Methane partial oxidation to methanol–solid initiated homogeneous methane oxidation

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The initiation temperature of methane partial oxidation was markedly lowered by platinum wire placed upstream of a high pressure reactor. Added hydrogen in the reactant gas promoted the methanol selectivity. The radicals formed on the platinum surface were desorbed from it and initiated the reaction.

Keywords: Methane oxidation; homogeneous reaction; platinum; methanol formation; hydrogen effect

1. Introduction

Extensive studies have been made on the partial oxidation of methane to methanol from the standpoint of the high potential as the alternative process [1–4]. Especially, homogeneous methane oxidation has been thought to be one of the promising direct processes to make methanol from methane [1].

Effects of reactor material, reaction conditions, and additives have been investigated for non-catalytic reaction in vapor phase [5]. Quartz or Pyrex tube was used as inert material for the reactor liner. High pressure (< 50 atm) and temperature range 400–450°C were favorable for high methanol selectivity. Hydrogen abstraction from methane is an initial step to determine the total conversion of methane. The initiation temperature was lowered by high pressure [5] and by ethane addition [1,4,5]. In the present study it was tried to initiate the partial oxidation of methane by means of platinum wire.

2. Experimental

Experiments were carried out in a high pressure flow type reactor made with stainless steel tube. A quartz tube was inserted in the reactor to prevent the direct contact of the reactant with the steel surface. The thermocouple centered

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in the reaction zone was also covered by a quartz tube. A platinum wire (0.10 mm, 20 cm) was placed upstream the reaction zone and the distance between the wire and the reaction zone was about 10 cm. The temperature of the Pt wire was about 250°C. Methane was purified by passing thorough columns of molecular sieve 5A and potassium hydroxide in series to remove water and carbon dioxide, respectively. The zeolite was also used for purifying air. Methane and air were first mixed and then supplied in the reactor. Reaction conditions were; temperature 380–500°C, pressure 41 atm, $CH_4/O_2/N_2 = 30/1/4$. Residence time was controlled by a quartz tube inserted in reaction zone. Reaction gas was sampled by a 6-way valve and a hot gas-tight injector. Products were analyzed by a gas chromatograph equipped with a methanator (Ru/Al_2O_3, 480°C). The methanol selectivity S (%) was calculated from equation:

$$S = \frac{F_{\text{MeOH}}}{C_{\text{CH}_4}} \times 100, \qquad (1)$$

where F_{MeOH} is the formation rate of methanol in mol/h and C_{CH_4} the methane conversion rate in mol/h.

3. Results and discussion

Methane conversion started at 420°C without Pt wire, while it started at 380°C in the presence of Pt wire (fig. 1). The methane conversion at 480°C without Pt was 2.2% and the selectivity to methanol was 22.0%. The same level

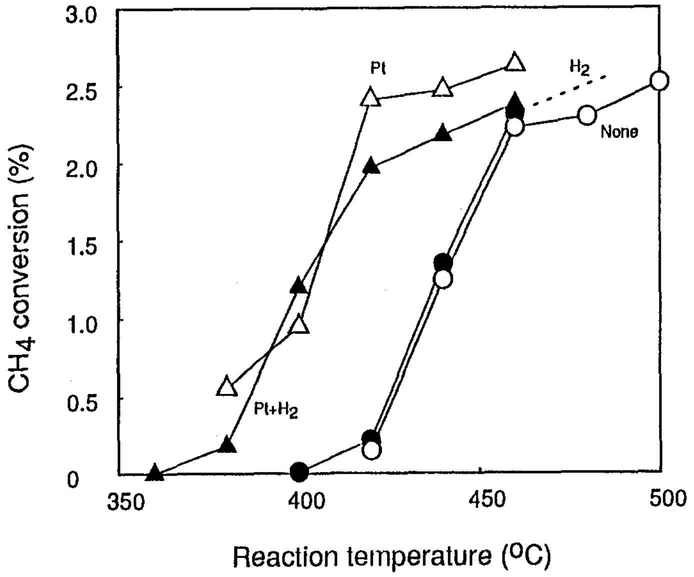

Fig. 1. Effect of platinum and hydrogen at 41 atm, residence time = 1 sec, methane/oxygen/nitrogen ratio = 30/1/4.

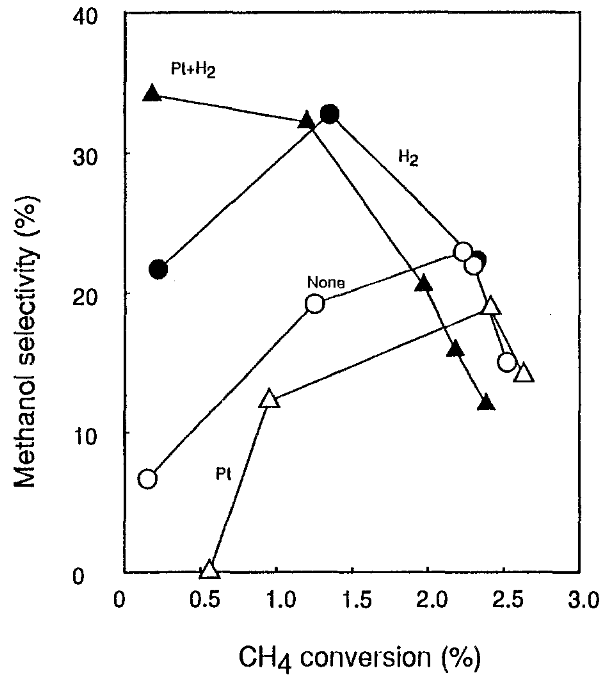

Fig. 2. Effect of platinum and hydrogen on methanol selectivity at 41 atm, residence time = 1 sec, methane/oxygen/nitrogen ratio = 30/1/4.

of methane conversion (2.4%) was attained at 420°C with the methanol selectivity of 18.8% in the presence of Pt wire. It is clear that the Pt wire promotes the initiation of reaction even when its temperature is much lower than reaction temperature.

Added hydrogen in methane (4 mol%) showed no effect on the initiation temperature either in the presence or absence of the Pt wire. The characteristic of hydrogen addition is the enhancement of methanol selectivity (fig. 2). The selectivity to methanol was 6.7% (0.2% CH_4 conversion) at 420°C in the CH_4-O_2 system, while it was 34.2% (0.2% CH_4 conversion) with hydrogen and Pt wire at 380°C.

Radicals should be formed by the reactions between CH_4 and O_2 and/or between H_2 and O_2 on platinum surface [6]. Then the radicals would be desorbed to initiate the vapor phase CH_4-O_2 reaction as shown below.

$$CH_4 + R^{\cdot} \rightarrow CH_3^{\cdot} + RH \tag{2}$$

$$CH_3^{\cdot} + O_2 \rightarrow CH_3O_2^{\cdot}. \tag{3}$$

The key step that determines methanol selectivity is the hydrogenation of the methoxy radical with transfer hydrogenation by methane [4]. The improved selectivity to methanol with added hydrogen either in the presence and in the absence of Pt wire suggests that hydrogen molecule promotes the hydrogenation of methoxy radical (eq. (4)).

$$CH_3O^{\cdot} + H_2 \rightarrow CH_3OH + H^{\cdot}. \qquad (4)$$

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