

A NEW METHOD FOR CONTROLLING THE PORE STRUCTURE OF POROUS CARBON USING PILLAR EFFECT

K. Miura, H. Nakagawa, K. Watanabe and Y. Harada

*Department of Chemical Engineering
Kyoto University, Kyoto 606-01, JAPAN*

Introduction

Carbon materials having uniform and controlled micropores are required for some applications such as molecular sieving, but methods for controlling the micropore distribution have not been established. Rather empirical and tedious methods have been employed for producing molecular sieving carbon (MSC).

We have previously presented a new and simple method for producing MSC from coal¹⁾ and phenolformaldehyde resin (PF)²⁾. The idea of the methods lies in the modification of coal and/or PF-resin by adding other organics. The methods are, however, still apart from the "synthesis of MSC". In this study, we propose to employ a well defined ion exchange resin as a starting material of MSC, and to control the micropore distributions of the carbonized resin by changing the cations exchanged. The proposed method would be a step for realizing "synthesis of MSC".

Experimental

The raw resin used was a spherical (≈ 0.5 mm diameter) polystyrene based ion exchange resin with sulfonic group as ion exchangeable group. First, the raw resin was treated by 1N hydrogen chloride to prepare H-type resin. Next, the H-type resin was treated by aqueous solutions containing various cations to exchange H⁺ for the other cations. The amount of cation exchanged was controlled by changing the pH of aqueous solutions. Each sample was represented by the kind and the amount (mol/kg-resin) of cation exchanged as Na-4.80, Zn-1.65, etc.. All the resins were dried in a vacuum oven at 70 °C for 1 day before use.

The resins were heated to be carbonized in a nitrogen stream at the rate of 10 °C/min up to a final temperature, T_f , at which they were maintained for 10 min. T_f was changed from 500 to 900 °C. The carbonized resins were characterized by accessible microporous volumes measured by the so-called molecular probe technique³⁾. CO₂, C₂H₆, n-C₄H₁₀ and iso-C₄H₁₀ were used as probe gases. The weight changes and gas formation rates during the carbonization of the resins were measured by use of a

TG-MS.

Results & Discussion

1) Effect of the exchanged cation type on the carbonization behavior of resins

Fig. 1 shows the changes of weight of the resins on cation free basis during the carbonization. The weight decrease profiles were greatly dependent on the kinds of cations exchanged. The weights of H-4.80 and Cu-1.95 decreased rapidly at around 300 °C, while the weights of other samples decreased at 350 to 750 °C. The yields at 900 °C are also dependent on the kinds of cations exchanged, varying from 0.42 for Cu-1.95 to 0.60 for Zn-1.65.

The differences in the weight decrease profiles among the samples are associated mainly with the decomposition behavior of the sulfonates. Then the formation rates of SO₂, a main product during the carbonization, are shown in Fig. 2. The formation rates of other sulfur containing compounds, H₂S, COS, and thiophene, were negligibly small. The peak temperatures of the SO₂ formation rates well corresponded to the temperature ranges at which the sample weight decreased rapidly in Fig. 1. The amounts of SO₂ produced, in other words the amounts of sulfur remaining in the carbonized samples, were also dependent on the kinds of cations exchanged as shown in Fig. 2. The cation except Cu²⁺ would prevent the decomposition of sulfonic groups. These results show that the carbonization behavior of the resins is significantly altered depending on the cations exchanged, and they well suggest that the micropores in the carbonized samples are also altered depending on the cations exchanged.

2) Effect of the exchanged cation type on the development of micropores

Fig. 3 shows the accumulated pore volume distributions of the samples carbonized at 900 °C. The distributions were significantly different among the samples as expected. Total micro-pore volumes of the samples prepared from the resins having di- or trivalent cations reached 0.12 ~ 0.15 cc/g, whereas those of the samples prepared from the resins having univalent cations were less than 0.04 cc/g. The

size of pore apertures shifted from 0.38 to 0.45 nm depending on the cations for the samples prepared from the resins having di- or trivalent cations. The pore apertures of Ni-1.82 and Cu-1.95 were almost uniform, whereas the aperture of Zn-1.65 was rather large and broad. Thus it was found that the micropore distributions of the carbonized resins can be controlled by changing the kinds of cations exchanged.

3) Role of cation on the development of micropores

Since the mechanism of the pore development, in other words the role of cation on the pore development, is of great concern, we have examined the changes of cation and sulfur during the carbonization in detail. X-ray diffractometry showed the existence of sulfides for the carbonized Ca-2.17 and Zn-1.65. Distinct X-ray diffraction peaks associated with crystalline metal appeared for only the carbonized Cu-1.95. XPS analysis showed the existence of some organic sulfur compounds in the carbonized Ca-2.17 and Zn-1.65. Fig. 4 shows the TEM images of Ni-1.82, Cu-1.95, and Zn-1.65 carbonized at 900 °C. Metals were found to be highly dispersed and to remain as particles of several nm.

Summarizing these results and above discussion, we can say that the cations in the resin affected the decomposition of sulfonates differently, leading to the different carbonized products. The metals and/or the sulfur remaining in the carbonized samples surely play significant roles on determining the micropore distributions. Pillar effects of the metals and/or the sulfur would be well expected.

This contribution clarified that the carbonization of the resins having different cations can be a method to control the micropore distribution and be a method for producing a tailored MSC. As an additional merit the samples prepared from the resins having di- or trivalent cations are hard and spherical particles. This is advantageous from practical view point.

Acknowledgements

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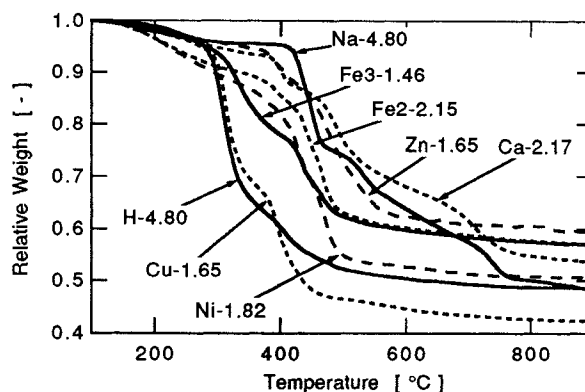


Fig.1 Weight Changes during carbonization

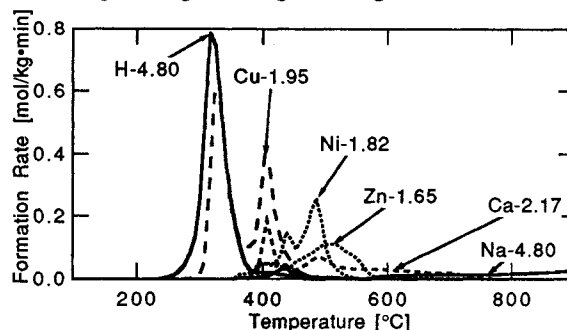


Fig.2 Formation rates of SO₂ during carbonization

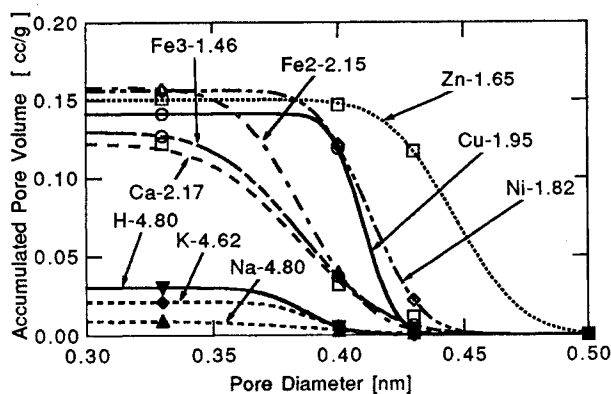


Fig.3 Micropore distributions of resins carbonized at 900 °C

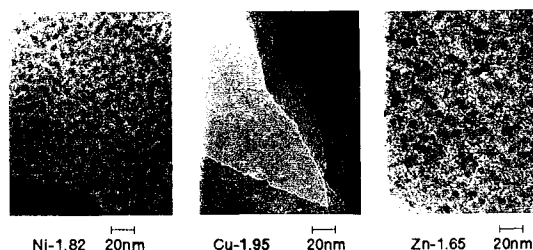


Fig.4 TEM images of resins carbonized at 900 °C