N	= number of tubes across the tube bundle in each coolant pass	[—]
Nu_w	= Nusselt number for heat transfer between the fluid and the coolant	[—]
Nu_w^*	= effective overall Nusselt number for heat transfer between the fluid and the coolant based on the radial mean fluid temperature used in one-dimensional model $= 4Nu_w/(4+Nu_w)$	[—]
R	= inside radius of the reactor tube	[m]
R_g	= the gas constant	
t	= pellet temperature $= R_g T'_p/E$	[—]
T	= fluid temperature $= R_g T'/E$	[—]
T'	= temperature of the fluid	[K]
T_c	= coolant temperature $= R_g T'_c/E$	[—]
T'_c	= temperature of the coolant	[K]
T'_p	= temperature of pellet	[K]
u	= interstitial fluid velocity	[m/s]
U	= fluid-to-coolant overall heat transfer coefficient	[W/s·m²·K]
z	= axial coordinate along the reactor tube $= z'/L$	[—]
z'	= length along reactor	[m]

ΔH	= heat of reaction	[J/mol]
ΔT_c	= temperature rise of coolant	
η	= effectiveness factor	[—]
θ	= reaction-diffusion modulus $= b\sqrt{A_0/D_{PA}}$	[—]
ρ, ρ_c	= densities of fluid and coolant respectively	[kg/m³]

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KINETICS OF CARBON DEPOSITION ON NICKEL METAL BY DECOMPOSITION OF CARBON MONOXIDE

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The kinetics of carbon deposition are reported for the temperature range 773–1023 K. A reaction model composed of adsorption and reaction steps is proposed and compared with experimental data. In this model the rate equation of carbon deposition takes into account the catalytic action of nickel. The calculated results are in good agreement with the experimental ones. The activation energy and the heat of adsorption of CO are 59.3 kJ/mol and 61.7 kJ/mol, respectively.

Introduction

Reduction of a metal oxide with CO is accompanied under certain conditions by the decomposition of carbon monoxide according to the reaction $2CO = C + CO_2$.[6,11] The presence of deposited carbon interferes with the gas flow and diffusion within a reactor, and therefore affects the reduction of the metal oxide. Thus, information concerning the mechanism and rate of carbon deposition is required in order to analyze the overall reduction process. Carbon deposition on metallic iron has been reported[5,9,13] when reduction of iron oxide occurred

with CO, and some rate equations have been obtained for this case. Taniguchi *et al.*[12] proposed a rate equation in which the catalytic action of iron carbide was taken into account. Further, Knapp *et al.*[4] proposed a Langmuir-Hinshelwood type equation for carbon deposition in the rate of magnetite reduction with carbon monoxide.

For nickel oxide, however, the equations mentioned above are not useful for estimating the reaction rate because nickel carbide is unstable at temperatures above 673 K.[1] Carbon deposition on nickel catalyst has been studied in relation with catalyst deactivation,[3,7,10] but a rate equation has not been obtained. In this study, experiments of carbon deposition catalyzed by nickel are carried out and a
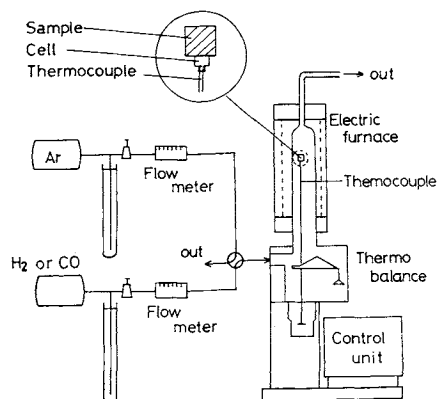
Fig. 1. Schematic diagram of experimental apparatus.

Fig. 2. Effect of NiO weight on reaction rate at 973 K.

Fig. 3. Effect of adsorption on reaction rate.

reaction model is proposed. In the model, the rate equation of carbon deposition on nickel is assumed to be influenced by the catalytic action of reduced nickel.

The mechanism which gives the maximum rate of carbon deposition at about 773 K[5,12] has not been understood very well. However, the model proposed in this study gives a possible explanation.

1. Experimental

Nickel oxide used in this study was pure NiO powder with an average diameter, measured with a microscope, of 6.5 μm. A solid sample was prepared as follows. About 200 mg of NiO powder was spread on a thin Ni plate (0.1 mm × 1 cm × 1 cm) to make a thin layer of the oxide, so that the maximum thickness of the layer could be less than 1 mm. The experimental apparatus is sketched in **Fig. 1**. The sample was placed in a cell, perpendicular to the gas flow in a reaction tube, and it was reduced by H_2 at the temperature at which carbon deposition occurred; then the reactant, CO or CO–Ar mixture was introduced into the reaction tube. The rate of carbon deposition was essentially independent of gas flow rate employed (1.0×10^{-3} m³ (N.T.P.)/min). The weight change of the sample was obtained with an automatic recording thermogravimetric unit. Reaction temperature was measured with a thermocouple placed near the sample as shown in Fig. 1, and was controlled by a P.I.D. control unit.

2. Experimental Results

Figure 2 shows the effect of the weight of NiO powder on the carbon deposition rate at 973 K. In this figure, experimental results are represented in the form

$$W = w/w_{Ni}$$

where w and w_{Ni} are the weight change of sample and the weight of nickel metal reduced from NiO with H_2, respectively. It can be seen from this figure that the deposition rate is independent of the NiO weight, that
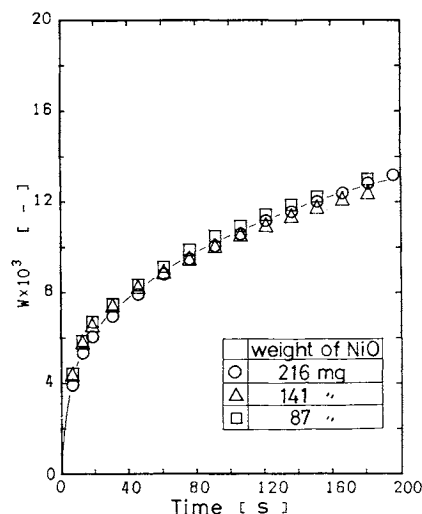
is, the thickness of the sample, so that the effects of the existence of the Ni plate and the resistance of gas diffusion within the sample layer on the overall rate can be neglected. Since it is inferred that an adsorption step affects the overall reaction rate,[8] the following experiments were carried out. CO gas was introduced for one minute at a reaction temperature ranging from 773 to 973 K, and was thereafter replaced by Ar gas. After 30 seconds the temperature was rapidly raised to 1273 K. The results are shown in **Fig. 3**. The weight change W increases rapidly in about the first 30 seconds (initial reaction stage). W decreases slowly in an atmosphere of Ar gas. However, it decreases rapidly to a constant value when the temperature is elevated to 1273 K. The final value of W at 973 K is higher than that at 773 K. It is revealed by this fact that the weight increase is mainly attributable to adsorption of CO at the initial stage of the reaction, and that in the range of 773–973 K the amount of deposited carbon increases with rising
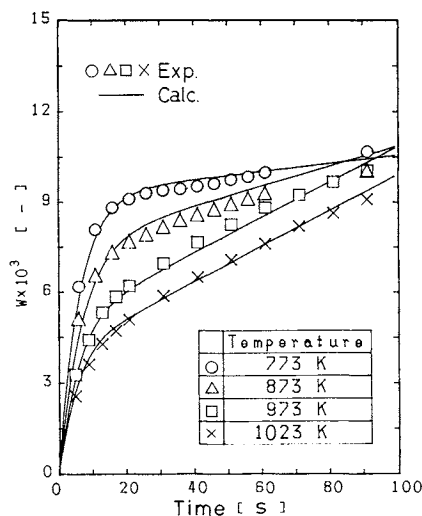
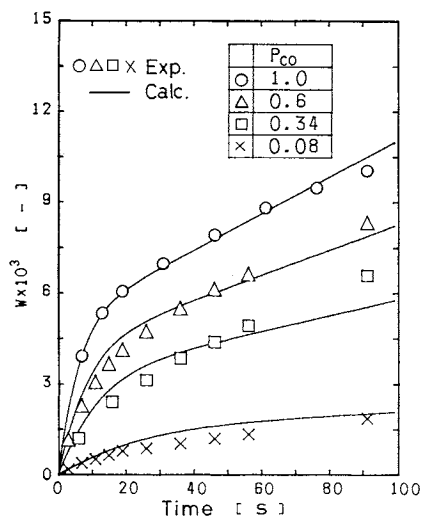Fig. 4. Carbon deposition at various temperatures and CO atmospheric pressure.

Fig. 5. Carbon deposition at various CO partial pressures and 973 K.

Fig. 6. dW/dt_i vs. P_{CO}.

reaction temperature.

Figure 4 shows the effect of reaction temperature on the carbon deposition rate. The reaction is fast at the initial stage, and gradually slows down to an almost constant value. It can also be seen from this figure that the lower the temperature is the higher the reaction rate at the initial stage. After about 30 seconds the rate increases with increasing temperature. These facts are in accordance with the experimental results reported by Turkdogan and coworkers.[13] That is, they reported that in the early stages of reaction the rate is highest at about 803 K and in the later stages of carbon deposition a maximum rate is obtained at about 1073 K.

Figure 5 shows carbon deposition at various CO partial pressures. The initial reaction rate depends on the CO partial pressure, but after 30 seconds its effect becomes small. In a logarithmic plot, shown in Fig. 6,
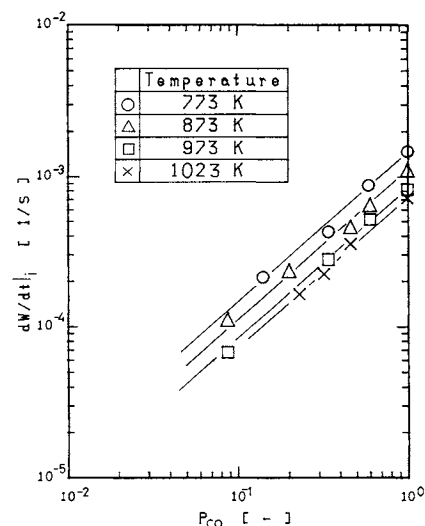
the relation between the initial rate, $dW/dt|_i$, and the partial pressure of CO, P_{CO}, is essentially linear. The initial rate was calculated from the data by the numerical differential method. The slopes of lines in Fig. 6 are almost unity.

3. Discussion

3.1 Determination of the rate equation for carbon deposition

The following two overall reactions can be considered.

$$2CO = C + CO_2 \tag{1}$$

$$2CO + 3Ni = Ni_3C + CO_2 \tag{2}$$
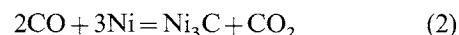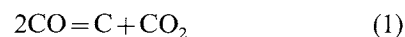
However, reaction (2) can be ignored because nickel carbide is unstable above 673 K.[1]

The reaction process will involve the adsorption of CO on the surface of solid to form a surface complex CO*. Two CO* may transform to carbon and a surface complex CO_2^*, which then desorbs to give a gaseous product CO_2. These steps, which are reversible in general, may be written as

$$CO + \sigma \rightleftharpoons CO^* \tag{3}$$

$$2CO^* \rightleftharpoons C + CO_2^* + \sigma \tag{4}$$

$$CO_2^* \rightleftharpoons CO_2 + \sigma \tag{5}$$
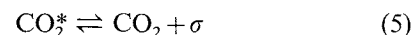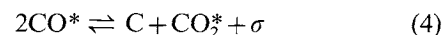
where σ designates an active adsorption site that is available to both CO and CO_2.

Assume the following restrictions in order to make the mathematical formulation tractable.

(1) The reaction takes place under isothermal conditions.

(2) Deposited carbon does not decrease the number of active adsorption sites.

(3) Desorption of CO_2 is so rapid that its effect on the overall reaction rate is negligible.

(4) The reverse reaction of Eq. (4) can be ignored when the bulk concentration of CO_2 is almost zero.

(5) Gas diffusion in the external gas film and intraparticle diffusion do not affect the overall reaction rate.

Then, the change of CO* concentration with time, dS_{CO}/dt, can be given by the following equation.

$$\frac{dS_{CO}}{dt} = k_1 C_{CO}(S_t - S_{CO}) - k_1' S_{CO} - 2k_2 S_{CO}^2 \qquad (6)$$

where k_1 and k_1' are CO adsorption and desorption rate constants, respectively, and k_2 is the reaction rate constant of Eq. (4).

The rate of weight change is expressed by Eq. (7):

$$\frac{dW}{dt} = M_{CO}\frac{dS_{CO}}{dt} + M_C k_2 S_{CO}^2 \qquad (7)$$

Initial conditions are as follows:

$$\text{At} \quad t=0 \quad S_{CO}=0, \quad W=0 \qquad (8)$$

Equations (6)–(8) can be rewritten in dimensionless form as

$$\frac{d\theta}{d\tau} = 1 - (1 + P_1)\theta - P_2\theta^2 \qquad (9)$$

$$\frac{dX}{d\tau} = \frac{d\theta}{d\tau} + \frac{P_2}{2}\frac{M_C}{M_{CO}}\theta^2 \qquad (10)$$

$$\text{I.C.} \quad \tau=0; \quad \theta=0, \quad X=0 \qquad (11)$$

where

$$\theta = S_{CO}/S_t, \qquad P_1 = 1/K_e C_{CO},$$

$$P_2 = 2k_2 S_t/k_1 C_{CO}, \qquad \tau = k_1 C_{CO}t,$$

$$X = W/S_t M_{CO}, \qquad K_e = k_1/k_1'$$

Using the Runge-Kutta-Gill method, the dimensionless weight X can be calculated. However, the values of the parameters S_t, k_1, k_1' (or k_e) and k_2 are necessary in order to calculate X.

3.2 Estimation of parameters

1) Estimation of S_t If the desorption rate of CO and the rate of reaction (4) are small enough compared with the adsorption rate of CO, Eq. (6) can be expressed as

$$\frac{dS_{CO}}{dt} = k_1 C_{CO}(S_t - S_{CO}) \qquad (12)$$

At the reaction temperature of 773 K, it should be noted from the weight change between 60 and 90 seconds in Fig. 3 that the desorption rate of CO is small enough. It should be also seen from the weight change after 30 seconds in Fig. 4 that reaction (4) scarcely takes place. Then the weight increase can be attributed to CO adsorption at the initial stage at 773 K and $W = M_{CO}S_{CO}$. **Figure 7** shows the relation between
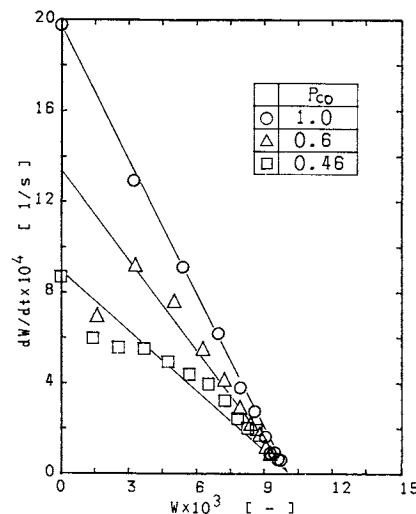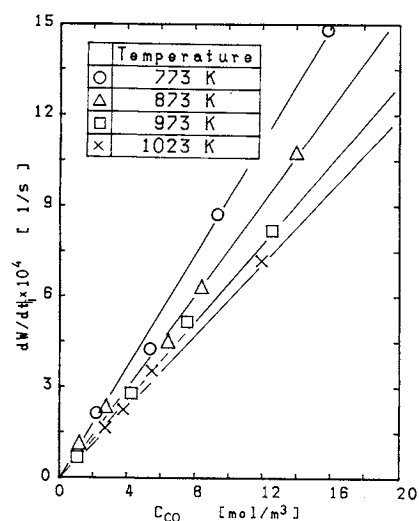

Fig. 7. dW/dt vs. W at 773 K.

Fig. 8. dW/dt_i vs. C_{CO}.

dW/dt and W at the initial stage at 773 K. The values of dW/dt in this figure are calculated from the data by the numerical differentiation method. The relation is almost linear. From the intersection between the lines and the abscissa, S_t is evaluated according to Eq. (13):

$$S_t = (W/M_{CO})|_{dW/dt=0} = 3.6 \times 10^{-4} \quad [\text{mol/g}] \quad (13)$$

2) Estimation of k_1 At the initial state, S_{CO} can be assumed to be zero, and then the adsorption rate is proportional to concentration of CO as given by Eq. (14).

$$\frac{dS_{CO}}{dt} = k_1 C_{CO}S_t \qquad (14)$$

The relation between the initial rate and the concentration of CO is shown in **Fig. 8**. It can be seen from this figure that the relation is almost linear. **Figure 9** shows the adsorption rate constant calculated from the slope of lines in Fig. 8. The dependence of k_1 on the temperature is small.
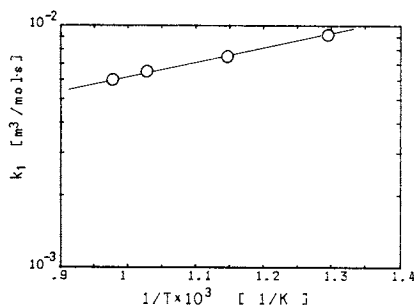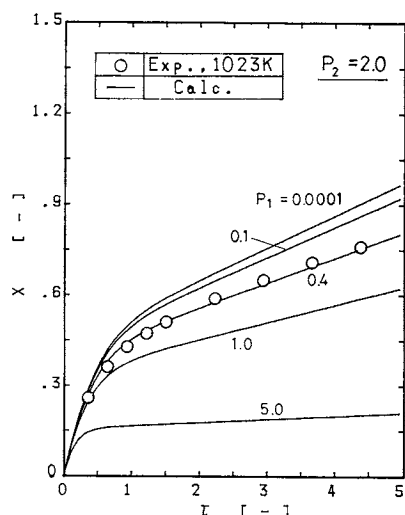
Fig. 9. Arrhenius plot of k_1.

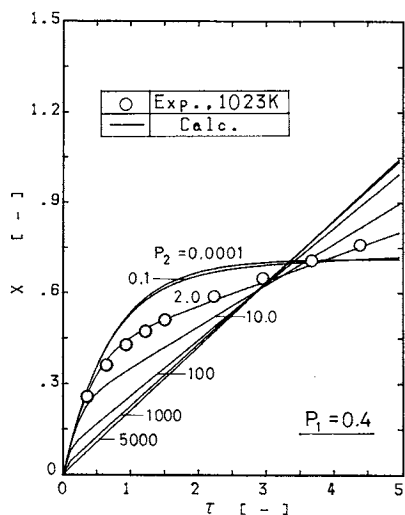**Fig. 10.** Effect of P_1 on calculated reaction rate.

Fig. 11. Effect of P_2 on calculated reaction rate.

$$\log (k_1) = -2.78 + 576/T \qquad (15)$$

3) Estimation of k_1' and k_2 k_1' and k_2 were calculated at each temperature from the values of P_1 and P_2, which give the most fittable values of W with respect to the experimental data. **Figures 10** and **11** show the relation between dimensionless deposition weight, X, and dimensionless time, τ, using $P_2 = 2.0$ and $P_1 = 0.4$ as fixed parameters, respectively. The
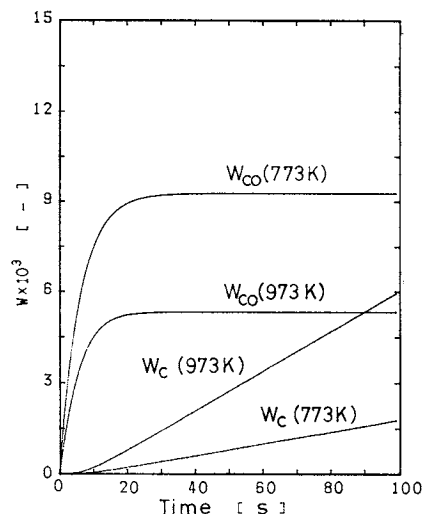

Fig. 12. Calculated weight of deposited carbon and adsorbed CO.

plots in these figures represent the experimental data at 1023 K.

3.3 Comparison of calculated results with experimental ones

In Fig. 4, the solid lines represent the results calculated from the model discussed above. The relation between W and time is obtained from X and τ which can be calculated by Eqs. (9)–(11), using the Runge-Kutta-Gill method with the values of the parameters P_1 and P_2 which gave the most fittable lines with respect to the experimental data at each temperature. Figure 5 shows a comparison of calculated results with experimental ones at various CO partial pressures and 973 K. The solid lines are the calculated results on the basis of the present model, using the values of the parameters P_1 and P_2 changed as follows:

$$P_1 = P_1\big|_{P_{CO}=1}/P_{CO}, \qquad P_2 = P_2\big|_{P_{CO}=1}/P_{CO}$$

The experimental results agree approximately with the calculated ones. The same results were recognized in all experiments at different reaction temperatures.

Figure 12 shows the calculated weight of adsorbed CO, W_{CO}, and the weight of deposited carbon, W_C, at 773 K and 973 K. The sum of W_{CO} and W_C is W. It is seen from this figure that the amount of adsorbed CO at 773 K is more than that at 973 K, but that the amount of deposited carbon is more at 973 K. The calculated weights of deposited carbon are about 0.5 (973 K) and 0.15 (773 K) at 90 seconds. These values are almost consistent with that of the final weight shown in Fig. 3. Thus, the model in this study gives a possible explanation for the fact that the rate decreases with increasing temperature in the early reaction stage.

Figure 13 shows the Arrhenius plots for k_2 calculated from the value of P_2 at each temperature. The
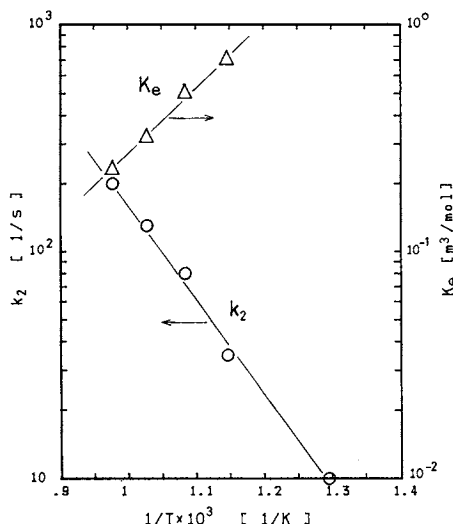
Fig. 13. Arrhenius plots of k_2 and K_e.

apparent activation energy is found to be 59.3 kJ/mol. In the same figure, the relation between K_e, calculated from the value of P_1, and the reciprocal of the absolute temperature is also shown. This relation is linear and the heat of adsorption is obtained as 61.7 kJ/mol from the slope of the line. The heat of adsorption of CO on transition metals lies generally between 55 and 146 kJ/mol.[2] The value obtained in this study also lies in that range.

Conclusion

The kinetics of carbon deposition was studied. A reaction model composed of adsorption and reaction steps was proposed. This model gives a possible explanation for the maximum rate of carbon deposition at about 773 K. The calculated results on the basis of the present model were in good agreement with the experimental data. The apparent activation energy and the heat of adsorption of CO was found to be 59.3 kJ/mol and 61.7 kJ/mol, respectively.

Nomenclature

C_{CO}	= concentration of CO	[mol/m³]
K_e	= adsorption equilibrium constant	[m³/mol]
k_1	= CO adsorption rate constant	[m³/mol·s]
k_1'	= CO desorption rate constant	[l/s]
k_2	= reaction rate constant	[g/mol·s]
M_C	= molecular weight of C	[g/mol]
M_{CO}	= molecular weight of CO	[g/mol]
P_{CO}	= partial pressure of CO	[—]
P_1	= dimensionless group $(1/K_eC_A)$	[—]
P_2	= dimensionless group $(2k_2S_t/k_1C_A)$	[—]
S_{CO}	= concentration of CO on Ni	[mol/g]
S_t	= total concentration of adsorption site	[mol/g]
T	= temperature	[K]
t	= time	[s]
X	= dimensionless weight change	[—]
W	= weight change of sample per weight of nickel (w/w_{Ni})	[—]
w	= weight change of sample	[g]
w_{Ni}	= weight of nickel metal	[g]
σ	= active adsorption site	
θ	= dimensionless concentration of CO* (S_{CO}/S_t)	[—]
τ	= dimensionless time $(k_1C_{CO}t)$	[—]

⟨Superscript⟩

*	= adsorption state	

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