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Kinetic Studies on Partial Oxidation of Methane over Samarium Oxides

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Abstract

Kinetic studies on the oxidative coupling of methane over Sm_2O_3 have been carried out. The experimental rate equation observed could be well explained in terms of the reaction mechanism proposed. The reaction is initiated by abstracting hydrogen atom from the methane adsorbed by the diatomic oxygen on the surface. The coupling of two $CH_3\cdot$ radicals leads to C_2H_6. Deep oxidation of $CH_3\cdot$ produces CO and CO_2. The large activation energy (149 kJ mol^{-1}) needed for the formation of $CH_3\cdot$ explains the sharp increase in the selectivity to C_2-compounds ($C_2H_6 + C_2H_4$) as raising temperatures. The oxygen species responsible for initiating the reaction was suggested to be O_2^{2-} or O_2^- on the surface.

Introduction

The oxides of rare earth metals have high catalytic activities and selectivities to the formation of C_2-hydrocarbons ($C_2H_6 + C_2H_4$) in oxidative coupling of methane [1, 2]. Among the rare earth metal oxides tested, Sm_2O_3 is the most active and selective catalyst in the reaction [1, 2]. The kinetic studies of the reaction over Sm_2O_3 showed that the overall oxidation of CH_4 can be written as follows:

$$\begin{tikzcd} CH_4 \arrow[rr, "I"] \arrow[dr, "III"'] & & C_2H_6 \arrow[r, "II"] \arrow[dl, "IV"] & C_2H_4 \\ & CO, CO_2 & & \end{tikzcd} \qquad (1)$$

Since the rate of path III is greater than that of path IV, the selectivity to the formations of C_2-compounds (C_2-selectivity) is determined by the relative rates of path I and III [2]. In order to get information about the reaction mechanism for paths I and III in detail, we have carried out kinetic studies on the partial oxidation of methane over Sm_2O_3. The oxygen species responsible for the reactions will be discussed.

Experimental

The Sm_2O_3 powder used was obtained from Asahi Chemical Industry Co. The purity of the catalyst was >99.9% and the surface area was 0.72 m^2 g^{-1}. The experiments were carried out using a conventional gas flowing system. Methane and oxygen were fed with a helium carrier over the catalyst (1.8–5.6 mg) placed at the bottom of a quartz reactor. Details about the experimental procedure and apparatus were described elsewhere [2]. The conversions of oxygen were controlled to be less than 5% for every kinetic experiments.

Results and Discussion

Kinetic Studies

Figure 1 shows the pressure effect of oxygen on the rates of formation of carbon oxides (CO_2 + CO), C_2H_6 and C_2H_4 at 700 °C. The selectivities to the C_2-compounds ($C_{2t} = C_2H_6 + C_2H_4$) are also plotted in Fig. 1. Here, the pressure of methane was kept constant at 18.2 ± 0.2 kPa. No other compounds such as CH_3OH, HCHO and higher hydrocarbons

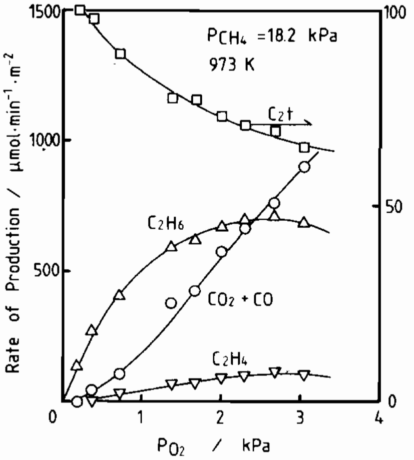

Fig. 1. Effect of $P(O_2)$ on the rates of formation of products and on the C_2-selectivity at 700 °C. The rates of formation of the products: △, C_2H_6; ▽, C_2H_4; ○, CO_2 + CO. □, selectivity to the C_2-compounds.

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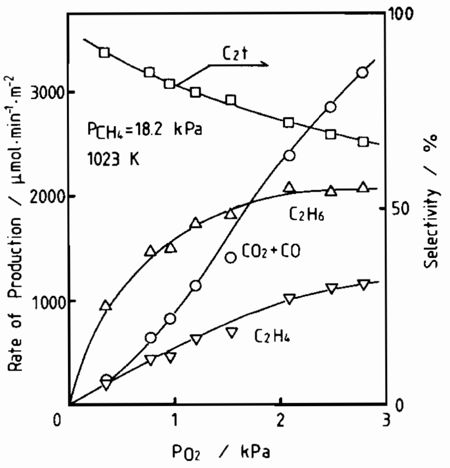

Fig. 2. Effect of $P(O_2)$ at 750 °C.

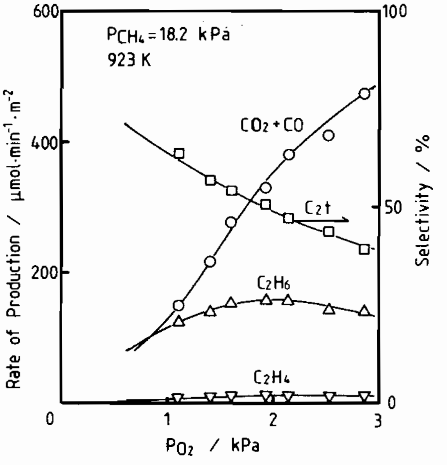

Fig. 3. Effect of $P(O_2)$ at 650 °C.

were produced. The effects of $P(O_2)$ were also examined at 750, 650, and 600 °C at the same $P(CH_4)$ 18.2 kPa. The results are shown in Figs. 2–4. Quite high selectivities (>90%) to C_2-compounds ($C_2H_6 + C_2H_4$) were observed at 700 and 750 °C at low oxygen pressure. However, the selectivities to C_2-compounds decreased with increasing the pressure of oxygen. Figures 1–4 show that the C_2-selectivity and C_2H_4:C_2H_6 ratio decreased sharply with lowering reaction temperatures at the same pressure of oxygen. C_2H_4 was not produced at all at 600 °C.

Figure 5 shows the effects of $P(CH_4)$ on the rates of formations of the products at 700 °C. The pressure of oxygen was kept constant at 0.98 ± 0.02 kPa. The effects of $P(CH_4)$ were also studied at 750, 650, and 600 °C (Figs. 6–8) under the same oxygen pressure 0.98 kPa. The C_2-selectivities increased with increasing $P(CH_4)$ at any temperatures tested.

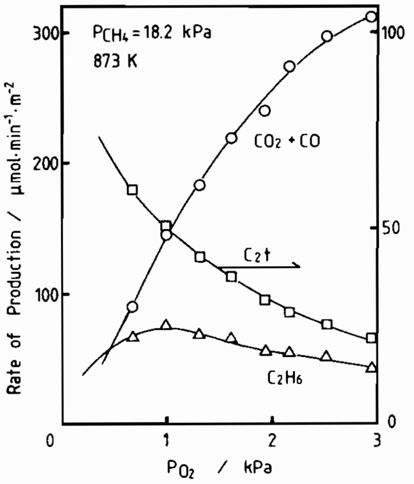

Fig. 4. Effect of $P(O_2)$ at 600 °C.

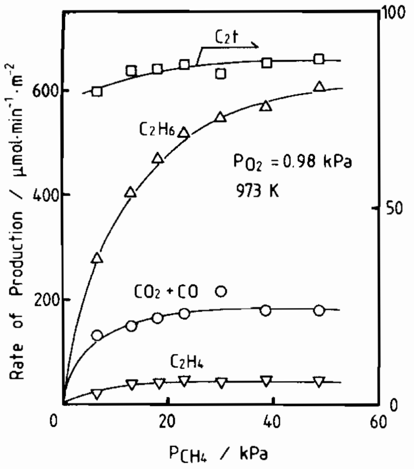

Fig. 5. Effect of $P(CH_4)$ at 700 °C.

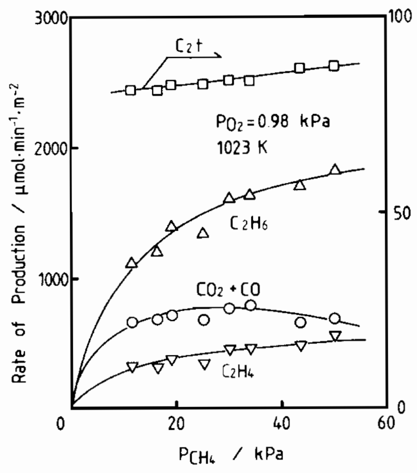

Fig. 6. Effect of $P(CH_4)$ at 750 °C.

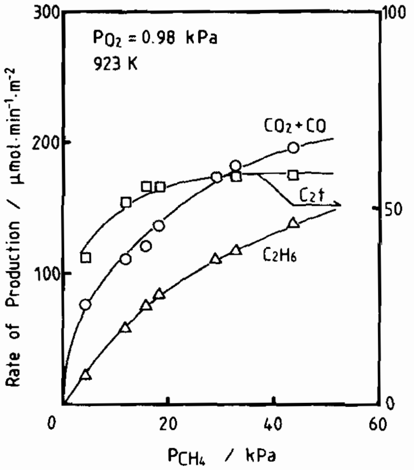

Fig. 7. Effect of $P(CH_4)$ at 650 °C.

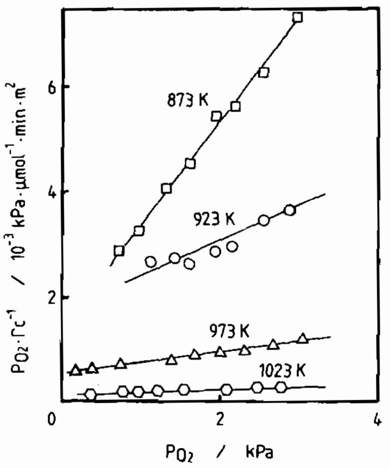

Fig. 9. $P(O_2)/r_c$ *vs.* $P(O_2)$ plot.

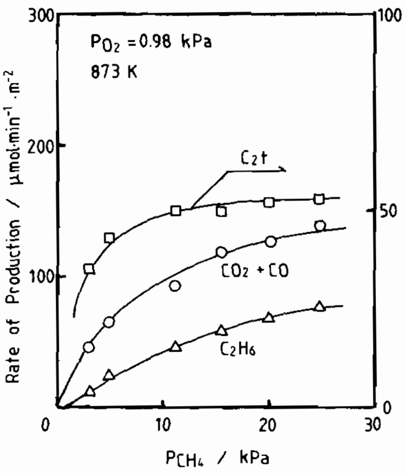

Fig. 8. Effect of $P(CH_4)$ at 600 °C.

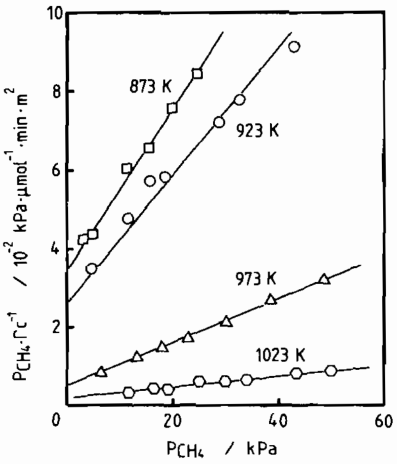

Fig. 10. $P(CH_4)/r_c$ *vs.* $P(CH_4)$ plot.

The effects of $P(O_2)$ and $P(CH_4)$ on the rate of conversion of methane (r_c) observed at 750–650 °C (Figs. 1–8) will be analyzed as follows.

Figure 9 shows the plot of $P(O_2)/r_c$ *vs.* $P(O_2)$ for the data obtained in the experiments for examining the pressure effects of oxygen. The good linear correlation observed in Fig. 9 shows that the rate equation for the conversion of methane can be written as follows:

$$r_c = k_o \frac{K_o' P(O_2)}{1 + K_o' P(O_2)} \tag{2}$$

where, k_o and K_o' are the constants at a fixed temperature.

Figure 10 shows the plot of $P(CH_4)/r_c$ *vs.* $P(CH_4)$ for the data obtained in the experiments for examining the pressure effects of CH_4 on the rates of formation of the products (Figs. 5–8). Good linear correlation between $P(CH_4)/r_c$ and $P(CH_4)$ can be seen for the data at different temperatures. The results in Figs. 9 and 10 show that the rate equation is written as follows:

$$r_c = k \frac{K_m' P(CH_4)}{1 + K_m' P(CH_4)} \times \frac{K_o' P(O_2)}{1 + K_o' P(O_2)} \tag{3}$$

where, k and K_m' are the constants which change with temperature.

We propose the following reaction mechanism to explain the kinetic results described above.

$$CH_4(g) \rightleftharpoons CH_4(a) \tag{i}$$

$$O_2(g) \rightleftharpoons O_2(a) \tag{ii}$$

$$CH_4(a) + O_2(a) \longrightarrow CH_3\cdot + HO_2\cdot \tag{iii}$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6 \tag{iv}$$

$$CH_3\cdot + O_2 \longrightarrow CH_3O_2\cdot \longrightarrow \longrightarrow CO, CO_2 \tag{v}$$

where, adsorptions of CH_4 and O_2, eqns. (i) and (ii), respectively, occur independently of each other on different active sites. Because of a high dissociation energy for the C–H bond of CH_4 (427 kJ mol^{-1}), it seems natural to consider that the abstraction of the hydrogen atom from CH_4 (eqn. (iii)) is the rate-determining step in the overall reaction. Here, it is assumed that the initiation (eqn. (iii)) is caused not by a monoatomic oxygen but by an adsorbed diatomic oxygen. A coupling of two $CH_3\cdot$ radicals produces C_2H_6 (eqn. (iv)). This reaction takes place either on the surface or in the gas phase near the surface [3, 4]. Deep oxidation may proceed through the oxidation of $CH_3\cdot$ radicals according to eqn. (v). This reaction may take place in the gas phase and on the surface. Therefore, the oxygen species contributing in the deep oxidation could be the oxygen in the gas phase and the oxygen on the surface (adsorbed O_2, O or lattice oxygen O^{2-}). C_2H_4 is produced by further oxidation of C_2H_6 as described previously [2].

The selectivity to C_2-compounds is determined by the competition between reactions (iv) and (v). The observation that the C_2-selectivity decreases as the pressure of oxygen rises (Figs. 1–4) can be ascribed to the relative increase in the rate of reaction (v) compared to the rate of reaction (iv) as $P(O_2)$ rises.

The temperature effect on the selectivities of the products indicated that the C_2-selectivity increased sharply as temperatures increased [2]. Reactions (iv) and (v) in the gas phase must proceed with very low or no activation energies [5]. This also may be true when the reactions occur on the surface. Therefore, the strong effect of temperature on the C_2-selectivity can not be explained by the difference in the activation energies between reactions (iv) and (v). Since the abstraction of H from CH_4 (reaction iii) requires high activation energy (149 kJ mol^{-1} as will be described later), the concentration of $CH_3\cdot$ radical must increase sharply with increasing temperature. The rate of reaction (iv) depends on the squares of the concentration of $CH_3\cdot$ radical. Thus, the increase in the rate of reaction (iv) with temperature must be greater than that of reaction (v), which explains the higher C_2-selectivity at higher temperatures.

According to the reaction mechanism (i–v) described above, the rate of conversion of CH_4 can be written as:

$$r_c = k_{iii}\theta(CH_4)\theta(O_2) \tag{4}$$

where k_{iii} is the rate constant of the rate-determining step iii and $\theta(CH_4)$ and $\theta(O_2)$ are the coverages of CH_4 and oxygen, respectively, adsorbed on different kinds of active sites. Assuming that the coverages of the sites adsorbed can be expressed by Lungmuir's adsorption isotherm, r_c is given as follows:

$$r_c = k_{iii}n_m n_o \frac{K_m P(CH_4)}{1 + K_m P(CH_4)} \times \frac{K_o P(O_2)}{1 + K_o P(O_2)} \tag{5}$$

where, n_m and n_o are the numbers of active sites per unit surface area for the adsorptions of CH_4 and O_2, and K_m and K_o are the equilibrium constants for the adsorptions of CH_4 and O_2, respectively. The rate eqn. (5) well explains the experimental rate eqns. (2) and (3). Thus the kinetic results obtained in this work strongly support the reaction mechanism proposed earlier (reactions i–v).

The slopes for the straight lines in Fig. 9 give the value $1/k'$ defined below,

$$1/k' = \frac{1 + K_m P(CH_4)}{k_{iii}n_m n_o K_m P(CH_4)} = \frac{1 + K_m P(CH_4)}{k K_m P(CH_4)} \tag{6}$$

where, $k = k_{iii}n_m n_o$. The slope-to-intercept ratio for each straight line in Fig. 9 gives K_o in eqn. (5) at

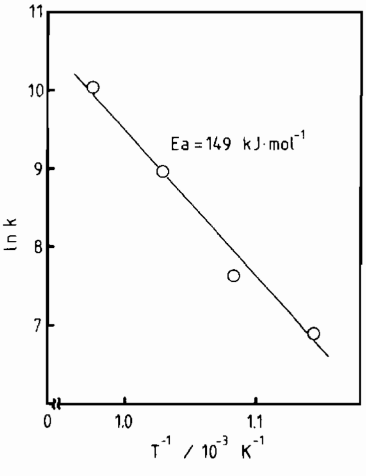

Fig. 11. ln(k) vs. $1/T$ plot.

TABLE I. Kinetic Parameters

Temperature (°C)	K_o (kPa^{-1})	k (mmol min^{-1} m^{-2})	K_m (kPa^{-1})	k (mmol min^{-1} m^{-2})
600	1.04	1.05	0.059	1.11
650	0.55	2.40	0.062	1.74
700	0.33	8.08	0.095	7.52
750	0.43	19.4	0.054	26.1

each temperature. K_m in eqn. (5) can likewise be calculated from the straight lines in Fig. 10. Introducing the K_m to eqn. 6, we can evaluate k because $P(CH_4)$ was kept constant (= 18.2 kPa) for the data in Fig. 9. The k values thus calculated are listed in the third column in Table I. Introducing the K_o calculated from Fig. 9 to the values of slopes in Fig. 10, we can also evaluate k. The values are shown in the fifth column in Table I. The k values in both columns agreed well with each other. The logarithm of the average value of k for the two columns was plotted *vs.* $1/T$ in Fig. 11. The straight line in Fig. 11 gives the activation energy for the activation of CH_4 (step iii) as 149 kJ mol^{-1}.

Oxygen Species Responsible for Activation of Methane

The idea that the oxidation of CH_4 is initiated by diatomic oxygen (reaction iii) is generally accepted for the reaction in the gas phase [6]. However, this is not so for the reaction over metal oxide catalysts. Liu *et al.* have demonstrated that surface O^- ions are the active oxygen species responsible for initiating the partial oxidation of CH_4 over MoO_3/cab–O–sil using N_2O as an oxidant. Ito *et al.* have suggested that $[Li^+O^-]$ centers are the active sites responsible for abstracting a hydrogen atom from CH_4 over Li-promoted MgO [4]. Thus, monoatomic oxygen species have been proposed as the active oxygen species responsible for activation of CH_4 [7]. The kinetic studies in this work, however, suggested that the adsorbed diatomic oxygen is the reactive oxygen species for initiating the reaction.

The kinetic studies cannot predict the kind of diatomic oxygen species responsible for the reaction. This might be O_2^-, O_2^{2-}, or a chemically adsorbed O_2 on the surface. Liu *et al.* [8] have implied that the active species over La_2O_3 may be a sorbed form of oxygen, e.g. O_2^-. They have confirmed the presence of O_2^- over La_2O_3 by ESR technique [8]. Very recently we have demonstrated that the reaction between CH_4 and Na_2O_2 proceeds smoothly, giving C_2-compounds with high selectivity at >300 °C in the absence of oxygen in the gas phase [9]. This observation suggested that the peroxide ions O_2^{2-} on the surface were very reactive for abstracting hydrogen atom from CH_4. These results suggest that the dioxygen species responsible for initiating the abstraction of H from CH_4 (reaction iii) could be O_2^{2-} or O_2^- as far as the reaction over rare earth metal oxides is concerned.

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