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PREPARATION OF MESOPOROUS CARBONS FROM POLYMER MATERIALS USING ORGANOMETALLICS

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We prepared mesoporous carbons using various vinylidene chloride copolymers, viz, vinylidene chloride/acrylonitrile, vinylidene chloride/vinyl chloride, and vinylidene chloride/methyl acrylate copolymers as precursors by steam activation. Mesoporous carbons were obtained by the addition of yttrium complex to these precursors. Mesopore surface ratios of porous carbons obtained from carbonized vinylidene chloride/methyl acrylate copolymer containing Y(acac)$_3$ were more than 90%, and 2.3–2.4 nm of pores were selectively developed.

Keywords: porous carbon; mesopore; vinylidene chloride copolymer

INTRODUCTION

Most activated carbons conveniently produced from various precursors are generally consisting of micropore. They have high specific surface area and are widely used as an excellent adsorbent for various low molecular weight compounds and gases. On the other hand, activated carbons mainly consisting of mesopore ($2 \sim 50$ nm) are expecting to be excellent for adsorption of large molecules in size. Previously, we reported that mesoporous activated carbons were obtained from pitch containing rare earth metal complexes by steam activation [1,2]. However, the pore size distribution of the mesoporous activated carbons obtained was wide.

In this work, we attempted to synthesize mesoporous carbons of narrow pore size distribution using various vinylidene chloride copolymers containing rare earth metal complex. The effects of metal content, activation time, and activation temperature were investigated.

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EXPERIMENTAL

As carbon precursors, vinylidene chloride/acrylonitrile copolymer (Poly(VDC/AN), $\overline{Mn} = 6.4 \times 10^4$), vinylidene chloride/vinyl chloride copolymer (Poly(VDC/VC), $\overline{Mn} = 7.1 \times 10^4$), and vinylidene chloride/methyl acrylate copolymer (Poly(VDC/MA), $\overline{Mn} = 6.1 \times 10^4$) were used. Carbon precursors containing rare earth metal complex were prepared by mixing of precursor with rare earth metal complex in tetrahydrofuran(THF), and then THF was removed by flash distillation. The preparation of carbons was conducted by activation of carbonized or oxidized precursors. The activation was performed by steam in N_2 gas.

As rare earth metal complex, yttrium acetylacetonate($Y(acac)_3$) was used because yttrium had a strong effect on mesopore formation in the preparation of activated carbons from pitch [1,2].

The pore characteristics of porous carbons was determined by N_2 adsorption isotherms using a Quantachrome Autosorb-6. Mesopore size and surface area were determined by BJH method.

RESULTS AND DISCUSSION

Poly(VDC/AN) Precursor

Table 1 shows the pore characteristics of porous carbons obtained from oxidized Poly(VDC/AN) containing ($Y(acac)_3$)(Y content : 2 wt%). Microporous carbon with specific surface area more than 2000 m^2/g was obtained from oxidized Poly(VDC/AN) without $Y(acac)_3$. With the addition

TABLE 1 Pore Characteristics of Activated Carbons Obtained from Oxidized Poly(VDC/AN)

Sample	Y content in polymer (%)	Activation (°C-min.)	Yield (%)	BET surface area (m^2/g)	Mesopore surface area (m^2/g)	Mesopore ratio (%)
Poly(VDC/AN)-Ox-0	0	900-20	26	2192	269	12
Poly(VDC/AN)-Ox-1	2	850-25	16	623	201	32
Poly(VDC/AN)-Ox-2	2	850-30	15	547	256	47
Poly(VDC/AN)-Ox-3	2	900-7	22	653	190	29
Poly(VDC/AN)-Ox-4	2	900-10	21	687	341	50
Poly(VDC/AN)-Ox-5	2	900-12	16	766	318	42
Poly(VDC/AN)-Ox-6	2	900-15	10	262	171	65
Poly(VDC/AN)-Ox-7	2	900-30	8	ND	ND	ND

Oxidation: 360°C, 1 h.

TABLE 2 Pore Characteristics of Activated Carbons Obtained from Carbonized Poly(VDC/AN)

Sample	Y content in polymer (%)	Activation (°C-min.)	(%)	BET surface area (m^2/g)	Mesopore surface area (m^2/g)	Mesopore ratio (%)
Poly(VDC/AN)-Carb-0	2	900-10	29	826	479	58
Poly(VDC/AN)-Carb-1	2	900-13	21	874	454	52
Poly(VDC/AN)-Carb-2	2	900-15	15	670	339	51
Poly(VDC/AN)-Carb-3	2	950-7	19	850	460	54
Poly(VDC/AN)-Carb-4	2	950-9	15	589	383	65

Carbonization: 600°C, 1 h.

of $Y(acac)_3$, BET specific surface area decreased. However, mesopore surface area scarcely increased for various activation conditions, viz, temperature and time. Table 2 shows the pore characteristics of porous carbons obtained from Poly(VDC/AN) containing ($Y(acac)_3$)(Y content : 2 wt%) carbonized at 600°C. Mesopore surface ratios of these porous carbons increased compared with those of oxidized poly(VDC/AN). Yttrium is supposed to take part in mesopore formation. However, as shown in Figure 1, the pore radius distributions of these carbons were relatively wide in the range of 4 nm< . Activation temperature and time scarcely affected pore size distribution.

Poly(VDC/VC) Precursor

Similarly to activated carbons from Poly(VDC/AN) precursor, we could not obtain porous carbons of high mesopore surface area from oxidized

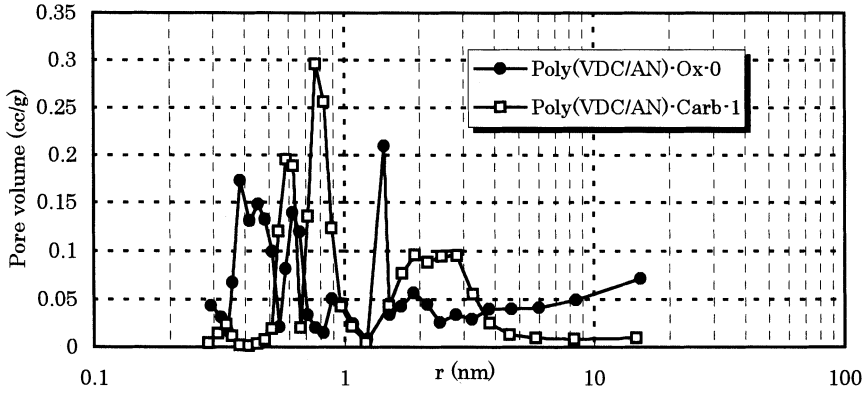

FIGURE 1 Pore radius distribution of Poly(VDC/AN)-Carb.

TABLE 3 Pore Characteristics of Activated Carbons Obtained from Carbonized Poly(VDC/VC)

Sample	Y content in polymer (%)	Activation (°C-min.)	Yield (%)	BET surface area (m^2/g)	Mesopore surface area (m^2/g)	Mesopore ratio (%)
Poly(VDC/VC)-Carb-1	2	900-40	24	732	586	80
Poly(VDC/VC)-Carb-2	2	950-20	19	324	323	100
Poly(VDC/VC)-Carb-3	2	950-25	18	148	157	94

Carbonization: 600°C, 1 h.

Poly(VDC/VC) by the activation of $13 \sim 56$ min at $800 \sim 950$°C. On the other hand, highly mesoporous carbons were obtained from carbonized Poly(VDC/VC) containing $Y(acac)_3$ as shown in Table 3. However, the pore radius distributions of these carbons were relatively wide in the range of $4\,\text{nm}<$.

TABLE 4 Pore Characteristics of Activated Carbons Obtained from Oxidized Poly(VDC/MA)

Sample	Y content in polymer (%)	Activation (°C-min.)	Yield (%)	BET surface area (m^2/g)	Mesopore surface area (m^2/g)	Mesopore ratio (%)
Poly(VDC/MA)-Ox-0	0	900-35	21	2315	31	1
Poly(VDC/MA)-Ox-1	2	900-15	18	805	618	77
Poly(VDC/MA)-Ox-2	2	850-20	13	468	308	66
Poly(VDC/MA)-Ox-3	2	950-7	24	1059	769	73

Oxidation: 360°C, 1 h.

TABLE 5 Pore Characteristics of Activated Carbons Obtained from Carbonized Poly(VDC/MA)

Sample	Y content in polymer (%)	Activation (°C-min.)	Yield (%)	BET surface area (m^2/g)	Mesopore surface area (m^2/g)	Mesopore ratio (%)
Poly(VDC/MA)-Carb-1	2	900-15	31	976	701	71
Poly(VDC/MA)-Carb-2	2	900-23	20	928	801	97
Poly(VDC/MA)-Carb-3	2	900-25	17	641	624	97
Poly(VDC/MA)-Carb-4	2	950-12	20	591	580	98
Poly(VDC/MA)-Carb-5	2	950-14	16	590	570	97

Carbonization: 600°C, 1 h.

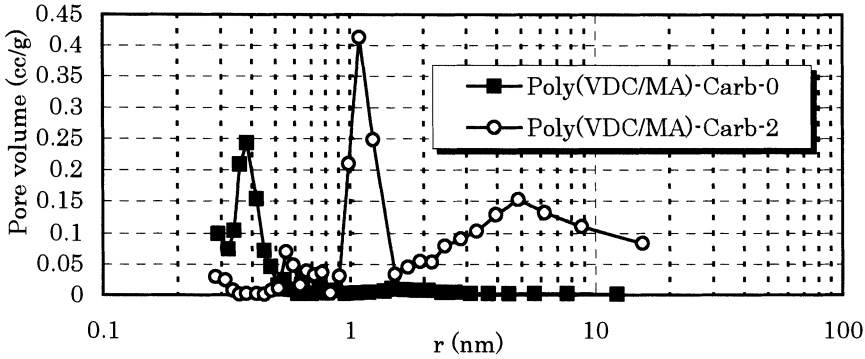

FIGURE 2 Pore radius distribution of Poly(VDC/MA)-Carb.

Poly(VDC/MA) Precursor

Table 4 and 5 show the pore characteristics of porous carbons obtained by activation of oxidized Poly(VDC/MA) containing $Y(acac)_3$ and carbonized one with steam, respectively. In both pretreated precursors, highly mesoporous carbons were obtained. Especially, mesopore surface area ratios of porous carbons obtained from carbonized Poly(VDC/MA) containing $Y(acac)_3$ were more than 90%. Pore size distributions of Poly(VDC/MA)-Carb-0 and -2 are shown in Figure 2. In these carbons, 2.3–2.4 nm of pores were selectively developed although we observe the formation of small amount of larger pores.

From these results, it is concluded that yttrium complex is an effective compound for the preparation of mesoporous carbons from pre-carbonized vinylidene chloride copolymer by steam activation.

In addition, from the point that methyl acrylate polymer is easily decomposed compared with acrylonitrile and vinyl chloride polymer by heat-treatment, it is suggested that copolymerization of acrylate monomer, whose polymer easily decomposed with heat-treatment, with vinylidene chloride is a useful way for the preparation of mesoporous carbons of uniform pore size.

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