

Transient Behavior of Methane Oxidation over Pt/SiO₂*

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Abstract

The transient behavior of methane oxidation over Pt/SiO₂ with wide exposing dispersion such as Dh=7, 16, 27, 40 and 81% was studied by using the transient response method at the temperature range 250~335°C. For the five catalysts used a common rate equation was derived:

$$r = (4.2 \times 10^{-3} \sim 2.5 \times 10^{-2}) \exp(-80 \sim -89/RT) P_{\text{CH}_4}^{0.49-0.96} P_{\text{O}_2}^0$$

The turnover frequency of the reaction was steeply reduced with increasing Dh suggesting a structure sensitive reaction. The mode of the transient response curves of CO₂ formed caused by the concentration change in methane at the inlet of the reactor was sensitively changed by the value of Dh, and they were characterized by two modes, either an instantaneous or overshoot types. To explain the drastic change in the mode, the reaction mechanism shifting the rate controlling steps from the surface reaction to the oxidation of the intermediates formed is proposed.

1. Introduction

The recent progress of surface science has rapidly clarified surface chemical processes in complex reactions so as to visualize the reconstruction of surface intermediates under in-situ conditions¹⁾. Especially, finely dispersed platinum particles easily change their own surface structure depending on environmental conditions such as temperature, pressure and gas composition. Chemical reactions catalyzed by surface metals are drastically influenced by the surface structure of metals^{2~4)}. The route of the catalytic reactions varies, therefore, depending on the change in surface structures which are easily reconstructed by the surrounding conditions. When the surface structure varies periodically, one can recognize a chemical oscillation which is catalytically induced^{2~7)}. When the population of active sites on the surface is varied by the percentage exposed (Dh, %) for platinum to the catalyst models used, one may recognize the reaction as a structure sensitive reaction. The structure sensitive reaction can thus be understood as the dynamic structural change of the catalyst surface during reaction, and as the change in the population of active sites depending on Dh. In the present

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study, the first aim is to reveal the structure sensitivity in the chemical oscillating behavior on the widely dispersed platinum particles supported on silica.

In our previous papers^{8,9}, we have shown that the transient behavior of products caused by a change in the concentration of reactant at the inlet of the reactor is fairly influenced by reaction mechanisms. The mode of the transient response curves can thus be classified depending on the reaction route⁹. To study the change in the reaction route depending on the percentage of exposed platinum particles supported on silicagel, the mode of the transient response curves may be effectively employed because of its characteristic behavior from which one can presume a mechanism⁹. There are many works for the oxidation of methane^{10,11}, and the reaction mechanisms proposed can be summarized by two streams: (1) the reaction of gaseous CH₄ with adsorbed oxygen and (2) the oxidation of the adsorbed intermediates formed from the decomposition of CH₄ due to the reaction with active oxygen species, for example on palladium catalysts¹²⁻¹⁷. The second aim of this study, therefore, is to clarify the shift of the reaction mechanism depending on the change in Dh.

2. Experimental Procedure

Catalysts: All the catalysts used in this study was kindly supplied by Professor R. L. Burwell, Jr. in Northwestern University^{18,19}. The details of the catalysts are presented in Table 1. The amount of platinum loaded was in the range 0.825~1.91 wt%, and the metal particles were supported on silicagel granules by both an incipient wetness and an ion exchange procedure. The population of metal atoms exposed to the surface was evaluated by the chemisorption of hydrogen and it was characterized as Dh=7, 16, 27, 40 and 81%. The average platinum crystalline size was determined by the analysis of X-ray diffraction profiles and evaluated to be 80~130 Å for Dh=7, 30-40 Å for Dh=27 and 20-30 Å for Dh=40¹⁹. Silicagel used was Davison Grade 62 which had a BET surface area of 285 m²/g, pore volume =1.2 cm³/g and average pore diameter=140 Å.

Gases and Analysis: The gases used in this study included CH₄ (99.9%), O₂

Table 1. Characterization of Pt/SiO (Prepared by Burwell, Jr., Butt and Cohen school)

Catalysts	Mesh	Pt/SiO ₂ (wt%)	Procedure	Dh (%)	L (Å)
# 68	120-140	0.825	Ion Exchange	81	—
# 65	40-70	1.10	Impregnation	40	20-30
# 70	120-140	1.50	Ion Exchange	27	30-40
# 69-2	70-80	1.48	Ion Exchange	16	—
# 88	120-140	1.91	Impregnation	7	80-130

(99.0%) and N₂ (99.0%) having the indicated levels of purity. All of the gases were analysed by using two gas chromatographs which were attached to Porapak Q (2 m) for the separation of CH₄, CO₂ and air; and with a 13 X Molecular Sieve (2 m) for the separation of N₂, CO and O₂. The Porapak Q column which was connected with TCD was operated at 60°C, and the 13 X Molecular Sieve which was connected with TCD was operated at 70°C.

Procedure: The reactor for this study consisted of a Pyrex glass tube (7 mm o. d.). The catalysts packed into the reactor were 2.37 g for Dh=7%, 1.88 g for Dh=16%, 2.09 g for Dh=27%, 1.00 g for Dh=40% and 1.76 g for Dh=81%. The reactor was immersed into a fluidized sand bath the temperature of which was well controlled within an accuracy of $\pm 1^\circ\text{C}$ (temperature controller: Ohkura EC-76A04) at the given temperature. Three flow controlling systems were prepared each of which could propose a different gas composition depending on the experimental schedule and they were used for the transient response method to quickly change the gas composition of the reactants at the inlet of the reactor making a step function of the reactant concentration with no change in the total gas flow rate. Two four-way valves were attached between the three flow controlling systems, and they were effectively used to make the step function of the reactant concentration at the inlet of the reactor.

The catalyst bed was kept in a pure nitrogen stream at 250~335°C for 2 hours prior to use, and the stream was then switched stepwisely over a given

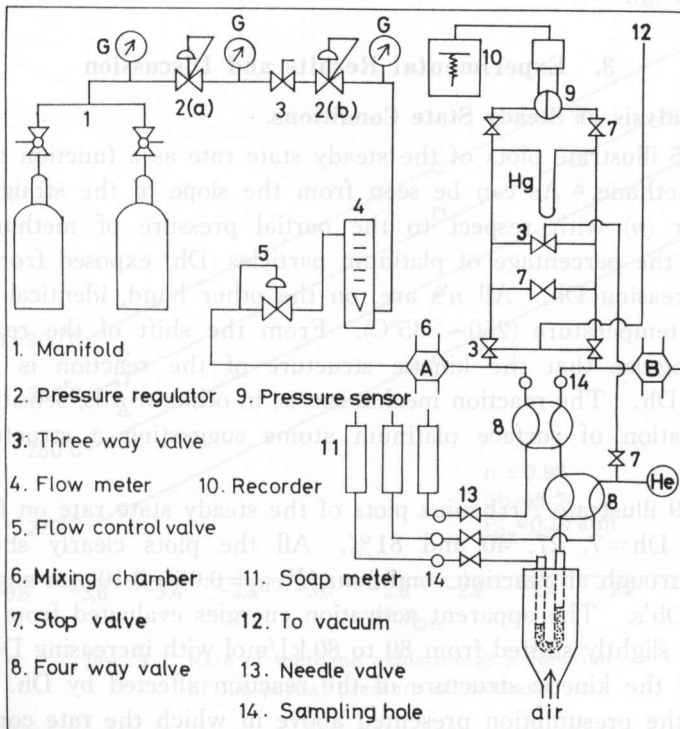


Fig. 1. Schematic diagram of apparatus for the transient response method.

reaction gas mixture, with no change in the gas flow rate at 160 (± 2) ml(NTP)/min. The transient response of the reaction gas components at the outlet of the reactor was followed by analysing the gas composition with two gas chromatographs. Special attention was paid to keep a constant flow rate and a constant total pressure in the reactor by watching a water manometer which detected any pressure difference between the three flow controlling systems. A detailed schematic diagram of the experimental apparatus is shown in Fig. 1. When the transient response was too fast to follow the change in the gas composition of the outlet stream, the same transient experiment was repeated a few times and the results obtained were superimposed to draw the response curves as continuously as possible. The further procedures for the transient response method will be found elsewhere^{8,20}.

The total conversion of methane was always kept to less than 10% to suit the differential reactor through all reaction conditions. The reaction rate thereby was calculated by using the following equation:

$$r = \frac{\Delta x}{\Delta(W/F)} = A \cdot f \cdot F_t \cdot \frac{1}{W(Pt)} \quad (1)$$

where x is the conversion of methane, F_t is the molar flow rate of methane (mol/min), f is the molar fraction of methane in a feed gas (-), F_t is the total molar flow rate of the feed stream (mol/min) and $W(Pt)$ is the weight of platinum of the catalyst (g).

3. Experimental Results and Discussion

3-1. Rate Analysis at Steady State Conditions.

Figs. 2~5 illustrate plots of the steady state rate as a function of the partial pressure of methane. As can be seen from the slope of the straight lines, the reaction order (n) with respect to the partial pressure of methane is varied depending on the percentage of platinum particles (Dh) exposed from $n=0.96$ to 0.49 with increasing Dh. All n 's are, on the other hand, identical with no dependence on temperature (250~335°C). From the shift of the reaction order, one may recognize that the kinetic structure of the reaction is fairly varied depending on Dh. The reaction mechanism is, in other words, sensitively affected by the population of surface platinum atoms suggesting a structure sensitive reaction.

Figs. 6~9 illustrate Arrhenius plots of the steady state rate on four different catalysts with Dh=7, 27, 40 and 81%. All the plots clearly shows a good straight line through all reaction conditions ($P^0_{\text{CH}_4}=0.03-0.10$ atm and $P^0_{\text{O}_2}=0.1-0.2$ atm) and Dh's. The apparent activation energies evaluated from the slope of the lines were slightly shifted from 89 to 80 kJ/mol with increasing Dh, suggesting the change of the kinetic structure of the reaction affected by Dh. This result may support the presumption presented above in which the rate controlling step shifts depending on Dh. The apparent reaction rate may be expressed:

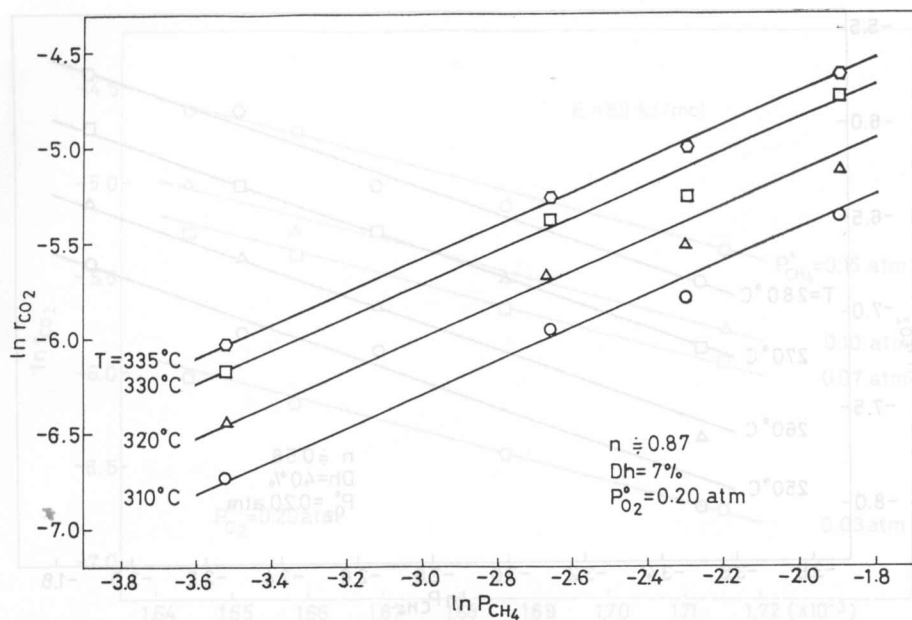


Fig. 2. Rate of methane oxidation as a function of the partial pressure of methane.

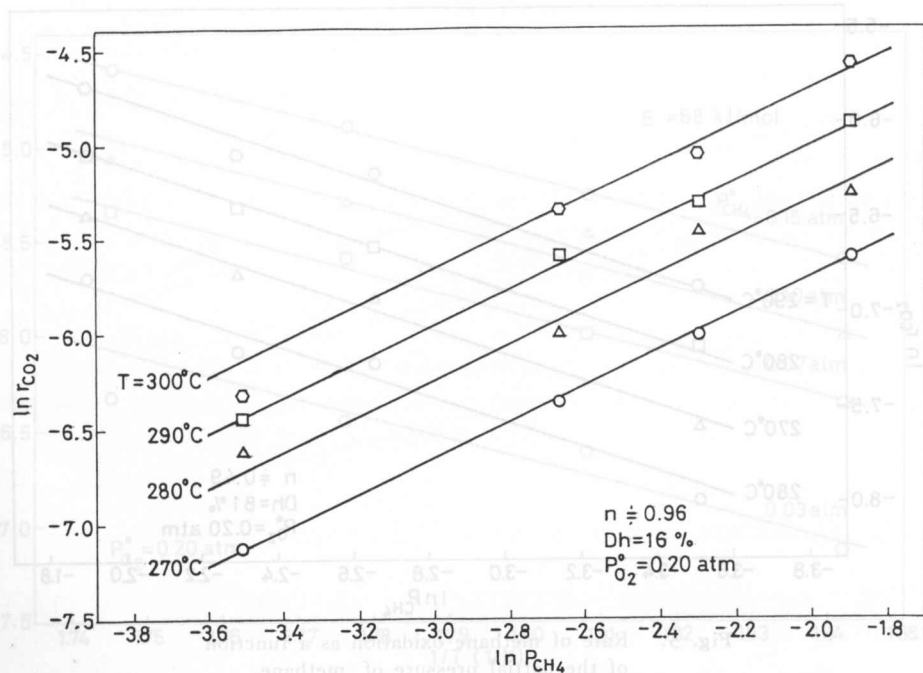


Fig. 3. Rate of methane oxidation as a function of the partial pressure of methane.

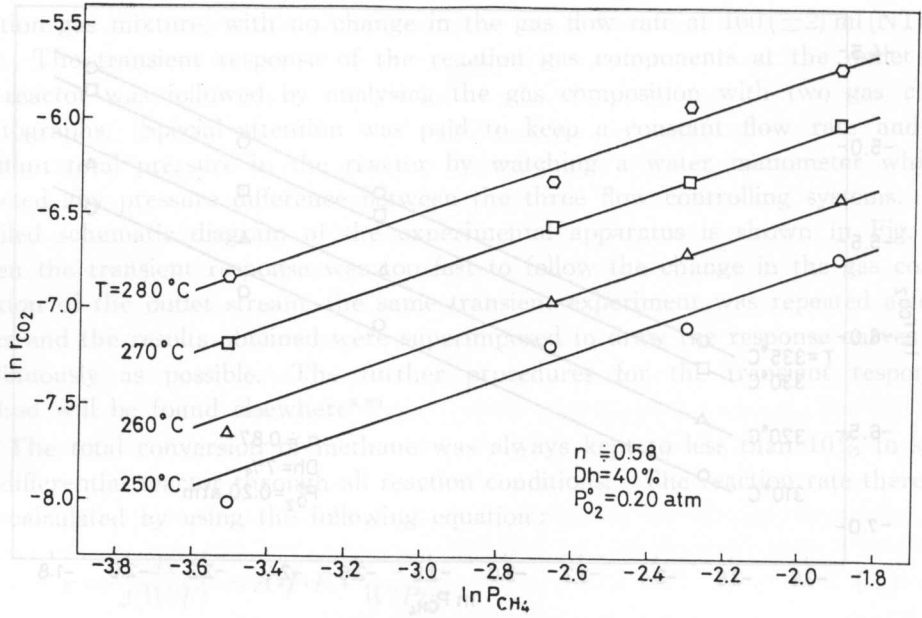


Fig. 4. Rate of methane oxidation as a function of the partial pressure of methane.

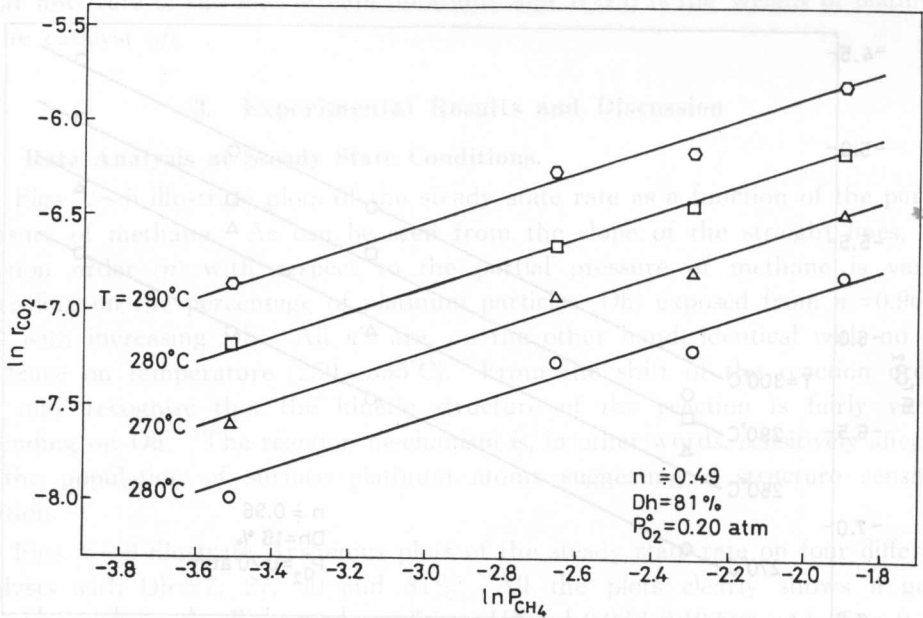


Fig. 5. Rate of methane oxidation as a function of the partial pressure of methane.

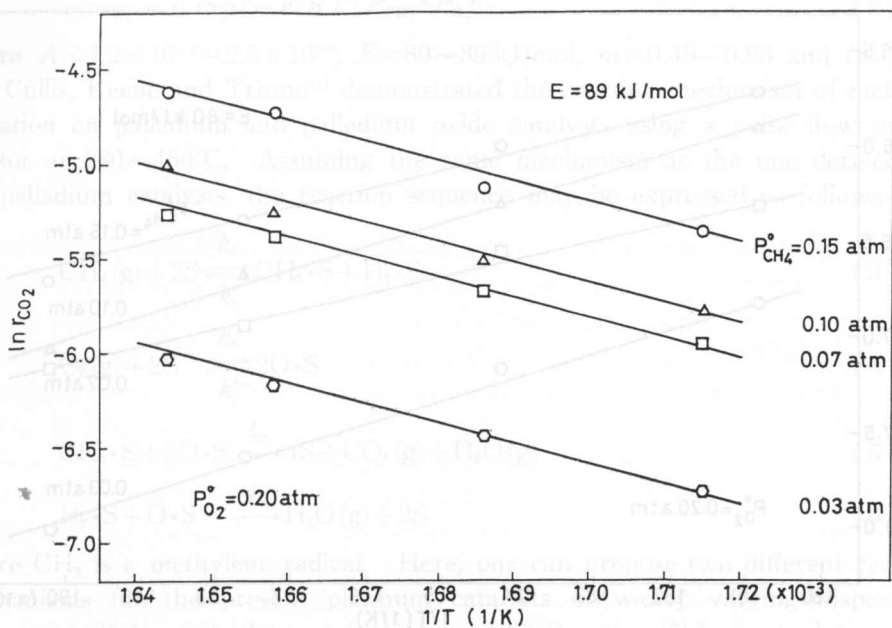


Fig. 6. Arrhenius plots of the apparent reaction rate for Dh=7%.

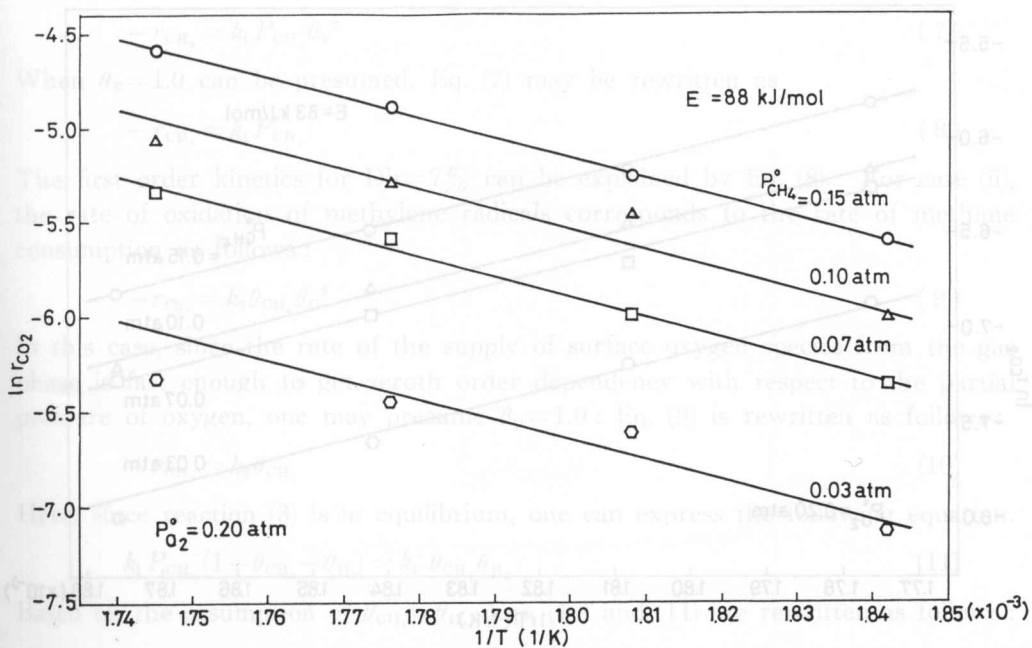


Fig. 7. Arrhenius plots of the apparent reaction rate for Dh=27%.

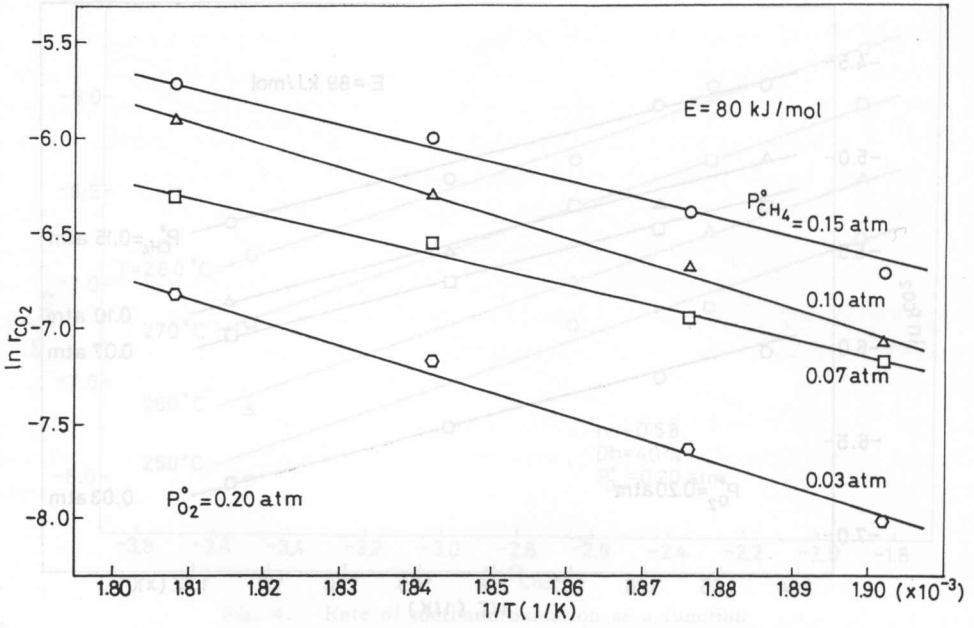


Fig. 8. Arrhenius plots of the apparent reaction rate for Dh=40%.

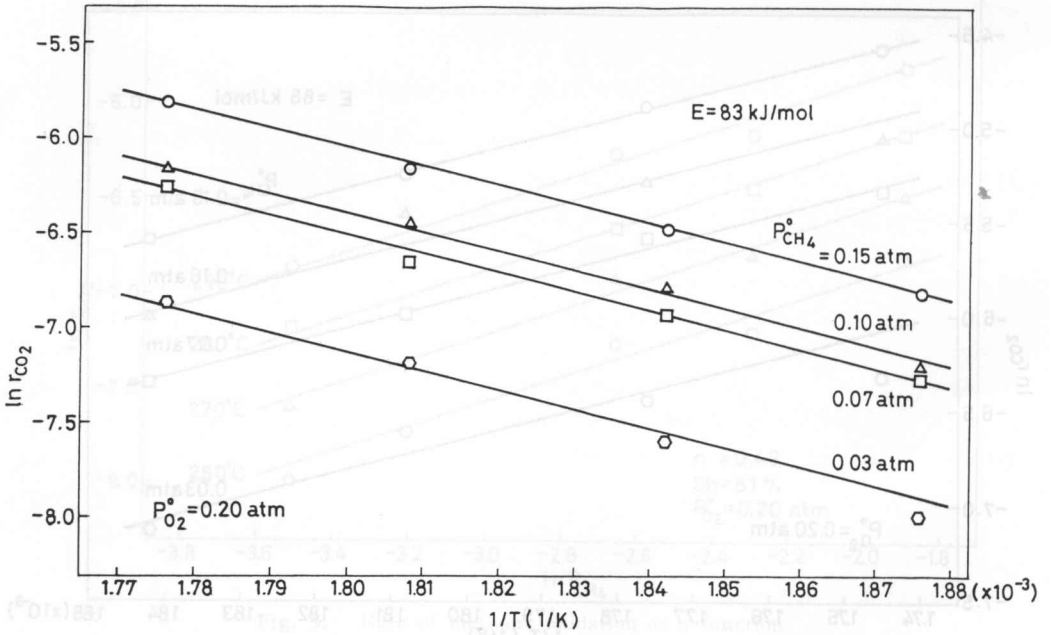
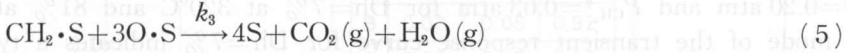


Fig. 9. Arrhenius plots of the apparent reaction rate for Dh=81%.

$$-r_{\text{CH}_4} = A \exp(-E/RT) P_{\text{CH}_4}^m P_{\text{O}_2}^l \quad (2)$$

where $A = 4.2 \times 10^{-3} \sim 2.5 \times 10^{-2}$, $E = 80 \sim 89$ kJ/mol, $m = 0.49 - 0.96$ and $l = 0$.

Cullis, Keene and Trimm¹⁷⁾ demonstrated the reaction mechanism of methane oxidation on palladium and palladium oxide catalysts using a pulse flow micro-reactor at 280~480°C. Assuming the same mechanism as the one derived for the palladium catalysts, the reaction sequence may be expressed as follows:



where CH₂ is a methylene radical. Here, one can propose two different reaction mechanisms for the present platinum catalysts of widely varying dispersion: (i) Reaction (3) is a rate determining step and (ii) Reaction (5) is a rate determining step.

For case (i), the rate equation is expressed as

$$-r_{\text{CH}_4} = k_1 P_{\text{CH}_4} \theta_{\text{V}}^2 \quad (7)$$

When $\theta_{\text{V}} = 1.0$ can be presumed, Eq. (7) may be rewritten as

$$-r_{\text{CH}_4} = k_1 P_{\text{CH}_4} \quad (8)$$

The first order kinetics for Dh=7% can be explained by Eq. (8). For case (ii), the rate of oxidation of methylene radicals corresponds to the rate of methane consumption as follows:

$$-r_{\text{CH}_4} = k_3 \theta_{\text{CH}_4} \theta_{\text{O}}^3 \quad (9)$$

In this case, since the rate of the supply of surface oxygen species from the gas phase is fast enough to get zeroth order dependency with respect to the partial pressure of oxygen, one may presume $\theta_{\text{O}} = 1.0$: Eq. (9) is rewritten as follows:

$$-r_{\text{CH}_4} = k_3 \theta_{\text{CH}_2} \quad (10)$$

Here, since reaction (3) is in equilibrium, one can express the following equation.

$$k_1 P_{\text{CH}_4} (1 - \theta_{\text{CH}_2} - \theta_{\text{H}_2}) = k_1' \theta_{\text{CH}_2} \theta_{\text{H}_2} \quad (11)$$

Based on the assumption of $\theta_{\text{CH}_2} = \theta_{\text{H}_2}$, Eqs. (10) and (11) are rewritten as follows:

$$-r_{\text{CH}_4} = k_3 \frac{P_{\text{CH}_4}^{1/2}}{2P_{\text{CH}_4}^0 + (k_1'/k_1)^{1/2}} \quad (12)$$

Since k_1 and k_1' are large enough compared to P_{CH_4} , from the previous assumption, Eq. (12) can be expressed

$$-r_{\text{CH}_4} = k_3 (k_1/k_2)^{1/2} P_{\text{CH}_4}^{0.5} \quad (13)$$

Eq. (13) thus can be explained by the observation of 0.5th order with respect to CH_4 on $\text{Dh}=81\%$.

Noting the shift of the reaction order depending on the value of Dh such as from first order to 0.5th order, one can thus reasonably presume the shift of the rate controlling step depending on Dh .

3-2. Transient Behavior of CO_2 in the Unsteady State of Methane Oxidation

Fig. 10 illustrates the transient response curves of CO_2 caused by the stepwise change in the gas composition from a pure N_2 stream to a reaction gas mixture (3% CH_4 , 20% O_2 and 77% N_2). The steady state of reaction is completed within twenty minutes and the rate seems to be stable at these reaction conditions ($P_{\text{O}_2}^0=0.20$ atm and $P_{\text{CH}_4}^0=0.03$ atm for $\text{Dh}=7\%$ at 320°C and 81% at 270°C). The mode of the transient response curve for $\text{Dh}=7\%$ indicates a typical instantaneous type whereas the curve for $\text{Dh}=81\%$ shows a typical overshoot type. From this big difference of the mode, one may recognize the change in the reaction sequences between the two catalysts each of which has a different value of Dh . The instantaneous mode strongly suggests a surface reaction controlling or an adsorption controlling of reactant for $\text{Dh}=7\%$. The overshoot mode, on the other hand, suggests a slow regeneration of surface active species for $\text{Dh}=81\%$. These results may propose a shift of rate determining step depending on Dh as a possible reaction model.

Fig. 11 illustrates the transient behavior of CO_2 caused by the stepwise change in the concentration of oxygen from $P_{\text{O}_2}^0=0.05$ atm to $P_{\text{O}_2}^0=0.15$ atm with a

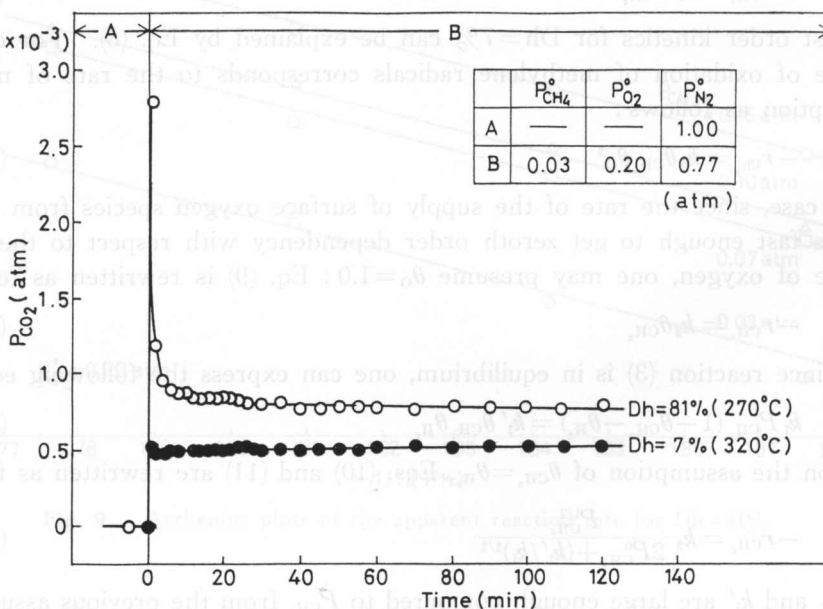


Fig. 10. CH_4 , O_2 (inc., 0)- CO_2 response.

common partial pressure of CH₄ ($P_{\text{CH}_4}^0=0.03$ atm). When the pure N₂ stream was switched over to a reaction gas mixture (3% CH₄, 5.4% O₂ and 91.6% N₂), a typical overshoot mode appeared. This overshoot mode was always observed through our all the reaction conditions and catalysts, suggesting possibly a reconstruction of surface platinum atoms resulting from the accumulation of reaction intermediates. Although the rate of CO₂ formation fluctuates at these reaction

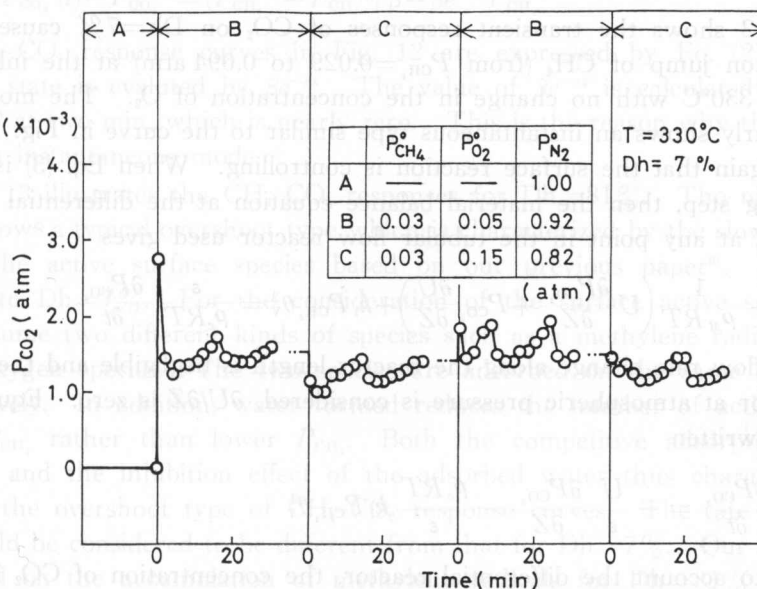


Fig. 11. O₂-CO₂ response for Dh=7%.

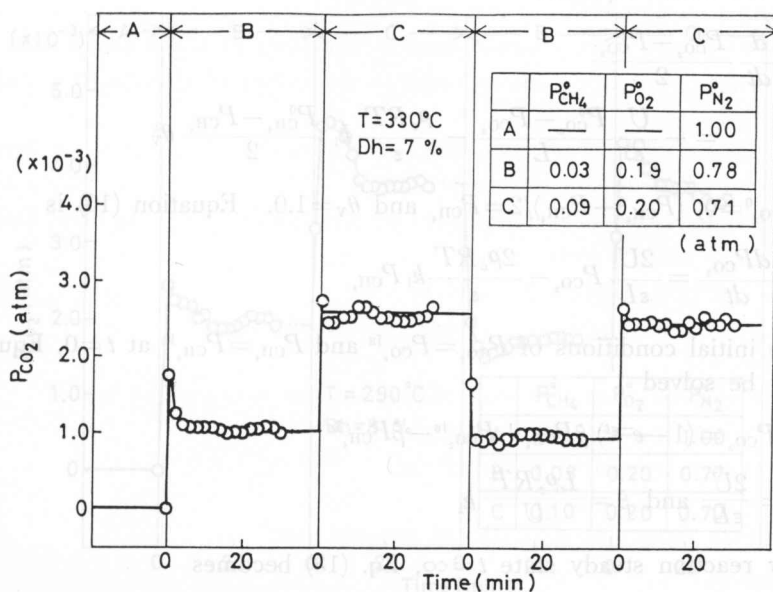


Fig. 12. CH₄-CO₂ response for Dh=7%.

conditions, the average conversion of CH_4 is constant with no depending on P_{O_2} , indicating a zeroth order of reaction rate with respect to P_{O_2} .

The fluctuation of CO_2 in Fig. 11 seems to result from chemical oscillation as demonstrated in CO oxidation. The period and the amplitude of the chemical oscillation are delicately changed at 20~25 min and $P_{\text{CO}_2}=3\sim 9\times 10^{-4}$ atm respectively, depending on the reaction conditions (reaction temperature, gas composition and Dh).

Fig. 12 shows the transient responses of CO_2 on Dh=7% caused by the concentration jump of CH_4 (from $P_{\text{CH}_4}=0.029$ to 0.094 atm) at the inlet of the reactor at 330°C with no change in the concentration of O_2 . The mode of the curves clearly shows an instantaneous type similar to the curve in Fig. 10. This suggests again that the surface reaction is controlling. When Eq. (3) is the rate determining step, then the material balance equation at the differential length of reactor dZ at any point in the tubular flow reactor used gives

$$-\frac{1}{\rho_M RT} \left(U \frac{\partial P_{\text{CO}_2}}{\partial Z} + P_{\text{CO}_2} \frac{\partial U}{\partial Z} \right) + k_1 P_{\text{CH}_4} \theta_v^2 = \frac{\varepsilon}{\rho_c RT} \frac{\partial P_{\text{CO}_2}}{\partial t} \quad (14)$$

Since the flow rate change along the reactor length is negligible and the ordinary flow reactor at atmospheric pressure is considered, $\partial U/\partial Z$ is zero. Equation (14) may be rewritten

$$\frac{\partial P_{\text{CO}_2}}{\partial t} = -\frac{U}{\varepsilon} \frac{\partial P_{\text{CO}_2}}{\partial Z} - \frac{\rho_c RT}{\varepsilon} k_1 P_{\text{CH}_4} \theta_v^2 \quad (15)$$

Taking into account the differential reactor, the concentration of CO_2 is linearly distributed along the reactor length. Equation (15) can be rearranged by the ordinary differential equation

$$\begin{aligned} \frac{d}{dt} \frac{P_{\text{CO}_2}^0 - P_{\text{CO}_2}}{2} \\ = -\frac{U}{\varepsilon} \frac{P_{\text{CO}_2}^0 - P_{\text{CO}_2}}{L} - \frac{\rho_c RT}{\varepsilon} k_1 \frac{P_{\text{CH}_4}^0 - P_{\text{CH}_4}}{2} \theta_v^2 \end{aligned} \quad (16)$$

where $P_{\text{CO}_2}^0=0$, $(P_{\text{CH}_4}^0 + P_{\text{CH}_4})/2 = P_{\text{CH}_4}$ and $\theta_v=1.0$. Equation (16) is

$$\frac{dP_{\text{CO}_2}}{dt} = \frac{2U}{\varepsilon L} P_{\text{CO}_2} - \frac{2\rho_c RT}{\varepsilon} k_1 P_{\text{CH}_4} \quad (17)$$

Using the initial conditions of $P_{\text{CO}_2}=P_{\text{CO}_2}^{\text{is}}$ and $P_{\text{CH}_4}=P_{\text{CH}_4}^{\text{is}}$ at $t=0$, Equation (17) can easily be solved

$$P_{\text{CO}_2} = (1 - e^{-\alpha t}) \beta P_{\text{CH}_4} + P_{\text{CO}_2}^{\text{is}} - \beta P_{\text{CH}_4}^{\text{is}} \quad (18)$$

where $\alpha = \frac{2U}{\varepsilon L}$ and $\beta = \frac{L\rho_c RT}{U} k_1$

At a new reaction steady state $t=\infty$, Eq. (18) becomes

$$P_{\text{CO}_2}^{\text{ns}} - P_{\text{CO}_2}^{\text{is}} = (P_{\text{CH}_4}^{\text{ns}} - P_{\text{CH}_4}^{\text{is}}) \beta \quad (19)$$

The rate equation at a steady state, therefore, may be derived

$$-r_{\text{CH}_4} = k_1 P_{\text{CH}_4} = \frac{U}{L\rho_c RT} P_{\text{CO}_2} \quad (20)$$

At the transient state after the stepwise change in the concentration of methane. Eq. (18) is rewritten

$$P_{\text{CO}_2}(t) - P_{\text{CO}_2}^{\text{is}} = (P_{\text{CH}_4}^{\text{ns}} - P_{\text{CH}_4}^{\text{is}}) \beta - \beta e^{-at} P_{\text{CH}_4} \quad (21)$$

The CH₄-CO₂ response curves in Fig. 12 are expressed by Eq. (21) and the transient state is evaluated by βe^{-at} . The value of βe^{-at} is calculated to be less than 10⁻⁶ at two min, which is nearly zero. This is the reason why the response shows an instantaneous mode.

Fig. 13 illustrates the CH₄-CO₂ responses for Dh=81%. The mode of the curves shows a typical overshoot type which is characterized by the slow regeneration of the active surface species based on our previous paper⁹⁾. This is in contrast to Dh=7%. For the consideration of the surface active species, one may presume two different kinds of species such as a methylene radical and an atomic oxygen species. The two species are adsorbed on the same active sites competitively. In addition, water formed reduces the number of active sites at higher P_{CH_4} rather than lower P_{CH_4} . Both the competitive adsorption of the reactants and the inhibition effect of the adsorbed water thus characterize the mode of the overshoot type of CH₄-CO₂ response curves. The rate controlling step should be considered to be different from that for Dh=7%. Our speculation is focused on the accumulation of methylene radicals for Dh=81% suggesting Eq. (4) to be a rate controlling step. Accordingly, the oxidation of methane is

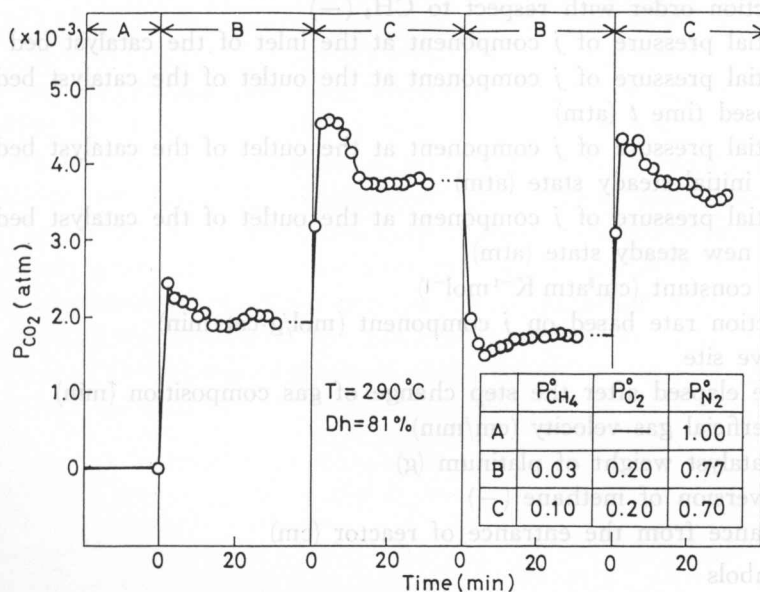


Fig. 13. CH₄-CO₂ response for Dh=81%.

clearly a structure sensitive reaction in which the rate controlling step is drastically changed depending on Dh.

4. Conclusions

The complete oxidation of CH₄ on Pt/SiO₂ is a structure sensitive reaction indicating the higher the Dh the lower the turnover frequency, the higher the Dh the lower the reaction order in P_{CH_4} , and the higher the Dh the lower the activation energy. In the proposed mechanism, the overall reaction rate is controlled by the dissociative adsorption of CH₄ for the lower Dh and by the oxidation of methylene radicals as a reaction intermediate for the higher Dh.

5. Acknowledgement

We thank Professor R. L. Burwell, Jr., in Northwestern University for kindly providing the Pt-SiO₂ catalysts.

6. Nomenclatures

- E : apparent activation energy (kJ/mol)
 F : molar flow rate of methane (mol/min)
 f : molar fraction of methane in the feed gas (-)
 F_t : total molar flow rate of the feed gas (mol/min)
 k_j : forward rate constant for step j (arbitrary unit)
 k'_j : backward rate constant for step j (arbitrary unit)
 L : total length of the catalyst bed (cm)
 l : reaction order with respect to O₂ (-)
 m : reaction order with respect to CH₄ (-)
 P_j^0 : partial pressure of j component at the inlet of the catalyst bed (cm)
 P_j : partial pressure of j component at the outlet of the catalyst bed and elapsed time t (atm)
 P_j^{is} : partial pressure of j component at the outlet of the catalyst bed and the initial steady state (atm)
 P_j^{ns} : partial pressure of j component at the outlet of the catalyst bed and the new steady state (atm)
 R : gas constant (cm³atm K⁻¹mol⁻¹)
 r_j : reaction rate based on j component (mol/g-cat·min)
 S : active site
 t : time elapsed after the step change of gas composition (min)
 U : superficial gas velocity (cm/min)
 $W(Pt)$: catalyst weight of platinum (g)
 X : conversion of methane (-)
 Z : distance from the entrance of reactor (cm)
- Greek symbols
 ϵ : void fraction of packed bed reactor (-)

- θ_j : surface coverage for adsorbed species j (-)
 ρ_c : catalyst bed density (g/cm³)
 ρ_M : molar density (mol/cm³)

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1. Introduction

Magnesium oxide has been well known as a less active catalyst for the oxidation of methane and carbon monoxide^{1,2,3}. Actually it has never been confirmed to be active for CO oxidation at temperatures higher than 200°C as we previously reported^{4,5}. In addition, the adsorption and reaction of CO and CCl₄ show extremely interesting behavior because of the multifunctional nature of the surface such as basicity, acidity and a variety of coordination unsaturation.^{6,7,8} The multifunctional nature of magnesium oxide induces variety in the activity of the adsorbed species, some of which are true intermediate for CO oxidation, and others which have a role as subspecies relating to the reaction route indirectly. The subspecies might control the surface diffusion

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