CONVERSION OF NATURAL GAS TO HYDROGEN AND CARBON BLACK BY PLASMA AND APPLICATION OF PLASMA BLACK

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Introduction

Natural gas is an environment-friendly resource as a clean fuel and a feed-stock for production of synthesis gas and power plant and it has provided the most abundant energy resource in the recent decade. In the future, it will play an important role as raw material for chemical supplies.

Most of natural gas conversion processing is to produce the synthesis gas in accordance with reforming of methane and then it synthesizes liquid fuels as methanol, DME (dimethyl ether) and other higher hydrocarbons (1).

Recently the direct conversion of methane, which is main component of natural gas, using various plasma technologies has widely been studied in order to obtain synthesis gas or hydrogen-rich gas without CO_2 emission (2,3). In general, there are many processes for production of hydrogen-rich gas with CO_2; steam reforming, partial oxidation, auto another reforming and carbon dioxide reforming of methane or natural gas. However, these processes cause the reduced efficiency due to the high cost of energy and device.

Therefore, the attention is being concentrated on the direct process, which makes decomposition of methane into the production hydrogen-rich gas. In this study, we will illustrate our recent research on the development of a microwave plasma-catalytic reaction process to produce hydrogen and carbon black from natural gas (4). In our plasma system of high power discharge, hydrogen and carbon black is produced by the decomposition of methane, which nearly resembles thermal cracking.

It may be assumed that decomposition of methane produces hydrogen and carbon black by the following single reaction:

$$CH_4 \quad + 75.3kJ/mol \rightarrow \quad C \quad + \quad 2H_2$$

Methane is a preferred raw material for the production of hydrogen from a hydrocarbon because of its high H to C ratio (H/C = 4), availability and low cost. Furthermore, the C produced can be sold as a co-product into the carbon black market (ink, paints, tires, batteries, etc). Several processes of carbon black production are currently used to produce furnace black, lampblack, channel black, thermal black, and acetylene black, which represent 95% of world production and consume primarily petroleum byproducts (5). In the present study, a plasma black was used as a for lithium ion battery. The carbon black is not only acts as an electron pathway by formation of a conducting network of active material but also improves electrical conductivity of interfacial electrode surface.

According to Fulcheri and Schwob (6), the total enthalpy of methane decomposition at 1600℃ is 181.8 kJ/mol, and the energy related to carbon mass varies approximately between 3 and 5 kWh per kg of carbon produced. This paper discussed the decomposition of methane by microwave plasma and possible application to CO_2-free hydrogen production.

Experimental

Figure 1 schematically shows the experimental apparatus for the microwave plasma system. In order to investigate the plasma catalytic reaction, the reactor was designed to be able to insert the catalyst pellet.

Plasma System Reactor In our experiments, microwave plasma (2.45GHz, iplas Co.) was used to produce hydrogen and carbon black from methane. The maximum microwave power is 6 kW. Plasma reactor consists of quartz tube of 6" O.D. that is connected to a microwave waveguide and resonator. It is mainly composed of (Figure 1):

-6kW magnetron power source and plasma generator (resonance)
-cold plasma reactive zone where methane is introduced
-separation bag filter of hydrogen and carbon
-water and air cooling and gas supply systems

Prior to characterization and plasma-catalytic reactivity measurements, the samples were annealed at 473K in the presence of N_2 and hydrogen gas could be used during reaction as plasma gas.

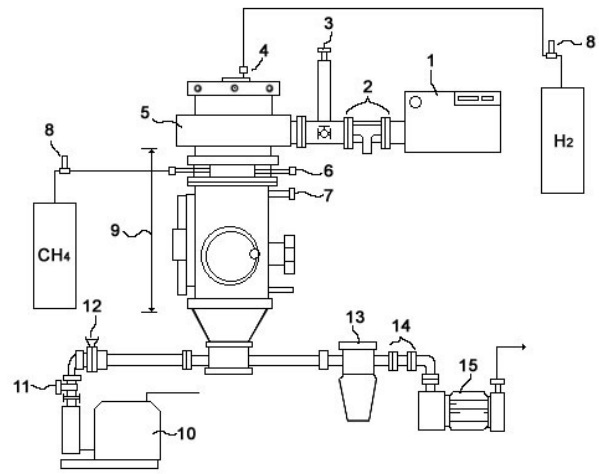


Figure 1. Experimental set for microwave plasma and catalytic reaction process; Magnetron (1), Waveguide (2), E-H tuner (3), microwave quartz tube (4), Plasma Generator (5), Jet inlet nozzle (6), Cooling line inlet, (7) MFC, (8) Microwave plasma reactor, (9) Vacuum pump, (10) Control valve for pressure (11, 12), Cyclone (13), filter (14), Mechanical diaphragm pump (15)

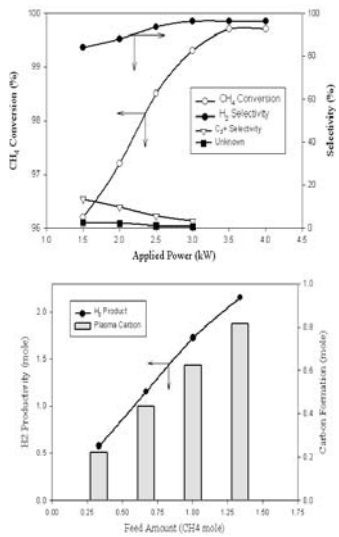
Thermal conductivity analyzer (Teledyne, 2000A-EU) analyzed the reaction product (hydrogen, methane and C2+ chemicals). Scanning electron microscopy (SEM) was used to observe the nano size of carbon black. SEM observation was conducted using a transmission electron microscopy operation at 15kV.

Plasma Black Characteristics The plasma black was treated at 800℃(PB800), 1300℃(PB1300) and 2100℃(PB2100) at 10^{-3} torr pressure in order to improve its conductivity. To determine the property of plasma black, surface area and porosity analysis, temperature programmed desorption (TPD), volume resistivity measurement experiments were performed.

Results and Discussion

Conversion of methane and yields of hydrogen and carbon black as a function of applied power are exhibited in Figure 2. The conversion of methane obtains up to 96% of a plasma and catalytic reaction at 3kW of applied power. Furthermore, the yield of hydrogen is from 83% to 95% at above condition. The yield with respect to carbon black and hydrogen increases with increasing applied power. When an input of 1 mole of methane was introduced, 0.6 mole of carbon and 1.62 mole of hydrogen were produced. Also, we carried out the microwave heating catalysis in order to improve

the performance of methane conversion. The microwave heating of the catalysts might have an important advantage over conventional thermal heating. The catalyst may play a role of abstracting more hydrogen from methane as improving the reactions of radicals. between catalyst surface and reactant gas. Our observation reveals that hydrogen and carbon black are produced at the rate of almost 2:1.



(a) (b)

Figure 2. Conversion of methane and yields of hydrogen and carbon black as a function of applied power (a) and the productivity of hydrogen and carbon as a function of feed amount (b).

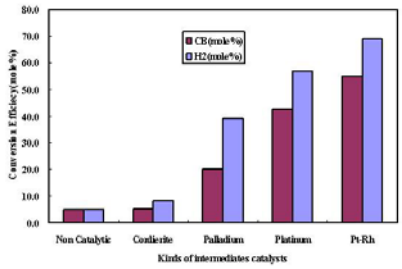


Figure 3. Comparison of various catalysts in the plasma-catalytic reaction; 200ml/min of flow rate, 30 torr of system pressure and applied plasma power is 3.0 kW.

Figure 3 illustrates the comparison of various catalysts in the plasma-catalytic reaction of methane decomposition. Among the novel metals, Pt-Rh catalyst is good for methane decomposition and production H2/carbon black. Conversion methane to hydrogen is 72% and to carbon black is 54%.

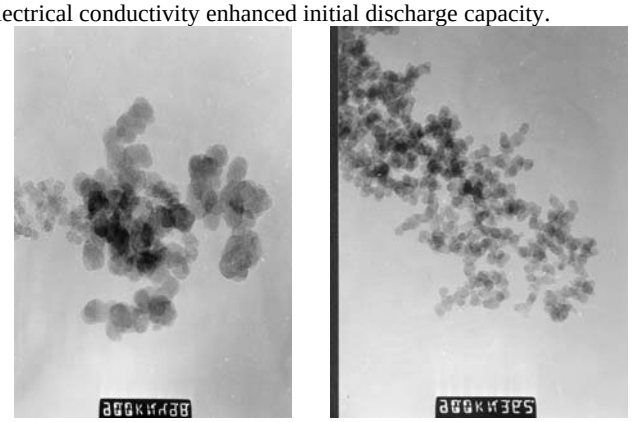
In order to determine the effects of heat treatment on surface area, surface heterogeneity, electrical resistivity and morphology of carbon black, we carried out electrochemical behavior of the carbon black as a conductor of lithium secondary battery electrode. The BET surface area of various carbon black as well as carbon black produced by plasma (plasma black) and average particle size were described as shown in Table 1. In order to compare the size, we determined the acetylene black and the plasma black by TEM as shown Figure 4.

The result of measurement of BET (213.23 m^2/g) showed that the carbon black by manufactured under a microwave plasma catalytic reaction system is very similar to classical furnace black.

Table 1. BET surface area of various carbon black

Carbon black	Surface area (BET : m2/g)	Surface area (Langmuir : m2/g)	Average particle size (nm)
Thermal black	50-120	75.7-171	40-200
Furnace black	100-ab. 200	150-300	ca. 20-30
Plasma black	213.23	293.05	20-30

Heat-treatment carbon black of produced plasma reaction has highest conductivity and highest purity. Four different samples including raw plasma black were added to $LiCoO_2$ to investigate effects of properties of plasma black as conductors on electrochemical characteristics as shown Figure 5. Plasma black conductors with low amount of surface functional groups and high electrical conductivity enhanced initial discharge capacity.



(a) (b)

Figure 4. High-resolution TEM photographs(x 900,000)of acetylene black(a) and plasma black(b)

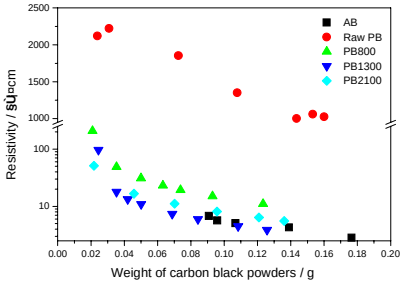


Figure 5. Volume resistivity of packed bed carbon black powders, AB(acetylene black), PB(plasma balck) and heat treated samples at 800℃, 1300℃, 2100℃.

Conclusions

An environment-friendly process for hydrogen and carbon black from natural gas was developed by microwave plasma and catalytic reaction. The high frequency discharge is an effective method to decompose methane to hydrogen and carbon black in the present catalyst. The catalytic reaction enhances the decomposition of methane to hydrogen and carbon black due to abstract more hydrogen electron from methane as activating the reaction of radicals. The plasma process appears to have better than conventional hydrogen production processes. And the performance of plasma black has almost the same electronic resistivity with that of acetylene black.

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References

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