Decomposition of Methanol over Some Supported Metal Catalysts by “On Board Reformer Process” (Part 1) Activity of Pt-SiO₂ Catalysts and Kinetic Study

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Carbon monoxide and hydrogen produced by decomposition of methanol will play an important role as a substitute motor gasoline. This process is known as “On Board Reforming Process”. These have some advantages compared with motor gasoline. The present research was undertaken to select a suitable catalyst for methanol decomposition process to form carbon monoxide and hydrogen, selectively. Some supported catalysts containing Cu, Cr, Ni, Pd, Rh, Ru, and Pt metals were tested and, consequently, it was found Pt/SiO₂ catalyst to be a suitable one among the catalysts tested. A kinetic study has been carried out using Pt-catalysts, and the rate equation is derived for use in design of a reactor. Reaction mechanism is also discussed.

1. Introduction

Energy shortage is now becoming a serious problem. Much efforts have been focused to resolve the problem. Utilization of synthesis gases obtained from coal reflects one of the efforts to save petroleum consumption. A modified Fischer-Tropsch process using synthesis gas has been developed to obtain lower olefins and gasoline, selectively. Another way of conserving petroleum is the utilization of methanol as substitute motor gasoline. Thus, the consumption of petroleum would be cut down and the petroleum saved would become available as raw materials for petrochemicals. Methanol can be used in three ways as a fuel^{1)~4)}; firstly, it is used directly as fuel for both diesel and gasoline engines; secondly, it is available for blending with gasoline for use in gasoline engines. On the other hand, methanol can be used indirectly; that is, methanol is first decomposed to form carbon monoxide and hydrogen, after which these gases are used as fuel for the gasoline engine. This decomposition process is known as the “On Board Reforming Process”.

Synthesis gases thus obtained by the reforming process have the following advantages as a motor fuel, in spite of their lower heat of combustion⁵⁾: (i) excellent combustibility which is due to a great amount of hydrogen, (ii) high thermal efficiency,

and (iii) clean emission.

Catalysts play an important role in methanol decomposition, and the following requirements are desirable: (i) high activity and selectivity at low temperatures, (ii) stable and inexpensive, and (iii) ease of preparation and regeneration.

It may be fair to say that it depends on the development of a suitable catalyst, regardless of whether or not the methanol is used largely as substitute motor gasoline.

The purpose of this paper is to assess the possibility of utilization of methanol to form substitute gasoline by catalysis, and to find a most suitable catalyst for the process. The reaction mechanism is also discussed.

2. Experimental

2.1 Preparation of Catalysts

Various catalysts were prepared by impregnation of silica or alumina with metal chloride or nitrate solution. Methanol synthesis catalyst was also prepared by a coprecipitation method. In all cases, 0.2—0.5 mm diameter particles of silica (apparent sp gr 0.8) and alumina (apparent sp gr 0.78) were used as catalyst carriers. These carriers were supplied from Sumitomo Chemical Ind. Ltd., Japan, and had 580 m²/g and 250 m²/g of surface area, respectively. ZnO of reagent grade was also used (Nihon Junyaku Ltd., Japan).

2.1.1 Noble Metal Catalysts

These catalysts were prepared by impregnating

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silica or alumina with noble metal chloride solutions to form 1 wt% metal supported catalysts, inclusive of Pt, Pd, Rh, and Ru metals.

2.1.2 Base Metal Catalysts

Cu/Zn/Al₂O₃ known as a methanol synthesis catalyst was prepared by coprecipitation⁶⁾ with atomic ratio of Cu:Zn:Al=60:35:5. Other catalysts were also prepared by an ordinary impregnation method using a known amount of each metal nitrate solution and thus, 1 wt% Cu/SiO₂, 5 wt% Cu+1 wt% Cr/SiO₂, and 16.6 wt% Cr/ZnO catalysts were prepared.

These catalysts were activated prior to the reaction at a certain temperature as follows: the pretreatments of the catalysts consisted of an oxidation and a hydrogenation at the same temperature. In most cases, the treatments were performed at 500 °C, while for Cu/Zn/Al₂O₃ and for 16.6 wt% Cr/ZnO catalysts at 300 and 450 °C, respectively.

2.2 Reaction

2.2.1 Closed Circulation System (dead volume 125 ml)

The reaction was carried out in a conventional closed circulation apparatus at 200–350 °C with 0.10–0.03 g of catalysts. In most cases, 45 mmHg (1 mmHg=133.3 N·m⁻²) of methanol was introduced to the catalyst bed in a U shaped glass reactor of 10 mm diameter. The product gases were analyzed by gas chromatography as a function of reaction time.

2.2.2 Flow System

The reaction was also carried out at 200–400 °C with 0.1–0.2 g of catalysts in a stream of He (10–40 ml/min). Methanol was fed to the reaction system in two ways: (1), methanol vapor at a constant temperature was carried by He carrier gas and (2), methanol was injected at the catalyst bed by a syringe into the He stream.

2.2.3 Analysis

Gas chromatography was used to analyze the

feed and product gases, in He flowing at rate 40 ml/min. Silica column of 0.45 m was used for the analysis of carbon dioxide and methane, while carbon monoxide and hydrogen were measured with 2.0 m molecular sieve 5A column at 80 °C. Methanol, ethylene, and diethyl ether were analyzed with a polyethylene glycol column at 60 °C.

3. Results and Discussion

3.1 Reaction in a Closed Circulation System

3.1.1 Cu-based Catalysts

Since a decomposition of methanol is a reverse reaction for methanol synthesis achieved with CO and H₂, the reaction was carried out over the Cu-based catalysts used for the production of methanol. The experiments were carried out with 45 mmHg methanol in a closed circulation apparatus at 250–300 °C, using a series of Cu catalysts, and the results are listed in **Table 1** (Nos. 1–6). These results do not conflict with those of Yasumori et al.⁷⁾ On the other hand, Mizuno⁸⁾ and Imai et al.⁹⁾ has also reviewed the same reaction system. The carbon balance of the products was not obtained completely as shown in **Table 1**, especially in reactions Nos. 1, 5, 6, and 7, which were conducted at low reaction temperatures. This is presumed to be due to adsorbed methanol on the catalyst surface, because the balance was increasingly higher as the reaction temperature increased, as shown in Nos. 7–9.

3.1.2 Noble Metal Catalysts

The catalytic activities of noble metal catalysts were also tested under the same reaction conditions, and the results are also given in **Table 1** (Nos. 7–12) with product distributions. It is noted that the selectivity of carbon monoxide is higher than that of Cu catalysts. On noble metal catalysts, however, methanation occurred as a side reaction instead of formation of methyl formate over the base metal catalysts. Dimethyl ether was also observed over the alumina carrier (No. 12).

Table 1 Reaction Results over Various Catalysts in Closed Circulation System (Initial Pressure of Methanol: 45 mmHg)

No.	Catalysts	React. temp. [°C]	Cat. wt [g]	Conv.* [%]	CO	Carbon balance [%] (selectivity)*			
						CH ₄	CO ₂	HCOOCH ₃	CH ₃ OCH ₃
1	CuO/ZnO/Al ₂ O ₃	250	0.03	94.9	69.8	2.0	8.5	2.0	0
2	"	270	"	95.0	71.9	1.8	—	2.4	0
3	"	300	"	95.4	91.3	3.8	4.9	1.0	0
4	16.6 wt% Cr/ZnO	300	0.1	68.6	73.7	0	—	0.8	0
5	1 wt% Cu/SiO ₂	250	"	53.9	9.5	0	10.8	62.3	0
6	5 wt% Cu+1 wt% Cr/SiO ₂	"	"	84.5	77.3	0	10.0	0.8	0.7
7	0.5 wt% Pt/SiO ₂	250	0.1	53.0	80.8	5.1	0.5	0	0
8	"	270	"	75.5	92.9	5.7	0.6	0	0
9	"	300	"	99.6	94.6	5.0	—	—	—
10	1 wt% Pt/SiO ₂	250	"	62.7	84.8	5.7	0.9	0	0
11	2 wt% "	"	"	79.8	87.8	7.7	0.2	0	0
12	0.5 wt% Pt/Al ₂ O ₃	"	"	96.7	47.0	3.6	2.3	0	47.0

* Values obtained after 60 min.

React. temp.: 250 °C, Loading amounts of metal: 1 wt%, Cat. wt.: 0.1 g, Partial pressure of methanol: 0.04 atm, Balance: He

Fig. 1 Comparison of Catalytic Activities on Reaction time over Some Metal Supported Silica Catalysts (Flow Method)

This is attributed to the dehydration of methanol caused by the acidic function of alumina carrier¹⁰.

3.1.3 Loading Effect of Pt on Silica

The loading effect of Pt catalyst was investigated at 250 °C with 0.1 g of catalyst. The reaction was performed using 45 mmHg methanol over 0.5–2.0 wt% Pt/SiO₂ catalysts. The results are also given in **Table 1** for both activity and selectivity. The activity of the catalyst increased as loading of Pt was increased, while the selectivity increased a little.

3.2 Reaction in a Flow System

3.2.1 Comparison of Catalytic Activity

It became clear that Pt catalysts were more suitable for methanol decomposition, compared with Cu catalysts, and hence the catalytic activities of a series of some noble transition metals supported on SiO₂ or Al₂O₃ were tested. In addition, Ni catalyst was also prepared by an impregnation method using a nickel nitrate solution and then tested. All the catalysts, that is, Pt, Pd, Ru, and Ni supported on silica were prepared to arrive at 1 wt% metal on silica carrier. The experiments were carried out at 250–300 °C with 0.1 g of each metal catalyst, and methanol vapor at 0.04 atm of partial pressure of methanol was carried by He gas to the reaction bed. The results are shown in **Fig. 1**.

It seems the order of activity of these catalysts to be as follows: Ni>Pd≈Pt>Ru, although the activity of Ni catalyst was not steady and decreased remarkably with reaction time. The catalytic performance of Ni catalysts will be dealt with in another paper¹¹.

It is to be noted that the results were obtained at lower conversion rates in order to facilitate comparison of their activities.

React. temp.: 250–400 °C, Cat. wt.: 0.2 g, Partial pressure of methanol: 0.8 atm, Balance: He

Fig. 2 Comparison of Selectivities [%] over Rh/SiO₂ and Pt/SiO₂ Catalysts (Flow Method)

3.2.2 Comparison of Selectivity

The selectivities of 1 wt% Pt/SiO₂ and 1 wt% Rh/SiO₂ were investigated at 250–400 °C using 0.2 g of the catalysts in the flow system. A mixture of methanol gas (7.9 ml/min) and He (2.1 ml/min) was introduced to the reaction system, at 3,600 ml/min·h of space velocity (SV). The distributions of the components in the effluent gas are shown in **Fig. 2**, in (a) and (b), in which a parameter is a reaction temperature. The former shows the results of 1 wt% Rh/SiO₂ and the latter gives the results of 1 wt% Pt/SiO₂. From a comparison of both figures, it follows that Pt/SiO₂ catalyst is a most suitable one for the decomposition of methanol in the present study. The selectivities of both Pt and Pd catalysts will be given in more details in another paper¹².

3.3 Kinetic Study

3.3.1 Activation Energy

To obtain activation energy in the reaction process, experiments were carried out in the closed system with catalysts having different Pt loading. The values of activation energy obtained by static method are compared with ones from the flow system and are shown in **Fig. 3**. The results (A, B, and C) and (D) in **Fig. 3** were obtained by static and flow methods, under the same conditions as shown in **Table 1** (static method) and **Fig. 2** (flow method), respectively. The correlation between Pt loading and initial CO formation is also given in **Fig. 3** as a dotted line. It is clearly seen that almost same values (about 16.3 kcal/mol [1 kcal=4.2 J]) are obtained in these experiments, while McKee¹³ obtained 14.2 kcal/mol of activation energy for the same reaction over Pt metal catalyst. It follows,

r_0 : Initial rate of CO formation in both static and flow methods

Mark	Key	Catalysts	Activation energy [kcal/mol]	Procedure
A	—△—	0.5 wt% Pt/SiO ₂	16.2	Static method
B	—○—	1 wt% "	16.3	
C	—□—	2 wt% "	16.0	
D	—●—	1 wt% "	16.5	Flow method

Fig. 3 Activation Energy on Pt/SiO₂ Catalysts

Table 2 Comparison of the Turnover Frequencies over Catalysts of Different Pt Loading (React. temp.: 250°C, Closed circulation apparatus)

Pt wt%	r_0 [μ mol/g·min]	Relative rate	H/Pt	Turnover freq. [min^{-1}]
0.5	49.4	1.0	0.99	1.93
1.0	99.5	2.0	0.98	1.94
2.0	140.0	2.8	0.80	1.71

therefore, that the same species of active sites are present on the surfaces in spite of the different Pt loading in the present study. The dispersion of Pt on the 2 wt% Pt/SiO₂ catalyst surface, however, seems to be low, judging from the relative rate of CO formation shown in **Table 2**. This fact is also confirmed by a hydrogen uptake over the catalysts, as shown in **Table 2**. The dispersion of Pt (H/Pt) in 2 wt% Pt/SiO₂ catalyst lowers to 0.80, while the values of 0.5 and 1 wt% Pt/SiO₂ catalyst are 0.99 and 0.98, respectively.

The turnover frequencies ($T.F.$ min^{-1}) are calculated based on the dispersion of Pt (H/Pt) as given in **Table 2**. It seems that $T.F.$ number based on effective Pt are almost constants (1.7–1.9) in these catalysts. This observation will also serve to explain the same activation energies on these catalysts.

3.3.2 Effect of Product Gases

It is desirable to know the inhibition effects of

Table 3 Effect of Product Gases on Initial Decomposition Rate of Methanol (React. temp.: 250°C, 1 wt% Pt/SiO₂, Closed circulation system)

Exp. No.	Feed	μ mol	Init. rate [μ mol/g·min]
1	Methanol	229.3	128.6
2	[Methanol] + H ₂	[229.3] [25.0]	124.4
3	[Methanol] + CO	[229.3] [39.3]	108.9

Catalyst: 1 wt% Pt/SiO₂, 0.1 g

Fig. 4 Reaction Orders of Methanol Decomposition

products gases on catalytic activity. The additional effects of carbon monoxide or hydrogen on the initial rate were examined at 250 °C with 0.1 g of 1 wt% Pt/SiO₂ catalyst using the closed circulation apparatus. The results are presented in **Table 3**.

The initial decomposition rate of methanol was obtained with or without CO or H₂. It is clearly seen that addition of carbon monoxide retards the decomposition rate, while no effect was observed in case of hydrogen.

3.3.3 Reaction Orders

Reaction orders of carbon monoxide and methanol were obtained with 0.1 g of 1 wt% Pt/SiO₂ catalyst, in closed or flow type apparatus. At first, the effect of carbon monoxide upon initial decomposition rate was studied at 250 °C, in a range of 39.3–93.9 μ mol of carbon monoxide, under constant amounts of methanol of about 230 μ mol. The results are shown in **Fig. 4** and it follows that the order of carbon monoxide is expressed as follows:

$$r_0 = k_1 [\text{CO}]^{-0.7} \quad (1)$$

where r_0 , k_1 , and $[\text{CO}]$ are initial rate by static method, rate constant and concentration of the remnant carbon monoxide, respectively.

Therefore, the rate is expressed in a general form

Table 4 Isotope Effect in Methanol Decomposition (React. temp.: 275°C, 1 wt% Pt/SiO₂, Cat. wt.: 0.05 g, Static system)

Reactant	Init. rate (μmol/g·mol)
CH ₃ OH	153.6
CH ₃ OD	142.2
CD ₃ OH	59.7

of as follows:

$$r = k_2 [\text{CH}_3\text{OH}]^\alpha [\text{CO}]^{-0.7} \quad (2)$$

where k_2 , $[\text{CH}_3\text{OH}]$, and α are rate constant, concentration and power of methanol, respectively. Then, in order to obtain the reaction order of methanol, the reaction rate was obtained at 300 °C over a range of 160–333 μmol/min of methanol, using the flow apparatus. The conversions of methanol were in a range of 11.9–20.5%, where 32.8–39.6 μmol/min of carbon monoxide was formed. The reaction order of methanol is also shown in Fig. 4, and then, the following rate law is obtained as a general rate equation for the reaction.

$$r = k_2 [\text{CH}_3\text{OH}]^{0.5} [\text{CO}]^{-0.7} \quad (3)$$

3.4 Reaction Mechanism

3.4.1 Isotope Effect

In order to elucidate the dehydrogenation mechanism of methanol, decomposition of methanol was carried out using deuterium labelled methanol over 1 wt% Pt/SiO₂ catalyst. The reaction was performed at 275 °C with methanol at initial pressure of 36 mmHg in the closed circulation system. The results are given in Table 4. An ordinary isotope effect was distinctly observed, and it follows that the rate is determined by a hydrogen transfer process from a methyl radical in the methanol. McKee also suggested the same rate determining step for the process from a comparison of activation energy of reaction for methanol¹³.

3.4.2 Mechanism

The following mechanism for the decomposition of methanol over Pt/SiO₂ catalyst is induced from these observations, taking into account the mechanism suggested by McKee;

Fig. 5 Effect of Contact Time on Methanol Decomposition (Methanol was injected by a syringe.)

where * represents an adsorption site.

In the present mechanism, the rate determining step is presumably step (6) which is a process of hydrogen transfer from methoxy radical, as seen in the isotope effect of methanol.

3.5 Rate Equation

The experiments were undertaken to prove the above mechanism by the flow method and an equation was derived based on the mechanism.

3.5.1 Contact Time

To obtain a rate equation for the decomposition of methanol, correlation between conversion of methanol and contact time (g·min/mol) was examined by changing the reaction temperature using 1 g of 1 wt% Pt/SiO₂ catalyst. The results are shown in Fig. 5. The reaction rates were obtained as a slope in each curve at any reaction time. All the calculated values used in the following parts were based on this figure.

3.5.2 Derivation of Equation

If the rate determining step is given in step (6), the rate equation is written as follows:

$$r = k_6 \theta_{\text{CH}_3\text{O}} \theta_{\text{H}} \quad (11)$$

where k_6 , $\theta_{\text{CH}_3\text{O}}$, θ_{H} are rate constant, surface concentration of CH₃O species and of dissociated hydrogen, respectively.

If the adsorption of methanol and carbon monoxide over the catalyst surface is stronger than

the other surface species, the rate equation is reduced to the more simple one as follows:

$$r = \frac{k p_{\text{OH}}}{(1 + K_{\text{OH}} p_{\text{OH}} + K_{\text{CO}} p_{\text{CO}})^2} \quad (12)$$

where k , K_i , and p_i are constant, adsorption term and partial pressure of each component, respectively.

Equation (12) is also expressed as follows:

$$r = k' p_{\text{OH}}^{\alpha'} p_{\text{CO}}^{\beta} \quad (13)$$

where α' and β are reaction orders, which should comply with the following limitation $1 > \alpha' > -1$, $0 > \beta > -2$.

It is seen, therefore, that Eq. (13) could explain the rate expression Eq. (3) obtained experimentally in the present study.

On the other hand, McKee derived the following rate equation, assuming a retardation of product, for the same reaction over Pt metal catalyst¹³,

$$r = \frac{k_{14}(a - x)}{1 + b x} \quad (14)$$

where k_{14} , a , b , and x are rate constants, the initial concentration of methanol, constant, and the amount decomposed after time t , respectively.

McKee's Eq. (14) can be expressed as the rate expression like Eq. (13), and shown as $\alpha' = 1$ and $0 > \beta > -1$, judging from the form of the function.

It is found, therefore, that the reaction order of methanol is different from the empirical Eq. (3) obtained in the present study.

Yasumori et al. presented also the reaction mechanism from kinetic studies on the decomposition of methanol over nickel¹⁴ and copper catalysts⁷. Madix¹⁵ reviewed the reaction mechanism of methanol on Cu catalysts and also, Trimm¹⁶ studied the adsorption state of labelled methanol over Cu catalysts.

3.5.3 Examination of Rate Equation

To clarify, the issues, Eq. (12) is arranged to a linear form as follows:

$$1 + K_{\text{OH}} p_{\text{OH}} + K_{\text{CO}} p_{\text{CO}} = \sqrt{k p_{\text{OH}} / r} \quad (15)$$

If a conversion of methanol (x) is used instead of the partial pressure, the equation can be written in a more simple form,

$$a' + b' x = \sqrt{(1 - x)/r} \quad (16)$$

where $a' = (1 + K_{\text{OH}} p_{\text{OH}}^0) / \sqrt{k p_{\text{OH}}^0}$, $b' = [K_{\text{CO}} - K_{\text{OH}}] / \sqrt{k p_{\text{OH}}^0}$, and p_{OH}^0 is an initial partial pressure of

SV [ml/ml·h]: 2,590—5,400

Fig. 6 Examination of Eq. (16) (Flow Method)

methanol.

A plot of $\sqrt{(1 - x)/r}$ vs. x should give a straight line and it is seen that this relation holds in Fig. 6, using the values calculated from the results shown in Fig. 5. The slope of the straight line is positive, when $K_{\text{CO}} > K_{\text{OH}}$. This means that adsorption of carbon monoxide is stronger than that of methanol on the catalyst surface. The difference in the strength in adsorption of both components, however, is seen to decrease with an increase of temperature as is shown by the decrease of slope in Fig. 6. It should be noted that the rate equation of the same form having a different constant can be derived kinetically, assuming step (5) as the rate determining step instead of step (6). Isotope effect in the present study, however, clearly shows that the reaction rate depends upon step (6), the elementary step.

If the rate determining step follows the abstraction of hydrogen from the absorbed methoxy radical instead of step (6),

The rate equation can be expressed as follows:

$$r = k_{6'} \theta_{\text{CH}_3\text{O}} \theta_v = \frac{k_{6'} K_4 K_5 p_{\text{OH}} / K_{\text{H}_2} p_{\text{H}_2}}{[1 + K_{\text{OH}} p_{\text{OH}} + K_{\text{CO}} p_{\text{CO}} + \dots + K_{\text{H}_2} p_{\text{H}_2}]^2} \quad (6'')$$

where $k_{6'}$, K_4 and K_5 are the rate constant of step (6)', equilibrium constants of steps (4) and (5) and

also, K_{OH} , K_{CO} , and K_{H_2} are adsorption equilibrium constants of each component.

This equation can be simplified in the following expression:

$$r = k p_{\text{OH}}^{\alpha''} p_{\text{CO}}^{\beta'} p_{\text{H}_2}^{\gamma} \quad (13)'$$

This power rate expression is not hold, however, in the present study, because it was found that hydrogen does not depend on the rate, as shown in **Table 3**.

4. Conclusion

The decomposition of methanol has been studied over various catalysts, including such as Cu, Cr, Ni, Pt, Pd, Rh, and Ru metals supported on SiO_2 or Al_2O_3 .

It was found that the Pt/ SiO_2 catalyst was the most suitable one for methanol decomposition in the present study.

The reaction orders were obtained for reaction over 1 wt% Pt/ SiO_2 catalyst as follows:

$$r = k_2 p_{\text{OH}}^{0.5} p_{\text{CO}}^{-0.7} \quad (3)'$$

From experimental results, the reaction mechanism was deduced, in which the rate determining step is a hydrogen transfer from the methyl radical in methanol. According to the mechanism, the following rate equation could be derived:

$$r = \frac{k p_{\text{OH}}}{(1 + K_{\text{OH}} p_{\text{OH}} + K_{\text{CO}} p_{\text{CO}})^2} \quad (12)$$

The equation was examined and found capable of explaining all the experimental results obtained in the present study.

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要 旨

**“On Board Reformer Process”における担持金属触媒によるメタノール分解反応（第1報）
Pt-SiO₂ 触媒の活性と速度論的検討**

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閉鎖循環型反応装置により各種金属担持触媒（Cu, Cr, Pt, Ni, Pd, Ru など）のメタノール分解活性を 250～300℃で比較し、結果を **Table 1** および **Fig. 1** に示した。

また、SiO₂ を担体とする 1 wt% Rh および Pt 触媒の選択性を **Fig. 2** に示した。これらの結果から、最適触媒として Pt-SiO₂ を選定した。この触媒による活性化エネルギーおよび TOF は、それぞれ、16.0～16.5 kcal/mol および 1.7～1.9 min⁻¹ である（**Fig. 3, Table 2**）。見掛け反応速度（ r ）は

Eq. (3) で示された（**Fig. 4, Table 3**）。

$$r = k_2 [\text{CH}_3\text{OH}]^{0.5} [\text{CO}]^{-0.7} \quad (3)$$

メタノール分解反応における同位元素効果を調べ（**Table 4**），反応機構を推定し，反応速度式を実験結果を用いて検討した（**Figs. 5, 6**）。その結果，Eq. (2) の反応速度式が帰納された。

$$r = \frac{k p_{\text{OH}}}{(1 + K_{\text{OH}} p_{\text{OH}} + K_{\text{CO}} p_{\text{CO}})^2} \quad (12)$$

Keywords

Carbon monoxide, Hydrogen, Methanol, Decomposition., Heterogeneous catalysis, Supported catalyst