

THE EFFECT OF STABILIZATION DEGREE ON THE CARBONIZATION AND ACTIVATION BEHAVIOR OF THE PITCH BASED ACTIVATED CARBON FIBER

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Introduction

Activated carbon fiber (ACF) has very high surface area and high adsorption-desorption rate compared with conventional activated carbon. Pitch-based ACF is typically produced through the pretreatment of a pitch, melt spinning of the pitch to form fiber, stabilization of the fiber, and carbonization and activation of the stabilized fiber. The fiber can be carbonized without melting only when it is stabilized beforehand. The stabilizing method most commonly employed is oxidation in air at less than 350 °C. The stabilization process of pitch fiber is well known to affect the carbonization and the activation processes. In this study the effect of stabilization degree on the carbonization and the activation behaviors was examined by utilizing various stabilized fibers prepared by changing the stabilization conditions.

Experimental

A pitch fiber prepared from a petroleum isotropic pitch was used as the raw material in this study. The diameter of the pitch fiber was about 15 μm . Its ultimate analysis is given in Table 1. It was oxidized in an air stream to prepare stabilized fibers of different stabilization degree, SF1, SF2 and SF3. Stabilization condition was changed for this purpose as given in Table 2. The ultimate analyses of the stabilized fibers are also listed in Table 1. The yield of the stabilized fiber increased with the increase of the degree of stabilization due to the uptake of oxygen.

Each stabilized fiber was heated in a nitrogen stream at the rate of 10 K/min up to 950 °C at which it was maintained for 10 min to be carbonized. Then the carbonized fiber was activated at 900 °C by steam of 0.5 atm of pressure at 900 °C to prepare ACFs of different activation levels.

The micropore volume distributions of the ACFs were estimated from adsorption isotherms of N_2 at 77K by use of the Dollimore and Heal method¹⁾. On the other hand, the micropore volume distributions of the carbonized fibers were estimated by the molecular probe technique²⁾. Adsorption isotherms of CO_2 , C_2H_6 , $n\text{-C}_4\text{H}_{10}$ and $\text{iso-C}_4\text{H}_{10}$ at 25 °C were used for this purpose. Each isotherm was analysed by the Dubinin-Astakhov equation³⁾ with $n=2$ to obtain limited micropore volume of each gas.

Results and Discussions

1) Carbonization behaviour of the fibers

Fig. 1 shows the weight changes of the pitch fiber and stabilized fibers during the carbonization, where the weight was normalized by the weight of the pitch fiber. The

weight of pitch fiber decreased slightly at around 250 °C, followed by the significant weight decrease at around 450 °C. At 450 °C pitch fiber was found to melt completely. A fairly large amount of tar is supposed to evolve in this temperature range. The yield of the carbonized fiber at 900 °C was 0.58. In the case of stabilized fibers, the weight decreased gradually from 300°C to 900 °C and the yield at 900 °C was much higher than the yield of the carbonized fiber prepared from pitch fiber, ranging from 0.7 to 0.8. This result clearly indicates that stabilization process increase the solid yield, although the yield of SF3, where the stabilization degree was the highest, was lower than that of SF2.

To examine the carbonization behavior in more detail, gas formation rates of H_2O , CO , CO_2 , CH_4 and H_2 were measured continuously by use of a mass spectrometer (Nichiden Anelva, AGS-211R). Fig. 2 shows the formation rates of CO , CO_2 and CH_4 during the carbonization of SF1 and SF3. The formation rate of CH_4 had a maximum at around 600 °C and it was much larger than the formation rates of CO and CO_2 for SF1, whereas the formation rate of CH_4 was much smaller than the formation rates of CO and CO_2 for SF3. The formation of CH_4 during the carbonization comes from the decomposition of aliphatic groups and the formations of CO and CO_2 come from the decomposition of oxygen containing functional groups such as carbonyl or carboxyl groups. Above result indicates that aliphatic groups were oxidized to form carbonyl and carboxyl groups during the stabilization. There also appeared a significant difference between SF1 and SF2 in the amounts of tar formed during the carbonization. The amount of tar formed during the carbonization of SF1 was 0.199 g/g-pitch fiber, which corresponded to 67% of total weight loss, whereas the amount of tar formed during the carbonization of SF3 was only 0.07g/g-pitch fiber. From the results of TG and MS analyses, it was clarified that stabilization of pitch fiber suppressed the formation of tar during the carbonization, resulting in high solid yield. However, excess stabilization decreased the solid yield by producing a large amount of CO and CO_2 during the carbonization as the result for SF3 indicated.

2) Micropore structure of the carbonized fiber

Fig. 3 shows the accumulated micropore volume distributions of the fibers after carbonization. Micropore diameter of all the carbonized fiber was less than 0.5 nm. Total micropore volume increased with the increase of stabilization degree, although the difference in the distributions among the samples was not so significant.

3) Activation rate of stabilized fibers

The activation of carbonized fibers was performed by use of TG in this study, therefore the weight change could be monitored continuously. Fig. 4 shows the weight change of the carbonized fibers during the activation. The weight decreasing rate, that is activation rate, of the carbonized fiber increased with the increase of degree of stabilization. This result indicates that the burn-off level based on carbonized fiber is dependent on the stabilization degree under the same activation condition. For example, the burn-off levels of the ACFs prepared from SF2 and SF3 are 0.36 and 0.40, respectively, when they are activated for 20 min.

4) Micropore structure of the activated carbon fiber

Fig.5 compares the accumulated micropore volume distributions of the ACFs at two burn-off levels of 0.3. The micropore volume distributions were not significantly different between the ACFs at same burn-off levels. The BET surface area of the ACF prepared from SF3 was about 10% larger than that prepared from SF2.

Conclusions

Stabilization of pitch fiber increased the carbonization yield. However, excess stabilization decreased the yield. Activation rate of carbonized fiber and BET surface area of ACF increased with the increase of the stabilization degree. In summary, it is important to control the stabilization degree for increasing productivity of ACF and to produce high quality ACF.

References

- 1) Dollimore D, Heal GR, J. Appl. Chem., 1964;14(3):109
- 2) Lamond TG et al., Carbon, 1965;3:59
- 3) Dubinin MM et al., J. Colloid Interface Sci., 1980;75:34.

Table1 Ultimate analyses of pitch and stabilized fibers[wt%]

	C	H	N	O(diff.)
Pitch fiber	92.2	5.6	1.7	0.5
SF1	87.0	4.3	1.8	7.9
SF2	83.9	3.8	2.1	10.2
SF3	71.6	2.2	2.2	24.0

Table 2 Stabilization condition of pitch fiber and the yield

	a	T _f	T _h	y
SF1	3.0	265	0	1.028
SF2	3.0	300	0	1.048
SF3	1.0	320	60	1.066

a : heating rate [°C/min] T_f : final temperature [°C]
T_h : holding time [min] y : yield [g/g-pitch fiber]

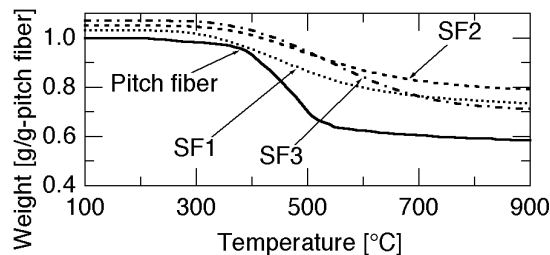


Fig. 1 Weight changes of stabilized fiber during the carbonization.

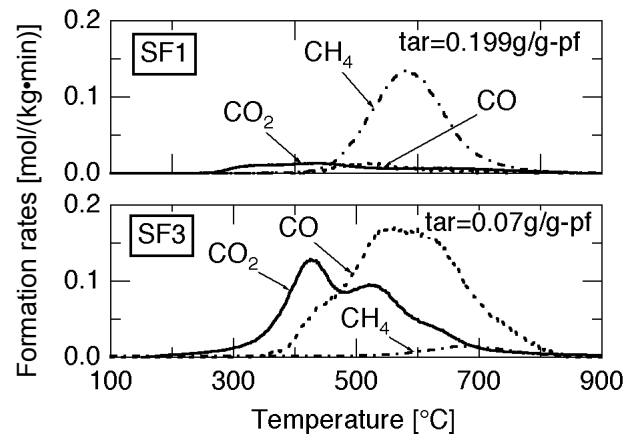


Fig. 2 Formation rates of CO, CO₂ and CH₄ during the carbonization for SF2 and SF3.

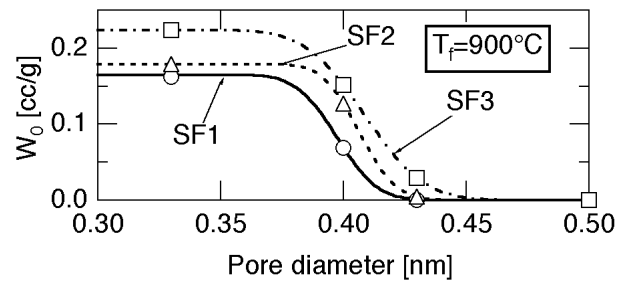


Fig. 3 Accumulated micropore volume distributions of carbonized fibers.

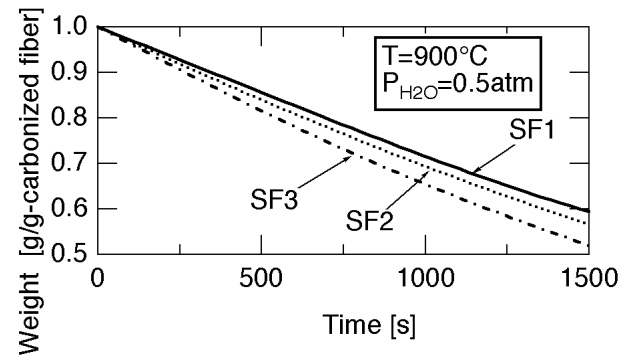


Fig. 4 Weight changes of carbonized fibers during the activation by H₂O (P=0.5atm) at 900 °C

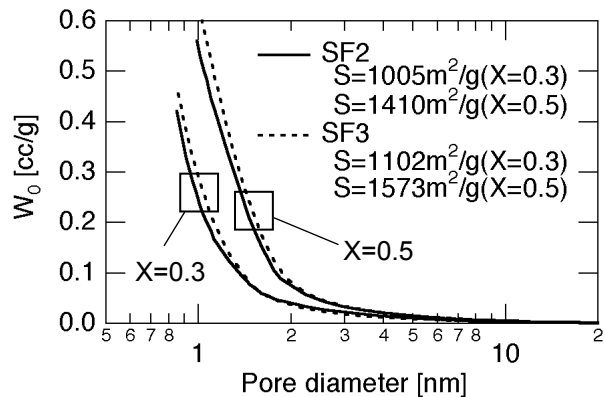


Fig. 5 Accumulated micropore volume distributions of ACFs prepared from SF2 and SF3.