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Kinetic study of methanol synthesis from carbon dioxide and hydrogen†

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Practical kinetic equations for methanol synthesis from CO_2 hydrogenation are necessary for designing a highly efficient reactor. The kinetic equations were deduced from the reaction mechanisms for methanol synthesis and CO formation as well as from various kinetic experiments over our Cu/ZnO-based catalyst. The accuracy of the equations deduced has been verified by the comparison between the values calculated from the kinetic equations and the data obtained from various experiments in a test plant (50 kg day^{-1} of MeOH). Therefore, the kinetic equations developed in the present study have been found applicable to the design of a highly effective reactor employing our developed catalyst. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: kinetic equation; carbon dioxide; methanol synthesis; hydrogenation; copper catalyst

NOTATION

R_M	rate of methanol production per unit mass of catalyst (mol h^{-1})
R_R	rate of CO production per unit mass of catalyst (mol h^{-1})
$P(x)$	partial pressure of component x (MPa)
K_M	equilibrium constant of reaction [1] thermodynamically determined
K_R	equilibrium constant of reaction [3] thermodynamically determined
K_x	adsorption equilibrium constant for component x
k_x	overall rate constant for component x (mol h^{-1} per kg of catalyst)
R	gas constant (8.314 J mol^{-1} K^{-1})
T	reaction temperature (K)

INTRODUCTION

The greenhouse effect of carbon dioxide has been recognized as one of the most serious problems in the world, and a number of countermeasures have so for been proposed. Methanol synthesis from CO_2 and hydrogen ($CO_2 + 3H_2 \equiv CH_3OH + H_2O$) has received much attention because it is useful for methanol engines, fuel cells, chemicals, and so on. The authors developed high performance Cu/ZnO-based catalysts that are highly active and selective in methanol synthesis, and are extremely stable for long periods in continuous operation.[1–3]

It is important to set up kinetic equations for CO_2 hydrogenation in order to develop a high-efficiency reactor for methanol synthesis from CO_2 and hydrogen. In the present study, the practical kinetic equations for methanol synthesis and CO formation over our Cu/ZnO-based catalysts have been developed, and high accuracy of the equations has been verified by a comparison between the data experimentally observed and the values calculated from the kinetic equations developed.

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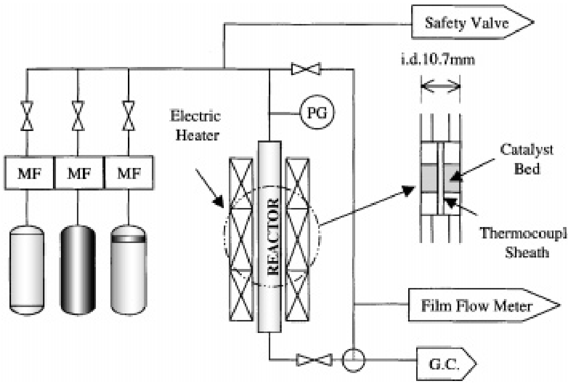

Figure 1 Flow diagram of a fixed bed reactor.

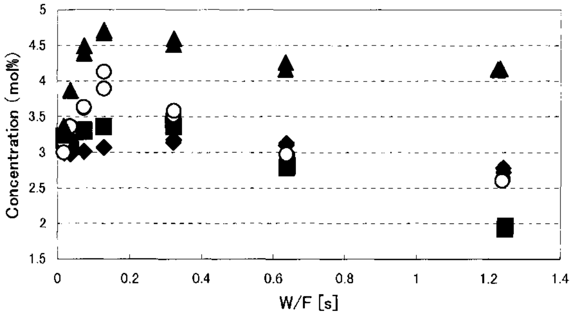

Figure 2 Change in CO concentration as a function of contact time: ◆, 200 °C; ■, 225 °C; ○, 250 °C; ▲, 275 °C.

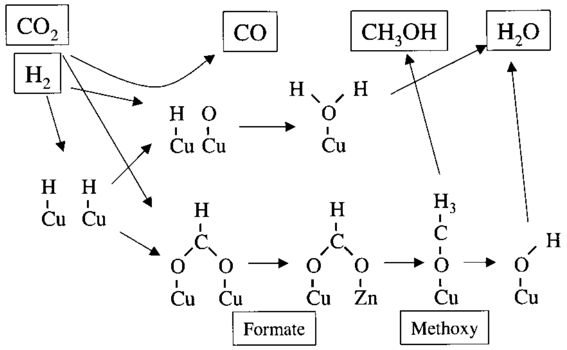

Figure 3 Reaction mechanisms for CO_2 hydrogenation employed for the present study.

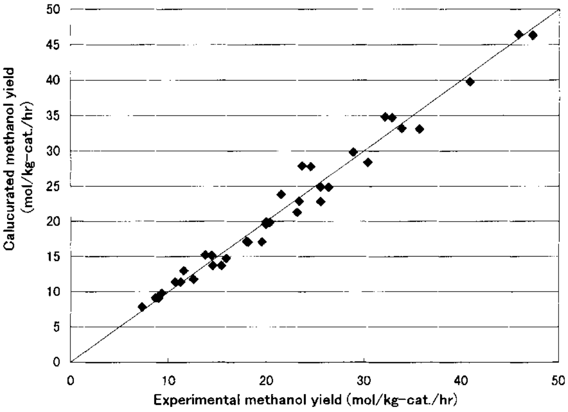

Figure 4 Parity plot for the rate of methanol synthesis under various conditions.

EXPERIMENTAL

A Cu/ZnO-based multicomponent catalyst (Cu/ZnO/ZrO_2/Al_2O_3/SiO_2) was prepared by a conventional coprecipitation method and pelletized to cylindrical shape (3 mm in diameter and 3 mm in height). Catalyst pellets were not crushed to smaller sizes for obtaining the kinetic equations for CO_2 hydrogenation, because the kinetic equations should be applied to the reactions in a test plant employing the catalyst pellets of the same dimensions as described above.

Figure 1 shows a flow diagram of the reactor used for collecting kinetic data. Methanol synthesis experiments were carried out using a one-pass tubular reactor with an internal diameter of 10.7 mm, which was packed with six pellets for differential reactions or with an optional number of the pellets for integral reactions. The flow rate of the reactant was controlled by mass flow controllers, and measured by a film flow meter in every sampling. All experiments to determine the parameters of kinetic equations were carried out at the same linear velocity of feed gas, which was high enough to avoid the influence of the laminar film. Space velocity for differential reactions was 100,000 h^{-1}, which was so high that low conversions of CO_2 can be obtained. The temperature of

Table 1 The choices of differential reaction conditions, reaction temperature, CO_2 partial pressure and H_2 partial pressure, for deciding parameters of kinetic equations

Temperature (K)	473	498	523	548
CO_2 partial pressure (MPa)	0.588	1.078	1.725	
H_2 partial pressure (MPa)	2.94	3.675	4.90	

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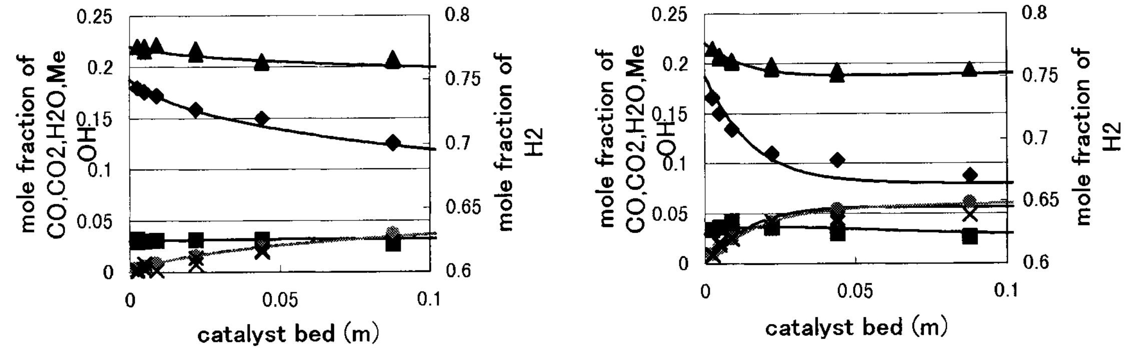
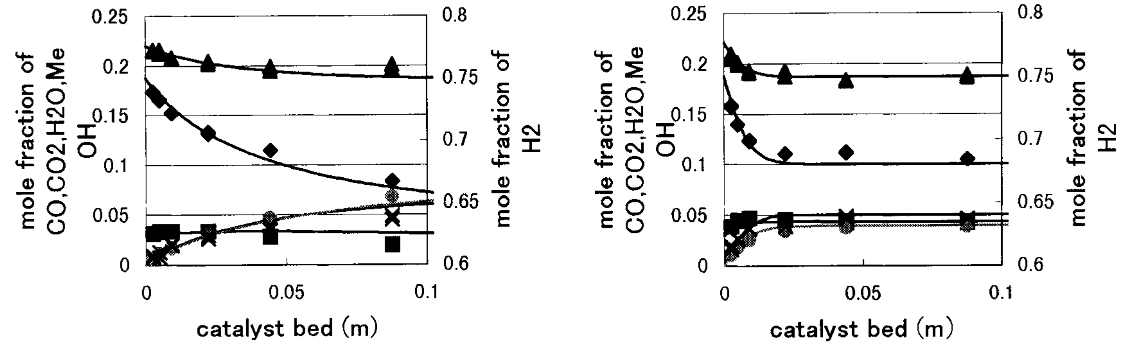


reaction temperature : 473 K

reaction temperature : 523 K



reaction temperature : 498 K

reaction temperature : 548 K

Figure 5 Calculated concentration profiles and observed values at various temperatures as a function of catalyst bed. ●: MeOH; ▲: CO_2; ■: CO; x: H_2O; ◆: H_2. Line: calculated value of each component.

the catalyst bed was measured by a thermocouple inserted in the catalyst bed, and controlled at 473, 498, 523, and 548 K. Before the kinetic study, the catalyst was treated in flowing diluted hydrogen at 573 K for 1 h, and then a standard feed gas mixture ($CO/CO_2/H_2$ = 3/22/75) was supplied to the catalyst bed at 523 K with a total pressure of 4.9 MPa until the activity was stabilized.

RESULTS AND DISCUSSION

Reaction mechanism and development of kinetic equations

The reaction paths for CO_2 hydrogenation over Cu/ZnO-based catalysts have been considered as follows: methanol is produced via reaction [1] not via reaction [2], and the reverse water-gas shift (RWGS) reaction [3] takes place simultaneously.

$$CO_2 + 3H_2 \equiv CH_3OH + H_2O \qquad [1]$$

$$CO + 2H_2 \equiv CH_3OH \qquad [2]$$

$$CO_2 + H_2 \equiv CO + H_2O \qquad [3]$$

The change in the concentration of the products was examined in integral reactions in order to make clear the reaction path for methanol synthesis. Figure 2 shows the change in the concentration of CO with increasing axial distance from the beginning of the catalyst bed. The concentration of CO rapidly increased at the beginning, and then gradually decreased with increasing axial distance.

This finding suggests that methanol should be synthesized directly from CO_2 not from CO produced by the RWGS reaction. It also suggests that the RWGS reaction should proceed in the

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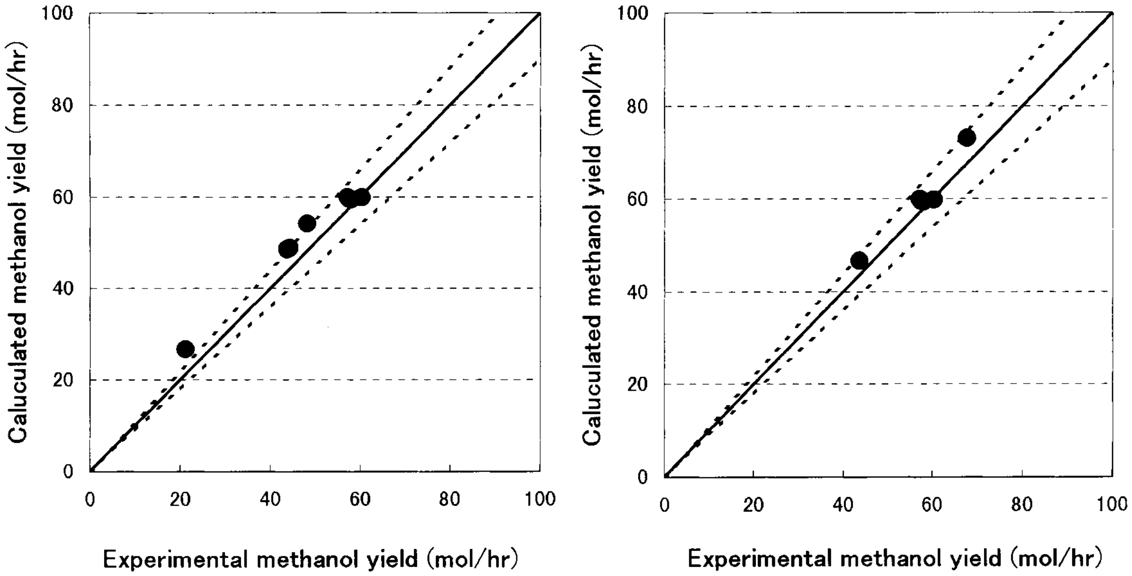
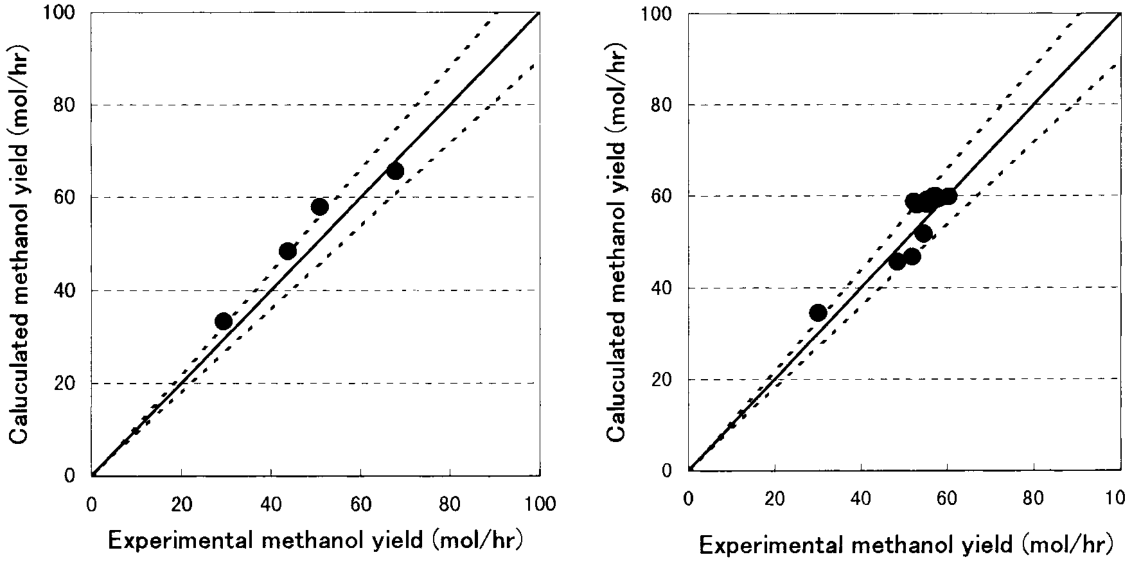


Change of temperature

Change of total pressure



Change of space velocity

Change of composition of reactant gas

Figure 6 Parity plot for the methanol yield of various conditions; temperature: 473, 503, 523, 543 K; total pressure: 3.5, 5, 7 MPa; space velocity: 5000, 10,000, 15,000, 20,000 h^{-1}; composition: H_2/CO_2 = 1–10; standard condition: 523 K, 5 MPa, 10,000 h^{-1}.

opposite way to maintain the equilibrium of the RWGS after the concentration of CO has reached a maximum, as suggested in our previous work.[2] Therefore, in this study, the methanol synthesis from CO *via* reaction [2] was ignored.

The kinetic equation for methanol synthesis was deduced on the basis of the assumptions that methanol should be produced *via* the intermediates of formate and methoxy species[4–6] and that the surface reaction between the formate species adsorbed on a copper–zinc site and hydrogen atoms adsorbed should be the rate-determining step (RDS), as shown in Fig. 3.[7] The RWGS reaction has been considered to take place either *via* a formate intermediate[8,9] or *via* direct decomposition of CO_2 to CO on the copper surface.[4] In the present study, the kinetic equation for the RWGS reaction was deduced on the assumption that the RWGS should proceed *via* the latter path.

The equations obtained were

$$R_M = \frac{k_M\{P(CO_2)P(H_2) - P(CH_3OH)P(H_2O)/[K_M P^2(H_2)]\}}{A^2}$$

$$R_R = \frac{k_R\{P(CO_2) - P(CO)P(H_2O)/[K_R P(H_2)]\}}{A}$$

$$\begin{aligned} A = 1 &+ K_{H_2}P(H_2)^{1/2} + K_{CO_2}P(CO_2) \\ &+ K_{H_2CO_2}P(H_2)^{1/2}P(CO_2) \\ &+ K_{H_2OH_2}P(H_2O)/P(H_2) + K_{H_2O}P(H_2O) \end{aligned}$$

Several terms of the kinetic equations were omitted for simplification; assuming that the change of $P(H_2)^{1/2}$ is small, and $P(H_2O)/P(H_2) \ll 0$, as a result the equations are

$$R_M = \frac{k_M\{P(CO_2)P(H_2) - P(CH_3OH)P(H_2O)/[K_M P^2(H_2)]\}}{[1 + K_{CO_2} \times P(CO_2) + K_{H_2O} \times P(H_2O)]^2}$$

$$R_R = \frac{k_R\{P(CO_2) - P(CO)P(H_2O)/[K_R \cdot P(H_2)]\}}{1 + K_{CO_2}P(CO_2) + K_{H_2O}P(H_2O)}$$

In the first step, the parameters k_M, k_R, and K_{CO_2} were estimated by the minimization of the sum of the squares of errors of the reaction rates experimentally measured in differential reactions under various conditions (see Table 1). The values obtained were

$$k_M = 3.2651 \times 10^4 \exp[-32093/(RT)]$$

$$k_R = 1.3831 \times 10^{12} \exp[-113390/(RT)]$$

$$K_M = \exp[7087/(T - 19.499)]$$

$$K_R = \exp[-4778/(T + 4.639)]$$

$$K_{CO_2} = 0.741$$

Figure 4 shows the correlation between the experimental data and the calculated value, clearly indicating that both values are in good agreement. This finding suggests that the simplified kinetic equations have high accuracy in differential reactions.

In the next step, the parameter K_{H_2}O was determined from the data obtained in integral reactions:

$$K_{H_2O} = 1.44511 \times 10^{-8} \exp[82215.3/(RT)]$$

The concentration profiles of the reaction products calculated by the kinetic equations are shown along with values observed at various temperatures in Fig. 5. The concentration curve calculated at each reaction temperature fitted very well the experimental values, indicating that the kinetic equations simplified on some assumptions are applicable to CO_2 hydrogenation in the one-pass reactor.

Application of the kinetic equations to methanol synthesis in a test plant

The kinetic equations developed were applied to CO_2 hydrogenation in our bench-scale test plant, which has a methanol synthesis capacity of 50 kg day^{-1} and is equipped with an isothermal tubular reactor with an internal diameter of 38 mm, as described in detail elsewhere.

The data obtained under various reaction conditions using the test plant were compared with the values predicted from the kinetic equations, as shown in Fig. 6. The solid line shows a perfect fit between the predicted and the experimental values, and the two broken lines show 10% differences from the perfect fit. The differences between the observed data and the predicted values were found to be smaller than 10%. Therefore, it is very clear that the kinetic equations developed in the present study are highly useful for designing a methanol synthesis reactor from CO_2 and hydrogen.

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The design of a methanol synthesis reactor from CO_2 and hydrogen based on the kinetic equations was performed in cooperation with Toyo Engineering Corp. (TEC), the results of which will be reported in another presentation.

CONCLUSIONS

(1) Kinetic equations for methanol synthesis from CO_2 hydrogenation have been obtained.
(2) The accuracy of the kinetic equations has been verified by a comparison between the values calculated from the kinetic equation and the data obtained from various experiments in a test plant.
(3) The kinetic equations developed have been found applicable to the design of a highly effective reactor employing our developed catalyst

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