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## KINETICS OF METHANATION OF CARBON MONOXIDE AND CARBON DIOXIDE

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**Key Words:** Chemical Reaction, Chemical Reactor, Methanation, Carbon Monoxide, Carbon Dioxide, Reaction Kinetics, Reaction Mechanism

The kinetics of reaction of carbon monoxide and carbon dioxide with hydrogen in a nickel catalyst tube wall reactor were investigated experimentally and the reaction mechanisms were clarified.

The observed rate laws were

$$-r_{\text{CO}} = \frac{k_1 P_{\text{H}_2} P_{\text{CO}}^{1/2}}{1 + K_{\text{CO}} P_{\text{CO}}} \quad \text{for carbon monoxide, and}$$

$$-r_{\text{CO}_2} = \frac{k' P_{\text{H}_2} P_{\text{CO}_2}^{1/3}}{1 + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}$$

for carbon dioxide at low partial pressure.

These reaction rate laws were derived theoretically from the proposed reaction mechanism. For a mixture of carbon monoxide and carbon dioxide the kinetics of the reaction proved to be well accounted for by the same reaction mechanism.

### Introduction

The methanations of carbon monoxide and carbon dioxide are well-known as industrial catalytic processes for fuel production.<sup>8)</sup> They have been studied extensively for their industrial applications. Moreover, as standard catalytic reactions their reaction mechanisms have been investigated intensively and the intermediates and reaction steps of methanation were gradually elucidated.<sup>7,9,10,11)</sup>

Several kinetic equations for the overall rates of

methanation have been proposed,<sup>2,4,5)</sup> but some of them are too simple to be extended to a wide range of conditions and some are difficult to apply to mixtures of carbon monoxide and carbon dioxide because they ignore the mutual interaction effect on the reaction rates.

In this work the authors studied kinetically the methanation of carbon monoxide and carbon dioxide with a nickel metal catalyst, and tried to derive reasonable and reliable rate equations for the system using a specially devised catalytic reactor, a tube wall catalytic reactor.<sup>3)</sup>

The methanation is exothermic and an increase in

Received April 6, 1984. Correspondence concerning this article should be addressed to M. Funakoshi.

the production rate of methane induces a severe temperature distribution inside the reactor. Such a temperature rise makes it difficult to operate the reactor safely and also accelerates the deactivation rate of the catalysts. Therefore, for such a highly exothermic reaction the removal of reaction heat from the reactor is an important consideration.

A tube wall catalyst reactor was found to be suitable for removal of reaction heat. Moreover, it proved useful not only for practical application, but valuable for catalytic reaction study by keeping the catalyst temperature uniform and removing diffusional resistance inside the tube when a reactor of small tube size and a high flow rate of reactant gas were used.<sup>6)</sup>

The reactor was a tubular aluminum one, on the inner wall of which nickel catalyst was deposited uniformly. The methanation proceeded at the catalyst wall and the evolved heat was transferred to the outside coolant directly.

## 1. Experimental

### 1.1 Methanation reactor and reaction conditions

The experimental apparatus is a conventional flow system. The details were described elsewhere,<sup>6)</sup> along with reaction conditions and experimental procedures.

A T.C.D. gas chromatograph was used for analysis of the reactants and products gas. As the sensitivity of this cell is about 100 ppm, gas of smaller amount could not be detected.

Within the experimental conditions no nickel carbonyl could be observed in the outlet gas and no appreciable carbon deposit on the catalyst surface could be observed.

### 1.2 Preparation of the tube wall nickel catalyst

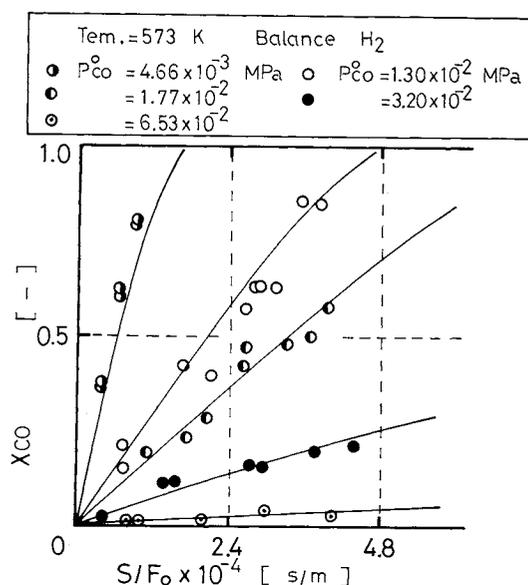
The tube wall catalyst was prepared by electrodeposition of nickel on the inner wall of the aluminum tube from rapidly flowing nickel chloride solution. Details of the procedures and the properties of the catalyst obtained were described in a previous paper.<sup>6)</sup> The nickel catalyst obtained was highly active, and its activity could be maintained constant for many months.

For methanation with this catalyst, diffusion of the reactants proved to have negligible effect on the methanation rate when tube diameter was less than 0.6 cm and reactant gas flow rate was greater than 20 ml/min.<sup>6)</sup>

## 2. Experimental Results

### 2.1 Methanation of carbon monoxide

After axial and radial mixing effects had been ascertained to be negligible, measurements of the methanation rate of carbon monoxide were carried out. **Figure 1** shows the conversion of carbon monoxide



**Fig. 1.** Correlation between conversion and contact time for methanation of carbon monoxide.

oxide at different flow rates of the reactant gas, and in **Figs. 2** and **3** the initial rate of methanation is plotted versus the partial pressures of carbon monoxide and hydrogen. In these figures  $S$  and  $F_0$  are the apparent surface area of the catalyst and the gas flow rate respectively, and the initial rates were derived from the reaction rate at low  $S/F_0$ , where the differential condition was ascertained.

Though these data showed tendencies similar to those of previous rate equations, data for a wide range of gas compositions could not be correlated by those rate equations.

The experimental data obtained were compared with several different rate equations, and the sum of the squares of the residue of each rate equation to the data are shown in **Table 1**, which also shows that the most suitable rate equation is:

$$r_{\text{CH}_4} = \frac{k_1 P_{\text{CO}}^{1/2} P_{\text{H}_2}}{1 + K_{\text{CO}} P_{\text{CO}}}, \quad (1)$$

though there still remains a small deviation in the dependency of the rate on hydrogen partial pressure between Eq. (1) and the experiments. The solid curves in **Figs. 1, 2** and **3**, which are plotted by use of Eq. (1) with suitable parameters, coincide with the experimental data.

From the temperature dependency it was found that the activation energy  $E_1$  of  $k_1$  was about 59 kJ/mol and the apparent adsorption energy of carbon monoxide was about 25 kJ/mol. The results of these data are tabulated in **Table 2**. Though the activation energy of the methanation might be smaller than in the previous works, the apparent overall activation energy of this reaction is about 84 kJ/mol

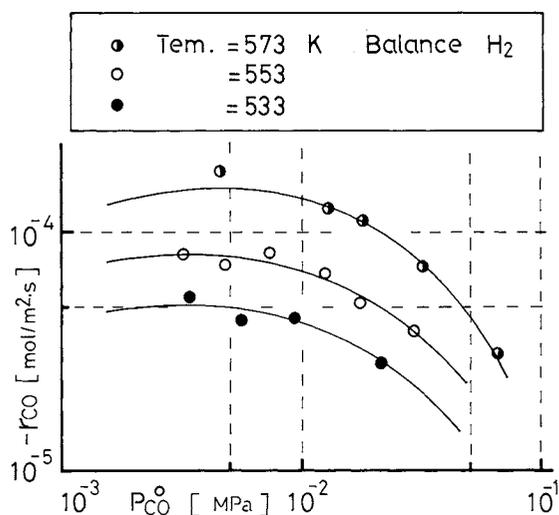


Fig. 2. Initial rate vs. CO partial pressure for methanation of carbon monoxide.

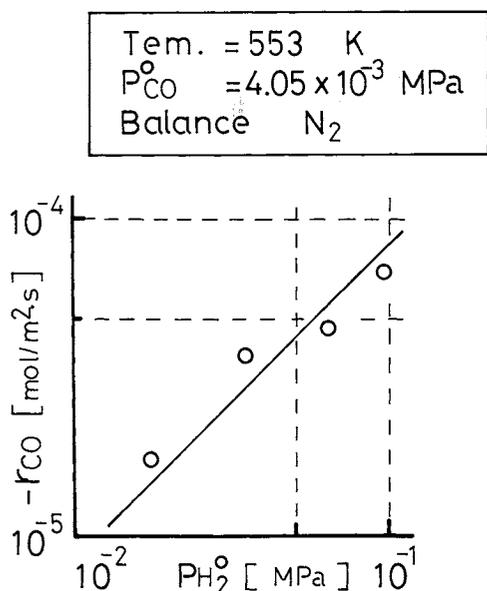


Fig. 3. Initial rate vs. H<sub>2</sub> partial pressure for methanation of carbon monoxide.

Table 1. Reaction rate equations analyzed and the sums of the squares of the residuals

Rate equations	Sums of the squares of the residuals
$r_{\text{CH}_4} = k_1 P_{\text{CO}}^{1/2} P_{\text{H}_2} / (1 + K_{\text{CO}} P_{\text{CO}})$	$s = 8.57 \times 10^{-4}$
$= k_1 P_{\text{CO}} P_{\text{H}_2} / (1 + K_{\text{CO}} P_{\text{CO}})^2$	$= 1.89 \times 10^{-3}$
$= k_1 P_{\text{CO}} P_{\text{H}_2}^2 / (1 + K_{\text{CO}} P_{\text{CO}})^3$	$= 1.79 \times 10^{-3}$
$= k_1 P_{\text{CO}} P_{\text{H}_2}^{1/2} / (1 + K_{\text{CO}} P_{\text{CO}})^2$	$= 2.04 \times 10^{-3}$
$= k_1 P_{\text{CO}}^{1/2} P_{\text{H}_2} / (1 + K_{\text{CO}} P_{\text{CO}}^{1/2})^2$	$= 1.04 \times 10^{-2}$

when the data are replotted according to the Freundlich rate form, and are at nearly the same level as in the previous works.<sup>10)</sup>

The heat of adsorption of carbon monoxide on nickel is found to be very large, and this low value of

Table 2. Catalytic rate parameters for methanation of carbon monoxide

Temperature (K)	$k_1^a$ (mol·m <sup>-2</sup> ·s <sup>-1</sup> ·MPa <sup>-3/2</sup> )	$K_{\text{CO}}$ (MPa <sup>-1</sup> )
533	$6.98 \times 10^{-6}$	266
553	$1.10 \times 10^{-5}$	243
573	$1.77 \times 10^{-5}$	178

<sup>a</sup>  $k_1$  is the catalytic rate constant per unit BET surface area of the nickel catalyst.

adsorption energy may be unusual, but the heat of adsorption changes with coverage from 125 kJ/mol to 16.7 kJ/mol,<sup>12)</sup> and the present reaction condition may correspond to its high coverage on the catalyst surface.

Moreover, from the rate equations derived from tube wall reactors having different BET surface areas, it was found that the reaction rate constant per unit BET surface area of the nickel catalyst was nearly constant. The results prove that the kinetic data obtained were not influenced by intraparticle diffusion of the deposited nickel film. The turnover number of methanation on this catalyst was calculated to be about  $6 \times 10^{-4} \text{ s}^{-1}$  under the condition<sup>10)</sup> that temperature is 275°C,  $P_{\text{H}_2} = 0.076 \text{ MPa}$  and  $P_{\text{CO}} = 0.025 \text{ MP}$ . The turnover number of newly prepared catalyst was very high, but it gradually decreased and settled on the level after continuous methanation.

## 2.2 Methanation of carbon dioxide

Figures 4 and 5 show the dependency of initial rates of methanation on hydrogen and carbon dioxide partial pressures, respectively.

In Fig. 6, the change of conversion with contact time,  $S/F_0$ , is plotted. In the experiments the products from carbon dioxide were mainly methane and water. Carbon monoxide was not observed in the product gas.

The experimental initial rates of methanation were correlated with several different rate equations similar to the case of carbon monoxide methanation. As a result, the following rate equation is found to represent the experiments fairly well, though other rate forms might also be applicable to the data within the allowable error.

$$-r_{\text{CO}_2} = \frac{k_2 P_{\text{H}_2}^{1/2} P_{\text{CO}_2}^{1/2}}{(1 + K_{\text{H}_2} P_{\text{H}_2}^{1/2} + K_{\text{CO}_2} P_{\text{CO}_2}^{1/2})^2} \quad (2)$$

The dotted lines in Figs. 4 and 5 express rate equation (2) with suitable parameters. Because the presence of water vapor in the reacting gas was observed experimentally to decrease appreciably the rate of methanation, rate equation (2) must include a term for the adsorption of water as illustrated in Fig. 6.

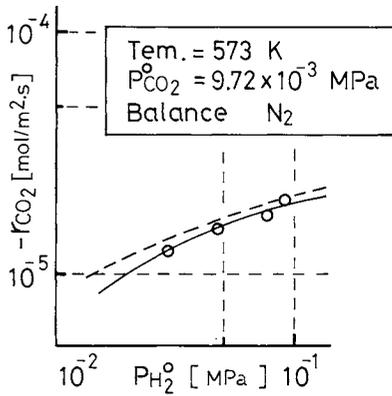


Fig. 4. Initial rate vs.  $H_2$  partial pressure for methanation of carbon dioxide.

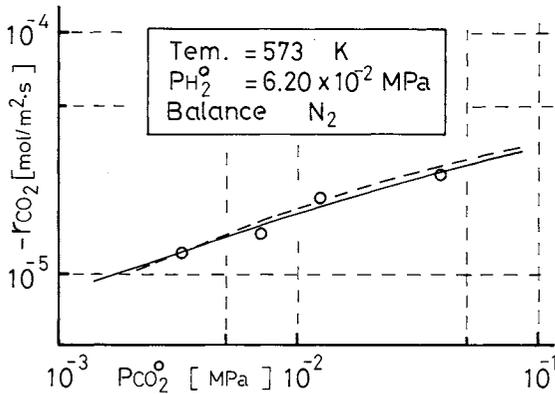


Fig. 5. Initial rate vs.  $CO_2$  partial pressure for methanation of carbon dioxide.

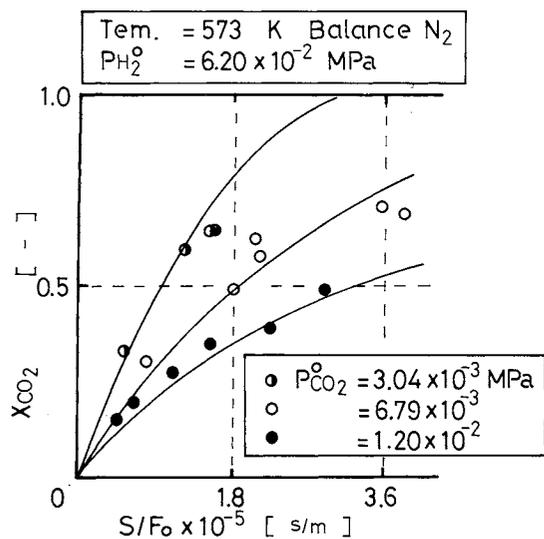


Fig. 6. Correlation between conversion and contact time for methanation of carbon dioxide.

In some experimental conditions, such as high partial pressures of carbon dioxide, carbon monoxide is produced as an intermediate in the methanation; and it decreases with increasing contact time. The selectivity,  $S_{CO}$ , defined by Eq. (3), is plotted in Fig. 7 for several different reaction conditions.

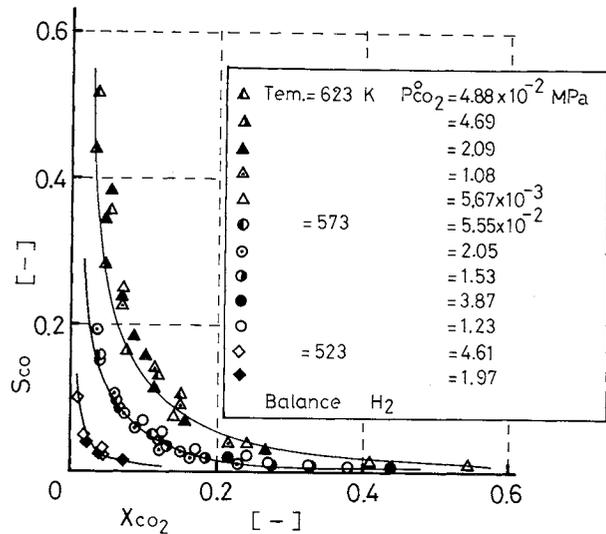


Fig. 7. Carbon dioxide conversion vs. carbon monoxide selectivity.

$$S_{CO} = \frac{\text{yield of carbon monoxide}}{\text{conversion of carbon dioxide}} \quad (3)$$

As is shown in this figure, the selectivity at each temperature is determined only by the degree of conversion,  $X_{CO_2}$ , independent of the initial carbon dioxide partial pressure. This characteristic is typical of the consecutive reaction system if the rate equations of the first and second steps have the same kinetic orders.

If the hydrogenation system is assumed to be a simple consecutive reaction system, the selectivity of carbon monoxide is derived by the following equation.

$$\frac{dP_{CO}}{dP_{CO_2}} = -1.0 + \beta \frac{P_{CO}}{P_{CO_2}} \quad (4)$$

$$\text{at } P_{CO_2} = P_{CO_2}^0 \text{ (initial condition), } P_{CO} = 0.$$

The solid curves in the figure are the theoretical relationships of  $S_{CO}$  vs.  $X_{CO_2}$  derived from Eq. (4), and are in accord with the experimental data.

From a comparison of the theoretical curves with the experimental data for different temperature,  $\beta$  is found to be about 1000, 200, and 60, at 523, 573, and 623 K, respectively.

### 2.3 Methanation of the mixture of carbon monoxide and dioxide

Figure 8 shows some of the results of experiments at 623 K. The analysis of this system requires detailed knowledge of the catalytic reaction mechanism.

### 3. Kinetic Analysis of Methanation

Experimentally obtained kinetic features of methanation may be summarized as follows:

1) In the hydrogenation of carbon monoxide, the rate is expressed by a Langmuir rate equation with a

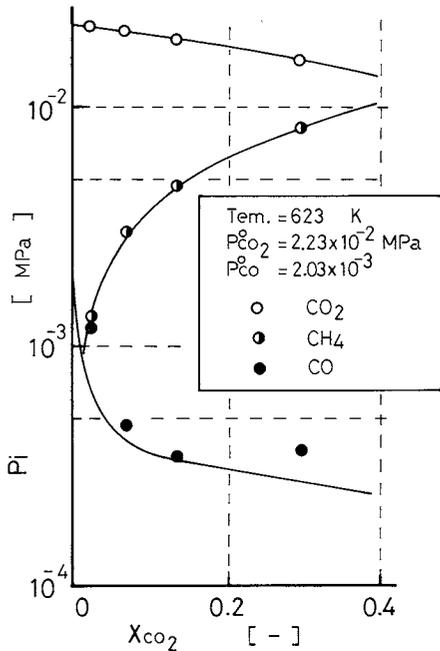


Fig. 8. Correlation between partial pressure of each component at the outlet vs. carbon dioxide conversion for methanation of carbon monoxide and carbon dioxide mixture.

numerator of  $P_{CO}^{1/2}$  instead of  $P_{CO}^1$ .

2) Similarly, the rate equation for carbon dioxide depends on  $P_{CO_2}^{1/2}$ , though the dependency of the rate on hydrogen partial pressure is different from the former case.

3) For reactions with high concentrations of carbon dioxide, carbon monoxide is produced as an intermediate, and the selectivity seems to be determined mainly by the degree of conversion, regardless of the initial concentration of carbon dioxide.

Based on the elementary reaction steps which had been extensively studied previously, the authors derived a mechanism which is consistent with the experimental rate data obtained.

In this mechanism the main assumptions about the adsorptions and reactions on the catalyst surface are as follows:

1) Carbon monoxide and carbon dioxide and hydrogen adsorb on the catalyst surface, but kinetically hydrogen adsorption takes no main part in the methanation.

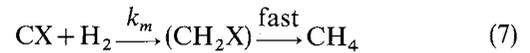
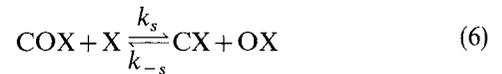
2) Adsorption of carbon monoxide is very strong in comparison with the adsorption of other reactants and products.

3) Adsorbed carbon monoxide or carbon dioxide dissociate on the surface of the catalyst and proceed to methane and water by the reaction with hydrogen.

4) The surface coverages of intermediate compounds are very small except for CO, CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O.

### 3.1 Methanation of carbon monoxide

The reaction scheme is



Here  $X$  represents active sites on the nickel catalyst, and the equilibrium for the adsorption of carbon monoxide is expressed as

$$\theta_{CO} = K_{CO} P_{CO} \theta_v \quad (9)$$

$\theta_v$  and  $\theta_i$  represent the fractions of vacant sites and of sites occupied by an adsorbed species  $i$ , respectively, and  $\theta_C$  and  $\theta_O$  may be reasonably assumed to be very small in comparison to  $\theta_{CO}$  or  $\theta_v$ .

$$\theta_C \text{ and } \theta_O \ll \theta_{CO} \text{ and } \theta_v$$

At steady state the surface concentration of  $CX$  is determined by the following equation:

$$k_s \theta_{CO} \theta_v - k_{-s} \theta_C \theta_O - k_m P_{H_2} \theta_C = 0 \quad (10)$$

and at the same time the production of methane and water must be equal; that is:

$$\begin{aligned} k_m P_{H_2} \theta_C &= k_h P_{H_2} \theta_O \\ \theta_O &= (k_m/k_h) \theta_C = \alpha \theta_C \end{aligned} \quad (11)$$

Therefore, from Eqs. (10) and (11),  $\theta_C$  and the rate of methanation are derived as Eqs. (12) and (13), respectively.

$$\begin{aligned} \theta_C^2 + (k_m P_{H_2} / \alpha k_{-s}) \theta_C - (k_s / \alpha k_{-s}) \theta_{CO} \theta_v &= 0 \\ \theta_C &= (1/2) [(k_m P_{H_2} / \alpha k_{-s})^2 \\ &+ (4k_s / \alpha k_{-s}) \theta_{CO} \theta_v]^{1/2} - (k_m P_{H_2} / \alpha k_{-s}) \end{aligned} \quad (12)$$

and

$$\begin{aligned} r_{CH_4} &= k_m P_{H_2} \theta_C \\ &= k_m P_{H_2} [(k_m P_{H_2} / 2\alpha k_{-s})^2 \\ &+ (k_s / \alpha k_{-s}) \theta_{CO} \theta_v]^{1/2} - (k_m P_{H_2} / 2\alpha k_{-s}) \end{aligned} \quad (13)$$

As the adsorption of carbon monoxide is very strong, the following condition is reasonably assumed:

$$(k_s / \alpha k_{-s}) \theta_{CO} \theta_v \gg (k_m / 2\alpha k_{-s}) P_{H_2}$$

and Eq. (12) becomes

$$\theta_C = [(K_s / \alpha) \theta_{CO} \theta_v]^{1/2} \quad (14)$$

where  $K_s = k_s / k_{-s}$ .

Therefore, the rate of methanation (13) is given as follows:

$$r_{\text{CH}_4} = k_m (K_s/\alpha)^{1/2} P_{\text{H}_2} (\theta_{\text{CO}} \theta_v)^{1/2} \quad (15)$$

$$= k_m (K_s K_{\text{CO}}/\alpha)^{1/2} P_{\text{H}_2} P_{\text{CO}}^{1/2} \theta_v \quad (16)$$

In this equation  $\theta_v$  can be written as

$$\theta_v = 1/(1 + K_{\text{CO}} P_{\text{CO}})$$

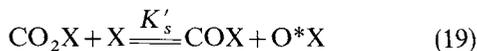
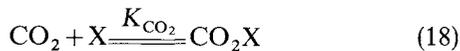
because the main adsorption species on the surface is carbon monoxide. Based on this derivation, the overall rate of methanation of carbon monoxide is

$$r_{\text{CH}_4} = k_m \left( \frac{K_s K_{\text{CO}}}{\alpha} \right)^{1/2} \frac{P_{\text{H}_2} P_{\text{CO}}^{1/2}}{1 + K_{\text{CO}} P_{\text{CO}}} \quad (17)$$

This equation corresponds to Eq. (1), which was derived from the experimental data analysis.

### 3.2 Methanation of carbon dioxide

For the results of the reaction in which the product is mainly methane and water, it is not necessary to consider the effect of carbon monoxide gas on the rate of methanation. In this system, the reaction steps can be written as follows:



and the adsorbed carbon monoxide thus produced, COX, changes to methane according to the mechanism of Eqs. (6), (7) and (8). In this carbon dioxide system the surface concentration of COX may be regarded as being very small, but the rate of methanation is expressed similarly as

$$r_{\text{CH}_4} = k_m (K_s/\alpha)^{1/2} P_{\text{H}_2} (\theta_{\text{CO}} \theta_v)^{1/2} \quad (15)$$

Based on the equilibrium relationships (18) and (19),

$$\theta_{\text{CO}_2} = K_{\text{CO}_2} P_{\text{CO}_2} \theta_v \quad (21)$$

$$\theta_{\text{CO}} \theta_{\text{O}^*} = K'_s \theta_{\text{CO}_2} \theta_v \quad (22)$$

In these equations  $K_{\text{CO}_2}$  and  $K'_s$  are the adsorption constant of carbon dioxide and the equilibrium constant of reaction (19), respectively. As the rate of disappearance of carbon dioxide is equal to the rate of the reaction  $\text{O}^*\text{X}$  to produce water at steady state:

$$\begin{aligned} (-r_{\text{CO}_2}) &= k'_h \theta_{\text{O}^*} P_{\text{H}_2} = k'_h K'_s P_{\text{H}_2} \theta_{\text{CO}_2} \theta_v / \theta_{\text{CO}} \\ &= (k'_h K'_s K_{\text{CO}_2}) P_{\text{H}_2} P_{\text{CO}_2} \theta_v^2 / \theta_{\text{CO}} \end{aligned} \quad (23)$$

And  $(-r_{\text{CO}_2})$  is equal to the rate of methanation.

$$(k'_h K'_s K_{\text{CO}_2}) P_{\text{H}_2} P_{\text{CO}_2} \theta_v^2 / \theta_{\text{CO}} = k_m (K_s/\alpha)^{1/2} P_{\text{H}_2} (\theta_{\text{CO}} \theta_v)^{1/2}$$

Then

$$\theta_{\text{CO}} = [k'_h K'_s K_{\text{CO}_2} / k_m / (K_s/\alpha)^{1/2}]^{2/3} P_{\text{CO}_2}^{2/3} \theta_v \quad (24)$$

Using this steady-state concentration of COX, the rate of methanation is derived as

$$\begin{aligned} r_{\text{CH}_4} &= k_m (K_s/\alpha)^{1/2} P_{\text{H}_2} (\theta_{\text{CO}} \theta_v)^{1/2} \\ &= [k_m^2 k'_h K'_s K_{\text{CO}_2} / \alpha]^{1/3} P_{\text{H}_2} P_{\text{CO}_2}^{1/3} \theta_v \end{aligned} \quad (25)$$

Here, under the assumption that  $\theta_{\text{CO}_2}$ ,  $\theta_{\text{H}_2}$  and  $\theta_{\text{H}_2\text{O}} \gg \theta_{\text{C}}$  or  $\theta_{\text{O}}$ ,  $\theta_v$  is given as

$$\theta_v = 1/(1 + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})$$

and the methanation rate, Eq. (25), becomes

$$-r_{\text{CO}_2} = \frac{(k_m^2 k'_h K'_s K_{\text{CO}_2} / \alpha)^{1/3} P_{\text{H}_2} P_{\text{CO}_2}^{1/3}}{1 + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}} \quad (26)$$

As the adsorption of carbon dioxide is not so strong as that of carbon monoxide, it is necessary to consider the effect of adsorption of hydrogen and product water. The solid curves in Figs. 4 and 5 are the initial rates calculated by the rate equation (26) with most probable values of  $K_{\text{H}_2}$ ,  $K_{\text{CO}_2}$ , and  $(k_m^2 k'_h K'_s K_{\text{CO}_2} / \alpha)^{1/3}$ .

The solid curves in Fig. 6 are the integral reaction progress in the tube wall reactor calculated by the rate equation. In this case the effect of produced water was considered, and the most probable value of the equilibrium constant of water was found to be about  $200 \text{ MPa}^{-1}$ . This figure shows that the experimental data are expressed well by the rate Equation (26).

The rate equation for unit BET surface area of the nickel catalyst is expressed as

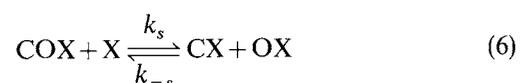
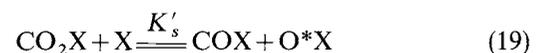
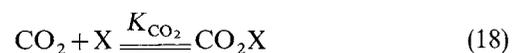
$$-r_{\text{CO}_2} = r_{\text{CH}_4} = \frac{(8.81 \times 10^{-6}) P_{\text{H}_2} P_{\text{CO}_2}^{1/3}}{1 + (30.3) P_{\text{H}_2} + (3.7) P_{\text{CO}_2} + (200) P_{\text{H}_2\text{O}}} \quad (26')$$

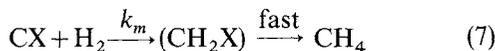
Though this equation (26') is different from the experimentally derived rate form (2), it is found to be well in accordance with the experimental data.

### 3.3 Methanation of the mixture of carbon dioxide and carbon monoxide

During the hydrogenation of carbon dioxide in the presence of carbon monoxide as an intermediate or a mixture of carbon monoxide and carbon dioxide, it is necessary to treat the interaction of both reaction processes.

As an extension of the previous reaction scheme, the whole process can be expressed by the following reaction steps.





In this reaction scheme, reaction step (5) must be considered as a rate process (5') rather than an equilibrium.

At steady state

$$\theta_{CO_2} = K_{CO_2} P_{CO_2} \theta_v$$

$$\theta_{CO} \theta_{O^*} = K_s' \theta_{CO_2} \theta_v$$

and as the rate of consumption of carbon dioxide is equal to the rate of water production from  $O^*X$ , ( $-r_{CO_2}$ ) is expressed as

$$\begin{aligned} -r_{CO_2} &= k_h' P_{H_2} \theta_{O^*} \\ &= k_h' K_s' P_{H_2} (\theta_{CO_2} \theta_v / \theta_{CO}) \\ &= (k_h' K_s' K_{CO_2}) P_{H_2} P_{CO_2} (\theta_v^2 / \theta_{CO}), \end{aligned} \quad (27)$$

and the production rate of methane from COX is similarly given by Eq. (15).

$$r_{CH_4} = k_m (K_s / \alpha)^{1/2} P_{H_2} (\theta_{CO} \theta_v)^{1/2} \quad (15)$$

As  $\theta_{CO}$  is kept constant at steady state, the disappearance rate of  $\theta_{CO}$  must be balanced with the production rate, that is:

$$k_{-CO} \theta_{CO} + r_{CH_4} = (-r_{CO_2}) + k_{CO} P_{CO} \theta_v \quad (28)$$

( $-r_{CO_2}$ ) and ( $r_{CH_4}$ ) being substituted by Eqs. (27) and (15), Eq. (28) leads to Eq. (29).

$$y + A(y)^{1/2} - B/y = K_{CO} P_{CO} \quad (29)$$

where

$$y = \theta_{CO} / \theta_v$$

$$A = (k_m / k_{-CO}) (K_s / \alpha)^{1/2} P_{H_2}$$

$$B = (k_h' K_s' K_{CO_2} / k_{-CO}) P_{H_2} P_{CO_2}$$

$$K_{CO} = k_{CO} / k_{-CO}$$

Based on Eq. (29),  $\theta_{CO} / \theta_v$  is estimated and the performance of this reaction process can be analyzed.

For some arbitrarily assigned values of  $A$  and  $B$  in Eq. (29), the relationships of  $y$  and  $K_{CO} P_{CO}$  are shown in Fig. 9. The whole field of this relationship may be divided into three regions as is shown in the figure.

In region  $L$ , where  $K_{CO} P_{CO}$  is very large,  $y$  is nearly proportional to  $K_{CO} P_{CO}$ , that is, the equilibrium of carbon monoxide is established on the catalyst surface and the rate of methanation is determined by carbon monoxide. In this case

$$y = K_{CO} P_{CO}, \quad (30)$$

and

$$\begin{aligned} r_{CH_4} &= k_m (K_s / \alpha)^{1/2} P_{H_2} (\theta_{CO} \theta_v)^{1/2} \\ &= k_m (K_s / \alpha)^{1/2} P_{H_2} \theta_v y^{1/2} \end{aligned}$$

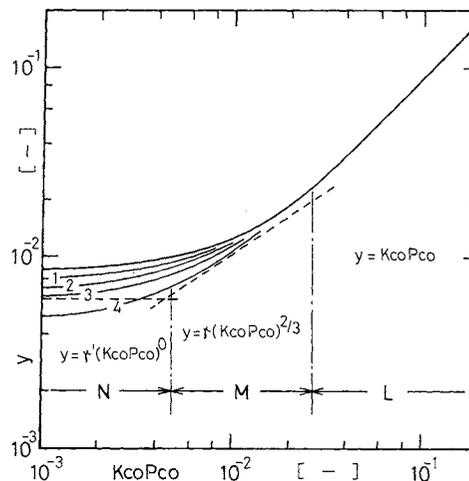


Fig. 9. The relationship of  $\theta_{CO} / \theta_v$  vs.  $K_{CO} P_{CO}$  (Eq. (29)).

which lead to Eq. (16).

In region  $N$ , where  $K_{CO} P_{CO}$  is very small,  $y$  is nearly independent of  $K_{CO} P_{CO}$  and is determined only by the value of  $A$  and  $B$ . In this condition, approximately:

$$\begin{aligned} y &= (A/B)^{2/3} \\ &= [k_h' K_s' K_{CO_2} P_{CO_2} / k_m / (K_s / \alpha)^{1/2}]^{2/3} \end{aligned} \quad (31)$$

From Eq. (31) the rate of methanation (25), obtained already, is derived as follows:

$$\begin{aligned} r_{CH_4} &= k_m (K_s / \alpha)^{1/2} P_{H_2} \theta_v y^{1/2} \\ &= [k_m (K_s / \alpha)^{1/2}]^{2/3} (k_h' K_s' K_{CO_2})^{1/3} P_{H_2} P_{CO_2}^{1/3} \theta_v \end{aligned} \quad (25)$$

Region  $M$  is the transition from  $N$  to  $L$ , that is, from the region where  $y = \gamma' (K_{CO} P_{CO})^0$  to the region where  $y = K_{CO} P_{CO}$ . In this transition region  $y$  depends not only on  $K_{CO} P_{CO}$  but also on  $P_{H_2}$  and  $P_{CO}$ . However, the relationship in this region can be expressed approximately as

$$y = \gamma (K_{CO} P_{CO})^{2/3} \quad (32)$$

which is shown by the dotted line in the figure. Moreover, by the progress of the reaction the partial pressure of hydrogen decreases appreciably, and accordingly the relationship changes from the original solid curve to curves 1, 2, 3, and 4 successively with the progress of the reaction. Then the approximation Eq. (32) may be more widely applicable to the transition region.

Here, to calculate the selectivity of the product by the progress of the reaction in this transition region, the mass balance equations for carbon dioxide and carbon monoxide in the tube wall catalytic reactor are expressed as follows:

$$\frac{F_o}{RT} \frac{dP_{CO_2}}{dz} = ar_{CO_2} = -(ak_h' K_s' K_{CO_2}) P_{H_2} P_{CO_2} \frac{\theta_v^2}{\theta_{CO}} \quad (33)$$

$$\frac{F_o}{RT} \frac{dP_{CO}}{dz} = a(k_{-CO}\theta_{CO} - k_{CO}P_{CO}\theta_v)$$

$$= (ak'_hK'_sK_{CO_2})P_{H_2}P_{CO_2} \frac{\theta_v^2}{\theta_{CO}} - ak_m(K_s/\alpha)^{1/2}P_{H_2}(\theta_{CO}\theta_v)^{1/2}$$
(34)

Here  $F_o$  and  $a$  are the gas flow rate and the surface area of catalyst per unit length of the tube wall reactor, respectively, and  $z$  is the coordinate of reactor length. From these equations,

$$\frac{dP_{CO}}{dP_{CO_2}} = -1.0 + \frac{k_m(K_s/\alpha)^{1/2}}{k'_hK'_sK_{CO_2}} \frac{(\theta_{CO}/\theta_v)^{3/2}}{P_{CO}} \frac{P_{CO}}{P_{CO_2}}$$
(35)

Equation (35) determines the selectivity for the production of carbon monoxide from carbon dioxide. By the application of Eq. (32), Eq. (35) can be written in a simple form.

$$\frac{dP_{CO}}{dP_{CO_2}} = -1.0 + \frac{k_m(K_s/\alpha)^{1/2}}{k'_hK'_sK_{CO_2}} \gamma^{3/2} K_{CO} \left( \frac{P_{CO}}{P_{CO_2}} \right)$$
(35')

This equation is in accord with Eq. (4), which was derived from the analysis of experimental data alone. Therefore

$$\beta = \frac{k_m K_{CO}}{k'_h K'_s K_{CO_2}} (K_s/\alpha)^{1/2} \gamma^{3/2} = 1000 \quad \text{at } 523 \text{ K}$$

$$= 200 \quad \text{at } 573 \text{ K}$$

$$= 60 \quad \text{at } 623 \text{ K}$$

For the catalytic reaction of a mixture of carbon monoxide and carbon dioxide, the progress of the reaction can be derived by Eq. (35), with the following initial condition.

$$\text{At } P_{CO_2} = P_{CO_2}^o, \quad P_{CO} = P_{CO}^o$$

The experimental results in Fig. 8 are analyzed according to this equation. The solid curves in Fig. 8 are theoretical ones, where the constant corresponding to  $\beta$  in Eq. (35') is equal to 60. Here it is found that the analysis is applicable to this system also.

## Conclusion

From the analysis of the overall reaction rate data, rate equations were derived for the methanation of carbon dioxide and carbon monoxide in the presence of nickel catalyst, and a reaction process was proposed corresponding to the rate equations obtained.

In this paper, the analysis is based only on the overall rate data for methanation under several different sets of conditions, and therefore there remain some ambiguities about the reaction intermediates. That is, the analysis neglects the reaction of adsorbed hydrogen and discrimination between the rate processes of water production and the adsorbed oxygen atoms,  $O^*X$  and  $OX$ .

In this analysis the reaction to produce carbon

dioxide from carbon monoxide and water was neglected since under the present experimental conditions the formation of appreciable amounts of carbon dioxide from carbon monoxide could not be detected. However, for the high-pressure methanation of carbon monoxide that process must be considered, as small amounts of carbon dioxide actually could be observed when a large amount of water was fed into the reactor system with carbon monoxide and hydrogen.

The rate equation derived for carbon dioxide, Eq. (26), is not so familiar, but nearly the same rate form was derived previously by Amenomiya<sup>1)</sup> for water-gas conversion by an alumina catalyst. He observed surface formate as an intermediate of the reaction, but we could not derive a reasonable mechanism expressing the rate based on the surface formate intermediate.

A more detailed discussion of the reaction scheme will require more accurate kinetic data and knowledge about the surface processes. However, from this study it may be said that a kinetic formulation of this complex reaction process can be derived and that reliable and reasonable basic data for reactor design and operations have been established.

## Nomenclature

$A$	$= (k_m/k_{-CO})(K_s/\alpha)^{1/2}P_{H_2}$	[—]
$B$	$= (k'_hK'_sK_{CO_2}/k_{-CO})P_{H_2}P_{CO_2}$	[—]
$E_i$	$=$ activation energy of $k_i$	[KJ · mol <sup>-1</sup> ]
$F_o$	$=$ total gas flow rate at inlet	[m · s <sup>-1</sup> ]
$i$	$=$ adsorbed species	[—]
$K_{CO}$	$=$ adsorption equilibrium constant of carbon monoxide	[MPa <sup>-1</sup> ]
$K_{CO_2}$	$=$ adsorption equilibrium constant of carbon dioxide	[MPa <sup>-1</sup> ]
$K_{H_2}$	$=$ adsorption equilibrium constant of hydrogen	[MPa <sup>-1</sup> ]
$K_{H_2O}$	$=$ adsorption equilibrium constant of water	[MPa <sup>-1</sup> ]
$K_s$	$= k_s/k_{-s}$	[—]
$K'_s$	$=$ equilibrium constant of Eq. (19)	[—]
$k'$	$=$ rate constant of carbon dioxide consumption rate	[mol · m <sup>-2</sup> · s <sup>-1</sup> · MPa <sup>-4/3</sup> ]
$k_1$	$=$ rate constant of Eq. (1)	[mol · m <sup>-2</sup> · s <sup>-1</sup> · MPa <sup>-3/2</sup> ]
$k_2$	$=$ rate constant of Eq. (2)	[mol · m <sup>-2</sup> · s <sup>-1</sup> · MPa <sup>-1</sup> ]
$k_{CO}$	$=$ rate constant of forward reaction in Eq. (5')	[mol · m <sup>-2</sup> · s <sup>-1</sup> · MPa <sup>-1</sup> ]
$k_{-CO}$	$=$ rate constant of reverse reaction in Eq. (5')	[mol · m <sup>-2</sup> · s <sup>-1</sup> ]
$k_h$	$=$ rate constant of Eq. (8)	[mol · m <sup>-2</sup> · s <sup>-1</sup> · MPa <sup>-1</sup> ]
$k'_h$	$=$ rate constant of Eq. (20)	[mol · m <sup>-2</sup> · s <sup>-1</sup> · MPa <sup>-1</sup> ]
$k_m$	$=$ rate constant of Eq. (7)	[mol · m <sup>-2</sup> · s <sup>-1</sup> · MPa <sup>-1</sup> ]
$k_s$	$=$ rate constant of forward reaction in Eq. (6)	[mol · m <sup>-2</sup> · s <sup>-1</sup> ]
$k_{-s}$	$=$ rate constant of reverse reaction in Eq. (6)	[mol · m <sup>-2</sup> · s <sup>-1</sup> ]
$P_{CO}$	$=$ partial pressure of carbon monoxide	[MPa]
$P_{CO}^o$	$=$ partial pressure of carbon monoxide at initial state	[MPa]
$P_{CO_2}$	$=$ partial pressure of carbon dioxide	[MPa]
$P_{CO_2}^o$	$=$ partial pressure of carbon dioxide at initial state	[MPa]

$P_{H_2}$	= partial pressure of hydrogen	[MPa]	oxygen	[—]
$P_{H_2O}$	= partial pressure of water	[MPa]	$\theta_{O^*}$	= fractions of active sites occupied by adsorbed $O^*$
$r_{CH_4}$	= methane production rate	$[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]$	$O^*$	[—]
$r_{CO}$	= carbon monoxide production rate	$[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]$	$\theta_v$	= fractions of vacant active sites
$r_{CO_2}$	= carbon dioxide production rate	$[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]$		[—]
$S$	= apparent surface area	$[\text{m}^2]$		
$S_{CO}$	= selectivity of carbon monoxide	[—]		
$T$	= temperature	[K]		
$X$	= active site	[—]		
$X_{CO}$	= conversion of carbon monoxide	[—]		
$X_{CO_2}$	= conversion of carbon dioxide	[—]		
$y$	= $\theta_{CO}/\theta_v$	[—]		
$z$	= reactor length	[m]		
$\alpha$	= $k_m/k_h$	[—]		
$\beta$	= constant in Eq. (4)	[—]		
$\gamma$	= function	[—]		
$\gamma'$	= function	[—]		
$\theta_C$	= fractions of active sites occupied by adsorbed carbon	[—]		
$\theta_{CO}$	= fractions of active sites occupied by adsorbed carbon monoxide	[—]		
$\theta_{CO_2}$	= fractions of active sites occupied by adsorbed carbon dioxide	[—]		
$\theta_i$	= fractions of active sites occupied by adsorbed species $i$	[—]		
$\theta_O$	= fractions of active sites occupied by adsorbed	[—]		

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