Evaluation of Thermal Plasma Synthesized Catalysts for Methane Pyrolysis

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Abstract: Methane pyrolysis is an endothermic reaction that requires higher reaction temperature and energy. To improve efficiency, synthetic catalysts are generally used in methane pyrolysis. One of the catalysts for methane pyrolysis is transition metals with high thermal conductivity, electric conduction, and 3d orbitals. We synthesized Ni-Co, Ni-CNT, and Cu-CNT using thermal plasma and analyzed methane conversion rate and hydrogen selectivity using them as catalysts for methane pyrolysis.

Keywords: Methane pyrolysis, Synthetic catalyst, Thermal plasma, Alloy, Metal-CNT

1. Introduction

Typical hydrogen production methods have grey, blue, green, and turquoise hydrogen. Most hydrogen is called grey hydrogen, produced through steam methane reforming (SMR) of fossil fuels, either coal or natural gas. Blue hydrogen is applying carbon capture and storage (CCS) to reduce CO_2 emissions by 50-90%. Green hydrogen is eco-friendly that does not emit CO_2, but the production cost is very high. Turquoise hydrogen is production methods like blue and grey hydrogen. However, it is produced solid carbon, not CO_2. One typical turquoise hydrogen production method is methane pyrolysis using an electric furnace. But, methane pyrolysis has high endothermic energy of $CH_4 \rightarrow C + 2H_2$ ΔH=75.6 kJ/mol. Therefore, this process needs a way to reduce the reaction energy and temperature. So, use a catalyst. Commonly used catalysts are transition metals and carbon-based materials. Transition metals have high thermal conductivity, electric conduction, and 3d orbitals. So, there are partially filled and can accept electrons from the C-H bonds of methane. transition metals like Ni, Fe, and Co have been widely studied as active species for methane pyrolysis using an electric furnace. Nickel is less toxic than cobalt and has higher efficiency than iron [4]. Therefore, Ni-based alloys and synthetic composites are mainly used. The methane pyrolysis is usually carried out at 500-700 ℃ with a Ni-based catalyst, 700-900 ℃ with a Fe-based Catalyst, 800-1000 ℃ with a carbon catalyst, and 1100-1600 ℃ with a non-catalytic [4]. Therefore, Ni-based catalysts are mainly used for methane pyrolysis using an electric furnace. But transition metals have lower stability than carbon-based catalysts, which have high stability and low efficiency [1]. So, we synthesized alloys and metal-CNT nanocomposites using thermal plasma for methane pyrolysis. Two types of micro-sized metals can be made into Nano-sized alloys. When metal nanomaterials are attached to the surface of CNT, which is a non-metallic catalyst, catalyst performance can be improved. Stability can be expected to increase at the same time. This study is a more straightforward method than chemical and physical methods. Therefore, this process can produce as inexpensive synthetic material as possible. An electric furnace carried out methane pyrolysis to measure the efficiency of the catalyst.

2. Experimental set-up

The catalysts were synthesized using thermal plasma under the conditions of Table. 1.

The electric furnace for methane pyrolysis has a size of 298 mm in width and 352 mm in length, with a quartz tube having a diameter of 50 mm and a height of 400 mm inside, schematic diagram of electric furnace for methane pyrolysis as shown in Fig. 1.

To evaluate the characteristics of the catalyst, the catalyst was injected into the electric furnace through a powder feeder because transition metals have low stability and tend to aggregate easily at high temperatures. This phenomenon was improved by injecting the catalyst with methane using the powder feeder. The gas after methane pyrolysis was analyzed by gas chromatography (GC, YL-6500), and then the CH_4 conversion rate and H_2 selectivity were calculated.

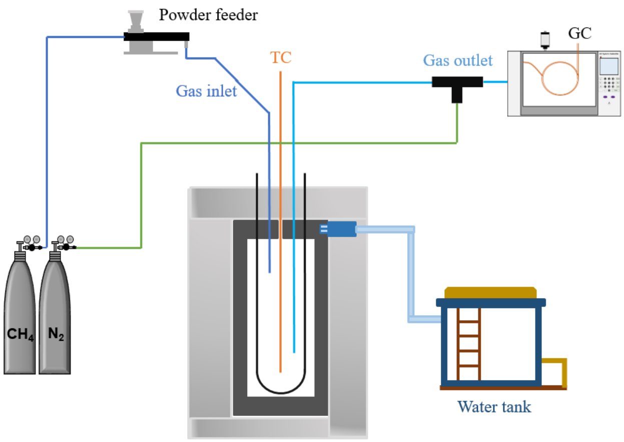

Fig. 1. Schematic diagram of electric furnace for methane pyrolysis.

Table. 1. Condition of synthesis catalyst using thermal plasma.

Gas	Molar ratio	The flow rate of plasma forming gas [L/min]	Plasma input power [kW]	Feeding rate of starting material [g/min]
Ni: Co	7:3	Ar 13, N_2 2	15	1.1
Ni: CNT	2:1	Ar 4, N_2 8	21	0.7
Cu: CNT	2:1	Ar 4, N_2 8	21	0.7

3. Result and discussion

The synthetic catalyst from thermal plasma was analyzed through FE-TEM and EDS.

Fig. 2 confirmed that Ni and Co metals are well synthesized into Ni-Co alloy using thermal plasma. However, a thin oxide layer was formed together [2]. It is judged that Ni-Co has a lower CH_4 conversion rate than Ni because of the formation of such a thin oxide layer. Nevertheless, it can be confirmed that most of the decomposed methane was converted to hydrogen when the Ni-Co catalyst was used.

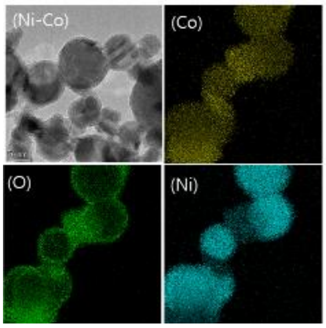

Fig. 2. FE-TEM and EDS image of Ni-Co.

Fig. 3 and Fig. 4 show that metal and CNT are well synthesized into metals-CNT using thermal plasma. However, a thin oxide layer was formed together [3].

When CNT is used in a catalyst, the CH_4 conversion rate and H_2 selectivity tend to be lower than that of the Ni catalyst or Ni-CNT catalyst. However, the case of Ni-CNT has a CH_4 conversion rate a little lower than that of Ni due to the thin oxide layer, but the H_2 selectivity tends to be higher. This seems to be the result of combining CNT's stability and Ni's high efficiency.

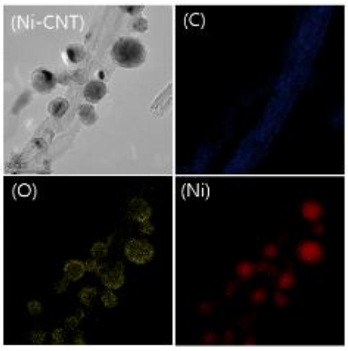

Fig. 3. FE-TEM and EDS image of Ni-CNT.

Fig. 5 shows that the CH_4 conversion rate and H_2 selectivity of methane pyrolysis at non-catalytic, high temperature has high efficiency. Fig. 6 shows the CH_4 conversion rate and H_2 selectivity of methane pyrolysis of each catalyst. The CH_4 conversion rate and H_2 selectivity were compared according to the CH_4 flow rate based on the Ni catalyst. As the CH_4 flow rate increased, the residence time decreased, which reduced the methane pyrolysis efficiency, as shown in Fig. 7. Ni has a high conversion rate than Ni-Co and Ni-CNT because Ni-Co and Ni-CNT synthesized by thermal plasma form a thin oxide layer in the process of capture after synthesis. It can be seen that the CH_4 conversion rate is lower than that of the micro-sized Ni catalyst, as shown in Fig. 7.

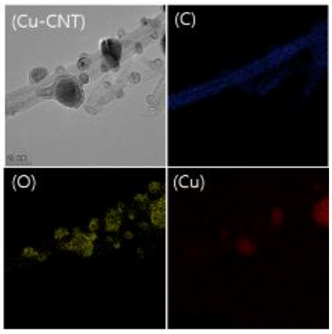

Fig. 4. FE-TEM and EDS image of Cu-CNT.

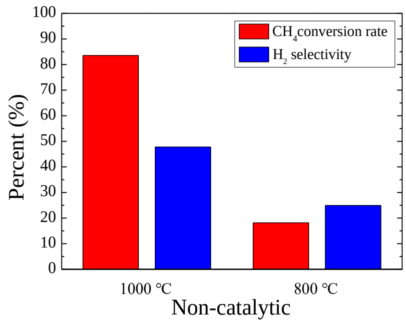

Fig. 5. CH_4 conversion rate and H_2 selectivity as a function of temperature in the non-catalytic.

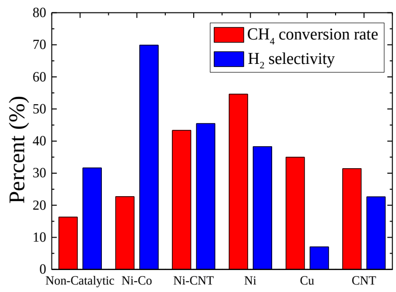

Fig. 6. CH_4 conversion rate and H_2 selectivity of catalysts.

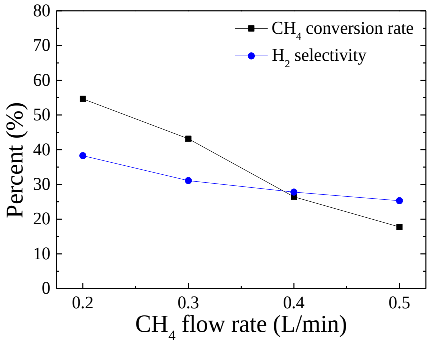

Fig. 7. CH_4 conversion rate and H_2 selectivity as a function of CH_4 flow rate based on Ni catalyst.

4. Conclusion

Compared with the physical and chemical methods, synthesizing the catalyst using thermal plasma has the advantages of low cost and massive production rate. In this work, the catalyst with a uniform size of 20-100 nm has been synthesized by using thermal plasma. Comparing the CH_4 conversion rate and H_2 selectivity of Ni-CNT catalyst has high H_2 selectivity than Ni catalyst. However, Ni-Co has a lower CH_4 conversion rate than Ni catalysts, because of synthetic catalysts, a thin oxide layer was formed during the collecting process, and the performance tended to decrease. In this work, nevertheless this drawback, We can synthesize an efficient catalyst in large quantities at a low cost by the one-step method of synthesis catalyst, and improved this drawback, we can synthesize more efficient catalysts.

References

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