

분위기 기체가 벗짚 활성화탄소의 표면 특성에 미치는 영향

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Effect of Environmental Atmospheres during Heat-treatment on Surface Characteristics of Porous Carbons from Rice Straws

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1. Introduction

The pore structure and surface properties of porous carbon can be controlled by the preparation conditions. The partial gasification of char with steam or CO₂ can create and/or destruct pores in the porous carbon in the way of opening constriction and widening of existing micropores [1]. It has been reported that the steam activation occurs mainly in the external parts of carbon, leading to increase mesoporosity, on the contrary, the CO₂ activation occurs by creation of new micropores as well as coalescence of existing micropores [2].

Recently, phenolic resin as precursor was heat treated under N₂ or CO₂ atmosphere and subsequently oxidized under acid solution [3]. It was found that the adsorption capacity of the sample carbonized under CO₂ decreases, however, that under N₂ increases with the treatment of acid solution. This indicates that the environmental atmospheres during carbonization influence the porosity evolution of resultant porous carbons. Even though numerous works have been devoted to investigate the different effects caused by the environmental atmospheres e.g. N₂, steam and CO₂ in the porosity development [4], surface properties of the resultant porous carbons have not been clearly studied. Thus, the aim of this work is to investigate the effect of environmental atmospheres on surface characteristics of porous carbons from rice straws.

2. Experimentals

2.1. Preparation of porous carbons

Rice straws chopped to 3cm in length were heated with 10°C/min to 800°C under N₂ or CO₂ atmosphere and kept under steam or CO₂ atmosphere for 1-3hrs. After heat treatment, furnace was cooled to room temperature under N₂ or CO₂ atmosphere.

2.2. Characterization

The BET surface area, the mean pore diameter, and the pore size distribution were obtained on Micromeritics instrument (ASAP 2010) by adsorption of N₂ at 77K. The effect of the environmental atmospheres on the gasification behavior of rice straws was examined by using Hi-Res TGA (Dupont, Hi-Res TGA 2950). The evolution of functional groups and the structural changes were monitored by FT-IR (Perkin Elmer, FT-IR Spectrometer Spectrum 2000), Boehm's method [5], and X-ray diffractometer (MXP 18XMF22-SRA).

3. Results and Discussion

3.1. Surface characteristics

In order to elucidate the formation of the surface functionality on samples prepared under various environmental atmospheres, the surface functionality change was monitored by Boehm's method, and shown in Figures 1 and 2, respectively. In the case of N₂ carbonization, the surface basicity increases with increase of carbonization temperature due to the removal of the heteroatoms by the devolatilization of nitrogen- and oxygen-containing compounds such as carboxylic and lactonic groups (Figure 1(b)). On the other hand, the surface basicity of samples carbonized under CO₂ tends to decrease. It is considered that the surface oxide groups such as carboxylic and lactone groups are introduced in the way of thermal reaction of carbon surface with CO₂. However, after activation the porous carbons prepared under CO₂ atmosphere show more acidic surface functionality in comparison with those under steam atmosphere. This trend can be explained by the reactivity of different activation agents. As steam has a higher reactivity than CO₂, it would favour for steam to decompose mainly both carboxylic and lactone type groups, and create phenol type groups, resulting in pyrone-type structures with a greater ability to donate electron pairs and behave as Lewis bases. On the other hand, as CO₂ is less reactive than steam, it would attack only carboxylic type groups instead of lactone type groups, which causes carbon surface to become more acidic in comparison with steam activation. When compared to the

effect of carbonization atmospheres on surface functionality of porous carbons, in the case of CO₂ activation, N80C3 (combination of N₂ carbonization and CO₂ activation) shows more acidic character than C80C3 (combination of CO₂ carbonization and CO₂ activation). However, in the case of steam activation, the opposite phenomenon was observed (C80S3 has more acidic character). This indicates that the environmental media during heat treatment play an important role in creating different surface characteristics on the resultant porous carbon, which can show different adsorption properties.

3.2. Porosity evolution

To compare the porosity development of porous carbons obtained under various environmental media, adsorption isotherms are shown in Figure 3. As the activation time increases, in the case of CO₂ activation, the nitrogen uptake of all samples increases due to the formation of pores by pore-drilling and pore-widening. The shape of isotherms of samples carbonized under CO₂ shows Type I, indicative of microporous character. On the other hand, that of samples carbonized under N₂ yields Type IV isotherm, indicating that the micropores as well as mesopores are developed. However, in the case of steam activation, the uptake of nitrogen tends to decrease as the activation time increases. It is considered that since the steam has more power to react with carbon substrate in comparison with CO₂, the pore-widening effect is predominant and would favour gasification in larger pores, giving rise to meso- and macroporosity development. It seems that for steam, micropores are created in the early stage of the activation and destroyed owing to coalescence and transition to larger pores. However, CO₂ seems to facilitate the process of the creation of new small pores, which is subsequently widened to meso- and macropores with increasing time of heat treatment.

4. Reference

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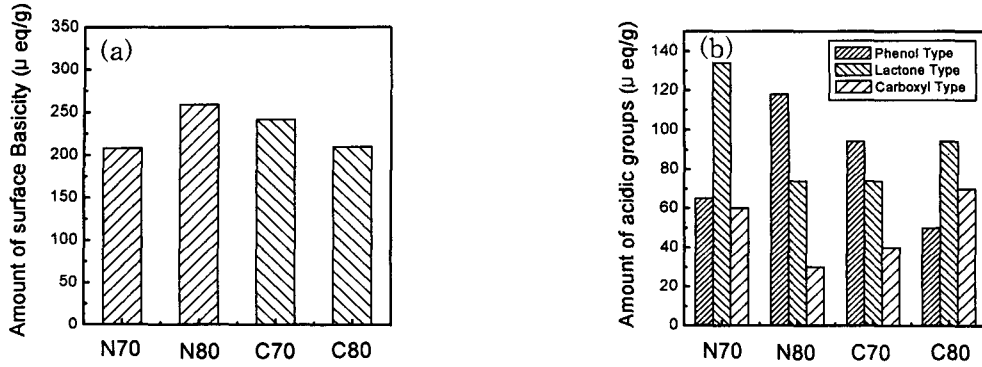


Figure 1. Surface functionality of carbonized samples:(a) surface basicity and (b) surface acidity.

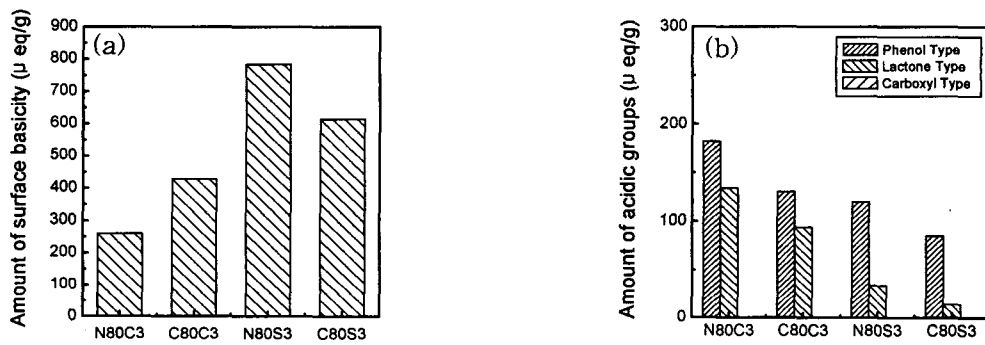


Figure 2. Surface functionality of porous carbons:(a) surface basicity and (b) surface acidity.

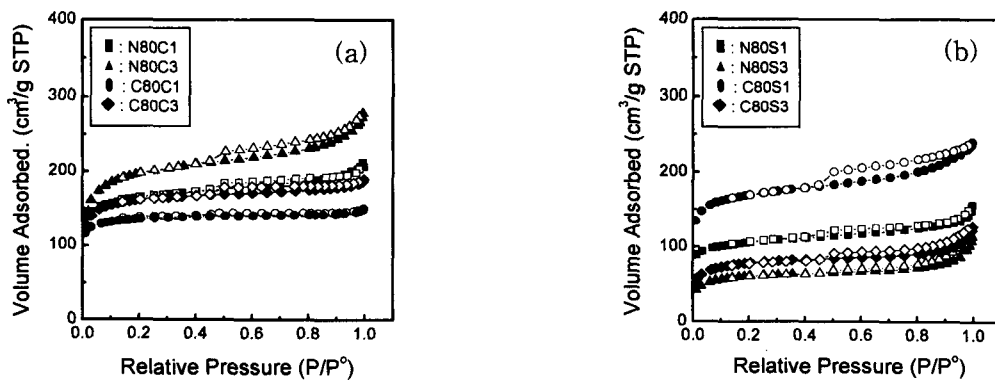


Figure 3. N₂ adsorption/desorption isotherms of porous carbons activated under (a) CO₂ and (b) steam.