

# Preparation of Porous CNFs by Selective Catalytic Gasification and their Characteristic Evaluation for Supported Catalysts

Jin-sung Jang,<sup>1,2</sup> Seongyop Lim,<sup>1,2</sup> Sang-Kyung Kim,<sup>2</sup>  
Dong-Hyun Peck,<sup>2</sup> Byungrok Lee,<sup>2</sup> Doohwan Jung<sup>1,2</sup>

<sup>1</sup>University of Science & Technology 113 Gwahangno  
Yuseong-gu Daejeon 305-333 Korea

<sup>2</sup>Fuel Cell Research Center, Korea Institute of Energy  
Research 102 Gajeong-ro Yuseong-gu Daejeon 305-343  
Korea

## Introduction

In the catalysts of polymer electrolyte membrane fuel cells, the durability as well as the catalyst activity has been a big issue of fuel cells. There are two reasons of catalyst degradation. The first is metal dissolution. (Including the particle growth) The second is carbon corrosion. Metal dissolution is governed by the interaction between carbon and metal catalysts and the crystallinity of metal. Its cause actual loss of precious metals and also increase of the particle size (Ostwald ripening). On the one hand, the electrochemical corrosion of carbon support is one of challenging issues in the electrode catalysts. Because of generally high crystallinity of carbon for improvement of anti-oxidation properties cannot be obtained by such treatments that make carbon materials of high surface area for high dispersion of catalyst nano-particles. High activity and high durability of catalysts seem to be very contradictory.

In this study, particularly channeled carbon nanofibers (CNF), which were synthesized by selective catalytic gasification [1], were applied to the catalyst. The selective catalytic gasification was adopted to make CNF with high surface area and at the same time.

Composition of methanol oxidation catalyst Pt and Ru used support material. Gasification reactant is nano sized catalyst particle and oxygen was used for selective gasification reaction [2], [3]. The gasification of catalyst made without removal as supported Pt and Ru catalyst.

Effects of the catalyst amount and species on formation of pores (channels) were investigated by TGA and BET. The channel structure was examined by HR-TEM. Also, Cyclic Voltammetry used for activation area of gasified catalysts

## Experimental

### 1. Preparation of carbon nano fibers for gasification

The novel metal supported on CNFs for gasification materials is prepared by impregnation method.

$H_2PtCl_6 \cdot 6H_2O$  (Aldrich) and  $RuCl_3 \cdot 3H_2O$  (Aldrich) were used as the precursors of the catalysts.

The precursors and platelet-CNF were mixed in deionized water. The solution was mixed at room temperature for one day. The metal ions were reduced in the  $NaBH_4$  solution for 1h.

After the impregnation, the catalyst loaded carbon was filtrated and dried at  $70^\circ C$  for 24h.

### 2. Catalytic gasification

The preparation process of the gasification is shown in Fig. 1. The air was used as source for catalytic gasification. PCNF, which is supported by catalyst, measured gasification behavior using by TGA. The result from measurement used gasification temperature ( $450^\circ C$  and  $500^\circ C$ ). The gasification progressed increasing rate of  $7^\circ C / min$  at tube-furnace. Mixed gas maintained for 1hour or 3hour, respectively. The flow rate of  $N_2$  and Air was 150cc/min and 50cc/min, respectively. After the progress, gasification yield has calculated.

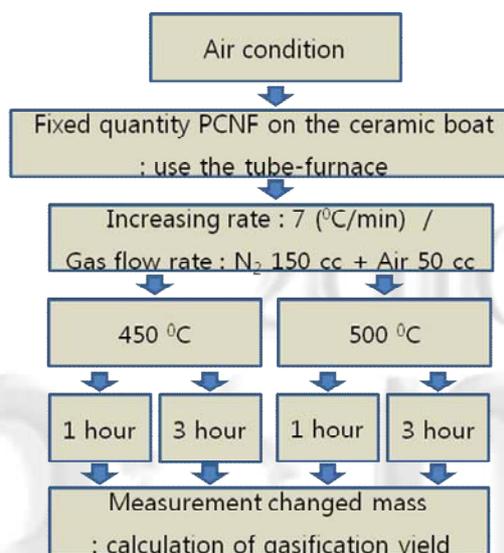


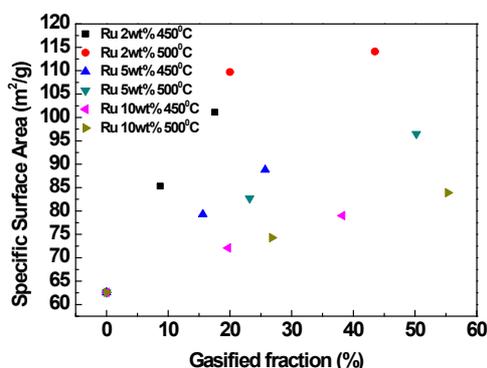
Fig. 1 The preparation process of the gasification.

### 3. Preparation of supported Pt-Ru catalysts for anode of DMFC

The Gasified carbons were mixed with  $H_2PtCl_6 \cdot nH_2O$  (Aldrich) and  $RuCl_3 \cdot nH_2O$ (Aldrich). The mixed solution was stirred over 24hours and the metal ions were reduced in the solution of  $NaBH_4$  for 1h. The molar ratio of  $NaBH_4$  to Ru and Pt metal were 15. After the impregnation, the catalyst loaded carbon was filtrated and dried at  $70^\circ C$  for 24h.

## Results

Fig. 2 shows a specific surface area distribution of PCNF gasified Ru 2,5,10 wt.% by gasified fraction in the air. The x-axis, which represents the amount of carbon consumed gasification, the y-axis is pore size distribution. First,  $450^\circ C$  case, PCNF to start is shown that the constant change rate. However, the more supported Ru amount, surface area increasing rate has been reduced sequentially. Second,  $500^\circ C$  case is shown that thermal oxidation more effect than oxidation by catalytic gasification.

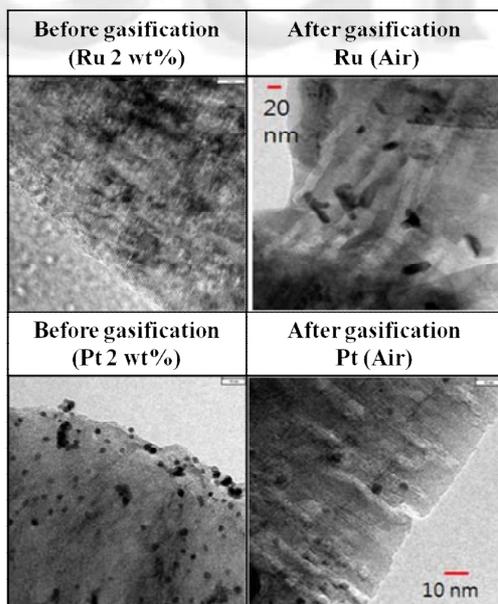


**Fig. 2.** Specific surface area distribution of PCNF gasified Ru 2,5,10 wt.% by gasified fraction (in air).

Fig. 3 shows TEM image of before and after gasification. The catalytic gasification of CNF with novel metal nanoparticles was effective to selectively develop the pore structure in CNF without structural defects forming on unsupported sites of PCNF.

The metallic Ru at the initial state was converted into RuO<sub>2</sub> simultaneously with growth of the particle size (into a rod type) during gasification in the air. The channels were preferentially formed in the direction perpendicular to the graphitic layer, using Ru on PCNF in the air.

On the other hand, the metallic Pt was converted into Pt simultaneously with growth of the general Pt particle size. The channels were formed in the direction parallel to the graphitic layer, using Pt on PCNF in the air.



**Fig. 3.** TEM image of before and after gasification.

## Conclusions

Particularly channeled carbon nanofibers (CNF) were applied to the catalyst support for preparation of highly active electrode catalysts for DMFC. Nano-structured carbons such as carbon were applied as support materials for the anode catalysts in direct methanol fuel cell.

Porous CNFs were prepared through selective gasification of CNF with nano-sized catalyst particles such as Ru and Pt in air. The gasification generated pores whose size corresponds to those of the catalyst particles. The channel length was controlled by the gasification time.

Several kinds of carbon-supported PtRu catalysts were prepared using the porous CNFs prepared in this study, and the catalyst activity for methanol oxidation is on test.

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## References

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