

# ROLE OF METALLIC SALT IN THE EVOLUTION OF PORE CHARACTERISTICS OF CELLULOSIC BIOMASS-BASED POROUS CARBONS

*S.H. Lee, C.R. Park, and C.H. Yun\**

*Enviro-Polymers Design Lab., Hyperstructured Organic Materials Research Center, and School of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea*

*\*School of Applied Chemistry and Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea*

## Introduction

Porous carbons can be manufactured from various raw materials such as polymers, coals, and plentiful agricultural by-products. These agricultural by-products are attractive feedstocks because they are inexpensive and abundant [1]. However, lignocellulosic materials have low char yield during heat treatment. Thus, numerous works have been devoted to increase char yield of these precursors. It has long been known that the char yield of cellulosic biomasses can be increased if the formation of levoglucosan is suppressed using various catalysts inclusive of phosphoric acid, sulfuric acid, etc.

In recent, it has been suggested that pore structure and size can be controlled by various methods of which examples include using ceramic template or metallic ions serving as pillars [2]. Thus, it was the aim of this work to study the impregnation effect of metallic salts that are expected to function as both catalysts and pillars on the evolution of pore characteristics of cellulosic biomass-based porous carbons.

## Experimental

Rice straws, chosen as cellulosic biomass precursor material, were chopped to 3cm in length and impregnated with  $\text{FeSO}_4$  (denotes as RFS) and  $\text{H}_2\text{SO}_4$  (denotes as RFS-HS) for 2hrs. Impregnated samples were carbonized at 1000 under  $\text{N}_2$  atmosphere (denotes as RFSC10). RFSC10 was subsequently washed with nitric acid solution (13vol.%) for 30mins at 40 (denotes as RFSC10Aw). Thermal degradation behavior of samples was examined by TGA (SEIKO, TGA/DTA220, Japan) and the pore characteristics were determined from  $\text{N}_2$  adsorption isotherms at 77K monitored on an automatic adsorption instrument (Micromeritics, ASAP2010, USA). The morphologies of samples were monitored by TEM (JEOL, TEM-200CX, Japan) and X-ray diffractometer (Mac Science Co., MXP 18XMF22-SRA, Japan).

## Results and Discussion

The thermal degradation behaviors of rice straws impregnated with  $\text{FeSO}_4$  together with additional acids were examined on TGA and the resulting thermograms were shown in Figure 1. It can be seen that the char yield tends to increase with increasing strength of acid, and the highest char yield is obtained when rice straws were treated with  $\text{FeSO}_4$  and an additional drop of  $\text{H}_2\text{SO}_4$  (RFS-HS samples). On the other hand, rice straws treated with  $\text{H}_2\text{SO}_4$  only or  $\text{FeSO}_4$  only have lower char yield than RFS-HS. It is considered that sulfuric acid facilitates the dissociation of  $\text{FeSO}_4$  in water solution. In this case, proton and sulfate ions promote the dehydration reaction of rice straws and result in the formation of dehydrated cellulose structure that gives rise to higher char yield [3].

Pore size distributions of carbons were shown in Figure 2. RFSC10 has the bimodal pore size distribution which consists in sharp intensity of pore diameter of 3nm and around 20nm. On the other hand, when RFSC10 was treated with nitric acid, the pores of the diameter of both 3 nm and above 20 nm disappear with concurrent appearance of the pores with the diameter of around 10nm.

By the impregnation with  $\text{FeSO}_4$  onto rice straws, Fe ions can react with hydroxyl functional groups on the surface of rice straws as well as in-between cellulose chains. During carbonization, Fe ions are oxidized and act as pillars between carbon layers, resulting in well-controlled pore size of carbons.

On a subsequent acid treatment, most of the crystal domains of metallic oxides were washed out from the carbon structure. However, it might be difficult for the Fe oxides located between the carbon layers to be dissolved out by acid. Indeed, from XRD patterns in Figure 3, it can be clearly seen that after acid washing, the XRD pattern attributed to diffraction of  $\text{Fe}_3\text{O}_4$  remained the same as that of RFSC10. Thus, the pores of around 10nm in diameter were formed by the pillar effect of  $\text{Fe}_3\text{O}_4$  between carbon layers. And it is considered that the pores with 3nm and larger than

10nm are originated from the voids in the self-aggregated  $\text{Fe}_3\text{O}_4$  crystals.

### References

- [1] Yun CH, Park YH, Park CR. Effects of pre-carbonization on porosity development of activated carbons from rice straw. *Carbon* 2001;39(4):559-567.
- [2] H. Nakagawa, K. Watanabe, Y. Haroda, K. Mura. Control on micropore formation in the carbonized ion exchange resin by utilizing pillar effect. *Carbon* 1999;37(9):1455-1461.

- [3] M. Jagtoyen, F. Derbyshire. Activated carbons from poplar and white oak by  $\text{H}_3\text{PO}_4$  activation. *Carbon* 1998;36(7-8):1085-1097.

### Acknowledgments

This work was financially supported by Korea Science and Engineering Foundation (KOSEF) and the Hyperstructured Organic Materials Research Center (HOMRC) at Seoul National University (SNU).

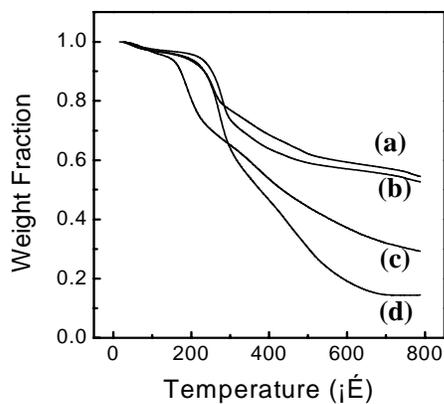


Figure 1. TGA thermograms of rice straws impregnated with (a)  $\text{FeSO}_4+\text{H}_2\text{SO}_4$ , (b)  $\text{FeSO}_4+\text{HCl}$ , (c)  $\text{H}_2\text{SO}_4$ , and (d)  $\text{FeSO}_4$ +acetic acid.

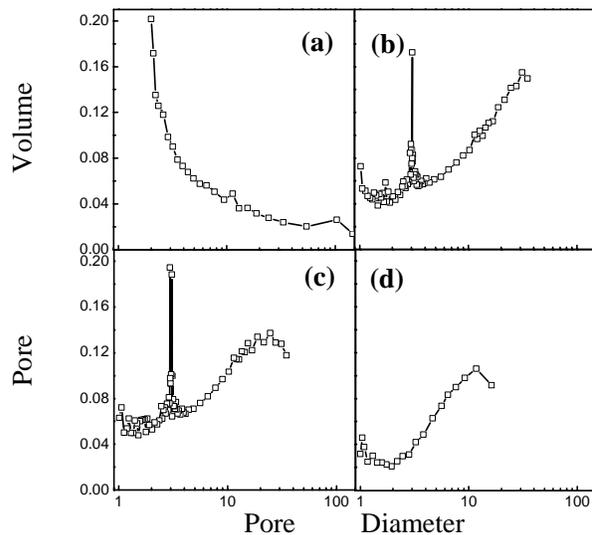


Figure 2. Pore size distribution of (a) rice straws, (b) RFSC10, (c) RFS-HSC10, and (d) RFSC10Aw.

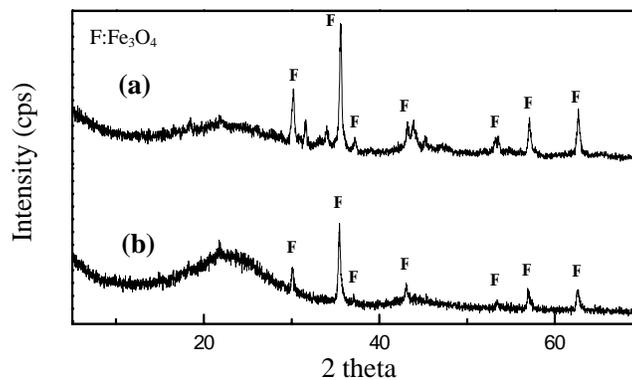


Figure 3. X-ray diffractograms of (a) RFSC10 and (b) RFSC10Aw.