A kinetic study of methanol decomposition catalyzed over plate-type palladium catalyst

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A kinetic study of the catalytic methanol decomposition to carbon monoxide and hydrogen has been carried out in the pressure range of methanol up to 8 atm at 200 and 250 °C over a palladium catalyst supported on an oxidized aluminum plate. The reaction pathway can be proposed as (i) dissociative adsorption of methanol to methoxyl groups and hydrogen adsorbed on palladium sites, (ii) decomposition of the methoxyl groups to carbon monoxide and hydrogen adsorbed, and (iii) desorption of the surface carbon monoxide and hydrogen species. It is suggested that the second step is rate-determining and the surface hydrogen species enhance the decomposition of the methoxyl groups.

Keywords: reaction rate, reaction mechanism, methanol decomposition, palladium

1. Introduction

Methanol can be synthesized from almost all carbon sources such as coal, natural gas, and bio-mass, which are more abundant resources than crude oil, and it is expected to be an alternative energy carrier as a fuel in the near future [1,2]. The methanol decomposition to carbon monoxide and hydrogen is endothermic; hence, the reaction can be utilized for recovery of the waste heat from industries and increases the heating value of methanol [3]. It is also applicable to a methanol-fueled automobile in which the heat of the exhaust gas can be recovered with the reaction and the decomposition gas is fed to the engine [4].

In a chemical process of a highly endothermic reaction such as the methanol decomposition, heat must efficiently be provided to a catalyst. However, the conventional fixed-bed reactor is disadvantageous, because the heat conductivity of the catalyst layer is usually poor. From this viewpoint, the plate-fin-type reactor in which catalytic materials are modified on the surface of a heat exchanger (plate-fin) was proposed [5,6]. It was shown that the reactor can respond quickly to the temperature of the heat medium, and is advantageous to a conventional fixed-bed reactor for higher thermal conduction and lower pressure drop [5].

In an attempt to design a heat recovery system, the present work deals with a kinetic study of a palladium catalyst supported on an aluminum plate whose surface is anodically oxidized. Palladium catalysts have been reported to be active to the methanol decomposition [7–12], and a kinetic study was carried out in the range of methanol pressure less than 1 atm [11]. However, because the practical system is usually operated under much higher pressure, we have investigated the reaction rates under methanol pressures up to 8 atm and found that the reaction rate decreases with increase in the partial pressure of methanol above ca. 1 atm.

2. Experimental

After an aluminum plate (JIS-A1050, 100 mm by 200 mm and 0.3 mm in thickness) was treated at room temperature for 3 min in an aqueous solution of sodium hydroxide (20 wt%), it was dipped in a nitric acid solution (30 wt%), and finally rinsed with distilled water. The surface of the plate was oxidized by anodizing at current density of 25 $\mathrm{A\,m^{-2}}$ in an aqueous solution of 4 wt% oxalic acid at 20 °C for 16 h and calcined in air at 350 °C. The plate was soaked in distilled water at 80 °C and calcined in air at 400 °C for 3 h. The thickness of the alumina layer formed on the surface was found to be ca. 50 μm by an SEM imaging technique. The plate was impregnated with an acetone solution containing palladium acetate (2 $\mathrm{mmol\,dm^{-3}}$) for 24 h at room temperature and calcined in air at 400 °C for 3 h. This process was repeated again, and the plate was finally treated in an acetone solution of sodium nitrate (10 ppm) at room temperature for 24 h to neutralize the acid sites on the surface of the Al_2O_3 layer; then, it was dried in air and calcined at 400 °C for 3 h. The content of palladium was 8 $\mathrm{g\,m^{-2}}$ and that of sodium was 0.25 $\mathrm{g\,m^{-2}}$. The dispersion of palladium was evaluated as 0.17 on the basis of the amount of hydrogen irreversibly adsorbed on the surface at 100 °C.

Catalytic tests were performed with a fixed-bed continuous-flow reactor. The aluminum plate loading palladium was cut into small pieces of 5 mm by 5 mm and 10–96 pieces were randomly packed in a stainless tube reactor

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with an inner diameter of 22 mm. After the reduction of the catalyst in a stream of 10 vol% hydrogen diluted with nitrogen at 400 °C for 2 h, the reactor was purged with a nitrogen stream and the temperature was reduced to the reaction temperature; then, 10–100 vol% of methanol in a stream of nitrogen was fed at 200 or 250 °C. The total flow rate was kept at 90 $dm^3 h^{-1}$ in STP using mass-flow controllers, and the total pressure was 1.7–8.5 atm. The outlet gas was analyzed by an on-line gas chromatograph (Shimadzu GC-14 BPTF). The reaction line except the methanol feeder was always kept heated at a temperature above 150 °C. The methanol conversion was usually kept less than 5% to fulfill the condition for a differential reactor, and the concentrations of the components employed in this study were the average values of the inlet and outlet gases.

3. Results and discussion

Methanol was decomposed mainly to carbon monoxide and hydrogen at 200 and 250 °C, being accompanied by dimethyl ether as a by-product. The selectivity to carbon monoxide was always above 95%. Figure 1 shows the formation rates of carbon monoxide at 200 and 250 °C as a function of methanol. The rate increased with increasing the partial pressure of methanol up to ca. 1 atm, and then it decreased.

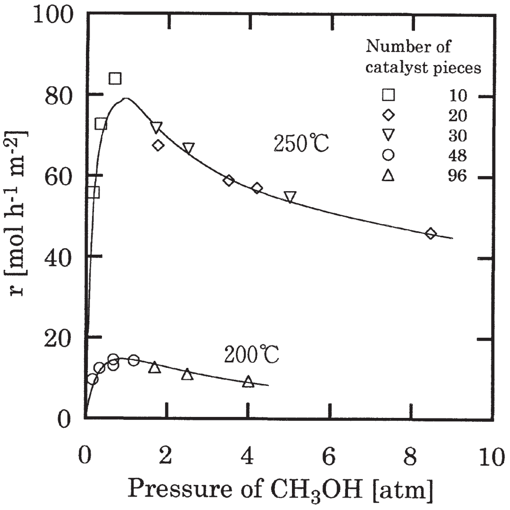

Figure 1. Formation rate of carbon monoxide vs. pressure of methanol over palladium supported on aluminum plate.

On the basis of surface science studies on methanol decomposition over clean palladium surfaces, it was assumed that the reaction takes place through the following three steps: (i) dissociative adsorption of methanol to methoxyl groups and atomic hydrogen species, (ii) decomposition of the methoxyl groups to carbon monoxide and atomic hydrogen species on the surface, (iii) desorption of carbon monoxide and hydrogen [13–17]. Fukuhara et al. proposed that the rate-determining step of the reaction over palladium supported on zirconium oxide is step (ii) and that the decomposition takes place through interaction between the methoxyl group and the atomic hydrogen species on the surface; however, in their study, the pressure range of methanol was too narrow to ensure the mechanism [11].

Assuming that step (ii) is rate-determining, the following elemental steps can be hypothesized as a probable pathway for methanol decomposition:

$$\mathrm{CH_3OH + 2Pd \rightleftharpoons CH_3O\text{–}Pd + H\text{–}Pd} \quad \text{(equilibrium constant } K_\mathrm{M}) \tag{1}$$

$$\mathrm{CH_3O\text{–}Pd + H\text{–}Pd \rightarrow CH_2O\text{–}Pd + H_2 + Pd} \quad \text{(rate constant } k_1) \tag{2}$$

$$\mathrm{CH_2O\text{–}Pd + 2Pd \rightarrow CO\text{–}Pd + 2H\text{–}Pd} \tag{3}$$

$$\mathrm{2H\text{–}Pd \rightleftharpoons H_2 + 2Pd} \quad \text{(equilibrium constant } K_\mathrm{H}) \tag{4}$$

$$\mathrm{CO\text{–}Pd \rightleftharpoons CO + Pd} \quad \text{(equilibrium constant } K_\mathrm{C}) \tag{5}$$

When the equilibrium states (1), (4), and (5) are set up and step (2) is rate-determining, the formation rate of carbon monoxide, r (the unit will be $\mathrm{mol\,h^{-1}\,m^{-2}}$), can be described as follows:

$$r = k_1 K_\mathrm{M} P_\mathrm{M} / \big(1 + K_\mathrm{M} K_\mathrm{H}^{1/2} P_\mathrm{M} P_\mathrm{H}^{-1/2} + K_\mathrm{H}^{-1/2} P_\mathrm{H}^{1/2} + K_\mathrm{C}^{-1} P_\mathrm{C}\big)^2,$$

where P_M, P_H, and P_C are partial pressures of methanol, hydrogen, and carbon monoxide, respectively. The reaction step (3) is considered to be much faster than step (2), because formaldehyde is easily decomposed to hydrogen and carbon monoxide on the surface of metal [18]; hence, step (3) does not contribute to the rate equation. In the case of $P_\mathrm{H} \ll 1$ and $P_\mathrm{C} \ll 1$, the rate equation can be simplified as $r = k_1 K_\mathrm{M} P_\mathrm{M} / (1 + K_\mathrm{M} K_\mathrm{H}^{1/2} P_\mathrm{M} P_\mathrm{H}^{-1/2})^2$, which can be transformed to

$$P_\mathrm{M}^{1/2} r^{-1/2} = k_1^{-1/2} K_\mathrm{M}^{1/2} K_\mathrm{H}^{1/2} P_\mathrm{M} P_\mathrm{H}^{-1/2} + k_1^{-1/2} K_\mathrm{M}^{-1/2}.$$

The plot of $P_\mathrm{M}^{1/2} r^{-1/2}$ vs. $P_\mathrm{M} P_\mathrm{H}^{-1/2}$ (figure 2) shows that this equation is consistent with the experimental results. The values of $K_\mathrm{M} K_\mathrm{H}^{1/2}$ at 200 and 250 °C are calculated to be 0.40 and 0.60 $\mathrm{atm}^{-1/2}$, respectively, and those of $k_1^{-1} K_\mathrm{H}^{1/2}$ are 0.0023 and 0.0048 $\mathrm{mol^{-1}\,m^2\,h\,atm^{1/2}}$, respectively.

The heat of hydrogen adsorption on palladium catalysts was reported to be 109–147 $\mathrm{kJ\,mol^{-1}}$ [19]. The heat of adsorption of methanol in reaction (1) and the activation energy of reaction (2) can be estimated from the data of $K_\mathrm{M} K_\mathrm{H}^{1/2}$ and $k_1 K_\mathrm{H}^{-1/2}$ at 200 and 250 °C using the heat of adsorption of hydrogen. That is, the heat of adsorption of methanol will be 37–56 $\mathrm{kJ\,mol^{-1}}$ and the activation energy will be 118–137 $\mathrm{kJ\,mol^{-1}}$. The heat of dissociative adsorption of methanol on Pd(100) was reported to be 45 $\mathrm{kJ\,mol^{-1}}$ [14], and our result is consistent with that. The apparent activation energy of the methanol decomposition over metallic palladium supported on zirconium oxide was ca. 100 $\mathrm{kJ\,mol^{-1}}$ [12].

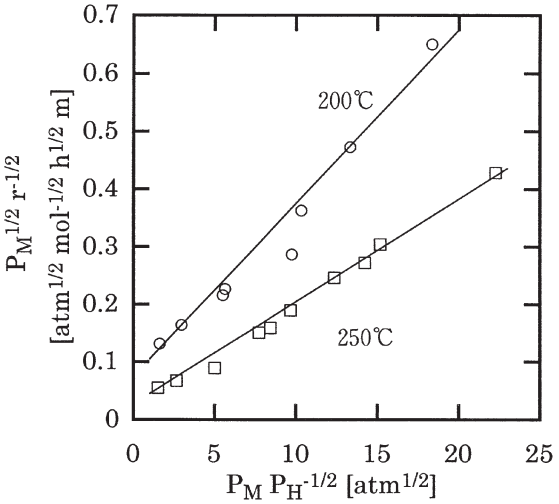

Figure 2. Plot of $P_M^{1/2} r^{-1/2}$ vs. $P_M P_H^{-1/2}$.

It can be supposed that the decomposition of the methoxyl group on the surface is promoted by abstraction of the hydrogen atom with a palladium site instead of reaction (2), that is,

$$CH_3O\text{–}Pd + Pd \rightarrow CH_2O\text{–}Pd + H\text{–}Pd \quad (\text{rate constant } k_2). \tag{6}$$

The following rate equation can be obtained under the steady state:

$$r = k_2 K_M K_H^{1/2} P_M P_H^{-1/2} / \left(1 + K_M K_H^{1/2} P_M P_H^{-1/2} + K_H^{-1/2} P_H^{1/2} + K_C^{-1} P_C\right)^2.$$

In the case of $P_H \ll 1$ and $P_C \ll 1$, the rate expression can be transformed into

$$P_M^{1/2} P_H^{-1/4} r^{-1/2} = k_2^{-1/2} K_M^{1/2} K_H^{1/4} P_M P_H^{-1/2} + k_2^{-1/2} K_M^{-1/2} K_H^{-1/4}.$$

The plot of $P_M^{1/2} P_H^{-1/4} r^{-1/2}$ vs. $P_M P_H^{-1/2}$ (figure 3) shows no linear relation; hence, the mechanism is less probable.

Supposing that the methoxyl group decomposes by itself, that is,

$$CH_3O\text{–}Pd \rightarrow CH_2O\text{–}Pd + (1/2)H_2 \quad (\text{rate constant } k_3) \tag{7}$$

the rate equation can be expressed as

$$r = k_3 K_M K_H^{1/2} P_M P_H^{-1/2} / \left(1 + K_M K_H^{1/2} P_M P_H^{-1/2} + K_H^{-1/2} P_H^{1/2} + K_C^{-1} P_C\right).$$

In the case of $P_H \ll 1$ and $P_C \ll 1$, the rate expression can be transformed into

$$r^{-1} = k_3^{-1} K_M^{-1} K_H^{-1/2} P_M^{-1} P_H^{1/2} + k_3^{-1}.$$

The plot of r^{-1} vs. $P_M^{-1} P_H^{1/2}$ (figure 4, open symbols) is not linear, showing that the mechanism is not appropriate.

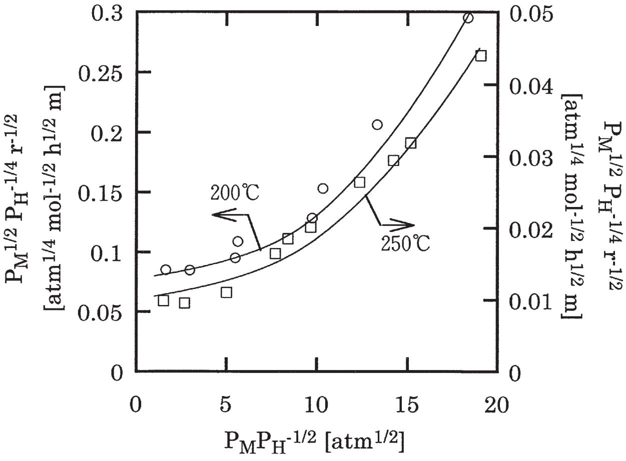

Figure 3. Plot of $P_M^{1/2} P_H^{-1/4} r^{-1/2}$ vs. $P_M P_H^{-1/2}$.

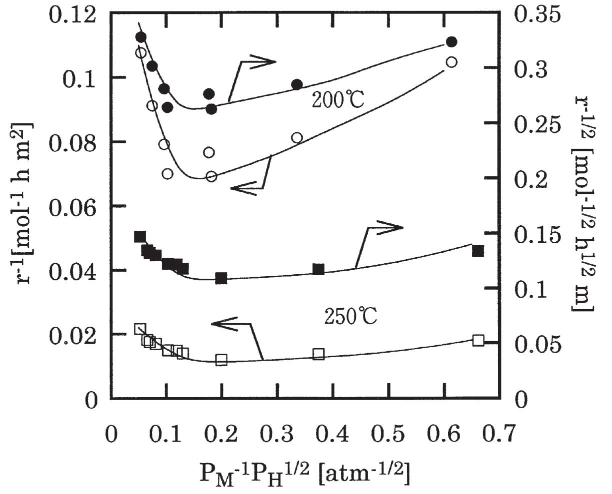

Figure 4. Plot of r^{-1} vs. $P_M^{-1} P_H^{1/2}$ (open symbols) and that of $r^{-1/2}$ vs. $P_M^{-1} P_H^{1/2}$ (solid symbols).

Iwasa et al. reported formation of methyl formate over palladium supported on zinc oxide [10]. When methyl formate is the intermediate of the methanol decomposition, the coupling of surface methoxyl groups, e.g.,

$$2CH_3O\text{–}Pd \rightarrow HCOOCH_3\text{–}Pd + Pd + H_2 \quad (\text{rate constant } k_4) \tag{8}$$

is considered to be rate-determining and the surface methyl formate species will rapidly be decomposed to surface carbon monoxide and hydrogen species. The rate equation will be

$$r = k_4 K_M^2 K_H P_M^2 P_H^{-1} / \left(1 + K_M K_H^{1/2} P_M P_H^{-1/2} + K_H^{-1/2} P_H^{1/2} + K_C^{-1} P_C\right)^2.$$

In the case of $P_H \ll 1$ and $P_C \ll 1$, the rate expression can be transformed into

$$r^{-1/2} = k_4^{-1/2} K_M^{-1} K_H^{-1/2} P_M^{-1} P_H^{1/2} + k_4^{-1/2}.$$

The plot of $r^{-1/2}$ vs. $P_M^{-1} P_H^{1/2}$ (figure 4, solid symbols) is not linear and this mechanism is denied.

Consequently, it is the most probable that decomposition of surface methoxyl groups through interaction with adsorbed hydrogen (reaction (2)) is the rate-determining step of the methanol decomposition to carbon monoxide and hydrogen over palladium. This mechanism can account for the decreasing of the reaction rate with increasing pressure of methanol above 1 atm. That is, the surface concentration of the atomic hydrogen species, which promote the decomposition of the methoxyl groups, will be too small under excessive pressure of methanol, because the methoxyl species are dominant in the equilibrium steps (1) and (4) at the initial stage of the reaction above 1 atm. It should be noted that the rate is proportional to the multiplication of the surface fractions of the methoxyl groups and the atomic hydrogen species.

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References

[1] W. Keim, ed., *Catalysis in C1 Chemistry* (Reidel, Dordrecht, 1983).
[2] J.M. Fox, Catal. Rev. Sci. Eng. 35 (1993) 169.
[3] *Reports of Eco-Energy City Project* (New Energy and Industrial Technology Development Organization and The Energy Conservation Center, Tokyo, 1997).
[4] National Research Council, *Catalysis Looks to the Future* (National Academy Press, Washington, DC, 1992).
[5] K. Murata, K. Yamamoto and H. Kameyama, Int. J. Hydrogen Energy 21 (1996) 201.
[6] H. Kameyama, M. Inoue, R. Yamanaka and K. Murata, Chem. Eng. 36 (1991) 42.
[7] H. Niiyama, S. Tamai, J.S. Kim and E. Echigoya, J. Jpn. Petrol. Inst. 24 (1981) 322.
[8] Y. Saitoh, S. Ohtsu, Y. Makie, T. Okada and Y. Terumuma, Bul. Chem. Soc. Jpn. 63 (1990) 108.
[9] D.T. Wickham, B.W. Logsdon, S.W. Cowley and C.D. Butler, J. Catal. 128 (1991) 198.
[10] N. Iwasa, O. Yamamoto, T. Akazawa, S. Ohyama and N. Takezawa, J. Chem. Soc. Chem. Commun. (1991) 1322.
[11] N. Fukuhara, S. Sekiguchi, H. Mutoh and T. Igarashi, Kagaku Kogaku Ronbunshu 21 (1995) 1002.
[12] Y. Matsumura, M. Okumura, Y. Usami, K. Kagawa, H. Yamashita, M. Anpo and M. Haruta, Catal. Lett. 44 (1997) 189.
[13] K. Christmann and J.E. Demuth, J. Chem. Phys. 76 (1982) 6308, 6318.
[14] G.A. Kok, A. Noordermeer and B.E. Nieuwenhuys, Surf. Sci. 135 (1983) 65.
[15] J.L. Davis and M.A. Barteau, Surf. Sci. 187 (1987) 387.
[16] J. Rask, J. Bontovics and F. Solymosi, J. Catal. 146 (1994) 22.
[17] R. Shekhar and M.A. Barteau, Catal. Lett. 31 (1995) 221.
[18] K. Aika, H. Sekiya and A. Ozaki, C_1 Mol. Chem. 1 (1984) 65.
[19] M.A. Vannice and P. Chou, *Strong Metal–Support Interactions*, ACS Symposium Series, Vol. 298, eds. R.T.K. Baker, S.J. Tauster and J.A. Dumesic (American Chemical Society, Washington, DC, 1986) p. 76.