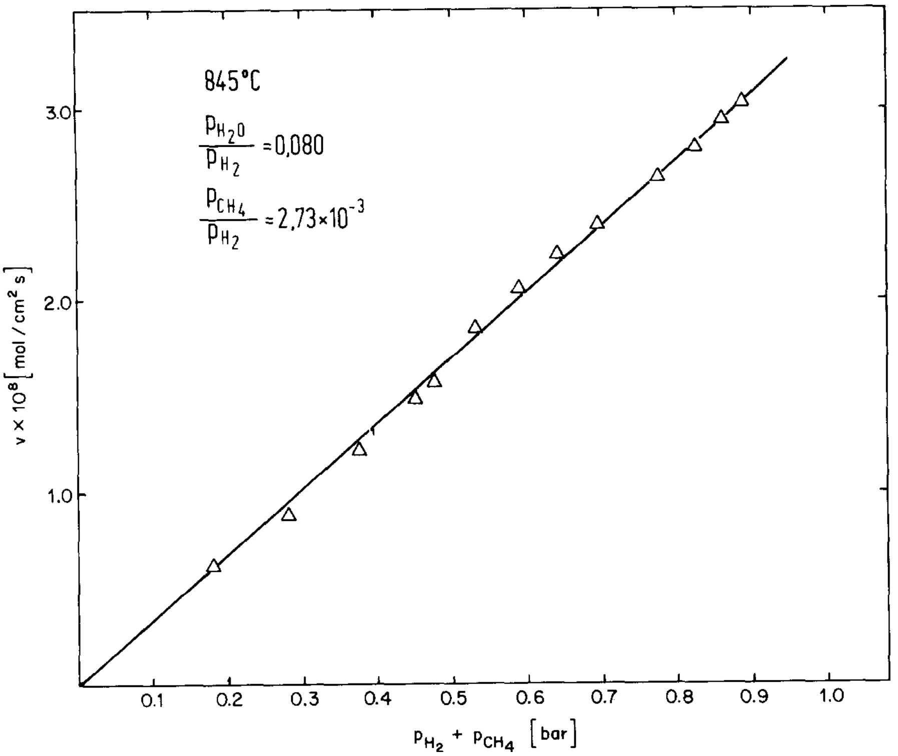

FIG. 7. Reaction rate of methane reformation as a function of $P = p_{CH_4} + p_{H_2}$ on nickel as catalyst.

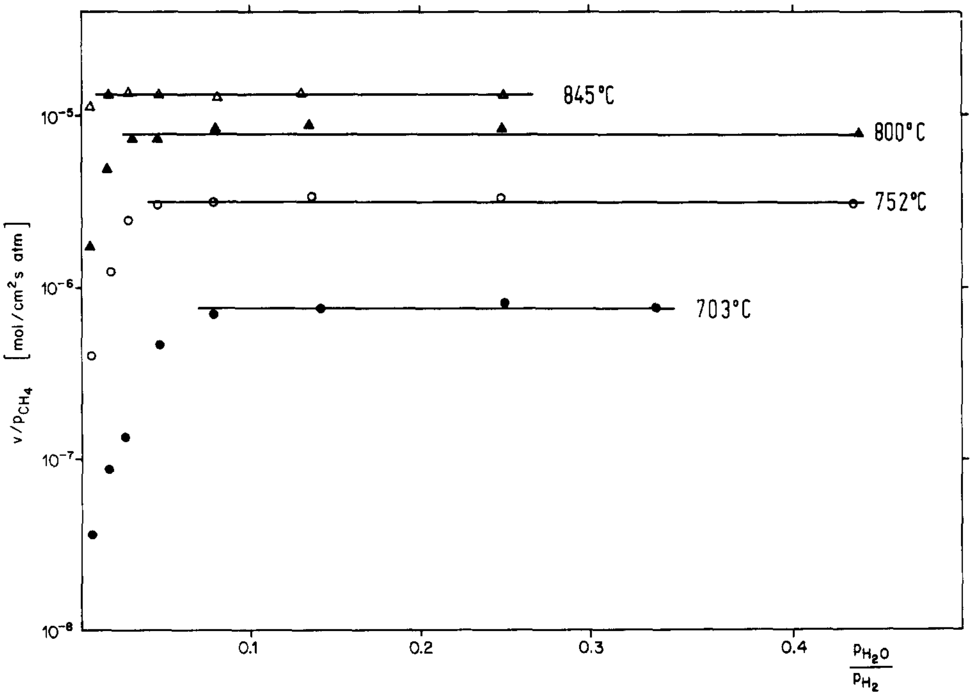

FIG. 8. Dependence of v/p_{CH_4} on p_{H_2O}/p_{H_2} at various temperatures for a nickel catalyst.

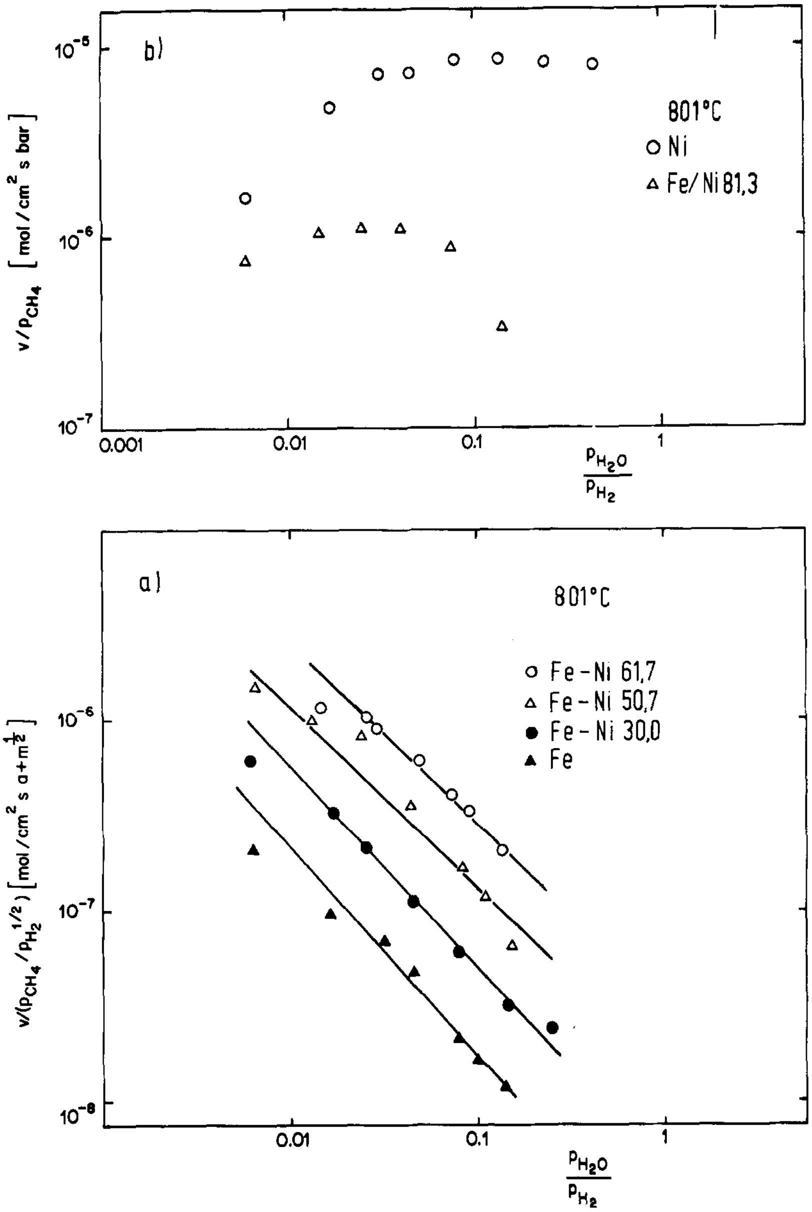

FIG. 9. (a) $v/p_{CH_4}/p_{H_2}^{1/2})$ as a function of p_{H_2O}/p_{H_2} for iron and iron-nickel alloys containing up to 60% Ni [see Eq. (7)]. (b) v/p_{CH_4} as a function of p_{H_2O}/p_{H_2} for nickel and iron-nickel alloy containing 81.3% Ni [see Eq. (11)].

partial pressures p_{CH_4} and p_{H_2} indicates that on iron and on iron-nickel alloys containing up to 60% Ni the decomposition of the CH_3 radical is the rate limiting elementary step of the methane decomposition (*1*, *2*). On nickel and on the nickel alloy with the highest Ni content (81.3%) the first step of the methane decomposition is rate determining (*1*, *9*).

The retardation of the reaction by adsorbed oxygen, which was observed with iron-nickel alloys (see Fig. 3), can be explained by surface site blocking beause of the high oxygen affinity of iron. To describe the oxygen adsorption on iron the Langmuir equation could only be applied to the results obtained at temperatures up to 750°C (*10*).

At higher temperatures this equation could not be applied, since with increasing temperature and increasing oxygen activity the catalyst surface shows facetting. Terraces and steps with different crystallographic orientations ar formed. Therefore, the Temkin isotherm, which is a generalization of the Langmuir equation for polycrystalline heterogeneous surfaces, was used to describe the oxygen adsorption on the iron catalyst:

$$\theta = g \cdot \ln a_O. \qquad (16)$$

For catalytic reactions on heterogeneous surfaces it can be assumed that the reaction rate decreases exponentially with the oxygen coverage of the surface. Then the rate equation reads:

$$v = k_1^{\mathrm{Fe}} \cdot e^{-f\theta} \cdot p_{CH_4}/p_{H_2}^{1/2}, \qquad (17)$$

and combined with Eq. (16) the experimental rate law of Eq. (15) results ($n = f \cdot g$). For iron–nickel alloys containing up to 60% nickel, a similar retardation of the reaction by adsorbed oxygen is also observed (see Fig. 9a).

With nickel as catalyst no retardation of the reaction by adsorbed oxygen is observed (see Fig. 8). The dependence of the rate on the oxygen activity in the range of low $p_{H_2O}/p_{H_2} = 0.1$ can be explained by a change of the rate-controlling step. Obviously the concentration of adsorbed oxygen is very low for such low oxygen activities and the reaction

$$\mathrm{O(ads)} + \mathrm{C} \rightarrow \mathrm{CO}, \qquad (18)$$

for which the rate is proportional to p_{H_2O}/p_{H_2} [see Eq. (10)] should be rate limiting. The rate constant for the reforming of methane on nickel [Reaction (1)], which is 8×10^{-6} mol/cm^2 s bar at 800°C, is in reasonable agreement with the rate constant of the carburization of nickel [Reaction (2)], which at 800°C is 2×10^{-6} mol/cm^2 s bar (*7*), considering that the two values were measured by different methods on different samples. This is another proof that the decomposition of methane is the rate-controlling step of Reaction (1).

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REFERENCES

1. Grabke, H. J., *Ber. Bunsenges. Phys. Chem.* **69**, 409 (1965).
2. Grabke, H. J., and Martin E., *Arch Eisenhüttenwes.* **44**, 847 (1973).
3. Grabke, H. J., and Tauber, G., *Arch. Eisenhüttenwes.* **46**, 215 (1975).
4. Williams, Möller R., AND Grabke, H. J., *High Temp. Sci.* **14**, 33 (1981).
5. Best, K. J., and Grabke, H. J. *Ber. Bunsenges. Physik. Chem.* **75**, 524 (1971).
6. Münster, P., and Grabke, H. J., *Arch. Eisenhüttenwes.* **51**, 319 (1980).
7. Lazar, K., and Konczos, G., *Hungarian Acad. Sci.* **86**, 1 (1977).
8. Grabke, H. J., Müller, E. M., and Konczos, G., *Scripta Met.* **14**, 159 (1980).
9. Grabke, H. J., Konczos, G., Müller, E. M., and Ramanathan, R., *Ber. Bunsenges. Physik. Chem.*, in preparation.
10. Münster, P., and Grabke, H. J., *Ber. Bunsenges. Physik. Chem.* **84**, 1068 (1980).
11. Schürmann, E., Schmidt, T., and Tillmann, F., *Giesserei-Forschung* **19**, 35 (1967).