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Hydrogen production by the thermocatalytic decomposition of methane in a fluidized bed reactor

Hyun Tae Jang[†] **and Wang Seog Cha***

Dept. of Chemical Engineering, Hanseo University, Seosan 356-706, Korea
*Dept. of Civil and Environ. Eng., Kunsan Nat'l University, Kunsan 573-701, Korea

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Abstract−CO_2-free production of hydrogen via thermocatalytic decomposition of methane in a fluidized bed reactor (FBR) was studied. The technical approach is based on a single-step decomposition of methane over carbon catalyst in air/water vapor free environment. The factors affecting Fe catalyst (Iron powder activity in methane decomposition reactions were examined. Carbon species produced in the process were characterized by SEM methods. The fluidization quality in a gas-fluidized bed of Fe (Iron powder) and Fe/Al_2O_3 catalyst was determined by the analysis of pressure fluctuation properties, and the results were confirmed with characteristics of methane decomposition. The effect of parameters on the H_2 yield was examined. Fibrous carbon formed over Fe catalyst surface. The hydrogen yield increased with increasing reactor temperature, and decreased with increasing superficial velocity of methane inlet stream. The conversion rate of methane is maintained by attrition of produced carbon on Fe catalyst surface in a FBR

Key words: Thermocatalytic, Methane Decomposition, Iron-based Catalyst, CO_2-Free Production of Hydrogen, Fluidized Bed

INTRODUCTION

Conventional processes of hydrogen production are among the major producers of CO_2 emissions. It has been proposed recently that CO_2 produced in steam reforming (SR) or partial oxidation (PO) processes could be captured and sequestered under the ocean or underground. However, CO_2 sequestration is an energy intensive and costly process associated with ecological uncertainties. Thus, CO_2-free production of hydrogen via thermocatalytic decomposition of hydrocarbon fuels is discussed as a viable alternative to the conventional processes [1-5].

Hydrogen plays an important role and has been used with a very large volume in chemical, food and refining industries [6]. In particular, production of pure hydrogen from hydrocarbons, principally methane, the major component of natural gas, has great practical importance. Non-oxidative thermocatalytic decomposition of methane is a source for producing a pure hydrogen stream. However, solid carbon deposited from gas-phase methane can cause severe fouling of the reactor, catalyst, and gas handling systems. Consequently, non-oxidative catalytic decomposition of methane has not been utilized commercially.

Muradov [7] has also attempted catalytic pyrolysis of methane to produce CO_2-free hydrogen using alumina-supported Fe_2O_3 and NiO (10 wt%) at 850 °C. He proposed reduction of oxide phase by methane to catalytically active metal and carbide phases followed by depletion of these active phases before reaching steady-state methane decomposition to yield 20 volume% hydrogen. Choudhary et al. [2] have used 10 wt% Ni on SiO_2, H-ZSM-5, and HY supports for hydrogen production by catalytic decomposition of diluted (20 volume%) methane in a stainless steel reactor. They observed maximum CH_4 conversions of 45% at 550 °C and observed prolonged release of substantial concentrations of CO (2,500 ppm going down to 750 ppm) and CO_2 (<500 ppm) in the product stream. Li et al. [1] have also used high Ni catalysts for production of hydrogen and nano-carbon from decomposition of methane. They found that the maximum methane conversion occurs at 650 °C irrespective of Ni loading. They also reported that the morphology of nano-carbon is influenced by hydrogen in the feed itself.

In the meantime, FBR could be particularly suitable for the hydrocarbon decomposition process since it allows adequate fluidization of catalyst particles and continuously removing carbon formed through the decomposition reaction from the reactor [8-12].

In the present work, thermocatalytic decomposition of methane to produce CO_2-free hydrogen using iron-based catalyst was studied in the FBR. The pressure fluctuation properties were measured to interpret the attrition of produced carbon and the decomposition characteristics of methane. And the effect of temperature and flow rate on the yield of methane decomposition was investigated.

EXPERIMENTAL

1. Experimental Apparatus

1-1. Catalyst Synthesis

Fe (Iron, electrolytic, powder, Junsei, Chemical Co. LTD., Mean diameter 0.087 mm) catalyst and alumina-supported Fe (0.138 mm, denoted as Fe/Al_2O_3) catalyst were prepared by impregnating an alumina support (γ-alumina, Aldrich, U.S.A.) with an aqueous solution of $FeCl_3$ (Junsei Chemical Co., Japan) at 323 K and drying up the impregnated samples at the same temperature. The samples were dried at 378 K for 48 h, and calcined at 673 K for 12 h in air. The Fe/Al_2O_3 catalysts were then pressed, crushed, and sieved to a 40-

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[†] To whom correspondence should be addressed.
E-mail: htjang@hanseo.ac.kr

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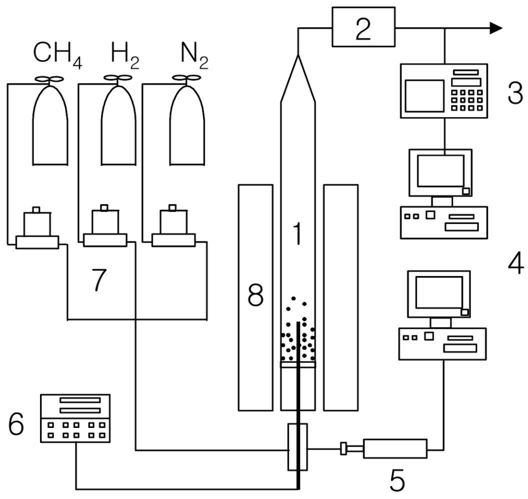

Fig. 1. Schematic of the experimental setup used for studying catalytic decomposition of methane.

1. Fluidized bed reactor
2. Filter
3. Gas chromatograph
4. Personal computer
5. Pressure transducer
6. Temp. controller
7. Mass flow controller
8. Electric

50 mesh size (mean diameter: 0.359 mm). The loading amount of Fe was adjusted to 5, 10, 15, 20 wt% with respect to the alumina support.

1-2. Apparatus and Analysis System

Fig. 1 is a schematic apparatus used for carrying out methane decomposition experiments. The continuous-flow reactor system consisted of a fluidized bed with quartz and an electrical heater controlled by a temperature controller. The quartz reactor was 50 cm long with 18.5 mm inside diameter. A porous frit with quartz at the bottom of the reactor was used as a gas distributor. The pressure transducer for measuring pressure fluctuations was inserted vertically along the plenum.

The analysis system consisted of a gas chromatograph (GC, HP-6890N, FID/Model 580, Gow-Mac Instrument Co.). The concentration of methane and hydrogen was monitored by an automated sampling system. Injections were made by a six-port external injection GC valve with a 150 μl automatic sample loop. The sample was then transferred to a GC with a carrier gas, pure nitrogen. The GC was equipped with HayeSep-Q packed column of 8 ft length and 1/8" outside diameter, and a thermal conductivity detector (TCD). The column (oven) and detectors (TCD, FID) were maintained at 323 K and 423 K, respectively.

Prior to the reaction, the Fe catalyst (aspect ratio (L/D): 1.5) was reduced at 973 K for 3 h with a flow of H_2/N_2 mixed gas with a volume ratio of 1/1 and a flow rate 100 mL/min. After reduction, the experimental setup was flushed with nitrogen until the GC showed no hydrogen peak to purge residual and physisorbed hydrogen from the system. After switching to the reaction gas (methane) at a fixed temperature, the reaction was started by adding methane into the reactor.

RESULTS AND DISCUSSION

1. Hydrogen Production from Decomposition of Methane

One of the conventional hydrogen production processes is decomposition of hydrocarbon fuels (e.g. natural gas, NG) into hydrogen and carbon:

$$CH_4 \xrightarrow[\Delta]{} C+2H_2 \quad \Delta H^0=17.8\ \text{kcal/mole} \tag{1}$$

Methane decomposition reaction is a moderately endothermic process [8-10]. The energy requirement per mole of hydrogen produced (8.9 kcal/mole H_2) is somewhat less than that for the SR process. In addition to hydrogen as a major product, the process produces a very important byproduct: clean carbon. Unlike SR and PO processes, the NG decomposition process does not include a water-gas shift reaction and energy intensive gas separation stages.

Figs. 2 and 3 demonstrate the hydrogen concentration curves from methane decomposition over Fe/Al_2O_3 catalyst (0.359 mm) at 973 K in the packed bed reactor (PBR) and FBR, respectively. PBR rather than FBR was followed by rapid drop in the catalytic activity and the decrease in methane decomposition rate. Methane decomposition using PBR and FBR reached quasi-steady state over 5-10 and

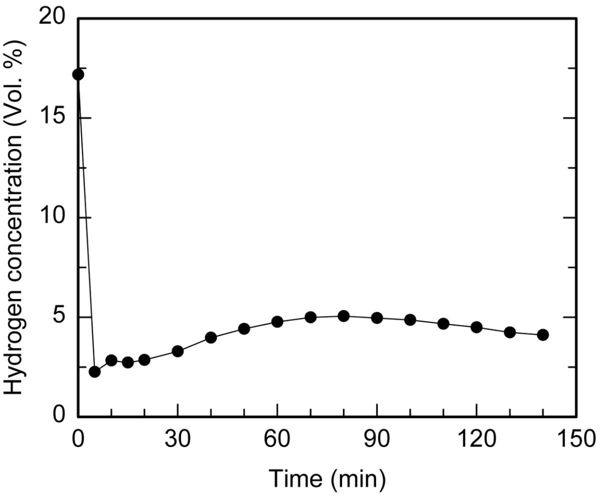

Fig. 2. Hydrogen production due to decomposition of methane over $Fe(5)/Al_2O_3$ catalyst at 973 K in the PBR.

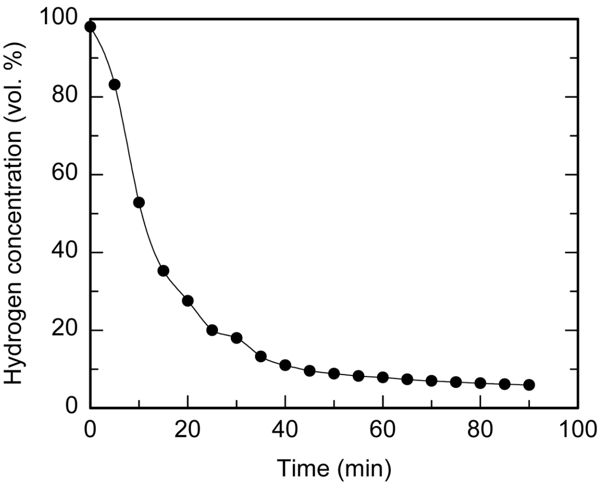

Fig. 3. Hydrogen production due to decomposition of methane over $Fe(5)/Al_2O_3$ catalyst at 973 K in the FBR.

40-50 min, respectively, and remained practically stable for several hours.

It was difficult to conduct long run experiments with PBR due to carbon build up within the reactor and potential reactor clogging. It is apparent that the continuous removal of carbon from PBR would be a daunting technical problem; therefore, this type of reactor is unlikely to be used in large scale hydrogen production units.

Fig. 4 shows the minimum fluidization velocity of Fe catalyst (Iron, electrolytic, powder, Junsei, Chemical Co. LTD., Mean diameter 0.087 mm) particles according to the fluidized bed temperature. Fig. 5 shows the mean pressure and standard deviation of pressure fluctuations of Fe catalyst particles in the FBR at 1,223 K bed temperature and 0.0354 m/sec superficial velocity. In Fig. 5, the mean pressure and standard deviation of pressure fluctuations changes according to operation time. Those values are related to the weight of bed material and bed voidage. The mean pressure is increased initially. After one hour, the mean pressure is decreased with operating time. Thus, the mean pressure according operation time is related to particle elutriation of carbon particles in the carbon growing particle system.

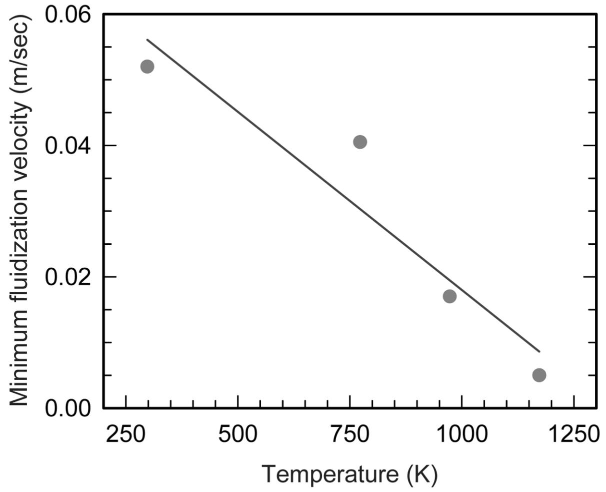

Fig. 4. Minimum fluidization velocity of Fe particles according to the fluidized bed Temperature.

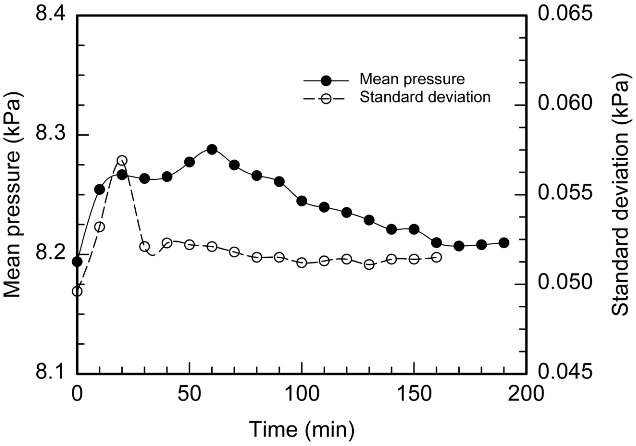

Fig. 5. Mean pressure and standard deviation of Fe/Al_2O_3 catalyst in the FBR at 1,273 K (superficial velocity: 0.0354 m/sec).

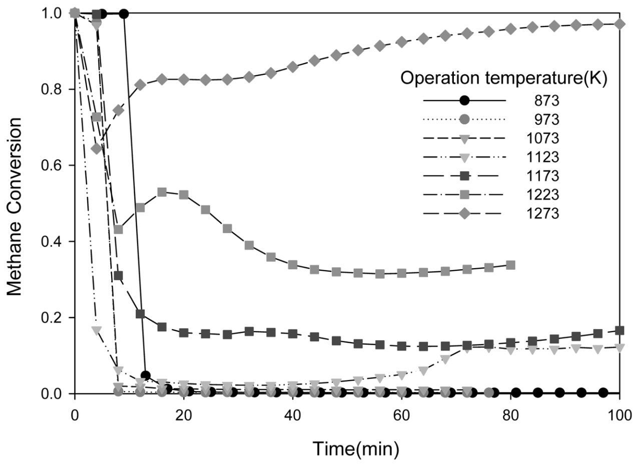

Fig. 6. Effect of the FBR temperature on methane conversion Fe catalyst.

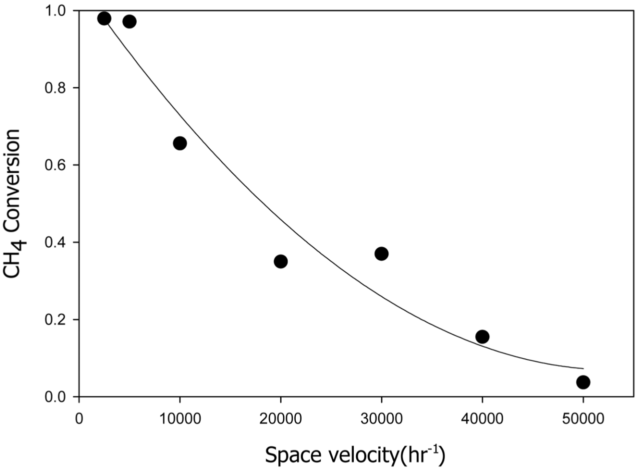

Fig. 7. Effect of superficial velocity on hydrogen production over Fe catalyst at 1,273 K in FBR.

As a whole, temperature is one of the most important factors in gas-solid heterogeneous reactions. Fig. 6 shows the effect of the FBR temperature on methane conversion over Fe catalyst. As already stated, it is known that the reaction of methane decomposition is endothermic process. That is, the reaction needs energy for decomposition of methane. As shown in Fig. 6, the conversion of methane in the effluent gas increases with increasing temperature. The attrition of produced carbon on the Fe catalyst is shown in Fig. 6; the slope of conversion is similar with mean pressure in Fig. 5. The conversion rate of methane is maintained by attrition of produced carbon on Fe catalyst surface in an FBR.

Fig. 7 depicts the effect of methane space velocity on hydrogen production over Fe catalyst at 1,273 K in the FBR. The concentration of hydrogen decreases with increasing methane superficial velocity related to the residence time within the FBR.

2. Carbon Characterization

Thermal catalytic decomposition of methane converts a gaseous methane inlet stream into a gaseous hydrogen outlet stream and solid carbon at high temperatures. SEM analysis was conducted to find out carbon formed by methane decomposition over Fe catalyst.

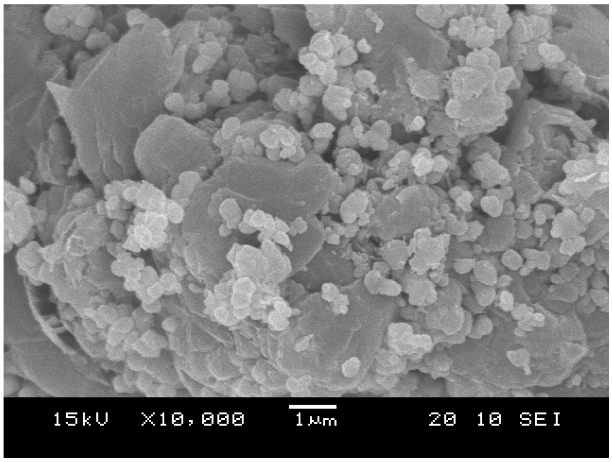

Fig. 8. SEM photographs of Fe catalyst under the operation of the packed bed at 1,173 K (10000 magnifications).

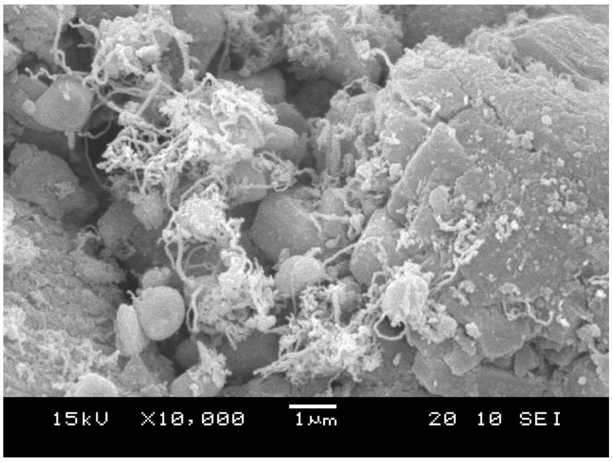

Fig. 9. SEM photographs of Fe catalyst under the operation of the fluidized bed at 1,173 K (10000 magnifications).

Figs. 8 and 9 show SEM photographs of Fe catalyst under the operation of packed and fluidized bed at 1,173 K. As shown in these figures, the fibrous carbon formed over Fe catalyst can be seen in the PBR. But, in case of the FBR, the carbon formed over catalyst surface was elutriated due to the attrition within the bed (see Fig. 5) and captured at the filter part. As illustrated in Fig. 10, nano-carbon captured by filter looks like carbon fibers. Most of this carbon is in the form of potentially valuable multi-walled nanofibers.

CONCLUSIONS

The technical feasibility of CO_2-free production of hydrogen via thermocatalytic decomposition of methane was demonstrated. Methane was efficiently converted into hydrogen and carbon by using Fe/Al_2O_3 catalyst. The effect of operational parameters on the hydrogen yield was determined in the FBR. In case of the reactor temperature, the hydrogen yield increased with increasing temperature. And the hydrogen yield decreased with increasing superficial velocity related to the residence time.

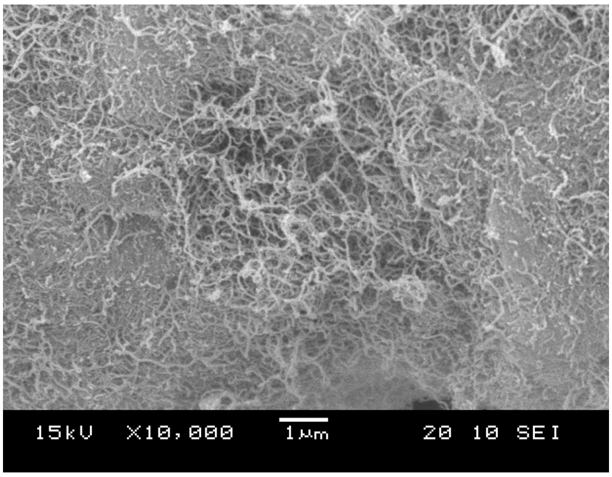

Fig. 10. SEM photograph of nano-carbon fibers (captured at the filter part) formed by decomposing methane over Fe catalyst in the FBR at 1,173 K.

ACKNOWLEDGMENTS

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