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Conversion of natural gas to hydrogen and carbon black by plasma and application of plasma carbon black

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Abstract

In a microwave plasma-catalytic system, methane decomposition was carried out with 2.45 GHz microwave plasma and then the high conversion and yield of hydrogen and carbon black were obtained efficiently. It was found that hydrogen and carbon black were produced at the mole ratio of 2:1, and carbon black of around 30 nm was produced, which is comparable to classical furnace black. In a study of catalyst effect, Pt-loaded catalysts showed higher activities than a Pd catalyst for the conversion of methane by plasma-catalytic process. The productivity of carbon black increased with platinum loading up to 3 wt.%.

Keywords: Microwave plasma; Plasma-catalytic reaction; Hydrogen; Plasma carbon black; Platinum

1. Introduction

The direct conversion of methane, which is the main component of natural gas, using various plasma technologies has widely been studied in order to obtain more valuable chemical products. During last decade, the new idea of manufacturing high value-added chemicals could have been achieved by the plasma-catalytic methane conversion [1].

The existing method that has been used to produce hydrogen from methane has significant effect on the global warming, since it releases CO_2 while producing hydrogen due to mixing methane with water and to increase of the reaction temperature. Therefore, the development of environmentally friendly method of producing hydrogen is very helpful in the aspect of preventing global warming and saving energy. When the current plasma is used to produce hydrogen and carbon black, it has been reported that CO_2 emission as well as the production energy will decrease [1,2].

The term ''carbon black'' refers to a group of industrial products involving furnace black, lampblack, channel black, thermal black and acetylene black processes, and it represents 95% of world production and consumes primarily petroleum byproducts [3]. Carbon black is widely used as filler in elastomers, plastics and paints to modify the mechanical, electrical and optical properties of materials in which they are dispersed and consequently determine their applications. Recently, it is more important raw material as a conductor in commercial cells, especially secondary lithium battery [4,5].

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 [2]. In our plasma system of high power discharge, carbon black and hydrogen is produced by the decomposition of methane, which nearly resembles thermal cracking. Hence, the plasma carbon black process is the new process for the manufacture of carbon black by plasma technology.

Since 1980s, many research efforts have been made to develop processes for direct conversion of methane, main component of natural gas, into more valuable hydrocarbons [6–8]. Methane is very stable due to the strength of C–H bond. Therefore, high temperature catalytic reactions of direct methane conversion lead to poor economics associated with a low yield of the specific chemical feedstock. It may be assumed that decomposition of

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methane produces hydrogen and carbon black by the following single reaction:

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

According to Fulcheri and Schwob [9], the total enthalpy of methane decomposition at 1873 °C is 182.7 kJ/mol, and the energy related to carbon mass varies approximately between 4 and 7 kW h per kg of carbon produced or 1 and 1.9 kW h per normal cubic meter of hydrogen produced.

In this study, we discussed the decomposition of methane by microwave plasma and the possibility of application to CO_2-free hydrogen production. Also, the effective use of carbon as an additive to lithium cells in order to determine the electrochemical characteristics of the electrode was investigated.

2. Experimental

Fig. 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. Prior to characterization and plasma-catalytic reactivity measurements, samples were annealed at 473 K in the presence of N_2. To generate hydrogen and carbon black from methane, plasma-catalytic reactions were carried out with the microwave plasma (2.45 GHz, iplas Co.). Before plasma-catalytic reaction, the system was evacuated by vacuum pump down to 10^{-5} Torr. The honeycomb type catalysts such as palladium and platinum were used and the diameter of honeycomb is almost 4.5 in. These catalysts were placed in the middle of reactor, designed specially. The reactor of 6 in. o.d. quartz tube was connected to a microwave waveguide and resonator as shown in Fig. 1. Mass flow controller (MFC) controlled the flow rate of natural gas and hydrogen gas into the plasma reactor. In order to find out the effect of addition of hydrogen, hydrogen was used as the plasma gas and the supply line of hydrogen installed at the top of microwave plasma-catalytic system. We analyzed the reaction product (hydrogen and others) by thermal conductivity analyzer (Teledyne, 2000A-EU). To analyze C_{2+} products, they were collected in the liquid nitrogen trap during the reaction and then vaporized into a bulb of known volume at room temperature. Eq. (1) is used to calculate the conversion or H_2/C_{2+} selectivity.

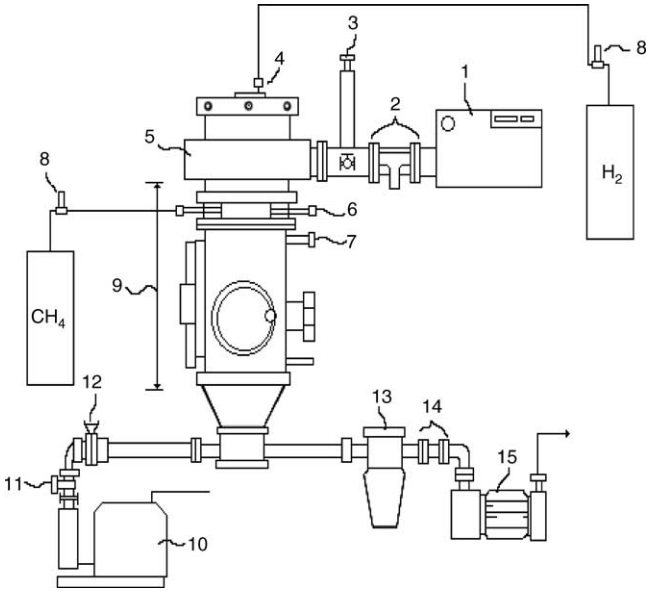

Fig. 1. Experimental set for microwave plasma and catalytic reaction process. Magnetron (1), waveguide (2), E–H tuner (3), microwave quartz tube (4), plasma generator (5), jet inlet nozzle (6), cooling line inlet (7), MFC (8), microwave plasma reactor (9), vacuum pump (10), control valve for pressure (11, 12), cyclone (13), filter (14), mechanical diaphragm pump (15).

$$\text{Conversion (or selectivity)} = \frac{2M_{H_2/C_{2+}}}{M_{CH_4}} \quad (1)$$

where $M_{H_2/C_{2+}}$ is the mole of the H_2 or C_{2+} products and M_{CH_4} is the mole of input methane.

Typical reaction conditions are 100–300 Torr of pressure, 1–5 kW of input power and 0.5–10 l/min of flow rate.

The microstructure and morphological properties of carbon black were examined using transmission electron microscope (TEM) and scanning electron microscopy (SEM), while the physical properties and the thermal decomposition behavior were studied by BET (Quantachrome Instruments, Autosorb-1) and thermogravimetric analysis (TGA, TA Instruments, SDT2960).

The electrochemical performance of carbon material was assessed by cyclic voltammetry (CV) using the method described in Ref. [10].

3. Results and discussion

Conversion and selectivity of hydrogen and carbon black as a function of applied power is exhibited in Fig. 2(a). The conversion of methane obtains up to 96% of a plasma and catalytic reaction at 3 kW of applied power, 100 Torr of pressure and 1.0 l/min of flow rate of methane. Furthermore, the selectivity of hydrogen is from 83 to 95% at above condition. The selectivity with respect to carbon black and hydrogen increases with increasing applied power. When an input of 1 mol of methane was introduced as described in Fig. 2(b), 0.6 mol of carbon and 1.62 mol of hydrogen were produced.

In case of lower plasma power (<3.0 kW), higher C2+ selectivity and lower methane conversion were observed. The C–H bonds of methane in this case are dissociated by plasma and recombined with unsaturated hydrocarbons [1]. Radicals are produced by methane plasma and then recombined each other; therefore, the stochiometric equation of the methane reaction is;

$$2CH_4 \rightarrow \alpha C_2H_6 + \beta C_2H_4 + \gamma C_2H_2 + (\alpha + 2\beta + 3\gamma)H_2 \quad (2)$$

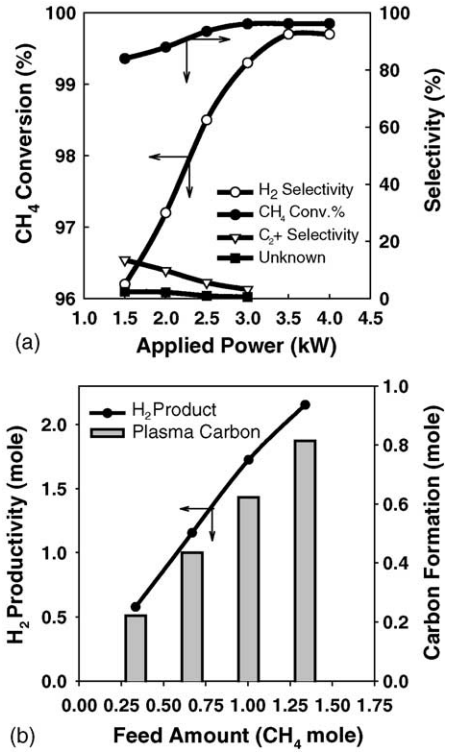

Fig. 2. Conversion and yields of hydrogen and carbon black as a function of applied power (a) and the productivity of hydrogen and carbon as a function of feed amount (b).

where $\alpha + \beta + \gamma = 1$. Otherwise, the selectivity of hydrogen was increased in higher plasma power (>3.0 kW). It seems to dissociate methane completely as increasing the free radicals like acetyl ($CH^{\bullet\bullet}$) and hydrogen radical ($H^{\bullet}$) and produce carbon and hydrogen with increasing plasma power.

The carbon black yield and conversion of methane as a function of methane injection rate in the bench scale reaction appeared in Fig. 3. In general, the calculation of various yield and conversion efficiency (CE) defined below [11]. Only feedstock containing methane (or natural gas) will be considered.

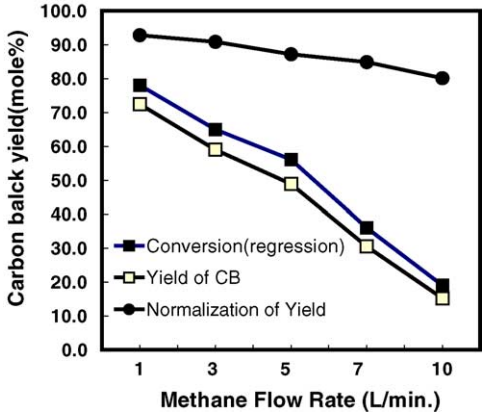

Fig. 3. Carbon black yield as a function of methane feed rate, plasma power is constant at 3 kW.

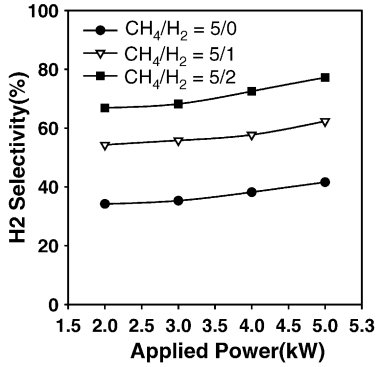

Fig. 4. Effect of reuse of hydrogen produced from plasma reaction.

Conversion efficiency (CE) is defined as

$$\mathrm{CE} = \left[1 - \frac{Q^{\mathrm{P}}_{\mathrm{CH_4}}}{Q^{\mathrm{in}}_{\mathrm{CH_4}}}\right] \times 100 \tag{3}$$

where $Q_{\mathrm{CH_4}}$ is volumetric flow rate of methane at standard temperature and pressure, the superscripts "P" and "in" denote the product stream and process feedstock inflow, respectively. The carbon basis yield (y) is generally defined as

$$y = \frac{\text{mass carbon contained in a particular product}}{\text{mass carbon input in feedstock inlet}} \times 100 \tag{4}$$

The yield of carbon black can be normalized to account for the fact that methane conversion is not complete. In this case, the yield is a measure of carbon black selectivity. The normalized yield is

$$y^{\mathrm{N}}_{\mathrm{carbon}} = \frac{y_{\mathrm{carbon}}}{\mathrm{CE}} \tag{5}$$

At a flow rate of 1.0 LPM, it achieved the maximum conversion of methane and yield of carbon black, the conversion and yield stated to decrease above 1.0 LPM flow rates. At an injection rate of 5.0 LPM, the measured yield has dropped to 50%. Fig. 3 showed the measured yield normalized to account for the measured decrease in conversion efficiency. The normalized yield is a measure of selectivity for conversion to carbon black. This normalization examines a significant portion of the observed decrease in carbon black yield. This represents that even

Table 1
Surface area and average particle size of various carbon black

Carbon black	Surface area (m^2/g)		Average particle size (nm)
	BET	Langmuir	
Thermal black	50–120	75.7–171	40–200
Furnace black	100–200	150–300	20–30 (approximately)
Plasma carbon black	213.23	293.05	20–30

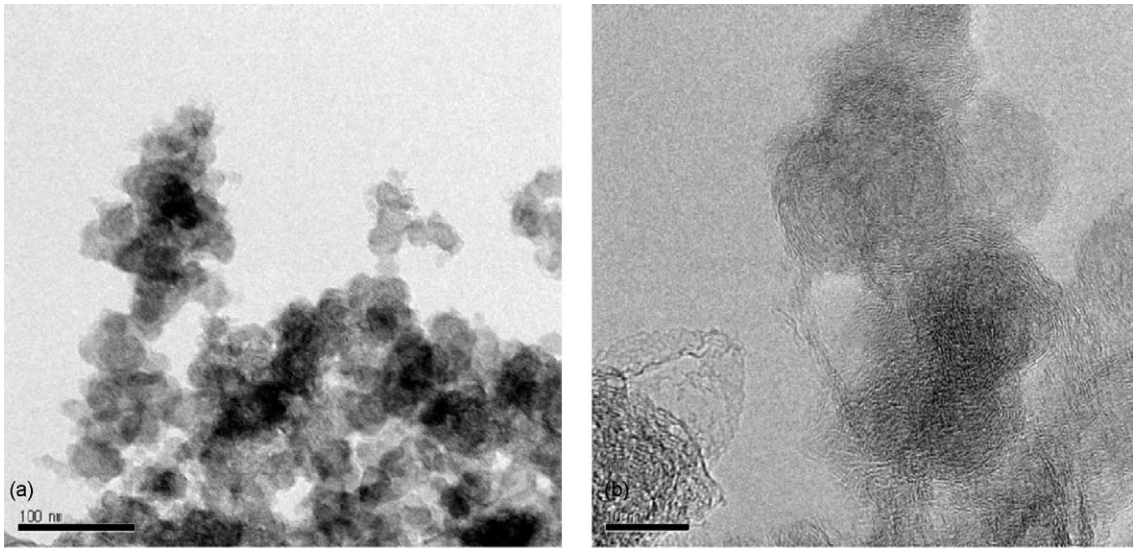

Fig. 5. High-resolution TEM photographs of plasma carbon black (a) and enlargement image (10 times) (b) of the same sample.

distribution of plasma zone or the minimization of the cold boundary layers through improved thermal design must be considered.

Fig. 4 described the effect of recycling of hydrogen as a plasma gas at 300 Torr of pressure and 7 l/min of flow rate in presence of catalyst. According to increase the recycle of hydrogen, the hydrogen selectivity increased. Herein, the appropriate recycle ratio was 30% of hydrogen. Methane decomposition in the plasma-catalytic system generates the methyl radical from collision of methane with electrons, ions and free radicals as well as exited molecules. And microwave field energy allows the catalyst to generate surface electric discharge making methane activated. As to add hydrogen, it considers that the dissociation of methane by collision with hydrogen electron and the recombination were occurred over the catalyst.

In order to investigate the effects of heat treatment on surface area, surface heterogeneity, electrical resistivity and morphology of carbon black, we carried out electrochemical behaviour of the carbon black as a conductor of lithium secondary battery electrode.

The BET surface areas of various carbon blacks as well as plasma carbon black produced by plasma and average particle size were described as shown in Table 1. In order to compare the size, we examined the acetylene black and the plasma black by TEM as shown in Fig. 5. The size of the plasma carbon black was determined by SEM as shown Fig. 6. Fine primary particles of 20–50 nm are identified from TEM in Fig. 5(a), and further example of the concentric, surface parallel orientation of the graphite layers in carbon black is illustrated in Fig. 5(b).

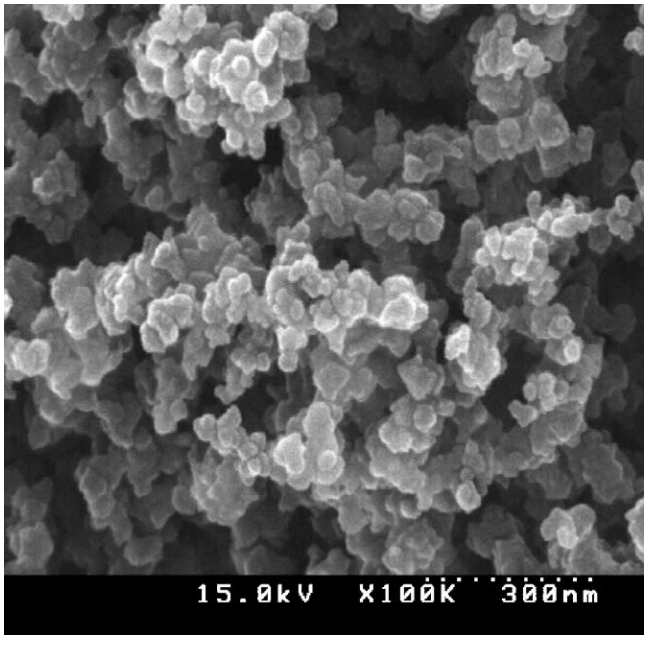

Fig. 6. SEM photograph of plasma black.

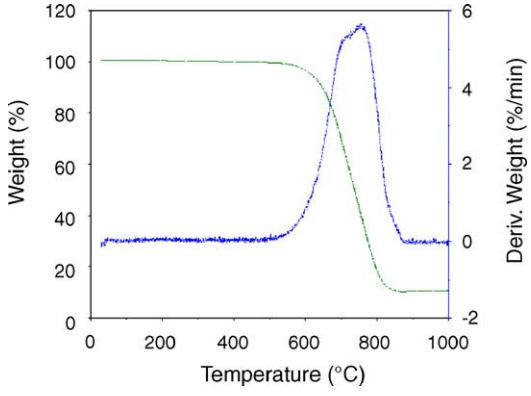

Fig. 7. Result of TG-DTA of plasma black.

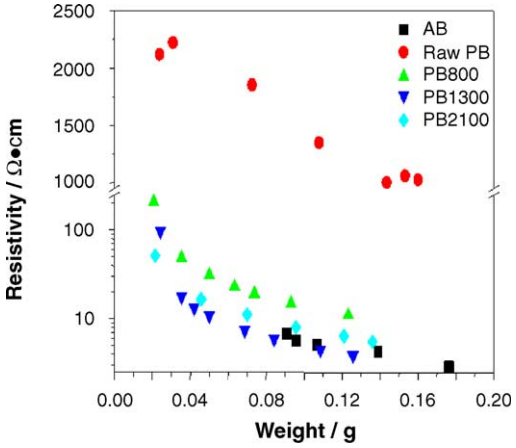

Fig. 8. Electrical resistivity of packed bed carbon black powders, AB, PB and heat-treated samples at 800, 1300 and 2100 °C.

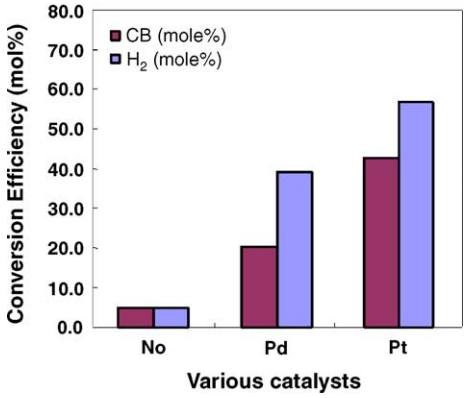

Fig. 10. Productivity of carbon black and hydrogen from methane by microwave plasma and catalytic reaction of Pd and Pt catalyst (plasma power: 3 kW, flow rate: 3 l/min).

SEM of carbon black aggregate is shown in Fig. 6. The fusion of spherical particle is evident in this image.

The results of measurement of BET (213.23 m^2/g) and TGA (Fig. 7) showed that the carbon black by manufactured under a microwave plasma-catalytic reaction system is very similar to classical furnace black. In Fig. 7, there is one significant weight loss, seen 580 °C. This loss corresponds to the decomposition of acetylene black.

Heat-treated carbon black of produced plasma reaction has highest conductivity and highest purity. Four different samples including raw plasma carbon black were added to $LiCoO_2$ to investigate the effects of properties of plasma black as conductors on electrochemical characteristics as shown in Figs. 8 and 9. Plasma carbon black (PB) prepared by plasma process of methane was treated at 800 (PB800), 1300 (PB1300) and 2100 °C (PB2100) under 10^{-2} Torr. In Fig. 8, the resistivity of plasma carbon black decreased with treatment temperature while the conductivity of plasma carbon black increased, and these properties are almost similar to acetylene black. The deterioration of rate capability and cyclability were observed for the plasma carbon black treated at 2100 °C, while the high cyclability of cell was obtained at 800 °C of heat treatment temperature in Fig. 9. Plasma carbon black conductors with low amount of surface functional groups and high electrical conductivity enhanced the cyclability and initial discharge capability [12].

Also, we carried out the experiment for the microwave heating catalysis in order to enhance the performance of methane conversion reactivity. As shown in Fig. 10, Pt catalyst leads to the high reactivity for the conversion of methane under plasma-catalytic process compare to Pd catalyst in condition of 3 kW of plasma power, 5 l/min of flow rate and 300 Torr of operation pressure. Furthermore, under plasma-catalytic reaction, the increasing of platinum loading up to 3 wt.% improved the conversion of hydrogen and carbon black as shown Fig. 11.

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

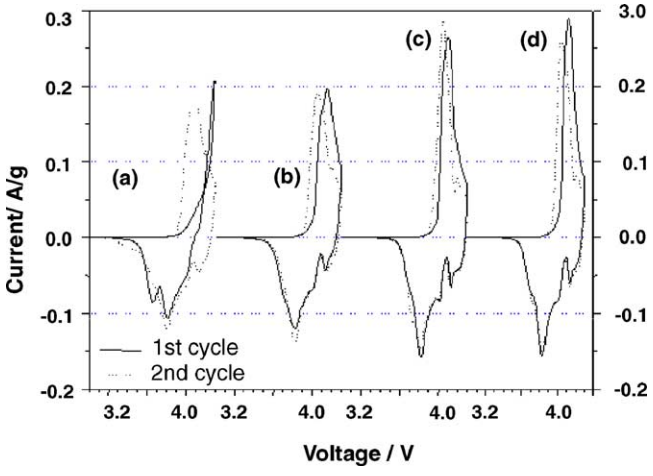

Fig. 9. Comparison of cyclic voltammograms of cathode employed plasma carbon blacks as a conductor in Li/l M-$LiPF_6$in EC: DMC: EMC/$LiCoO_2$ cell (scan rate: 0.1 mV/s, cutoff voltage: 3.0 and 4.3 V). (a) PB, (b) PB800, (c) PB1300 and (d) PB2100.

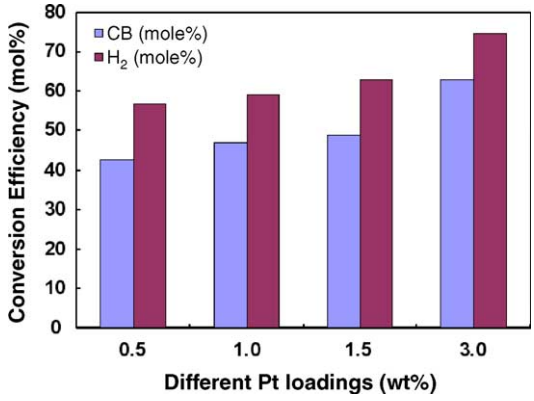

Fig. 11. Productivity of carbon black and hydrogen on Pt catalyst by plasma according to Pt loading amount (plasma power: 3 kW, flow rate: 3 l/min).

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 2:1.

Hydrogen and carbon black production appears to be augmented by the plasma treatment in both the postprocessing and the preprocessing configuration [13]. Plasma-catalytic system in this study is preprocessing configuration because of increasing the yield of hydrogen and carbon black by heating the catalyst region. It seems that the higher catalytic reactor temperature improved the catalyst activity and then enhanced the reactivity of plasma-catalytic reaction.

A detailed study of the mechanisms behind the plasma-catalytic formation of hydrogen and carbon black is presently underway and will be the subject of our future work.

4. Conclusions

An environmentally friendly process for hydrogen and carbon black from methane 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 catalysts. 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.

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