



Conversion of natural gas to C₂ product, hydrogen and carbon black using a catalytic plasma reaction

Wonjun Cho^{a,*}, Young Chai Kim^b, Seung-Soo Kim^{c,**}

^a Korea Gas Corporation R&D Center, 973 Dongchun-Dong Yeonsu-Ku, Incheon, 406-130, Republic of Korea

^b Department of Chemical Engineering, Hanyang University, Seoul, 133-781, Republic of Korea

^c Department of Chemical Engineering, Kangwon National University, Samcheok, Gangwon-do, 245-711, Republic of Korea

ARTICLE INFO

Article history:

Received 30 June 2009

Accepted 5 August 2009

Keywords:

Plasma catalytic methane conversion

Microwave plasma

Radio frequency plasma

Methane activation

Kinetics and mechanism

ABSTRACT

In the microwave and RF plasma catalytic reaction at room temperature, the decomposition of natural gas over Pd–NiO/γ-Al₂O₃ was carried out. The decomposition of methane is caused by collision by excitation of unstable electronic state. Measuring the flow rate and plasma power can represent kinetic data and mechanism. The conversion of C₂ hydrocarbons was increased from 47% to 63.7% in the microwave plasma catalytic reaction within electric field. Comparing the activities of catalysts, Pd–NiO/γ-Al₂O₃ bimetallic catalyst was more active than Pt–Sn/γ-Al₂O₃ catalyst because of modifying the surface of catalysts by carbon formation. In RF plasma catalytic reaction, we obtained high C₂ yield of 72%, in which the conversion and selectivity of C₂ hydrocarbons were related to the applied power and feed rate of natural gas.

© 2010 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

1. Introduction

Conversion of natural gas, using various plasma technologies, to obtain more valuable chemical products has been researched widely. Natural gas is the most abundant energy resource in the recent decade and it will play an increasingly important role in chemical supplies in the future. It is noted that methane, a major constituent of natural gas, has been converted to higher hydrocarbons by multi-step reaction processes. Direct conversion of methane to C₂ hydrocarbons has been attracted in the natural gas industry. Therefore many researches have been carried out with the aim to use it as the gas-to-liquid (GTL) processes in order to produce the synthesis gas, ethane, ethylene, acetylene as well as C₂ hydrocarbons [1–4]. For decades, steam-reforming process of natural gas has been known to be the most efficient and widely used process for the production of hydrogen.

Methane activation, however, of the strong and stable bond between carbon and hydrogen is the crucial step involved in the reaction. Many methods have been developed for methane activation, such as reaction with super-acids, coordination to metal complexes, and selective oxidation catalyzed by metal oxides.

At last decade, the new idea of manufacture valuable chemicals is available by the plasma catalytic methane conversion. In our previous paper, we have reported the experimental results obtained by the catalytic plasma reaction [5–8]. The yield of C₂ hydrocarbons increased from 30% to 42% with increasing the plasma power and decreasing flow rate of methane. When the catalysts were used for the reaction of natural gas, the selectivity of ethylene and acetylene increased while the yield of C₂ hydrocarbons was remained constant. Among the catalysts used, Fe catalyst showed the highest ethylene selectivity of 30%. When natural gas as a feedstock was introduced in the reaction, C₂ hydrocarbons of 46% were obtained due to the other constituents such as ethane and propane.

In this paper we will illustrate our recent research for radio frequency plasma in low temperature, which results are compared to our previous research for microwave plasma [9], for the purposes of kinetic studies of natural gas decomposition.

2. Experimental

2.1. Catalyst preparation

The bimetallic catalysts (Pd–Ni/γ-Al₂O₃ and Pt–Sn/γ-Al₂O₃) were prepared by successive impregnation of γ-alumina (Sumitomo Chemical, Japan, Model AKS-GT-20, BET surface area ~160 m²/g). Pd, Ni and Sn were impregnated 1%, 8–11% and 3% on γ-alumina, respectively. An appropriate amount of Pd(NO₃)₂ (Aldrich Co.) or H₆PtCl₆ (Junsei Co.) was impregnated first into the support and excess water was removed by rotary-evaporation

* Corresponding author. Tel.: +82 32 810 0321; fax: +82 32 810 0330.

** Corresponding author. Tel.: +82 33 570 6544; fax: +82 33 570 6535.

E-mail addresses: wicho@kogas.re.kr (W. Cho), sskim2008@kangwon.ac.kr (S.-S. Kim).

followed by drying at 110 °C for more than 3 h using dry evaporation method. The loaded supports were finally calcined at 550 °C for 2.5 h in air. The solids thus obtained were subsequently impregnated with aqueous Ni(NO₃)₂ (Aldrich Co.) or C₆H₆O₇Sn (Aldrich Co.) solution and treated in the same way as described above. The calcined bimetallic catalysts were reduced at 450 °C for at least 3 h in a flow of 5 vol.% H₂ in nitrogen.

2.2. Plasma catalytic reaction procedure and apparatus

The experimental apparatus used in this work is a low temperature plasma system, which have two different types, a microwave and a radio frequency generator. A microwave generator equipment used in this work operates at 2.45 GHz (ASTEX Co.), which is the most common operating frequency for microwave devices. The microwave power available to the sample is possible to generate maximum power of 120 W. Schematic diagram of plasma catalytic reactor system is shown in Fig. 1, and quartz tube was used as plasma reactor. Experimental of radio frequency plasma was carried out in a solid state power generator (Model OEM-12A) manufactured ENI Co., Inc. operating at a frequency of 13.56 MHz and a power of 1.2 kW. A mass flow controller was used to control the flow rate of methane (99.99%, Matheson Co.). Before reaction, a turbo-molecular pump down to 10⁻⁷ Torr evacuated the system. Plasma quartz reactor with a 25 mm O.D. was connected to a microwave/RF cavity. The forward and reflected powers of plasma generator were monitored during the experiments. The plasma phase was initiated with a Tesla coil while evacuated through the reactor. The catalyst was selected to take part in methane activation. The products were evaluated by a gas chromatograph (HP6890) with a Porapak N, QT column. The temperatures of injector, oven (column) and detector (TCD) were 50 °C, 100 °C and 150 °C, respectively. For this system, the methane conversion was defined as follows:

$$\text{CH}_4 \text{ conversion (\%)} = \frac{\text{moles of CH}_4 \text{ consumed}}{\text{moles of CH}_4 \text{ introduced}} \times 100 \quad (1)$$

The selectivity and yields of C₂ hydrocarbons were:

$$\text{Selectivity of C}_x\text{H}_y \text{ (\%)} = 2 \times \frac{\text{moles of C}_x\text{H}_y \text{ formed}}{\text{moles of CH}_4 \text{ consumed}} \times 100 \quad (2)$$

$$\text{Yield of C}_2 \text{ hydrocarbons} = \text{CH}_4 \text{ conversion} \times \sum (\text{selectivities of C}_x\text{H}_y) \quad (3)$$

where $x = 2$ and $y = 2, 4, 6$ of C₂H₆, C₂H₄, and C₂H₂, respectively.

To determine the variation of catalyst during catalytic plasma reaction, mercury intrusion method was applied by Micromeritics AutoPore III. Thermogravimetric analysis (TGA) was also performed using a TA SDT 2960 instrument in order to characterize the Pd-Ni/γ-Al₂O₃ and Pt-Sn/γ-Al₂O₃ catalysts and to investigate the property of carbon black (plasma black) produced from RF plasma. The morphology of the carbon blacks was investigated by scanning electron microscope (SEM), JEOL JSM-35 at magnifications of up to 2500×.

3. Results and discussion

3.1. Microwave plasma catalytic reaction

The reactions were carried out at the same experimental conditions (pressure: 10 Torr, plasma power: 40–120 W, flow rate: 2–40 ml/min). Fig. 2 shows the plasma methane conversion in the absence of catalysts to investigate the rate of methane decomposition. The decomposition rate of methane in the microwave plasma can be expressed to follow first-order rate equation as follows [10]:

$$-\frac{d[\text{CH}_4]}{dt} = k_1[\text{CH}_4] \quad (4)$$

where [CH₄] is the concentration of methane at time t , and k_1 notes the overall-all rate constant for first-order decomposition of methane.

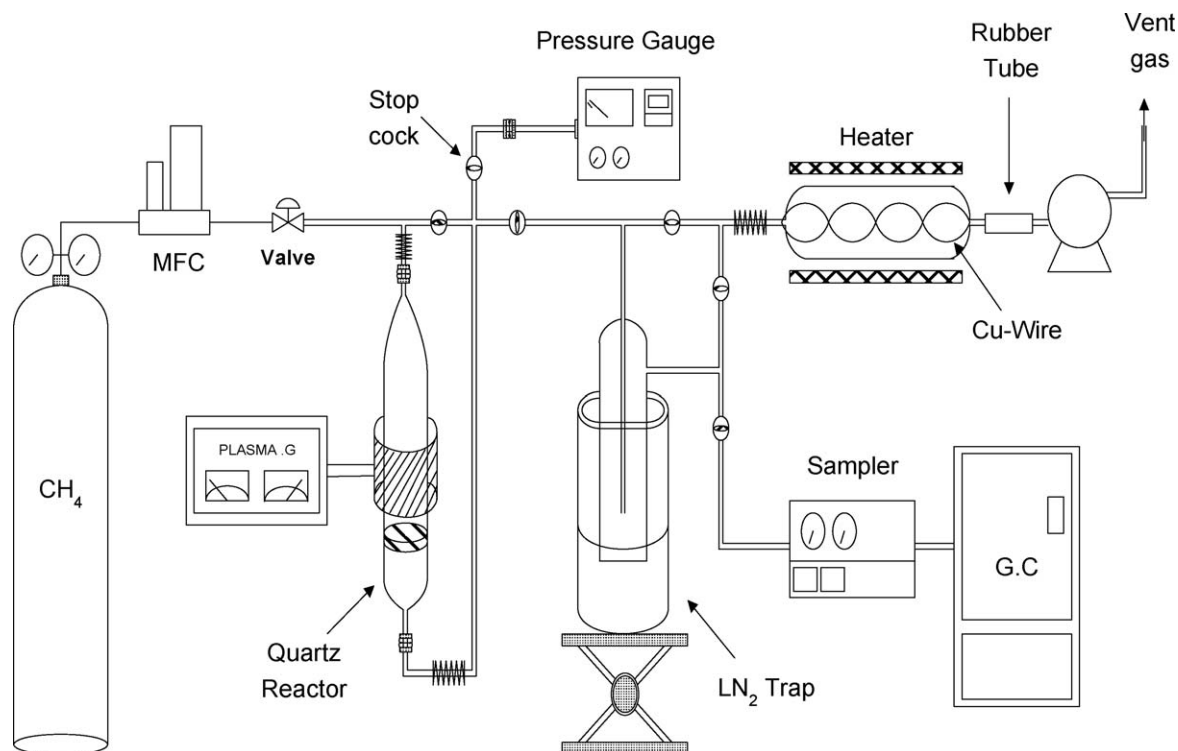


Fig. 1. Schematic diagram of a catalytic plasma reactor system.

Download English Version:

<https://daneshyari.com/en/article/228865>

Download Persian Version:

<https://daneshyari.com/article/228865>

[Daneshyari.com](https://daneshyari.com)