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Sulfur Poisoning of Boudouard and Methanation Reactions on Nickel Catalysts

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The Boudouard and methanation reactions were studied over a nickel catalyst under conditions where both reactions could be followed simultaneously. The dynamics of the reactions during a sulfur poisoning were followed in a thermogravimetric apparatus. During the drastic deactivation, the selectivity was constant, which indicates that the two reactions have the same intermediate. The poisoning of the methanation reaction was further studied on presulfided samples. The effect of sulfur is strongly nonlinear, but the activation energy remains constant. This indicates that the poisoning is geometrical, and that the methanation reaction requires an ensemble with several nickel atoms.

1. INTRODUCTION

The Boudouard reaction

$$2CO = C + CO_2 \qquad (-\Delta H_{298}^\circ = 172 \text{ kJ/mol}) \quad (1)$$

represents a potential risk of carbon formation in processes involving high concentrations of carbon monoxide over nickel catalysts, or nickel-containing construction materials. Examples are methanation for the production of synthetic natural gas (SNG) (*1*), and the manufacture of reducing gas for direct reduction of iron ore (*2*). Carbon formation on the catalyst may result in blockage of the pore mouths, or breakdown of the catalyst with a resulting increase in pressure drop. In preheaters and heat exchangers the carbon formed on the nickel may react with chromium resulting in carbide formation and leading to the so-called metal dusting corrosion (*3*). The corroded surface may function as a methanation catalyst, resulting in uncontrolled overheating.

The present work deals with a study of the Boudouard and methanation reactions under conditions where both reactions could be followed simultaneously.

Thermodynamics Aspects

When a catalyst is present, it is necessary to consider also the following reactions

$$CO + 3H_2 = CH_4 + H_2O \qquad (-\Delta H_{298}^\circ = 206 \text{ kJ/mol}), \quad (2)$$

$$CO + H_2O = CO_2 + H_2 \qquad (-\Delta H_{298}^\circ = 41 \text{ kJ/mol}). \quad (3)$$

The risk of carbon formation is normally evaluated by means of the so-called principle of equilibrated gas (*4*) which predicts carbon formation if the gas shows affinity for reaction 1 after the establishment of the methanation and shift equilibria. Dent and Cobb (*5*) observed that the thermodynamic data to be used for these calculations were influenced by the carbon modification involved. Our studies (*6*) con-

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firmed this observation which implies that the equilibrium constant observed on the catalyst is smaller than that based on graphite. This means that higher contents of carbon monoxide are allowed before carbon formation. A similar deviation from graphite data was observed for the decomposition of methane.

As outlined earlier (*6*) this effect can be ascribed to the whisker-like structure of the carbon formed on the catalyst. The large surface to volume ratio of the whiskers results in a contribution from the surface energy comparable with the observed deviation. The effect is favored by small nickel crystals as the whisker diameter is close to that of the nickel crystals.

Kinetics and Mechanism

Thermogravimetric studies by Tøttrup (*7*) showed that the rate of carbon formation from the Boudouard reaction did not vary with time after an induction period. This behavior has been observed also for other systems (*8*). The rate was found to increase with the partial pressure of the carbon monoxide, and it was possible to fit the data to a Langmuir-type expression (*7*). The addition of small amounts of steam caused a significant decrease of the reaction rate and an increase of the CO_2 of the exit gas. The presence of alkali did not influence the retarding effect of steam. Addition of hydrogen also caused a decrease in the reaction rate, although the effect was less pronounced. At the same time the exit gas showed a small content of methane being insignificant compared with the equilibrium value. The data thus indicated a competition for sites of the Boudouard reaction, the shift reaction, and the methanation reaction, and that the shift reaction proceeds much faster than the methanation reaction (*7*).

Tøttrup estimated the activation energy of the Boudouard reaction to be 134 kJ/mol at low temperature, which is very close to the value found at low temperature for other systems (*8*). The activation energy is also very close to the activation energy of diffusion of carbon through nickel. This has formed the basis of explanations of the whisker growth (*9*, *10*) in which the diffusion of carbon through the nickel crystal is a step (and at low temperature the rate-determining step) in the growth of carbon whiskers.

The Influence of Sulfur

It is well known that sulfur chemisorbs on nickel surfaces (*11*) forming well-defined structures, and that above a certain coverage, a so-called two-dimensional surface sulfide is formed in which the nickel atoms are probably bound more strongly to the sulfur atoms than to the nickel atoms in the bulk (*12*). The saturation layer was found to contain 0.54 Ni atom per S atom (*11*) equivalent to $44.5 \cdot 10^{-9}$ g S/cm^2 Ni (*12*). Oliphant *et al.* (*13*) found this ratio to be 0.7, which, however, is in conflict with the structures identified by LEED (*12*, *14*, *15*).

It was shown that the surface sulfide eliminates the segregation of carbon from nickel (*16*) as well as preventing carbon formation from the Boudouard reaction (*6*, *11*). The sulfur, therefore, blocks the nickel surface and thereby the diffusion of carbon through the nickel crystal. The sulfur also poisons the adsorption of carbon monoxide (*15*, *17*, *18*) and the methanation (*19*) and reforming reactions (*11*).

With this background it was decided to study the dynamics of the Boudouard and methanation reactions in a thermogravimetric system during a sulfur poisoning. The studies were supplemented by experiments investigating the influence of sulfur coverage of the nickel surface on the methanation rate.

2. EXPERIMENTAL

Thermogravimetric Studies

Apparatus. The experiments were carried out in a thermogravimetric system described in detail earlier (*6*). A catalyst

pellet was hung in a microbalance (REEC–EMB1; sensitivity, 100 mV/mg). During the experiments weight changes of 0.1 mg could be followed. The catalyst was placed in a reactor (internal diameter = 19 mm) surrounded by an electrically heated furnace. The reactor and the microbalance were separated by a helium sealing system.

During the tests, the gas temperature was measured by a thermocouple situated just below the catalyst pellet. The temperature was adjusted by means of a thyristor controller. The exit gas line was connected to a gas chromatograph.

Gases. All gases were taken from cylinders. Helium was used as diluent. H_2S was added as a premixed gas, H_2/H_2S, containing 50 ppm H_2S. All gases were used unpurified. Gas chromatographic analysis indicated impurities (mainly CH_4 in CO) to be less than 0.01%.

Catalyst. The catalyst pellet was nickel on magnesium aluminum spinel as a 4.4 × 4.4-mm cylinder. The nickel content was 13 wt%, and the sulfur capacity determined by chemisorption (*11*) was 260 ppm corresponding to a nickel area of 0.6 m^2/g. The nickel crystallite size observed in an electron microscope was in the range of 300 to 3500 Å. The effective diffusion of CO at test conditions was calculated to be 0.08 m^2/hr on the basis of the pore volume distribution.

Procedure. A mixture of CO and H_2 diluted with He was passed over the catalyst pellet at 400°C and atmospheric pressure. The weight changes of the catalyst were followed, and gas samples were passed through the chromatograph. The CO/H_2, CO and H_2S/H_2 ratios were varied by maintaining a constant He flow (3 liters STP/hr). The rates r_B and r_m of the respective Boudouard and methanation reactions were calculated from the measured inlet flows, the recorded weight increase, and the exit gas analyses. The selectivity of carbon formation was expressed by the ratio of the two rates r_B/r_m.

Methanation Studies of Presulfided Catalysts

Apparatus. The activity was measured at atmospheric pressure in a differential once-through flow reactor with a fixed catalyst bed. The reactor, which was copper-lined, had an internal diameter of 6 mm, and the temperature was measured in a central thermowell with external diameter of 2.3 mm. The reactor was surrounded by an electrically heated furnace, and the temperature was adjusted by thyristor control. The maximum temperature variation in the catalyst was estimated to be less than ±2°C. The inlet flows were measured on capillary flowmeters. The CH_4 content of the exit gas was measured on an infrared analyzer (URAS1).

Gases. CO, H_2, and N_2 were taken unpurified from a bottle as above. N_2 contained less than 10 ppm O_2.

Catalyst. The catalyst was nickel on stabilized alumina as 0.3- to 0.5-mm particles. The nickel content was 25 wt%, and the sulfur capacity was ca. 4000 wt ppm, corresponding to a nickel area of 9 m^2/g.

Presulfided samples of the catalyst were prepared by exposing 0.5 g of the catalyst to a flow of H_2S/H_2 mixtures in a quartz reactor with an internal diameter of 10 mm. The bed temperature was kept within ±2°C.

The H_2S/H_2 inlet gas was made by mixing H_2 with H_2S/H_2 gas from a cylinder containing 200 or 20 ppm H_2S. The gas cylinder was coated inside with Teflon in order to prevent H_2S from reacting with the iron wall. It was necessary to saturate the inlet gas with water in order to avoid hydrogen sulfide uptake on the catalyst carrier. This was done by saturating the H_2 in H_2O at 20°C before mixing the H_2S/H_2.

The sulfidation was carried out at 300, 500, or 800°C with H_2S/H_2 varying between $8.4 \cdot 10^{-9}$ and $5.7 \cdot 10^{-6}$ to obtain a broad range of coverages. The sulfidation was terminated when the inlet and exit concentrations were equal. The concentrations

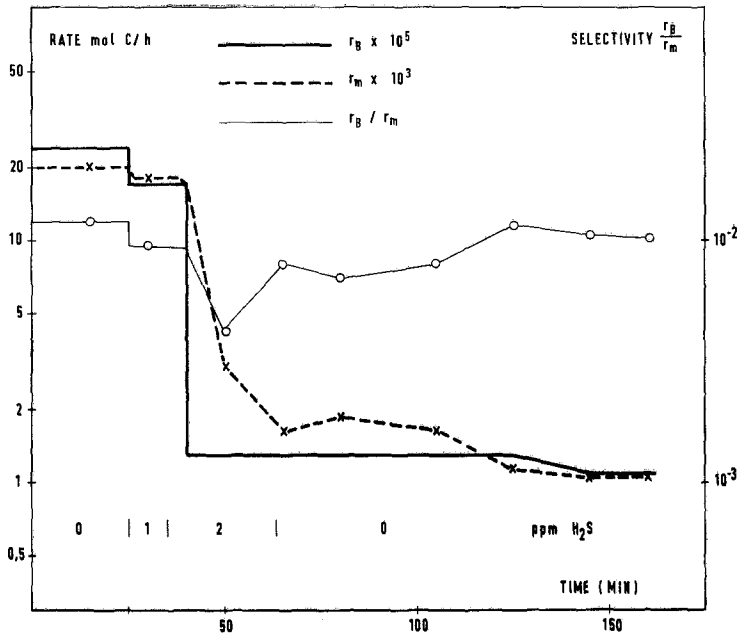

FIG. 1. Sulfur poisoning of Boudouard and methanation reactions. 400°C, 1 atm abs., 0.1 g cat. in TGA. Inlet flows (liters STP/hr): $H_2/CO/He = 5/7/3$.

of H_2S were measured with Dräger tubes, which were able to determine concentrations down to ~10 ppb. Concentrations in this range were required to obtain low coverages at 300°C. The chemisorption equilibrium data will be discussed in a later paper.

After sulfidation, the catalyst samples were unloaded and divided for sulfur analysis (s), sulfur capacity (s_0), and activity determination. The coverage was calculated as s/s_0.

Procedure. A sample of 0.05 to 0.1 g of the presulfided catalyst was placed in the reactor heated to 300°C in N_2, and exposed to the CO/H_2 feed gas (40–100 liters STP/hr). The CO concentration was varied (0.5–10%) to establish conditions of zero-order kinetics (*20*). This was done to measure the activity without the inhibition of CO. The relative activity was calculated by dividing the activity with that measured on the unpoisoned catalyst.

Calculations indicated no mass transfer restrictions in the film or in the pore system (Thiele modulus less than $(6)^{\frac{1}{2}}$), and the temperature increase over the gas film was estimated to be less than 0.2°C. The used catalyst was analyzed for sulfur to check the coverage. In no case did the difference exceed 10%.

3. RESULTS

Thermogravimetric Tests

At 400 to 470°C a mixture $CO/H_2 = 0.33$ ($P_{CO} = 0.2$ atm) showed no carbon formation in accordance with the principle of equilibrated gas predicting no carbon formation between 350 and 660°C, with the estimated equilibrium constant over 3500-Å crystals (*6*). (For graphite data the carbon free zone was 415–800°C, thus predicting carbon for the test at 400°C.)

With a mixture $CO/H_2 = 0.7$ ($P_{CO} = 0.33$ atm), significant carbon formation was observed at a constant rate. The principle of equilibrated gas predicts carbon at 400°C for Ni-crystals larger than 2500 Å. The methanation rate was not affected by

the carbon formation, and the selectivity of the Boudouard reaction was calculated to be $12 \cdot 10^{-3}$.

The effect of adding hydrogen sulfide to the feed is illustrated in Fig. 1. A small period with 1 ppm H_2S resulted in only a small decrease of the reaction rates of the Boudouard and methanation reactions, whereas the addition of 2 ppm H_2S resulted in a fast decrease of both reaction rates by approximately a factor of 20. After interruption of the addition of hydrogen sulfide, the rates remained at this low level. The desorption rate of hydrogen sulfide at these conditions is negligible due to a very low driving force ($H_2S/H_2 \sim 10$ ppb at equilibrium).

It should be noted that the selectivity for the Boudouard reaction was almost unaffected by the drastic deactivation. When increasing the CO/H_2 ratio, however, the selectivity of the Boudouard reaction increased as shown in Fig. 2. This was mainly caused by an increased rate of the Boudouard reaction, whereas the rate of the methanation reaction remained nearly constant. The result is in accordance with the kinetics of the two reactions for sulfur-free catalyst. As mentioned before (*7*) the rate of the Boudouard reaction increases with the partial pressure of carbon monoxide, whereas the rate of the methanation reaction at atmospheric pressure and at 400°C is nearly zero order with respect to hydrogen and carbon monoxide (*21*).

Analysis of the used catalyst pellet showed a sulfur content of 70 wt ppm, whereas the total sulfur capacity of the pellet was determined to 260 wt ppm. Thus the strong deactivation has taken place with only a part coverage of the nickel surface. The result cannot be explained in terms of diffusion restrictions due to a shell poisoning of the pellet. Calculated diffusion rates of carbon monoxide through the core were higher than the measured methanation rate by a factor of 50. Moreover, the equilibrated gas in the core would still have had affinity for the Boudouard reaction. The results should rather be explained in terms of a nonlinear poisoning of the active ensembles for the two reactions. This possibility was proven in the activity tests on the presulfided catalysts.

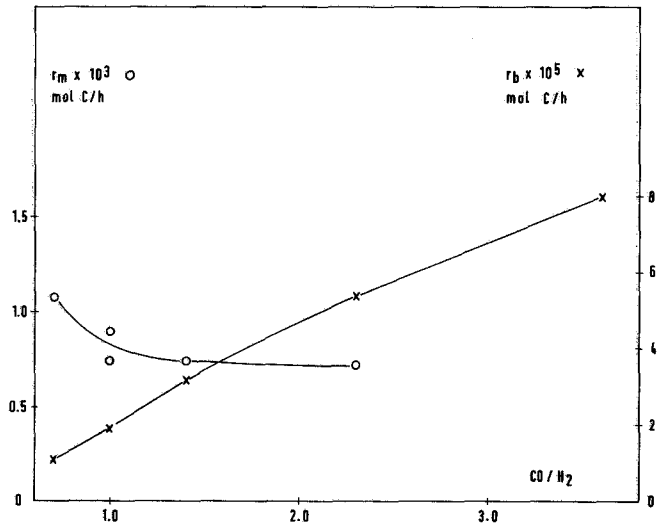

FIG. 2. Boudouard and methanation reactions on S-poisoned catalyst. 400°C, 1 atm abs., 0.1 g cat. in TGA. Total inlet flow: 15 liters STP/hr. $P_{CO} + P_{H_2} = 0.8$ atm.

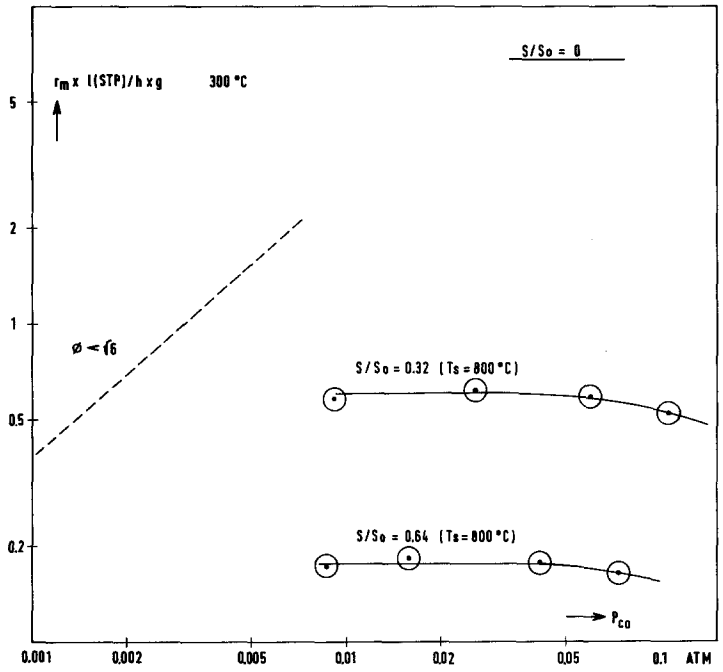

FIG. 3. Methanation rates of poisoned and unpoisoned catalyst. 300°C, 1 atm abs., total flow =40 liters STP/hr. Catalyst: 0.05 to 0.1 g. Data for unpoisoned catalyst extrapolated from Fig. 5. Limit for mass transfer restrictions indicated by dotted line. T_s = sulfidation temperature.

Methanation Tests

Typical activity plots from measurements at 300°C on presulfided catalysts are shown in Fig. 3 illustrating the zero-order kinetics.

The activity depends strongly on the sulfur coverage. Figure 4 shows a log–log plot of the relative activity as a function of the free-nickel surface area (or nickel site concentration). A straight line is fitted with a slope of −4.3. Hence the rate can be expressed by:

$$r_m = k(1 - s/s_0)^{4.3}. \quad (4)$$

Additional measurements at 330°C indicated that the temperature dependence of the rate was independent of sulfur coverage as illustrated in Fig. 5. An activation energy of 92 kJ/mol was calculated for the unpoisoned and poisoned catalysts as well. This value is within the range of published data (*1*, *20*).

A progressive deactivation was observed at prolonged exposure to 330°C as indicated for one experiment in Fig. 5. This phenomenon which was most pronounced at high S-coverages, was ascribed to encapsulation by carbonaceous deposits as shown in Fig. 6. However, it is unclear whether the sulfidation temperature has had any influence on this phenomenon. The deactivation did not change the activation energy.

4. DISCUSSION

Although the thermogravimetric experiments were subject to an undefined sulfur distribution in the pellets, the results are consistent with the assumption that the methanation and Boudouard reactions involve the same intermediate. Sulfur "blocks" the sites for the formation of this intermediate and hence it retards the Boudouard and methanation reactions to the same extent. A number of recent studies (*22–27*) have given evidence that

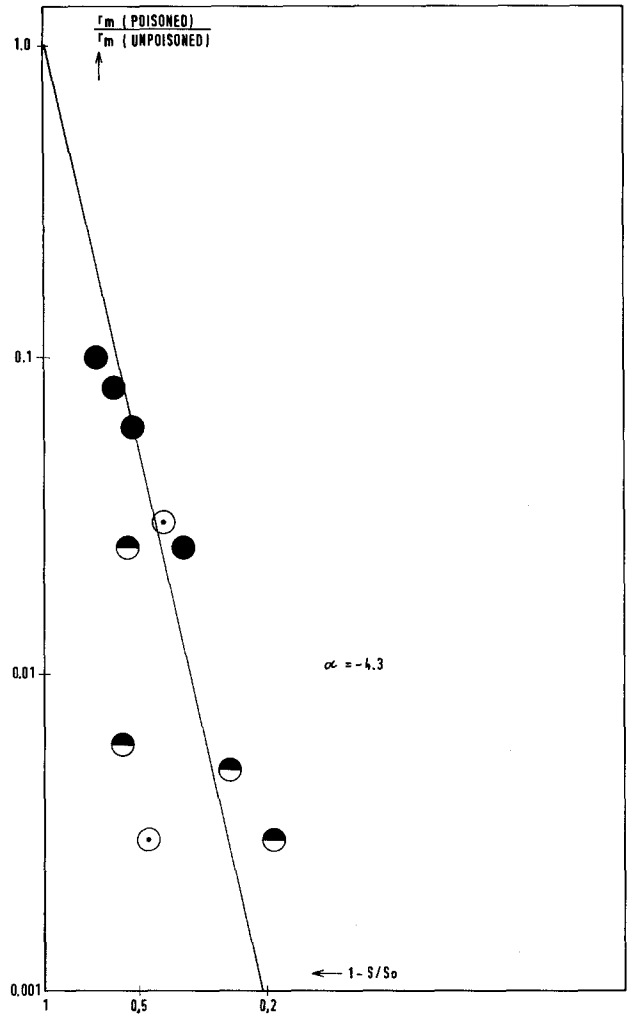

FIG. 4. Methanation activity of presulfided catalysts at 300°C, 1 atm abs., 0.05 g cat. (0.3–0.5 mm). Sulfidation temperature: filled circles, 800°C; half-filled circles, 500°C; unfilled circles, 300°C.

this intermediate may be adsorbed carbon. With the terminology of Wise *et al.* (*22*, *23*) as used in Fig. 6, this means that αC may react either with methane or be dissolved in nickel for the subsequent nucleation of carbon and growth of the whisker from the bottom of the nickel crystal (*9*). The whisker growth does not affect the methanation rate because the original nickel surface is still available for reaction. This behavior is similar to that observed for steam reforming (*11*).

The strong and nonlinear deactivation of the methanation reaction was accompanied by no change of the activation energy. This indicates that several nickel atoms are involved in the methanation reaction and that the sulfur poisoning involves site blocking.

For a zero-order reaction, requiring an ensemble of n atoms, the rate can be expressed by,

$$r_m = k(1 - \theta_1)^n, \qquad (5)$$

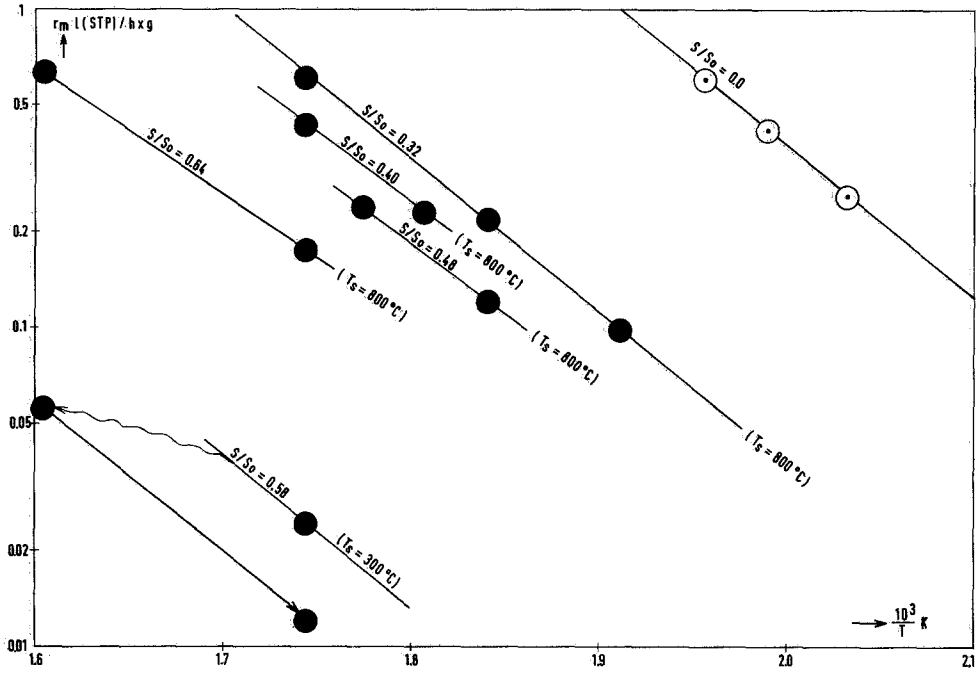

FIG. 5. Temperature dependence of zero-order methanation rates for poisoned and unpoisoned catalyst. 1 atm abs. Total flow = 40 liters STP/hr. Catalyst: 0.05 to 0.1 g. T_s = sulfidation temperature. Deactivation at prolonged operation at 350°C is indicated.

in which θ_1 is the fraction of blocked nickel atoms. At high coverages of immobile layers a correction should be introduced (*28*), but there are indications of high surface mobility of the adsorbed sulfur atoms (*15*).

The adsorption of the poison may result in saturation for a number of poison atoms (molecules) which may be only a fraction α of the nickel surface atoms. For sulfur on nickel α was found to be close to 0.54 mentioned above, which means $\theta_1 \sim 0.5\ s/s_0$.

Moreover, each adsorbed poison atom (molecule) may "quench" (deactivate) more than one nickel atom. This number, β, may change with the coverage because of the increasing interaction of the adsorbed poison atoms. On this basis (5) can be rewritten

$$r_m = k(1 - \alpha \cdot \beta s/s_0)^n. \qquad (6)$$

It may be argued that two nickel atoms are "quenched" by the adsorption of one sulfur atom ($\beta = 2$) since no nickel atoms are active at full surface coverage ($\theta_1 \sim 0.5$). If so, Eq. (4) should reflect the fact that methanation requires an ensemble of four nickel atoms.

However, this treatment is strongly simplified assuming ideal Langmuir adsorption. As shown by Erley and Wagner (*15*) the deactivation plot may be more complex because of phase transitions of the surface structure of the chemisorbed sulfur.

The data support other observations that methanation requires several nickel atoms. Erley and Wagner (*15*) observed a similar strong nonlinear effect of sulfur on the adsorption of carbon monoxide at room temperature. At low coverages one sulfur atom was estimated to block nine sites for carbon monoxide adsorption, and sulfur completely eliminated the adsorption for $\theta_1 > 0.33$, which is equivalent to $s/s_0 = 0.6$. For this coverage the results in Fig. 4 indicate a reduction of the methanation rate by a factor of 60.

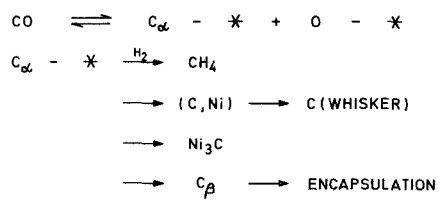

FIG. 6. Reaction sequence for CO reactions on nickel.

Martin *et al.* (*24*) found that four nickel atoms were required to dissociate carbon monoxide. Yu *et al.* (*29*) found the same number of atoms to be involved for hydrogen adsorption when coadsorbing hydrogen and carbon monoxide on nickel copper alloys. Bond and Turnham (*30*), who studied methanation on rhodium–copper alloys, concluded that the reaction required an ensemble of four rhodium atoms. The methanation studies of Araki and Ponec (*25*) on nickel–copper alloys also indicated that carbon monoxide can be dissociated only on places where carbon atoms can be bound to several nickel atoms simultaneously. Araki and Ponec claimed that the effect of copper was geometrical only. Therefore, the effect of adding copper to the catalysts resembles very much the effect of sulfur poisoning.

It is interesting to note that steam reforming is less sensitive to sulfur than methanation. This was demonstrated in studies of steam reforming of ethane at 500°C (*11*). After an initial drop in activity by a factor ca. 2, the deactivation appeared to be linear. The difference is still to be clarified.

5. CONCLUSIONS

The Boudouard and methanation reactions proceed simultaneously at conditions for which carbon formation is predicted by the principle of equilibrated gas. Reaction rates and thus the selectivity remain constant with time.

Both reactions are strongly poisoned by sulfur, but the selectivity is not changed during the deactivation. This supports the assumption that both reactions have the same intermediate, probably adsorbed carbon atoms.

The sulfur poisoning of the methanation reaction is nonlinear with a 4th power dependence on the relative sulfur coverage, whereas the activation energy is unaffected. This indicates that the methanation, and hence the Boudouard reaction, requires a large ensemble of nickel atoms.

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