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Catalytic Decomposition of Methanol over Nickel Wire

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The kinetic studies of the decomposition of methanol have been undertaken under pressures of up to 20 mmHg and at temperatures between 300 and 430°C. The initial rate (r_0) of decomposition which turns methanol into carbon monoxide and hydrogen was found to be expressed by the equation, $r_0=aP_m/(1+b\sqrt{P_m})^2$ where P_m is the initial pressure of methanol and where a and b are constants. The addition of carbon monoxide to the reactant was found to depress the rate of reaction, while a slight promotion was observed upon the addition of hydrogen to the system. On the other hand, when the kinetics of the decomposition of formaldehyde, which was regarded as the intermediate product in the methanol decomposition, was studied, it was found that formaldehyde decomposed to cabon monoxide and hydrogen, and that the rate was much larger than that of methanol decomposition. On the basis of these results and the exchange reaction of methanol with deuterium, the processes of methanol decomposition were discussed in detail and a possible mechanism of reaction was proposed in which the surface reaction between the adsorbed methoxy radical and the hydrogen atom, both produced by the dissociative adsorption of methanol, is the rate-determining step of the reaction.

Though a substantial amount of research has been carried out on the catalytic decomposition of methanol, much of this research has attempted to find effective catalysts for the methanol synthesis or to obtain information on the production of methyl ether, methylformate, and formaldehyde.

The kinetics of the decomposition has also been studied by the use of oxide catalysts, ZnO1) and $ZnO\text{-}Cr_2O_3$2), in which the mechanisms of the reaction were supposed to be successive, passing through formaldehyde as an intermediate.

Recently, Kemball and Daby3) obtained a rate equation for the reaction over a Fischer-Tropsch cobalt catalyst;

$$-\frac{d[\mathrm{MeOH}]}{dt}=\frac{\alpha[\mathrm{MeOH}]}{1+\beta[\mathrm{CO}]}$$

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1) H. Dohse, *Z. Physik. Chem.*, **B8**, 159 (1930).

2) M. Tamura and S. Shida, *Progress Phys. Chem. Japan*, **16**, 71 (1942).

3) P. W. Daby and C. Kemball, *Trans. Faraday Soc.*, **53**, 832 (1957).

where α and β are constants. However, little work has yet been undertaken over pure metallic catalysts except for an infrared spectroscopic study[4] of adsorbed methanol by the use of a silica-supported nickel catalyst.

In a previous study of the present authors on the adsorption of methanol on a nickel wire catalyst,[5] which was reduced and sintered at 550°C, it was suggested that there are at least two types of irreversible adsorption, and that one of them, being dominant above 80°C, is dissociative like CH_3O+H on the surface and may be responsible for the catalytic decomposition of methanol.

In the present work, in an attempt to elucidate the mechanism of the methanol decomposition, the kinetics of the decompositions of methanol and formaldehyde, regarded as an intermediate product of the reaction, has been investigated over a nickel wire catalyst, together with that of the exchange reaction of methanol or formaldehyde with deuterium, and also the effects of added hydrogen or carbon monoxide on the reaction rate.

Experimental

Catalyst and Samples. Pure nickel wire 0.2 mm in diameter, such as is used for vacuum tubes, was obtained from the Nippon Denkyu Kogyo Co., Ltd., and used as the catalyst. The spectroscopic analysis of this wire indicated that its purity was 99.99% by weight.

Methanol of an analytically-pure grade was distilled three times in the presence of metallic magnesium to remove a trace of water.

Degassed para-formaldehyde of a pure grade, obtained from the Yoneyama Chemical Co., was used to produce formaldehyde by heating it at about 80°C.

Apparatus and Procedure. For the rate determination a static system was used, as is shown in Fig. 1. The reaction vessel (100 m*l*) was made of quartz; its temperature was maintained within 0.1°C during the course of the reaction by the use of a cromel-alumel thermocouple and an automatic controlling system.

A number of coiled wire catalysts, each 30 cm long, were oxidized together in air of 95 mmHg at 600°C for 2 hr and then reduced in hydrogen of 700 mmHg at 550°C for 5 hr. These treatments were repeated until a constant activity was attained, and then the catalysts were stored in a reservoir.

After a high vacuum of about 10^{-6} mmHg had been obtained for the system, the stop cock (5) was opened to transfer a catalyst wire from the reservoir into the vessel with a magnet, a definite amount of methanol or formaldehyde vapor was diffused into the reaction vessel, and the reaction was started.

The progress of the reaction was accompanied by a change in the total pressure, a change which was followed with a glass Bourdon gauge.

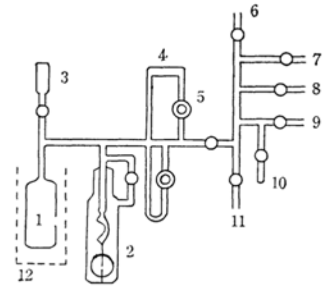

Fig. 1. Apparatus.

1. Reaction vessel
2. Bourdon gauge
3. Sampling tube
4. Nickel reservoir
5. Stop cock
6. To vaccuum system
7. CH_3OH
8. CO
9. H_2
10. Trap
11. To manometer
12. Electric furnace

All the reactants and products in the reactions were analyzed by mass spectrometry and infrared spectroscopy, using Hitachi RMU-5B and Perkin-Elmer 125 spectrometers respectively.

Results

Kinetics of Methanol Decomposition. It was found that the products of the decomposition of methanol over a nickel wire catalyst consisted of only hydrogen and carbon monoxide in the beginning of the reaction; however, small amounts of water and methane (1—2%) were formed when the system was kept at the reaction temperature for about 1 hr.

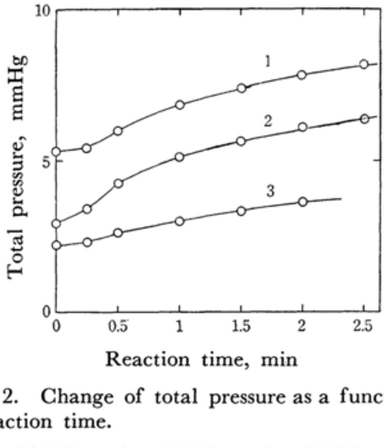

Fig. 2. Change of total pressure as a function of reaction time.

1: 380°C 2: 430°C 3: 360°C

A series of experiments was carried out at initial methanol pressures of up to 20 mmHg at 300, 340, 360, 380, 400, and 430°C.

Typical runs of this series are shown in Fig. 2. An induction period of about 10 sec was observed in every case before the decomposition commenced.

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[4] G. Blyholder and I. D. Neff, *J. Catalysis*, **2**, 138 (1963).

[5] E. Miyazaki and I. Yasumori, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1033 (1965).

Therefore, the maximum slope on the pressure-time curve was taken as the value of the initial rate of reaction.

The initial rate was adopted in the form:

$$r_0 = aP_m/(1+b\sqrt{P_m})^2, \tag{A}$$

where P_m is the methanol pressure and where a and b are constants, since the linear relationship between $1/\sqrt{r_0}$ and $1/\sqrt{P_m}$ was confirmed to be as is shown in Fig. 3.

The temperature dependence of the a constant in Eq. (A) is shown in Fig. 4, from which the apparent activation energy may be estimated to be 18.3 kcal/mol.

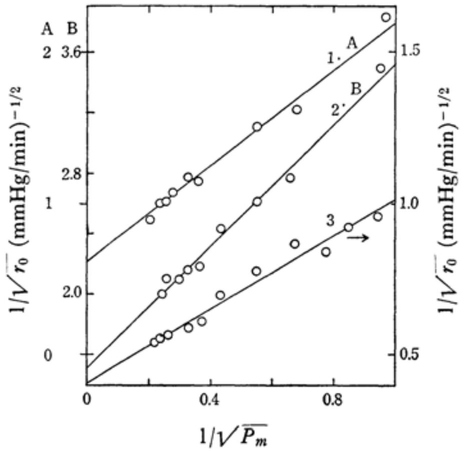

Fig. 3. Linear relation ship between $1/\sqrt{r_0}$ and $1/\sqrt{P_m}$ in methanol decomposition over nickel wire catalyst.

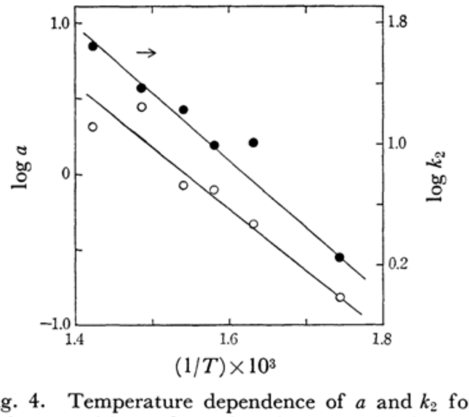

Fig. 4. Temperature dependence of a and k_2 for decomposition of methanol over nickel wire catalyst.

Effects of Added Hydrogen and Carbon Monoxide. In order to observe the effects of the decomposition products on the reaction rate and also on the induction period, methanol vapor of pressures up to 7 mmHg, mixed with hydrogen or carbon monoxide of partial pressures up to 8 mmHg, was used as the reactant.

These effects of added gases on the initial rate are shown in Fig. 5. It is clear that the decomposition is retarded by carbon monoxide, but, on the contrary, is somewhat promoted by the addition of hydrogen. It was also found that the presence of hydrogen shortens the induction period, and that its effect becomes more appreciable as the temperature increases.

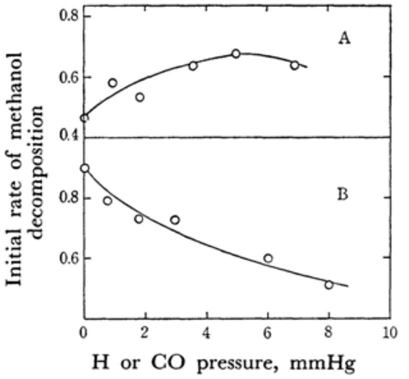

Fig. 5. Influence of added hydrogen or carbon monoxide to reactant on initial rate of methanol decomposition.

A: Hydrogen B: Carbon monoxide

The Exchange Reaction of Methanol with Deuterium. In order to see in what states the adsorbed methanol exists on the nickel wire catalyst, the exchange reaction with deuterium was studied during the course of decomposition, and also at a low temperature where decomposition does not occur. The results are shown in Fig. 6.

It was found, from the existence of a O—D bending vibration, as confirmed by infrared spectroscopy,

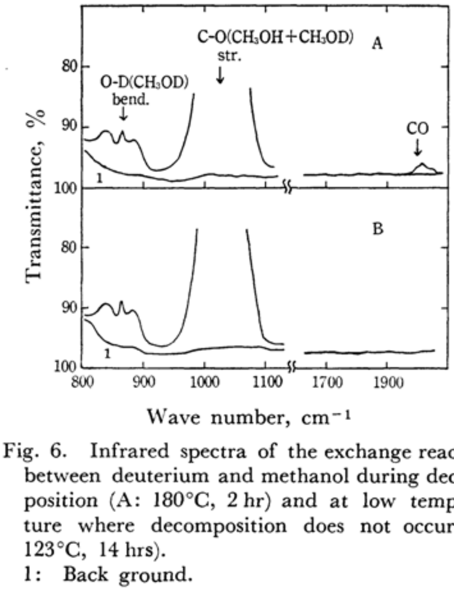

Fig. 6. Infrared spectra of the exchange reaction between deuterium and methanol during decomposition (A: 180°C, 2 hr) and at low temperature where decomposition does not occur (B: 123°C, 14 hrs).

1: Back ground.

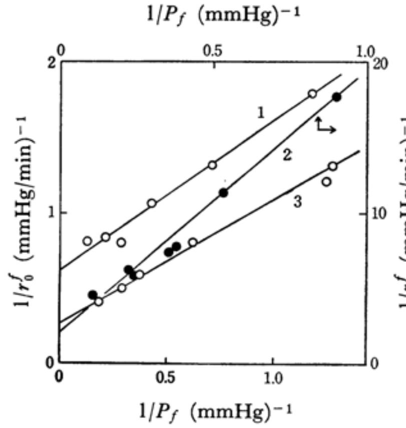

Fig. 7. Linear relationship between $1/r_0^f$ and $1/P_f$ in formaldehyde decomposition over nickel wire catalyst.

1: 161°C 2: 120°C 3: 180°C

that the present catalyst was active for the exchange reaction, and that the only product due to exchange was CH_3OD; these results correspond to those obtained by Kemball and Anderson on evaporated nickel film.[6]

From these results it is most likely that methanol is adsorbed on the nickel surface in such a dissociative form as $CH_3O(a)+H(a)$; this also agrees with the result obtained from the previous studies[5] of methanol adsorption on a nickel wire catalyst described above.

Furthermore, the exchange reaction of formaldehyde with deuterium was examined by the same procedure as that used for methanol, in temperature range of 80—120°C. However, no change was observed here, not even during decomposition.

Decomposition of Formaldehyde over the Nickel Wire Catalyst. The kinetics of formaldehyde was studied over the nickel wire catalyst since it was regarded as the intermediate product of methanol decomposition.

Formaldehyde started the reaction at a temperature lower than in the case of methanol by about 100°C, and decomposed to hydrogen and carbon monoxide as well as in methanol decomposition; it thus seems that the high reactivity of formaldehyde is the reason why it was not observed in the gas phase while methanol was decomposing.

The initial rate (r_0^f) of the reaction was expressed in the following equation:

$$r_0^f = \frac{k_f K_f P_f}{1+K_f P_f} \tag{B}$$

where P_f is the pressure of formaldehyde, and where k_f and K_f are constants, being deduced from the linear relationship between $1/r_0$ and $1/P_f$ (shown in Fig. 7), which differed from that in methanol.

If the adsorption of formaldehyde suitable for the decomposition is of the Langmuir type, k_f and K_f may correspond to the rate constant of reaction and the equilibrium constant for the "reactive" adsorption of methanol.

Therefore, the decomposition of formaldehyde adsorbed on the nickel surface was supposed from Eq. (B) to be the rate-determining step, and the true activation energy and heat of adsorption for "reactive adsorption" were evaluated as 15.6 kcal/mol and almost zero respectively from the dependencies of ln k_f and ln K_f against $1/T$ (Fig. 8).

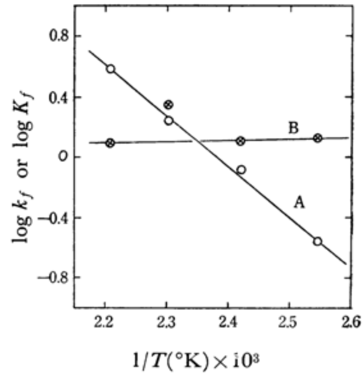

Fig. 8. Temperature dependence of k_f or K_f for formaldehyde decomposition over nickel wire catalyst.

Discussion

Mechanism of the Reaction. On the bases of the above results and the adsorption studies of hydrogen[7] and methanol[5] reported in previous papers, it seems that the adsorbed species, such as $CH_3O(a)$, $CH_2O(a)$, $CO(a)$ and $H(a)$, exist during the process of methanol decomposition on the nickel surface.

Among the reaction processes with these surface species, the decomposition of adsorbed formaldehyde can not be accepted as the rate-determining step, since it is much more rapid than that of methanol, providing that the conditions described above are also valid during the decomposition of methanol.

Moreover, the fact that the decomposition of methanol was accelerated by the presence of hydrogen suggests that the adsorbed hydrogen atom is relevant to the rate-determining step in methanol decomposition. In view of these facts, the mechanism of methanol decomposition over a nickel wire catalyst may be set down as follows:

$$CH_3OH(g) \underset{}{\overset{K_1}{\rightleftarrows}} CH_3O(a) + H(a) \tag{1}$$

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[6] J. R. Anderson and C. Kemball, *Trans. Faraday Soc.*, **51**, 966 (1955).

[7] E. Miyazaki and I. Yasumori, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 415 (1964).

$$CH_3O(a) + H(a) \xrightarrow{k_2} CH_2O(a) + H_2(g) \quad (2)$$

$$CH_3O(a) \overset{K_3}{\rightleftarrows} CHO(a) + H(a) \quad (3)$$

$$CHO(a) \overset{K_4}{\rightleftarrows} CO(a) + H(a) \quad (4)$$

$$CO(a) \overset{K_5}{\rightleftarrows} CO(g) \quad (5)$$

$$2H(a) \overset{K_6}{\rightleftarrows} H_2(g) \quad (6)$$

where the symbol (a) denotes an adsorbed species, and where K_i and k_i are the equilibrium constant of adsorption and the rate constant for the i step respectively.

It is characteristic of this mechanism that the adsorbed hydrogen atom which is produced by the dissociative adsorption of methanol abstracts one of the three hydrogen atoms in the adsorbed methoxy radical to form a hydrogen molecule; this step is assumed to be rate-determining, while the others remain in the pre-equilibrium state.

Formulation of the Reaction Rate. By assuming that the Langmuir-Hinshelwood theory can be applied to the elementrary reactions, (1) to (6), the following equations are obtained for all the process except (2):

$$K_1P_mS^2 = \theta_1\theta_5 \quad (1')$$

$$K_3\theta_3S = \theta_4\theta_6 \quad (3')$$

$$K_4\theta_4S = \theta_5\theta_6 \quad (4')$$

$$K_5\theta_5 = P_{co}S \quad (5')$$

$$K_6\theta_6^2 = P_hS^2 \quad (6')$$

where θ represents the coverage of surface species, where θ_1, θ_3, θ_4, θ_5, and θ_6, correspond to the $CH_3O(a)$, $CH_2O(a)$, $CHO(a)$, $CO(a)$ and $H(a)$ species respectively, where S is the fraction of the unoccupied sites on the surface, given by:

$$S = 1 - (\theta_1 + \theta_3 + \theta_4 + \theta_5 + \theta_6),$$

and where P_m, P_{co} and P_h denote the pressures of methanol, carbon monoxide, and hydrogen respectively.

The rate of methanol decomposition (r) is given by:

$$r = k_2\theta_1\theta_6 \quad (2)'$$

By combining (1′) to (6′) with (2′), the rate may be expressed as a function of P_m, P_{co}, P_h, K_i as follows:

$$r = \frac{k_2K_1K_6P_hP_m}{\left(\begin{array}{c}\{K_1K_6P_m + (K_3{}^{-1}K_4{}^{-1}K_6{}^{-1/2}P_h{}^{3/2} \\ + K_4{}^{-1}P_h + K_6{}^{1/2}P_h{}^{1/2})K_5{}^{-1}P_{co} \\ + K_6{}^{1/2}P_h{}^{1/2} + P_h\}^2\end{array}\right)} \quad (7)$$

When the hydrogen pressure is put at zero in Eq. (7), the rate of reaction becomes zero, which means that it takes some induction period for the reaction to attain the threshold of decomposition.

Equation (7) also indicates that carbon monoxide acts as an inhibitor of the reaction: this agrees well with the results shown in Fig. 5.

In the beginning of the reaction, carbon monoxide does not exist; hence, the initial rate of reaction (r_0) may be written approximately as;

$$r_0 = \frac{k_2K_1K_6P_hP_m}{(K_1K_6P_m + K_6{}^{1/2}P_h{}^{1/2} + P_h)^2} \quad (8)$$

A maximum in rate will be observed as P_h is varied, since the rate is a function of P_m and also of P_h.

The initial rate of reaction was defined as a maximum value in the course of the decomposition described above; therefore, the relationship between the hydrogen and methanol pressure at this point is obtained from the $(\mathrm{d}r_0/\mathrm{d}P_h)_{P_m}=0$ condition as follow:

$$P_h = K_1K_6P_m \quad (9)$$

By substituting Eq. (9) into Eq. (8), the initial rate (r_0) is finally expressed in the form:

$$r_0 = \frac{k_2K_1P_m}{(1+2\sqrt{K_1P_m})^2} \quad (10)$$

which can be rewritten as:

$$1/\sqrt{r_0} = 1/\sqrt{k_2K_1P_m} + 2/\sqrt{k_2} \quad (11)$$

It is clear that the a and b constants in the observed rate equation (A) correspond to k_2K_1 and $2\sqrt{K_1}$ in Eq. (10) respectively, and that the linear relationship between $1/\sqrt{r_0}$ and $1/\sqrt{P_m}$ was confirmed to be as is shown in Fig. 3.

On the other hand, from the dependence of the rate constant, k_2, in (2′) on the temperature (Fig. 4), the true activation energy could be evaluated as 20.3 kcal/mol; hence, by combining this value with that of the apparent activation energy obtained from the temperature dependence of a, the heat of the adsorption of methanol during decomposition was calculated to be 2.0 kcal/mol. Such a small value for the "reactive adsorption" had been expected in a previous study on methanol adsorption.[5]

The results of thermal desorption study[8] also show that there are several kind of adsorbed states of methanol on the nickel surface, and that some of them are responsible for the decomposition. It is, therefore, important to distinguish them in their structure and behavior and to verify the above kinetical consideration; attempts to do so be described in the following series of papers.

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[8] N. Monma, E. Miyazaki and I. Yasumori, to be published.