KOH RECYCLE PROCESS FOR REPEATING ACTIVATION OF MESOPHASE PITCH BASED CHOPPED CARBON FIBER

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Introduction

There are numbers of papers on the activation of carbon into porous one of high surface area. Among the activation procedures, activation with KOH has been reported to provide the largest surface area over 2000m2/g [1]. One-pass use of KOH increases the cost. Repeated use of KOH is the key point to be developed. In the present study mesophase pitch based carbon fiber was activated to prepare active carbon fiber with high graphitability and large surface. Hence a process of activation, trap and regeneration was examined to design the repeated use of KOH where KOH oxidizes the fiber to be reduced into metallic K, vaporizing to be trapped by down stream fiber which was oxidized back into KOH on the fiber by steam for the second activation of trapping fiber. Figure 1 describes the concept for recycle use of KOH in the present study.

Experimental

Figure 2 illustrate the reactor of the present activation. The sample was mesophase pitch based chopped fiber (carbonized at 650℃). 0.6g of CF and KOH 2.4g were placed in the bottom of the reactor. Another package of CF was placed in the upper part or down stream of the reactor as a trap. Activation conditions were temperature 800 or 700℃, holding times 1～7h, gas flow rate 0.6 or 0.3l/min. After activation, CF was washed with water and dried under vacuum for 12h. CF used as trap was also activated after hydration of trapped K. The surface area of activated CF was measured, using Sorptmatic 1990. Potassium remaining in activated CF was measured by titration.

Results and Discussions

Table 1 summarizes surface area, yield and remaining K on CF after the activation of ACF at 700℃. When the gas flow rates were 0.6 and 0.3l/min. respectively at KOH/CF ratio 4 by weight. 1900m^2/g were obtained by 0.6/min. while smaller surface area of 1192m^2/g was obtained by 0.3l/min. The yield of ACF and remaining K were 75 ～ 78% and 32 ～ 33%, respectively regardless of the flow rates. Table 2 summaries the surface areas of the trapping fibers after hydration and activation. The lowest trapping CF (Trap 1 lower) which collected KOH at KOH/CF ration of 0.75 obtained surface area 1528m^2/g, holding KOH of 0.2. CFs of other positions did not trap any KOH, and hence were not activated. Table 3 summarizes the remaining KOH by the activation at 800℃. 30% of charged KOH remained regardless the time. Table 3 summarizes the activation of trapping CF in the horizontal reactor. Much more K was transferred to the trapping CF reducing the remaining K. The trapping CF catching K by weight rate of 2.7 obtained surface area as large as 1700m^2/g which is comparable to that obtained any physical mixing. In contrast, trapped CF of zone 2, obtained small surface area due to small amount of K. The temperature of trap appears very important to capture K. The low part of trap 1 trapped K at 725℃, while the high the part failed at 675℃. The critical temperature appears to be 700℃.

Conclusion

The present study proved that the cycle procedure of KOH for repeated activation of CF consisting of activation, vaporize, trapping, hydration and second activation of trapping CF provides large surface area of 1500-1700m^2/g to the mesophase pitch based carbon fiber. The finally, large amount of K required to the starting activation is the problem. Rather constant amount of remaining KOH regardless of the reaction time suggests poor contact with the fiber. Since the trapping fiber is well activated by much less amount of KOH(2 ～ 3 by weight), start of the activation with the impregnated CF can reduce the remaining KOH.

References

1. Arnold N. et al., US Patent 3,817,874(1974)

Table 1 Activation of Pitch CF by KOH [b)]

Flow Rate	0.6/min	0.3/min
Surface area[m^2/g]	1898	1192
Yield[%]	75	78
Remaining KOH [c)]	33.3	32.1

Table 2 Surface Area of Trapped CF (in a vertical reactor)

	Surface area[m^2/g]	Starting KOH/CF [ratio]	Potassium Residue
ACF [a)]	1627	4	1.1
Trap CF1 lower	1528	0.75	0.2
Trap CF1 upper	3.4	N.D.	N.D.
Trap CF2	N.D.	N.D.	N.D.

Table 3 Surface Area of Trapped CF (in a horizontal reactor)

	Surface area[m^2/g]	Starting KOH/CF [ratio]	Potassium Residue
ACF [a)]	1657	4	0.6
Trap CF1	1712	2.56	-
Trap CF2	32.8	0.34	-

CF=800℃ T1=700℃ T1U=675℃ T1L=725℃ T2=600℃

Table 4 Potassium Residue of ACF (in a vertical reactor) [b)]

Holding times	Remaining KOH [%]
1h	33.4
3h	32.2
5h	33.2
6h	31.1
7h	28.1

a) 800℃ 5h hold 0.6l/min flow rate

b) 700℃ 0.6l/min KOH/CF=3

c) % To changed KOH

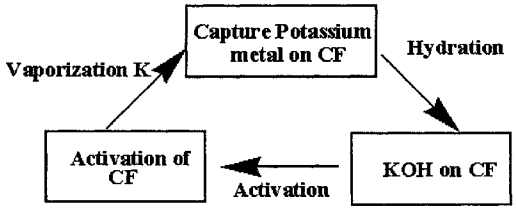

Fig.1 Cycle of KOH

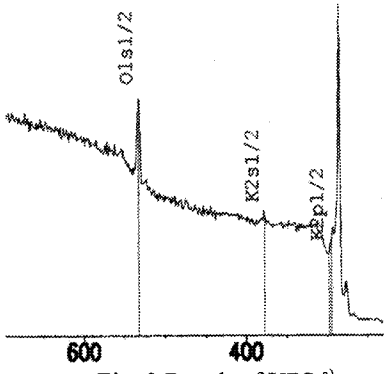

Fig. 3 Result of XPS [a)]

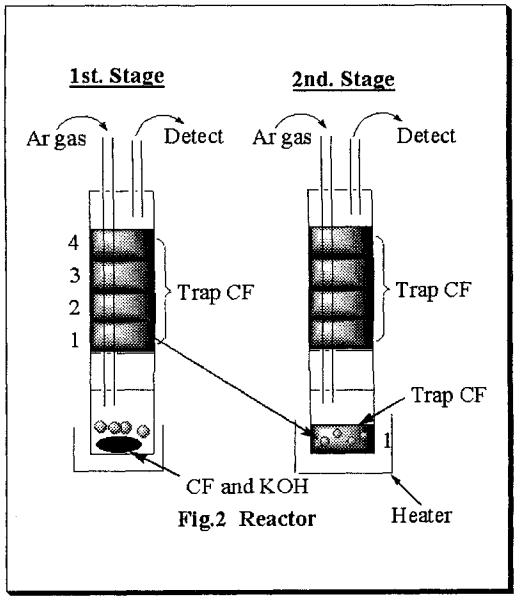

Fig.2 Reactor