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Kinetics of Decomposition of Carbon Monoxide on a Supported Nickel Catalyst

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The decomposition of carbon monoxide has been studied in a thermogravimetric flow system in the temperature range 280–400°C. The reaction proceeded at a constant rate after a certain initial period. Both the pressure of carbon monoxide and of carbon dioxide influenced the reaction rate. This could be described by a rate expression derived from a sequence with the dissociation of adsorbed carbon monoxide as rate-determining step. Steam and hydrogen had a retarding reversible effect on the rate. Presence of alkali on the catalyst showed no effect on the reaction rate.

INTRODUCTION

The present work is part of a study of carbon formation on nickel catalysts and deals with the decomposition of carbon monoxide, i.e., the Boudouard reaction:

$$2CO = C + CO_2. \qquad (1)$$

In the presence of hydrogen and steam this reaction is competing with the methanation and the shift reactions:

$$CO + 3H_2 = CH_4 + H_2O, \qquad (2)$$

$$CO + H_2O = CO_2 + H_2. \qquad (3)$$

Carbon formation by reaction (1) can take place if the gas has affinity for decomposition of carbon monoxide. The reaction is of industrial importance in the methanation of gases with high contents of carbon monoxide. But although the gas composition at the inlet to the catalyst bed shows affinity for decomposition of carbon monoxide, carbon formation is normally prevented by operating with such an excess of steam and hydrogen that thermodynamics, after equilibrium is established, predicts no formation of carbon.

It was the purpose of the present work to estimate the rate of carbon monoxide decomposition and to determine some physical and chemical factors which might influence the rate of reaction. The experiments were performed on a supported nickel catalyst in the temperature range 280–400°C.

By Auger electron spectroscopy Madden and Ertl (*1*) have previously investigated the (110) nickel/carbon monoxide system in the temperature range 100–375°C. Build-up of carbon and oxygen on the surface were found by interaction of electron beams with chemisorbed carbon monoxide and by heating the clean surface in carbon monoxide. The results indicated that the primary reaction was dissociation of adsorbed carbon monoxide to individually bound carbon and oxygen atoms, and that this reaction was followed by combination of surface oxygen with carbon monoxide and immediate desorption of formed carbon dioxide. From the results, Madden and Ertl (*1*) could moreover rule out the disproportionation reaction, proposed by Edmonds and Pitkethly (*2*) and by Gregg and Leach (*3*), which would leave carbon dioxide and carbon on the surface.

The carbon monoxide decomposition reaction was followed by Bousquet *et al.* (*4*) in a study of the mechanism of the methanation reaction (2). By use of a gravimetric technique a constant reaction rate was observed after an initial rapid weight increase had taken place.

Two different reaction products were reported by Escoubes and Eyraud (*5*). At temperatures below 300°C only Ni_3C was observed, whereas at temperatures above 340°C elementary carbon was the only product. In the intermediate temperature range, both Ni_3C and carbon were reported as products. Ni_3C and elementary carbon were also observed by Coad and Rivière (*6*) using Auger spectroscopy, and Ni_3C was found to decompose by heating above 400°C. Renshaw *et al.* (*7*) have discussed the existence of an intermediate carbide phase at temperatures above 400°C.

The equilibrium of the carbon monoxide decomposition reaction was studied by Rostrup-Nielsen (*8*) in the temperature range 450–700°C. Equilibrium constants were obtained which implied deviations from constants based on graphite data, and examination of the carbon formed showed a whisker-like structure with a nickel crystallite placed on the tip of the whisker. Deviations from graphite data could be explained by a disordered structure and by a higher surface energy depending on the whisker diameter.

Baker *et al.* (*9, 10*) investigated the exothermic decomposition of acetylene on nickel and proposed a mechanism with diffusion of carbon through nickel crystallites as rate-determining step.

The solubility, S_m, and the diffusion coefficient, D, of carbon in nickel were investigated by Lander *et al.* (*11*) in the temperature range 700–1300°C. The solubility of carbon showed a temperature dependence corresponding to an apparent activation energy of 9.7 kcal/mol. The diffusion coefficient was calculated by measurement of the rate of diffusion of carbon through a disk of nickel with thickness L. At steady state the rate was described by

$$r_{diff} = D \cdot S_m / L. \qquad (4)$$

The diffusion coefficient showed a temperature dependence corresponding to an apparent activation energy of 40.1 kcal/mol. Massaro and Petersen (*12*) estimated the diffusion coefficient in the temperature range 350–700°C by a similar technique and found an apparent activation energy of 20 kcal/mol for the temperature dependence of the diffusion coefficient.

By observation of LEED patterns and Auger spectra Blakely *et al.* (*13*) found a reversible segregation of carbon to the (100) surface of nickel in the temperature range 225–525°C.

METHODS

Apparatus

The experiments were performed in the thermogravimetric flow system described previously by Rostrup-Nielsen (*8*). A perforated basket of Inconel with an external diameter of 10.5 mm was placed in a reactor with an internal diameter of 20.5 mm. The gases were taken from cylinders and were introduced through needle valves and capillary flowmeters. CO and CO_2 were used unpurified. Gas chromatographic analyses showed impurities, mainly N_2, to be less than 0.3%. H_2 and N_2 were purified over Cu wire at 260°C. Steam was generated by passing the equivalent amount of H_2 and some N_2 over wires of copper oxide at 280°C.

Catalyst

The nickel catalyst was supported on η-Al_2O_3. Reduction of the catalyst was performed in hydrogen for a period of 2 hr at 800°C in a separate reactor. The content of reduced nickel was 9.9 wt%. The total surface area was measured as 116.9

m^2/g by the BET method, and from measurement of the sulfur capacity (*14*) the nickel area was estimated to be 6.6 m^2/g. The pore volume distribution was measured by the Ritter–Drake method (*15*, *16*) in an Aminco porosimeter, and the mean pore radius was calculated to be 41.9 Å.

Procedure

The catalyst was generally crushed to 2–3 mm particles, and a sample of 0.58 g was placed in the basket in each experiment.

The heating up was performed in H_2 until temperature and sample weight had stabilized. After N_2, CO_2, or H_2O had been introduced, the CO flow was admitted, replacing the H_2 flow, and the change of catalyst weight with time was recorded.

In all experiments the total volume of gas flow in the reactor was kept constant at 3.1×10^{-4} g mol/s. N_2 was used as a diluent, assuming that N_2 did not influence the rate of CO decomposition. The gas flow was measured by a gas meter and the gas composition was checked by gas chromatography.

RESULTS

The graphs of weight increase versus process time from experiments performed at constant gas composition are shown in Fig. 1. After an initial rapid weight increase the reaction rate speeds up again and arrives at a constant value, r_c.

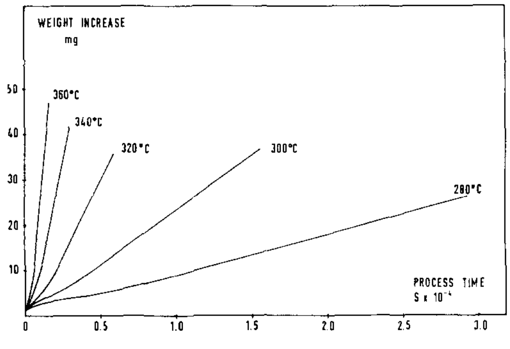

FIG. 1. Weight increase of catalyst sample vs process time at different temperatures. Feed 20% CO, 80% N_2.

TABLE 1

Influence of d_p on Rate of Reaction[a]

d_p (mm)	r_c (μg/s)
1.2–2.0	1.98
3.0–4.2	2.12
4.2–5.66	2.08

[a] $T = 300°C$; feed = 20% CO, 80% N_2.

Experiments at 300°C with the catalyst crushed to different particle sizes showed that the particle diameter of the catalyst, d_p, influenced neither the graph nor the reaction rate, r_c. The results are listed in Table 1.

A blank experiment with the nickel-free support did not result in any weight increase.

Influence of Temperature

From the graphs in Fig. 1 the reaction rates, r_c, were estimated, and the temperature dependence of r_c indicated an apparent activation energy of 32.8 kcal/mol for the rate of carbon deposition.

Influence of p_{CO} and p_{CO_2}

The influence of the partial pressures of CO and CO_2 on the rate of CO decomposition was estimated in gas mixtures of CO, CO_2, and N_2 at 300, 320, and 340°C.

The estimated reaction rates, r_c, from experiments with different partial pressures of CO are plotted versus p_{CO} in Fig. 2.

CO_2 showed no influence on the reaction at 300°C, but the results at 320 and 340°C showed the reaction rate, r_c, to decrease with increasing amounts of CO_2 in the feed gas. In Fig. 3, the estimated reaction rates are plotted versus p_{CO_2}.

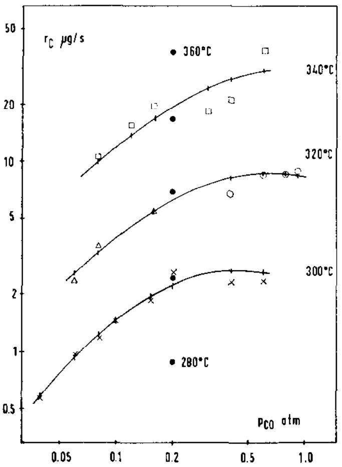

FIG. 2. Influence of p_{CO} on reaction rate. (×) 300°C, $p_{CO_2} = 0.2$ atm; (△) 320°C, $p_{CO_2} = 0.12$ atm; (○) 320°C, $p_{CO_2} = 0$ atm; (□) 340°C, $p_{CO_2} = 0$ atm; (●) Data from Fig. 1; (|) calculated from rate expression (9).

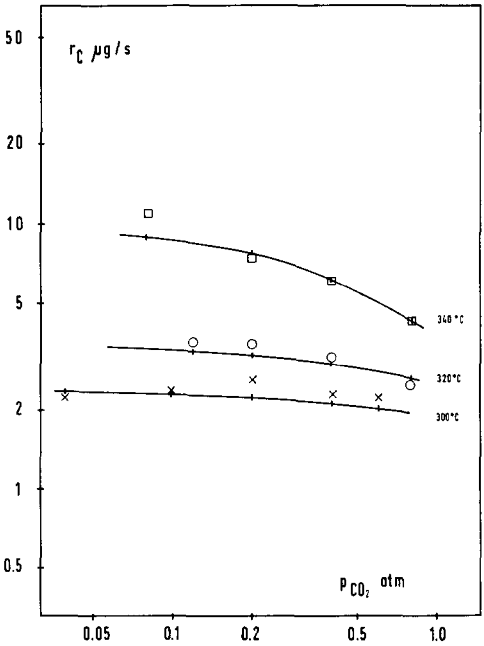

FIG. 3. Influence of p_{CO_2} on reaction rate. (×) 300°C, $p_{CO} = 0.2$ atm; (○) 320°C, $p_{CO} = 0.08$ atm; (□) 340°C, $p_{CO} = 0.08$ atm; (|) calculated from rate expression (9).

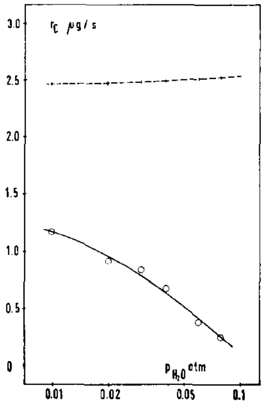

FIG. 4. Influence of p_{H_2O} on reaction rate at 300°C. (○) Experimental results, $p_{CO} = 0.8$ atm, $p_{CO_2} = 0$ atm; (– – –) calculated from rate expression (10) assuming the shift reaction (3) in equilibrium.

Influence of H_2O and H_2

The influence of steam on the reaction rate was investigated at 300°C in experiments performed in gas mixtures of H_2O, CO, and N_2 with fixed $p_{CO} = 0.8$ atm and with various contents of steam. In Fig. 4 the estimated rates are plotted as a function of p_{H_2O}.

Addition of steam caused a decrease in the raction rate. By alternatively allowing and blocking the addition of steam, the reaction rate changed between the normal level experienced without steam present and the low rate experienced with steam present. Thus, the retarding effect of steam on the reaction rate is reversible.

Addition of H_2 caused also a decrease in the reaction rate, and the effect was also demonstrated to be reversible. The retarding effect of H_2 was less than that of steam.

Whereas the addition of H_2 resulted in but a small content of CH_4 in the exit gas, the addition of H_2O to the CO_2-free feed gas resulted in a considerable increase of the content of CO_2 in the exit gas. As the small content of CH_4 found in the exit gas was insignificant compared with the equilibrium proportion, it could be concluded that the shift reaction proceeded much faster than both the CO decomposition reaction and the methanation reaction.

Effect of Alkali

Some experiments were performed to estimate the influence of alkali. This was of interest due to the well-known effect of alkali in enhancing steam adsorption and depressing carbon formation in steam reforming (*17*, *18*).

The rates of CO decomposition on the standard catalyst and the catalyst impregnated with alkali (2.9 wt% K) were compared at 300°C. Comparisons in Table 2 show identical rates on the standard catalyst and the alkali impregnated catalyst in the presence of H_2O and H_2, respectively, whereas in the absence of these components the rate is slightly less on the alkali impregnated catalyst than on the alkali-free catalyst.

Investigation of Spent Catalyst

Investigations of samples of spent catalyst by X-ray diffractometry showed the presence of Ni, Ni_3C, and C in varying amounts. The line widths and displacements showed the carbon depositions to be nonideal and disordered, but the disordering as calculated by the line width could not be correlated with the treatment temperature. The heights of the phase lines were used to compare the relative amounts of Ni and Ni_3C present, and the results are summarized in Table 3. Between 300 and 340°C, Ni_3C was present together with elementary Ni and C, but above 360°C, elementary Ni and C were the only phases present.

TABLE 2

Influence of H_2O and H_2 on Rate of Reaction[a]

Feed fixed: 80% CO	r_c (μg/s)	
	Standard catalyst	Catalyst impregnated with 2.9 wt% K
20% N_2	2.50	1.60
4% H_2O, 16% N_2	0.63	0.62
4% H_2, 16% N_2	1.00	1.17

[a] Effect of impregnation with alkali. $T = 300°C$, $p_{CO} = 0.8$ atm.

TABLE 3

Investigation of Spent Catalyst by X-Ray Diffractometry[a]

Temp (°C)	Ni	Ni_3C
300	18	100
320	<6	81
340	<6	72
360	74	—[b]
400	88	0
Unused catalyst	100	0

[a] The numbers indicate the relative amounts of phase present in percent of the observed maximum amount.

[b] Trace.

Examination in an electron microscope of catalyst samples showed the carbon to be present in whisker-like structures with the same tubular appearance as that described by Rostrup-Nielsen (*8*).

DISCUSSION

The graphs of weight increase as a function of process time showed that after a certain initial period with an initial rapid weight increase a constant rate of carbon monoxide decomposition took place. The graphs are in accordance with those reported by Bousquet *et al.* (*4*), and it may be assumed that the initial weight increase is caused partly by adsorption of carbon monoxide. A monolayer with one carbon monoxide molecule per nickel atom would result in a weight increase of 1.5 mg.

In the temperature range 280–340°C the conversion obtained by the decomposition of carbon monoxide was insignificant compared to the conversion necessary for establishment of equilibrium, and the reactor could be considered differential. By approximation of the results in Fig. 2

to a first order reaction with respect to carbon monoxide the pore diffusion restriction was calculated to be of no importance, and this result is in accordance with the results in Table 1, showing no influence of the particle diameter on the reaction rate. At temperatures above 340°C the pore diffusion restriction might become important.

Both the partial pressure of carbon monoxide and of carbon dioxide influenced the reaction rate, as shown in Fig. 2 and Fig. 3. At low partial pressures of carbon monoxide the reaction is approximately first order with respect to carbon monoxide. Increasing content of carbon monoxide caused the reaction order to decrease. The partial pressure of carbon dioxide had no significant influence at 300°C, but increasing temperature caused the reaction order with respect to carbon dioxide to decrease.

In order to find a suitable rate expression the following simple sequence was considered:

$$CO + S = CO\text{–}S, \qquad (5)$$

$$CO\text{–}S + S = C\text{–}S + O\text{–}S, \qquad (6)$$

$$CO\text{–}S + O\text{–}S = CO_2 + 2S, \qquad (7)$$

$$C\text{–}S = C + S. \qquad (8)$$

S means an empty site on the nickel surface, and Eq. (5) implies adsorption of carbon monoxide with one molecule per site. It is well-known that there are several species of adsorbed carbon monoxide on nickel, including both linear and bridged attachments of carbon monoxide (*19*).

TABLE 4

Results from Linear Regression Analysis of Rate Expression (10)

T (°C)	k (μg/s/atm)	K_A (atm^{-1})	K_B ($\times 10^2$)
300	25.7	2.36 ± 0.13	4.3 ± 1.9
320	54.1	1.56 ± 0.09	1.6 ± 0.9
340	148.3	1.20 ± 0.27	5.6 ± 1.5

Equation (6) describes the dissociation of adsorbed carbon monoxide to atomic carbon and oxygen, and immediate demorption of carbon dioxide after reduction of the surface oxygen by adsorbed carbon monoxide is proposed in Eq. (7). These reactions are in accordance with the results of Madden and Ertl (*1*).

Empty sites are necessary for the reaction to take place, and in a steady state the amount of empty sites must be constant. This means that the carbon formed must either diffuse on the surface or be dissolved in the nickel lattice. The empty sites are formed again in reactions (7) and (8).

By using Langmuir equations and thus assuming a homogeneous surface, the rate expressions for the reaction system (5)–(8) with one rate-determining step could be derived. The steps (5) and (7) could be ruled out as being rate determining. By assuming that the dissociation of adsorbed carbon monoxide is a rate-determining step and that the other steps in the sequence are in quasi-equilibrium, the following rate expression is derived:

$$r = k\frac{p_{CO}}{[1 + K_A p_{CO} + K_B(p_{CO_2}/p_{CO})]^2}. \qquad (9)$$

The second and third term in the denominator result from the steps in quasi-equilibrium and account for the surface coverages of adsorbed carbon monoxide and atomic oxygen, respectively. By rearranging a linear form in K_A and K_B was obtained:

$$\frac{(p_{CO})^{\frac{1}{2}}}{r^{\frac{1}{2}}} = \frac{1}{k^{\frac{1}{2}}} + \frac{K_A}{k^{\frac{1}{2}}}p_{CO} + \frac{K_B}{k^{\frac{1}{2}}}\frac{p_{CO_2}}{p_{CO}}. \qquad (10)$$

This equation enabled K_A and K_B to be calculated by linear regression analysis, and the results together with the calculated standard deviations are listed in Table 4. K_B was found to be less important and less exactly estimated than K_A which decreased with temperature with a dependence corresponding to an apparent heat of adsorption of $Q_A = 11.8 \pm 1.3$ kcal/mol. The apparent activation energy of the rate constant, k, was 31 ± 3 kcal/mol.

The reaction rates at the experimental conditions were calculated by using rate expression (9) and the data in Table 4, and in Figs. 2 and 3 the rates are plotted together with the experimental rates. The good agreement between calculated and experimental rates indicates, but does not prove, that the assumptions about the reaction mechanism are correct.

Steam and hydrogen showed a reversible retarding effect, while impregnation of the catalyst with alkali had no effect on the reaction rate. It may be assumed that adsorption of steam and hydrogen and subsequent reaction of these components with adsorbed carbon monoxide by the methanation (2) and the shift (3) reactions, respectively, compete with the dissociation of adsorbed carbon monoxide. The shift reaction was found to proceed faster than the methanation reaction, and this may explain that steam shows a more retarding effect than does hydrogen.

From the temperature dependence of the reaction rate in Fig. 1 an apparent activation energy of 32.8 kcal/mol was calculated. This result is within the range of apparent activation energies of 29–35 kcal/mol for the decomposition reaction rates of hydrocarbons reported by Baker *et al.* (*9, 10*) and Lobo *et al.* (*20*). These authors propose a model for decomposition of hydrocarbons with diffusion of carbon through nickel crystallites as the rate-determining step, and the model is based on observed zero order reaction with respect to hydrocarbon and agreement in apparent activation energies for the decomposition rate and for diffusion of carbon through nickel. In the present study of the decomposition rate of carbon monoxide the pressure dependence with respect to carbon monoxide was estimated to differ from zero order. In addition it must be emphasized that the temperatures at which the diffusion of carbon through nickel has been investigated are much higher than the reaction temperatures in this study. This fact makes the value of comparison between the estimated apparent activation energy of the reaction rate of 32.8 kcal/mol and the apparent activation energy of the diffusion coefficient for carbon in nickel questionable.

CONCLUSIONS

1. The rate of decomposition of carbon monoxide on nickel in the temperature range 300–340°C may be described by a rate expression for a mechanism with the dissociation of adsorbed carbon monoxide as the rate-determining step.
2. Addition of steam and hydrogen decreases the reaction rate, which indicates that adsorption of steam and hydrogen and subsequent reaction of these components with adsorbed carbon monoxide compete with the dissociation of adsorbed carbon monoxide.
3. The addition of alkali to the catalyst has no effect on the reaction.

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REFERENCES

1. Madden, H. H., and Ertl, G., *Surface Sci.* **35**, 211 (1973).

2. Edmonds, T., and Pitkethly, R. C., *Surface Sci.* **15**, 137 (1969).

3. Gregg, S. J., and Leach, H. F., *J. Catal.* **6**, 308 (1966).

4. Bousquet, J. L., Gravelle, P. C., and Teichner, S. J., *Bull. Soc. Chim. Fr.* 3693 (1972).

5. Escoubes, M., and Eyraud, C., *Bull. Soc. Chim. Fr.* 1369 (1966).

6. Coad, J. P., and Rivière, J. C., *Surface Sci.* **25**, 609 (1971).

7. Renshaw, G. D., Roscoe, C., and Walker, P. L., Jr., *J. Catal.* **22**, 394 (1971).

8. Rostrup-Nielsen, J. R., *J. Catal.* **27**, 343 (1972).

9. Baker, R. T. K., Barber, M. A., Harris, P. S., Feates, F. S., and Waite, R. J., *J. Catal.* **26**, 51 (1972).

10. Baker, R. T. K., Harris, P. S., Thomas, R. B., and Waite, R. J., *J. Catal.* **30**, 86 (1973).

11. Lander, J. J., Kern, H. E., and Beach, A. L., *J. Appl. Phys.* **23**, 1305 (1952).

12. Massaro, T. A., and Petersen, E. E., *J. Appl. Phys.* **42**, 5534 (1971).

13. Blakely, J. M., Kim, J. S., and Potter, H. C., *J. Appl. Phys.* **41**, 2693 (1970).

14. Rostrup-Nielsen, J. R., *J. Catal.* **11**, 220 (1968).

15. Ritter, H. L., and Drake, L. C., *Ind. Eng. Chem., Anal. Ed.* **17**, 782, 787 (1945).

16. Drake, L. C., *Ind. Chem. Eng.* **41**, 780 (1949).

17. Andrew, S. P. S., *Ind. Eng. Chem. Prod. Res. Develop.* **8**, 321 (1969).

18. Rostrup-Nielsen, J. R., *J. Catal.* **31**, 173 (1973).

19. Little, L. H., *in* "Chemisorption and Reactions on Metallic Films" (J. R. Anderson, Ed.), Chap. 6. Academic Press, London, 1971.

20. Lobo, L. S., Trimm, D. L., and Figueiredo, J. L., *Proc. Int. Congr. Catal., 5th, 1972* **2**, 1125 (1973).