The promoting effect of energetic activation of a methane molecular-beam in the direct catalytic partial oxidation of methane†

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Received (in Cambridge, UK) 12th May 2006, Accepted 6th July 2006
First published as an Advance Article on the web 3rd August 2006
DOI: 10.1039/b606763h

Energetic activation of a methane molecular-beam promoted remarkably the direct catalytic partial oxidation on Pt and Rh foils, in particular, hydrogen formation was dramatically enhanced.

Many studies on the interaction between methane molecules and metal surfaces have been carried out extensively,[1–9] because methane dissociation on a metal surface is a very important elementary step in methane steam reforming and the catalytic partial oxidation of methane. These catalytic reactions have been utilized for the production of hydrogen and synthesis gas (CO + H_2) from natural gas.[10–12] Fundamental studies on the reaction of methane on metal surfaces have been carried out using single crystal metal surfaces with or without the combination of the molecular-beam technique.[1–9] In almost all the cases, the researchers have focused on the elementary step of methane dissociation and the measurement of the sticking probability. The gaseous products have often been unclear and the surface temperature was much lower than that for methane partial oxidation and steam reformation. In contrast, catalytic partial oxidation of methane under steady-state conditions and at high reaction temperatures, with the product distribution, is reported in this communication. Hickman and Schmidt have reported that a Pt- or Rh-coated monolith gave high CH_4 conversion to synthesis gas with short contact times (10^{-3} s) and high spatial velocities (10^6 h^{-1}) through direct catalytic partial oxidation of methane.[13] On the other hand, we have reported that the selective formation of synthesis gas is possible by the partial oxidation of hydrocarbons such as C_4H_{10} under the molecular-beam reaction conditions.[14,15] However, methane has very low reactivity compared to other alkanes,[14] therefore, we have investigated the effect of the energetic activation of methane on Pt or Rh using a nozzle heating and seeding technique.

A molecular-beam reaction apparatus consists of a single chamber equipped with a free-jet nozzle for O_2, a free-jet heatable nozzle for methane and a differentially-pumped quadrupole mass spectrometer (QMS, QME200: Pfeiffer Vacuum Technology AG).[15,16] Reaction gases were introduced as molecular-beams through the nozzles, and they collided with the Pt or Rh foil (12.5 × 25 mm). The nozzle for methane is made of ceramic and it is surrounded by a thin graphite heater.[16] This is utilized for making the thermally-activated methane beam. The foil was positioned at about 15 mm away from the nozzles. The surface temperature (T_S) of the foil and the temperature (T_N) of the nozzle for methane were measured by chromel–alumel thermocouples, which were calibrated by a pyrometer. Even when T_N was raised up to 1100 K, the pyrolytic products of methane were below the detection limit of QMS. Furthermore, a molecular-beam of methane diluted in helium was also used. The helium dilution in conjunction with a supersonic expansion is regarded as a seeding technique, and the effect is to increase the translational energy of the methane molecules.[17] The rotational energy of the methane molecule is much lower than translational and vibrational energies. This is because the molecular-beam is cooled during the initial part of the free-jet expansion.[18] The reaction between methane and oxygen over metal foils supplied by the molecular-beams under each reaction condition was observed for 0.5 h at least. The Pt or Rh surface was pretreated at 1400 K by flowing O_2 for the removal of surface contaminants. The amounts of both the reactants and the products, except H_2O, were analyzed by the differentially-pumped QMS, where the background pressure level was about 1×10^{-8} Torr. This makes the accurate determination of the formation rate of products possible, even under the low conversion levels. The experimental error bar in the measurement of the formation rate of each product can be estimated to be $\pm 0.5 \times 10^{15}$ cm^{-2} s^{-1} based on the mass signal fluctuation. The production rate of H_2O was calculated on the basis of the production rates of CO, CO_2 and H_2. The beam flux was controlled using mass flow controllers, and transformed on the basis of the surface area that the molecular-beam impinges, which was estimated to be 2 cm^2.

Fig. 1 shows the formation rates of the products in methane oxidation over a Pt foil as a function of surface temperature. Products were CO, CO_2, H_2 and H_2O. Hydrocarbons other than methane were not detected. The activity at each temperature was almost stable during this measurement; *i.e.*, the steady-state activities are reported here. When methane without the energetic activation was used, the main products were CO and H_2O, and the reaction formula is expressed as $CH_4 + O_2 \rightarrow CO + 2H_2O$ (Fig. 1 (a)). In the case of the heated methane (Fig. 1 (b)), the production rate of CO and H_2O became a little higher, although the product distribution was similar to the case of methane without the energetic activation. On the other hand, when the heated and seeded methane was utilized, the product distribution was drastically changed (Fig. 1 (c)). In both cases, methane without the energetic activation and the heated methane, hydrogen formation was very small even at high temperatures. In contrast, hydrogen production was promoted drastically by the heated and

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† Electronic supplementary information (ESI) available: Schematic diagram of molecular-beam reaction apparatus. See DOI: 10.1039/b606763h

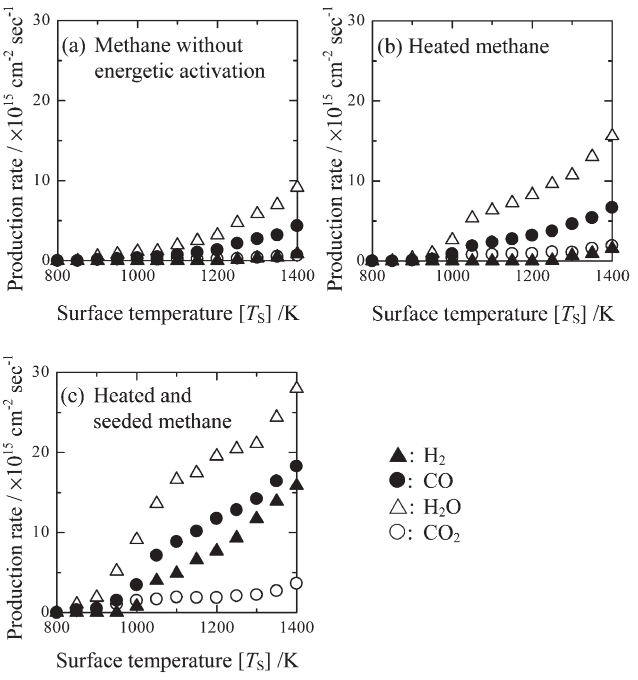

Fig. 1 Surface temperature dependence of product distribution in methane oxidation over Pt foil. CH_4 = 1.0 × 10^{18} cm^{-2} s^{-1}, CH_4/O_2 = 5. (a) Methane without energetic activation: 100% CH_4, T_N = rt. (b) Heated methane: 100% CH_4, T_N = 1100 K. (c) Heated and seeded methane: 10% CH_4, T_N = 1100 K.

seeded methane, and the rate became twenty times higher compared to the case of methane without the energetic activation at T_S = 1400 K. It should be noted that the effective pressure of the gases on the foil surface with the molecular collision is estimated approximately to be 5 × 10^{-2} Torr, which was calculated using the relation between collision flux and pressure. On the other hand, the pressure in the reaction chamber was about 1 × 10^{-2} Torr under these flux conditions. Considering the pressure difference between on the surface and in the chamber, it is expected that the reactant molecule can have only a chance to collide with the foil surface under these reaction conditions, therefore it is interpreted that hydrogen can be formed by direct catalytic partial oxidation of methane, and the heating and seeding of methane molecules can open the reaction route for the catalytic partial oxidation. In addition, the apparent activation energy of the methane conversion rate can be estimated from the data in the temperature range of 1150–1400 K. The activation energies of the oxidation of methane without the activation, the heated methane, and the heated and seeded methane are 73, 48 and 31 kJ mol^{-1}, respectively. The energetic activation of methane can decrease the activation energy of the reaction. The results suggest that the energy in methane is transferred to the activation energy, in particular, the step of methane dissociation.

The results at T_S = 1400 K over Rh foil are listed in Table 1. In the case of no activation, the main products were CO and H_2O. On the other hand, the methane heating promoted hydrogen formation, and the heated and seeded methane decreased H_2O formation and made the H_2/CO ratio close to 2, where the partial oxidation of methane is the main reaction route. The value of CH_4/O_2 was 200 on Rh foil, and this is much higher than the case for Pt foil. We also obtained the data on Rh foil at CH_4/O_2 = 5, which was applied to Pt foil. Hydrogen formation on Rh foil was negligible even in the oxidation of the heated and seeded methane. This can be related to the higher oxygen affinity of Rh than Pt.[19] Under the same O_2 flux conditions, the oxygen coverage on Rh foil can be much higher than that on Pt. This high oxygen coverage can suppress hydrogen formation.

Table 1 Effect of energetic activation of methane on methane oxidation over a Rh foil[a]

CH_4 molecular-beam			Production rate/ × 10^{15} cm^{-2} s^{-1}			
	Nozzle temp. (T_N)/K	Concentration in He (%)	H_2	CO	CO_2	H_2O
(a)	rt	100	0.0	0.8	0.0	1.5
(b)	1100	100	4.3	3.7	0.0	3.1
(c)	1100	10	17	9.0	0.0	0.8

[a] Reaction conditions; T_S = 1400 K, CH_4 = 2.1 × 10^{18} cm^{-2} s^{-1}, CH_4/O_2 = 200. (a) No activation: 100% CH_4, T_N = rt. (b) Heated methane: 100% CH_4, T_N = 1100 K. (c) Heated and seeded methane: 10% CH_4, T_N = 1100 K.

In the oxidation of the heated and seeded methane over Pt foil, the effect of the methane nozzle temperature was investigated and the results are listed in Table 2. The reaction rate of methane oxidation increased remarkably with increasing the methane nozzle temperature. An important point is that the hydrogen is, among the products, influenced most strongly by the methane nozzle temperature. Furthermore, we also investigated the effect of the seeding concentration of methane (Table 2). The addition of He gas to the methane stream promoted methane oxidation. In particular, in this case, hydrogen is also influenced most strongly by the seeding concentration. As a result, it is found that hydrogen formation *via* direct partial oxidation of methane is promoted remarkably by the energetic activation of methane with heating and seeding.

Fig. 2 illustrates the production rate as a function of O_2 flux in methane oxidation over a Pt foil at T_S = 1400 K. In the oxidation of methane without the energetic activation, the production rate decreased with increasing O_2 flux. As a result, the reaction order of the methane conversion rate with respect to O_2 flux is determined to be −0.5. This negative order with respect to O_2 means that the adsorbed oxygen species can suppress the dissociative adsorption of methane in the case of methane without the energetic activation. In the case of the oxidation of the heated and seeded methane, the production rate of products except for hydrogen increased with increasing O_2 flux, and this behavior is much different from that the case of methane without the energetic activation. As a result,

Table 2 Effect of the methane nozzle temperature on the reaction rate in the oxidation of heated and seeded methane on a Pt foil[a]

CH_4 molecular-beam		Production rate/ × 10^{15} cm^{-2} s^{-1}			
Nozzle temp. (T_N)/K	Concentration in He (%)	H_2	CO	CO_2	H_2O
600	10	0.4	3.5	0.2	7.1
800	10	3.0	6.0	1.4	12
950	10	7.2	11	2.0	18
1100	10	15	19	3.0	29
1100	30	6.7	13	3.8	27
1100	100	1.7	7.9	3.9	22

[a] Reaction conditions: T_s = 1400 K, CH_4 = 1.0 × 10^{18} cm^{-2} s^{-1}, CH_4/O_2 = 5.

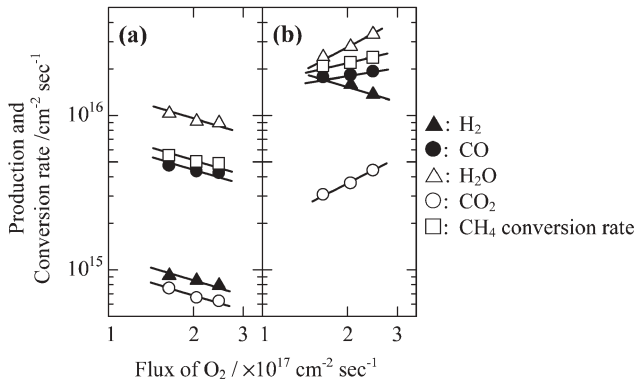

Fig. 2 Production rates as a function of the flux of O_2 in methane oxidation over a Pt foil at T_S = 1400 K. (a) Methane without energetic activation: 100% CH_4, T_N = rt. (b) Heated and seeded methane: 10% CH_4, T_N = 1100 K. Reaction conditions: O_2 flux = 1.6–2.5 × 10^{17} cm^{-2} s^{-1} at a constant CH_4 flux of 1.0 × 10^{18} cm^{-2} s^{-1}.

the reaction order of the methane conversion rate with respect to O_2 flux is determined to be 0.3. The heating and seeding changed the reaction order remarkably with regards to O_2. This positive order suggests that the adsorbed oxygen species can promote the dissociative adsorption of methane, and this is another characteristic feature in the oxidation of the heated and seeded methane. In addition, the error bar of the reaction order of methane conversion is determined to be lower than ±0.08 based on the inaccuracy in the measurement of formation rates.

There have been some reports on the effect of preadsorbed oxygen on the dissociative sticking probability of methane over metal single crystal surfaces. On Ni{100},[9] Pd{110},[2] Pt{111},[3] and Pt{110}–(1 × 2),[4] the adsorbed oxygen suppressed the dissociative adsorption of methane. On the other hand, it has also been reported that the adsorbed oxygen enhanced the reaction probability of methane on Cu{100}[8] and Pt{111}.[6] Furthermore, the effect of the translational energy of the methane molecules on the dissociation probability of CH_4 has been investigated at a surface temperature below 750 K.[3] It has been reported that the dissociation probability of methane in the translational energy range of 60–125 kJ mol^{-1} for oxygen preadsorbed Pt{111} is always smaller than that for clean Pt{111}. On the other hand, it has also been reported that the oxidation probability of CH_4 on Pt{111}–(2 × 2)–O was higher than the dissociative chemisorption probability on Pt{111} at a surface temperature of 500 K, in the translational energy range 10–25 kJ mol^{-1}.[4] The reasons for the disagreement are not clear. Compared to these previous reports mentioned above, the reaction proceeded catalytically under steady-state conditions in the present study, and the surface temperature was much higher. At high surface temperatures, adsorbed oxygen species can diffuse on the surface. In this experiment, oxygen is always supplied from the gas phase, and it has also been reported that nascent oxygen species, which are formed just after the dissociation of oxygen molecules, can be highly reactive.[20,21] The active oxygen species involved in the catalytic methane oxidation at high surface temperatures can be different from the preadsorbed oxygen reported previously. Further investigations on the catalytically active oxygen species, which can promote partial oxidation of methane, are necessary for the elucidation of the reaction mechanism.

From the results, it is found that the energetic activation of methane promotes hydrogen formation, therefore, the formation route of hydrogen is discussed here. In the case of methane without the energetic activation, the main reaction in methane oxidation is $CH_4 + O_2 \rightarrow CO + 2H_2O$ even at high surface temperatures. Based on the temperature programmed desorption profile of oxygen on a Pt metal surface,[22,23] it is expected that the coverage of the adsorbed oxygen species is very small at high surface temperatures. Therefore, low coverage of oxygen can not explain the switching of the reaction route by the energetic activation of methane. One possible explanation is that the energetically activated methane reacts with adsorbed oxygen species to give a precursor for hydrogen formation such as methoxy and hydroformyl species, although the dissociative adsorption of methane without the energetic activation can be inhibited by the adsorbed oxygen. These differences are represented by the reaction schemes as shown below.

$$CH_4 + O_a \nrightarrow CH_{3a} + H_a + O_a$$

$$CH_4^* + O_a \rightarrow CH_3O_a + H_a$$

$$CH_4^* + O_a \rightarrow CH_2O_a + 2H_a$$

(CH_4 and CH_4^*: without and with the energetic activation, respectively.)

According to the results of HREELS (high resolution electron energy loss spectroscopy) analysis for the reaction of methane with preadsorbed oxygen on Ni{100},[7] hydroformyl species have been observed and this supports our interpretation.

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