

## Reaction Mechanism of Partial Oxidation of Methane to Synthesis Gas over Supported Ni Catalysts

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**Abstract**—A mechanistic study on the partial oxidation of methane to synthesis gas ( $H_2$  and CO) was conducted with supported nickel catalysts. To investigate the reaction mechanism, pulse experiments,  $O_2$ -TPD, and a comparison of the moles of reactants and products were carried out. From the  $O_2$ -TPD experiment, it was observed that the active catalyst in the synthesis gas production desorbed oxygen at a lower temperature. In the pulse experiment, the temperature of the top of the catalyst bed increased with the pulses, whereas the temperature of the bottom decreased. This suggests that there are two kinds of reactions, that is, the total oxidation of methane (exothermic) at the top and reforming reactions (endothermic) at the bottom. From the comparison of the moles of reactants and products, it was found that the moles of  $CO_2$ ,  $CH_4$  and  $H_2O$  decreased as the moles of  $H_2$  and CO increased. The results support the mechanism that synthesis gas is produced through a two-step reaction mechanism: the total oxidation of methane to  $CO_2$  and  $H_2O$  takes place first, followed by the reforming reaction of the produced  $CO_2$  and  $H_2O$  with residual  $CH_4$  to form synthesis gas.

Key words: Supported Nickel Catalyst, Synthesis Gas, Oxidation of Methane (Partial), TPD, Pulse Reaction, Mechanistic Study

### INTRODUCTION

Synthesis gas is one of the most important commodity chemicals for the production of various important industrial chemical products. It has been commercially produced by the steam reforming of natural gas [Pena et al., 1996; Craciun et al., 1998; Trimm, 1999; Rostrup-Nielsen and Alstrup, 1999; Dong et al., 2001]. The process is highly endothermic and consumes much energy. On the other hand, synthesis gas production by the partial oxidation of methane is mildly exothermic and consumes less energy than the steam reforming process. Therefore, much effort to produce synthesis gas by the partial oxidation of methane has been carried out by many researchers [Grunwaldt et al., 2001; Elmasides and Verykios, 2001; Ji et al., 2001; Liu et al., 2002; Hohn and Schmidt, 2001].

There has been a controversy about the reaction mechanism of the partial oxidation of methane to produce synthesis gas. Some researchers proposed a one-step reaction mechanism [Pena et al., 1996; Foulds and Lapszewicz, 1994; Au et al., 1998; Tand et al., 1998]. This mechanism assumes that synthesis gas is directly produced from methane and oxygen. On the other hand, others proposed a two-step reaction mechanism [Ruckenstein, 1999; Hofstad et al., 1998; Piga and Verykios, 2000; Nakagawa et al., 1999]. This mechanism assumes that total oxidation of methane is taking place first, and then followed by the reforming of the produced  $H_2O$  and  $CO_2$  with residue  $CH_4$  to form synthesis gas.

This study was conducted to elucidate the reaction mechanism of the partial oxidation of methane to synthesis gas. Pulse experi-

ments,  $O_2$ -TPD experiments, and measurement of the moles of reactants and products were conducted.

### EXPERIMENTAL

#### 1. Preparation of Catalysts

The active component of catalysts was Ni, and supports were MgO, BaO, and CaO. The chemicals used to prepare the catalysts were  $Ni(NO_3)_2 \cdot 6H_2O$  (Junsei Chemicals Co.), MgO (Duksan Chemicals Co.), BaO (Kanto Chemicals Co.), and CaO (Junsei Chemicals Co.). Catalysts were prepared by the impregnation method. The prepared catalysts were dried at 120 °C for 24 h in a drying oven, then the dried catalysts were calcined at 800 °C for 2 h under flowing air of 30 mL/min. The calcined catalysts were then crushed, sieved through an 80-100 mesh sieve, and used for this study without reduction pretreatment.

#### 2. Synthesis Gas Production

The reaction to produce synthesis gas was carried out at 750 °C, 1 bar and  $CH_4 : O_2 = 2 : 1$  in a fixed-bed quartz reactor whose length and diameter were 50 cm and 3/8 inch, respectively. The catalyst used was 13-wt% Ni/MgO, 13-wt% Ni/BaO and 13-wt% Ni/CaO, and 0.1 g of the catalysts was used for the reaction. The temperature of the reactor was controlled by a thermocouple directly contacting on the catalyst bed. The reactants and products were analyzed by a GC equipped with carbosphere column (Alltech,  $\phi$  1/8 in  $\times$  2 m) to separate the effluent mixture. To remove water produced by the reaction, an ice bath and a silica gel moisture trap were placed between the reactor and the sampling valve. The amount of produced water was calculated by a hydrogen balance.

#### 3. Pulse Experiment

The pulse experiment was carried out to examine a temperature change caused by the reaction at the top and bottom of the catalyst

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\*This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

bed by monitoring the temperatures. For the pulse experiment, two thermocouples were located top and bottom of the catalyst bed to measure the temperature changes at both ends. To do this experiment, He gas was flowed down the catalyst bed and the temperature of the reactor was held constant at 750 °C by a thermocouple contacted at the outside of the reactor, and pulses of the reactants ( $\text{CH}_4 : \text{O}_2 = 2 : 1$ ) were introduced into the reactor by a sampling loop whose volume was 9.12 mL. With introducing pulses of the reactants, the temperatures of the both ends were measured and recorded. After one set of pulse experiments, another pulse was introduced to the reactor after the temperatures of the both ends were restored to 750 °C.

#### 4. $\text{O}_2$ -TPD Experiment

To get valuable information about the mechanism of this reaction, an  $\text{O}_2$ -TPD experiment was carried out. TPD experiments were performed with 0.1 g catalyst. The catalysts were pretreated at 200 °C with flowing He in a flow rate of 30 mL/min for 1 h and then cooled to 50 °C with flowing He. Then, at that temperature,  $\text{O}_2$  was adsorbed on the catalysts by flowing  $\text{O}_2$  in a flow rate of 30 mL/min for 1 h. After the adsorption, the catalysts were cooled to room temperature with flowing He. Finally, the temperature of the catalysts was raised to 900 °C with a rate of 10 °C/min. Desorbed gases were then detected by a TCD detector, providing TPD curves.

### RESULTS AND DISCUSSION

#### 1. Pulse Experiment

The temperatures of the top and bottom of the catalyst bed were measured with pulses of reactants. If synthesis gas is directly produced from methane and oxygen, the temperatures at both ends will be raised because the reaction is exothermic. Thus, it is expected that the temperatures at both ends must be higher than that of the outside (750 °C). On the other hand, if the synthesis gas is produced by the two-step reaction, it is expected that the temperature of the top will rise and the temperature of the bottom will fall because the total oxidation reaction is exothermic and the reforming reaction is endothermic. With pulses, the temperature at the top of the catalyst bed rose to 753 °C and the temperature at the bottom of the bed fell to 744 °C. This observation was continued up to ten pulses. From this result, it is suggested that there are two kinds of reactions, that is, the total oxidation reaction (exothermic) at the top and reforming reactions (endothermic) at the bottom. Because the temperature of the reactor was controlled and held constant at 750 °C by a thermocouple located at the outside of the reactor, there is no way to explain this falling in the temperature at the bottom without any endothermic reaction.

Nakagawa et al. [1999] performed this reaction with an Rh/SiO<sub>2</sub> catalyst in a horizontal reactor and reported a rise in the temperature at the top of the catalyst bed and a fall in the temperature at bottom of the catalyst bed. They explained this by the two-step reaction. Diskin et al. [1998] carried out a pulse experiment with supported nickel catalysts, analyzing the produced gas by a mass spectrometer, and they reported that the main product was CO<sub>2</sub>. From our work and literatures, it can be supposed that the partial oxidation of methane to synthesis gas on 13-wt% Ni/MgO catalyst is taking place by the two-step reaction pathway.

#### 2. $\text{O}_2$ -TPD Experiment

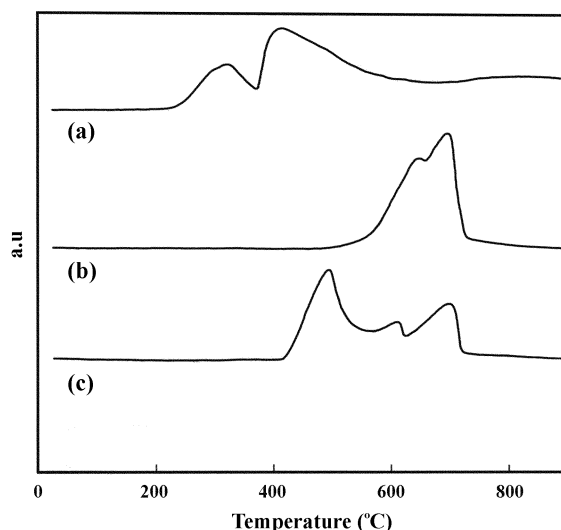


Fig. 1.  $\text{O}_2$ -TPD curves for (a) 13-wt% Ni/MgO, (b) 13-wt% Ni/BaO, and (c) 13-wt% Ni/CaO catalysts.

$\text{O}_2$ -TPD experiment was performed to characterize the catalysts and to get information on the reaction mechanism. Fig. 1 shows  $\text{O}_2$ -TPD curves for three nickel catalysts supported on three different supports-MgO, BaO, and CaO. Three kinds of  $\text{O}_2$  desorption peaks are observed in Fig. 1: one peak around 300 °C, peaks around 500 °C, and peaks around 700 °C. Among the three catalysts used in this study, 13-wt% Ni/MgO catalyst showed the highest methane conversion and selectivity to synthesis gas as published elsewhere [Kim et al., 2003]. In Fig. 1, 13-wt% Ni/MgO catalyst desorbed  $\text{O}_2$  at a lower temperature than the other catalysts. It is generally known that the oxygen desorbed at a lower temperature is responsible for the total oxidation of methane and the one desorbed at a higher temperature is responsible for the partial oxidation of methane [Hegarty et al., 1998; Arai et al., 1986; Jeon and Seo, 2002]. In this study, the catalyst which showed the highest activity in the synthesis gas production desorbed oxygen at a lower temperature. From these results, it may be assumed that there is a close relationship between

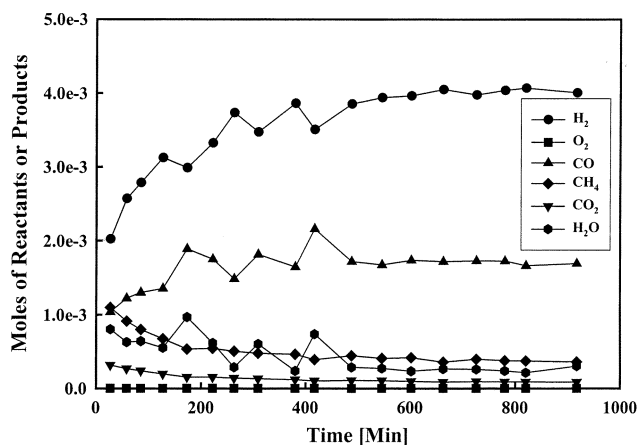


Fig. 2. Changes in the moles of reactants and products as a function of reaction time for 13-wt% Ni/MgO catalyst; ( $\text{CH}_4 : \text{O}_2 = 2 : 1$ ,  $T = 750$  °C).

the production of synthesis gas and the total oxidation of methane.

### 3. The Changes in the Moles of Reactants and Products

The changes in the moles of reactants and products were measured to get any information on the reaction mechanism and depicted in Fig. 2 for 13-wt% Ni/MgO catalyst. As shown in Fig. 2, there exists a noticeable trend in the moles of reactants and products: up to around 600 min, with the decrease in the moles of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$ , the moles of  $\text{H}_2$  and  $\text{CO}$  increased; and, after around 600 min, when the moles of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  held nearly constant, the moles of  $\text{H}_2$  and  $\text{CO}$  were also held nearly constant. These results show that there exists a close relationship between the moles of ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ) and ( $\text{H}_2$ ,  $\text{CO}$ ). This means that all the  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  contribute to the formation of  $\text{H}_2$  and  $\text{CO}$ . Putting these results together, it is supposed that the reaction takes place by a two-step reaction.

### CONCLUSIONS

In the pulse experiment, the temperature at the top of the catalyst bed rose, while the temperature at the bottom of the catalyst bed fell. From this it can be proposed that there exist two kinds of reactions: an exothermic reaction at the top and endothermic reactions at the bottom. The exothermic reaction must be the total oxidation of methane and the endothermic reactions may be the reforming reactions of the produced  $\text{CO}_2$  and  $\text{H}_2\text{O}$  with residual methane to form synthesis gas. From the  $\text{O}_2$ -TPD experiment, it is found that the catalyst facilitating the total oxidation of methane facilitates the synthesis gas production. Through the comparison of the moles of reactants and products, it is found that there exists a close relationship between the moles of ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ) and ( $\text{CO}$ ,  $\text{H}_2$ ). Putting these results together, it is concluded that on 13-wt% Ni/MgO catalyst, synthesis gas is produced by the two-step reaction mechanism.

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