

Effects of Synthesis Conditions and Starting Materials' Properties on Porosity of Template Carbons

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Template materials, carbon ingredients and their impregnation state into templates are important factors for synthesis of new porous carbon materials by template method. The synthesis conditions are assumed to have marked influence on pore development of the specimens. Particularly, pore volume in microporous and mesoporous region, specific surface area and yield point or yield constant of the specimens are extremely interested for practical application of the materials. In this research, several porous carbon specimens have been prepared under different conditions by the use of several kinds of natural soils or clays for templates, and we have investigated effects by the above conditions; filling period of ingredient for carbon, fill pressure, carbonization temperature, and so on. Qualitative difference of template materials has been also examined from viewpoints of synthesis procedures.

Keywords: application of natural resources, carbon, porous materials, template carbon materials, template technique.

1. INTRODUCTION

Porous materials have been used for various industrial and hygienic applications in current days. In addition, synthesis of further unique and fine porous materials is an attractive issue. Particularly, porous carbons surpass other artificial porous materials in safety, stability and levity, and they play a prominent role for adsorbents of various kinds of chemical substances in industrial and hygienic applications [1-4]. Furthermore, currently, new porous carbon materials synthesized by template technique have attracted much interest, and there are many studies of their scientific properties [5-14]. The technique realizes more precise pore size control and unique porous structure, which are based on template materials, as compared with other synthesis approaches of porous carbon materials.

In the previous reports, we have prepared several porous template carbon materials using several kinds of natural soils or clays and minerals for templates [15-18]. The carbon specimens have certain unique pore developments, and some of them show more effective adsorbability of several kinds of organic solvents' vapors as compared with a common activated carbon. In this research, we have synthesized several porous carbon materials by the above templates, under different synthesis conditions.

In fact, impregnation state of carbon ingredients into templates is assumed to be the most important factor for effective synthesis of the template carbons. From this viewpoint, we have used several kinds of template materials, carbon ingredients and different conditions of impregnation in synthesis of the specimens. Then

their effects on porosity of the specimens have been investigated, particularly concerning pore development in microporous and mesoporous region, specific surface area and yield constant of them.

2. EXPERIMENTAL

We have used 2 types of natural porous materials (T1 and T2, some kinds of volcanic ash soils or clays, products of SEIWA PRO Corp., Osaka, Japan) for templates in this research. The detailed particulars of the materials are described in the previous reports [15-18]. They are almost composed of allophanic soils. T1 is soil aggregate forming loamy layer of the Kanto Plain in Japan, and T2 is volcanic ash soil forming a layer which is immediately beneath of the loamy layer. In their X-ray diffraction (XRD) profiles, we have also confirmed intensive peaks corresponding to quartz (SiO_2) in T1, and $\alpha\text{-CaSiO}_3$ (wollastonite, $\text{CaO} \cdot \text{SiO}_2$) in T2.

Figure 1 shows the flow chart of synthesis procedure of the carbon specimens in this research. The ingredients of carbon are furfuryl alcohol (2-Furanmethanol), sucrose, and glucose (D(+)-Glucose, anhydrous). All of test reagents are products of Wako pure chemical industries Inc., and sucrose and glucose are used as approximately saturated aqueous solutions at room temperature ($T \approx 298 \text{ K}$).

In the case of furfuryl alcohol, most of the specimens are prepared at normal pressure. We have prepared several specimens which have different soaking period for each template, because the filling of ingredient into template is

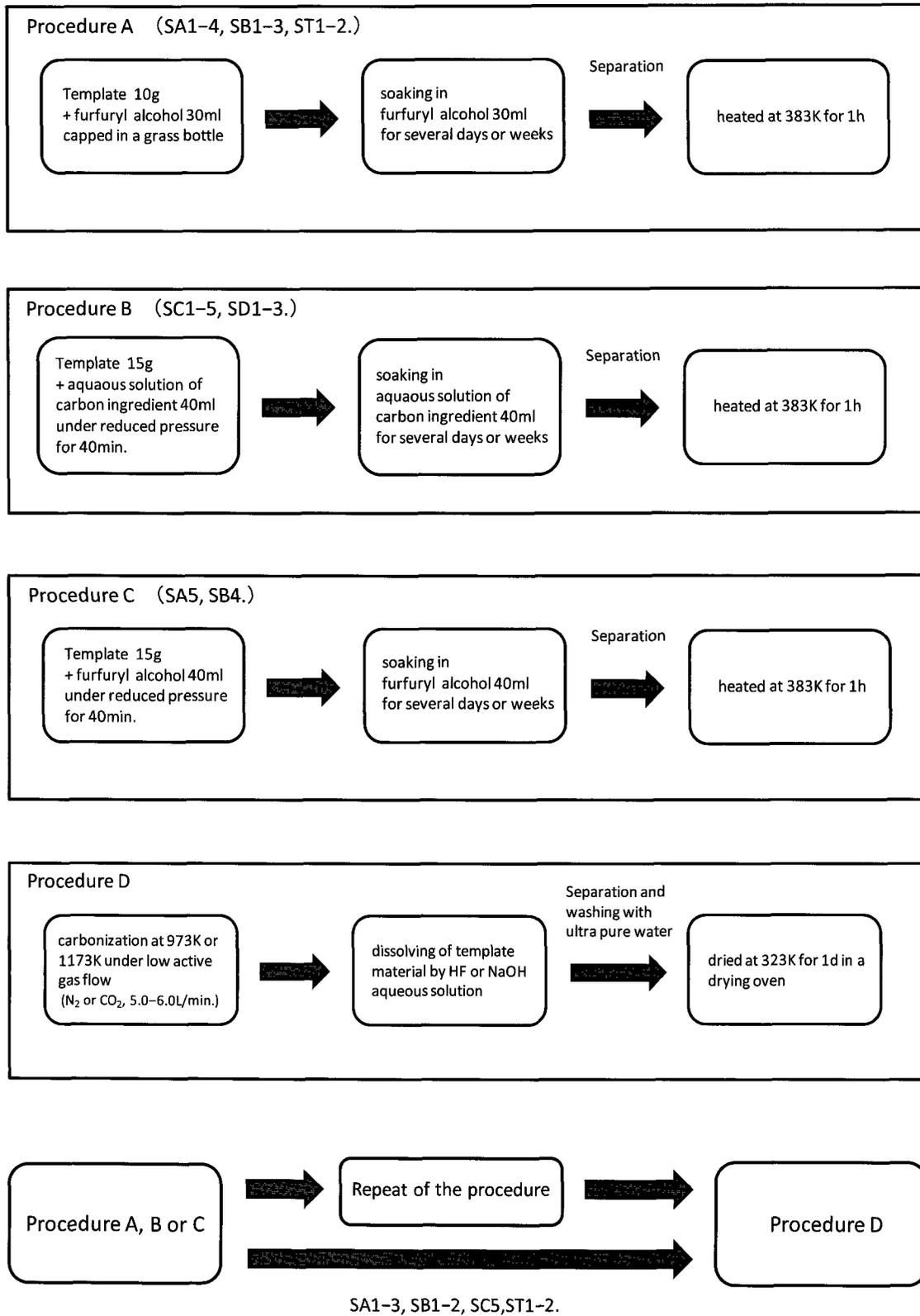


Fig.1. Flow chart of the synthesis procedure for template carbon specimens in this research.

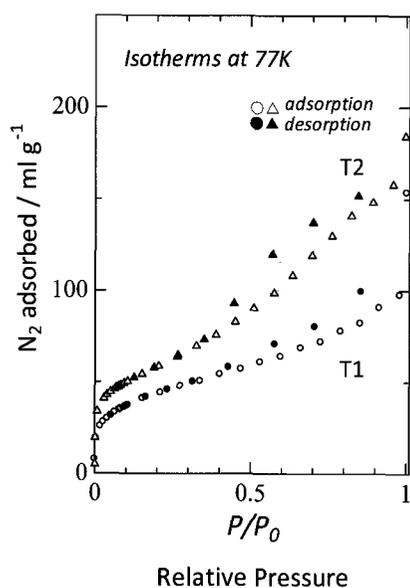


Fig.2. N_2 adsorption and desorption isotherms at $T=77$ K of the template materials T1 and T2.

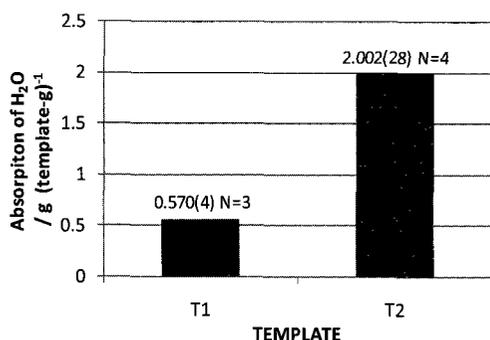


Fig.3. Comparison of H_2O absorption quantities by T1 and T2.

expected to have marked influence on the synthesis. After the soaking, the mixture material is separated by filtration, and moved into a melting pot. The material in the pot is heated at $T=383$ K for 1 h in air in a muffle furnace (FP100, Yamato Scientific Corp.).

In contrast, in the case of glucose or sucrose aqueous solution, the carbon ingredients can not be injected sufficiently into the template materials at normal pressure. In this research, the aqueous solutions are impregnated into the template materials under reduced pressure for 40 min., and the soaking is carried out as previously noted. After the soaking, the mixture material is separated by filtration, and moved into a melting pot. The material in the pot is heated at $T=383$ K for 1 h in air in the muffle furnace. We have controlled above-mentioned fill pressure by the use of Markos Mefer Suction Pump SP20 or Nihon BÜCHI V-702 Vacuum Pump System. The latter system can control lower fill pressure more minutely and accurately.

Table I

Porous properties of template materials in this research. V_{micro} is pore volume calculated by MP method, and V_{meso} is that calculated by D-H method.

SAMPLE	Template T1	Template T2	Reference (Activated carbon)
N_2 -BET specific surface area / $m^2 g^{-1}$	134.9	205.7	1379
$V_{\text{micro}} / ml g^{-1}$	0.057	0.0326	0.595
$V_{\text{meso}} / ml g^{-1}$	0.0806	0.1857	0.0625

Table II

Results of elemental analysis of the template materials. Error of each measurement is ≤ 0.3 mass %.

SAMPLE	Content / mass %		
	C	H	N
Reference (Activated carbon)	92.0	0.5	0.2
T1	1.0	4.3	0.1
T2	0.1	2.2	0.0

The above pretreatment procedures are carried out for one time or several times according to the specimens. Then the mixture materials are carbonized at $T=973$ K (most of the furfuryl alcohol specimens) or 1173 K (sucrose and glucose specimens) for 30 min. with low active gas flow (N_2 or CO_2 , 5.0–6.0 L/min.) in the furnace. Furfuryl alcohol has high inflammability, and it can be carbonized sufficiently at lower temperature as compared with sucrose or glucose. In this regard, some of the furfuryl alcohol specimens have been also synthesized by carbonization at $T=1173$ K or impregnation of carbon ingredient under reduced pressure.

After cooling to room temperature, the materials are grinded, and dealt with hydrofluoric acid or sodium hydroxide aqueous solution to dissolve the templates. Finally, the carbon materials are washed with ultra pure water for several times, and dried at $T=323$ K for 1 d in a drying oven.

N_2 -BET specific surface area and pore size distribution of the specimens have been measured by BELSORP 36 (BEL JAPAN Inc.) with N_2 gas (≥ 99.9995 %). Pore volumes and pore size distributions of the specimens are calculated by MP method (microporous region (radius of pores; $r < 1.0$ nm)) and Dollimore-Heal (D-H) method (mesoporous region (radius of pores; $1.0 \text{ nm} < R < 25 \text{ nm}$)). Elemental analysis (CHN) has been also carried out by PerkinElmer 2400 II CHNS/O analyzer on the specimens. In addition, we have performed XRD measurements by RIGAKU RINT 2200 and X-ray fluorescent (XRF) analysis by RIGAKU RIX 2000 on the template materials.

3. RESULTS AND DISCUSSION

3.1 Template materials

Figure 2 shows isotherms by N_2 adsorption and desorption at $T= 77$ K for T1 and T2, and Table I shows porosity of the template materials. They are both mesoporous materials, and they have similar chemical components. However, they have also several different characters in physical and chemical qualities.

At first, their hysteresis loops in the isotherms have different shapes, and these features indicate that their porous configurations are also different. T1 is assumed to have wedge type pores, and T2 is assumed to have bottleneck type pores [18–20]. In addition, Figure 3 shows H_2O absorption by T1 and T2. The absorption quantity is defined by amount of H_2O (ultrapure water) absorption after soaking in a glass bottle filled with H_2O for 24 h. From the results, T2 shows approximately 3.5 times of H_2O absorption as compared with T1. In this way, T2 has higher water-absorbing property, that is to say, hydrophilicity. Table II shows results of elemental analysis (CHN) for the template materials. T2 has almost no carbon content. In contrast, T1 has albeit only slightly carbon content. These results indicate existence of organic constituents in T1, and the properties are expected to contribute to make difference in hydrophilicity of the template materials.

3.2 Carbon specimens

Carbonization temperature is also assumed to be an important factor in synthesis of porous carbon materials. Figure 4 shows comparison of specific surface areas of carbon specimens synthesized from furfuryl alcohol and T1 or T2 by carbonization at different temperatures. SA1 and SB1 have been carbonized at $T= 973$ K, and ST1 and ST2 have been carbonized at $T= 1173$ K. Pretreatments of ST1 and ST2 are respectively almost similar to those of SA1 and SB1. We have found that the carbonization at $T= 973$ K has more preferable effect on specific surface area for the specimens by both template materials. At least for synthesis from furfuryl alcohol in this research, particular high treatment temperature seems to be rather unnecessary.

Table III shows porous properties and synthesis conditions of the carbon specimens in this research. Normal pressure means approximately $P= 101.3$ kPa. In addition, results of elemental analysis (CHN) for the carbon specimens are represented in Table IV. The yield constant of the specimens is defined as mass ratio of yield point of the carbon specimens and their template materials (carbon specimen / template material).

Figure 5 (a) shows specific surface areas of carbon specimens synthesized from template T1

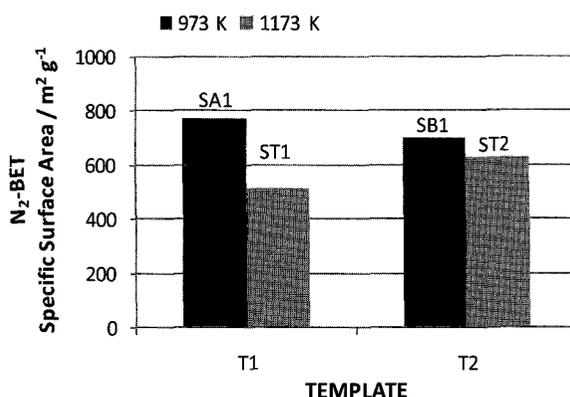


Fig.4. Comparison of specific surface areas of carbon specimens synthesized from furfuryl alcohol and template T1 or T2 by carbonization at different temperatures ($T= 973$ K and $T= 1173$ K).

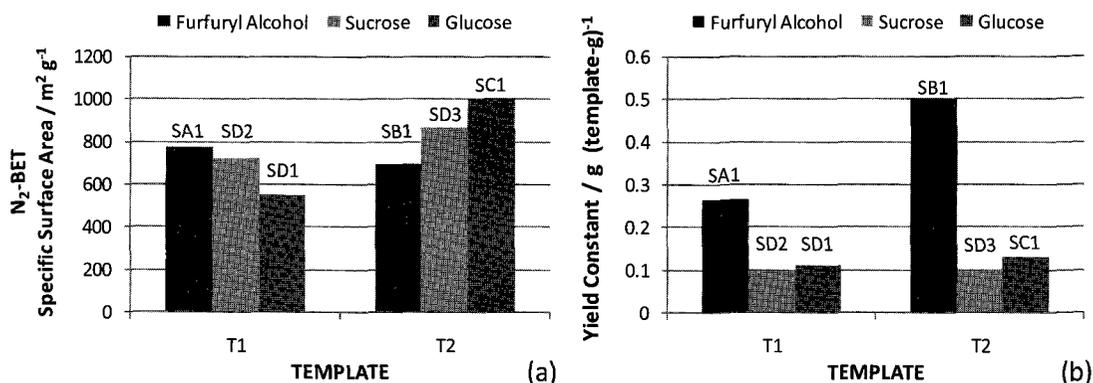


Fig.5. Specific surface areas (a) and yield constants (b) of carbon specimens synthesized from template T1 or T2 and different carbon ingredients.

Table III
Porous properties and synthesis conditions of the carbon specimens in this research.

SAMPLE	SA1	SA2	SA3	SA4	SA5
TEMPLATE	T1	T1	T1	T1	T1
RAW SUBSTANCE	Furfuryl alcohol				
SOAKING PERIOD	12 d	13 d	27 d	10 d × 2	10 d + 15 d
FILL PRESSURE / kPa	Normal	Normal	Normal	Normal	84
CARBONIZATION TEMPERATURE / K	973	973	973	973	973
N ₂ -BET specific surface area / m ² g ⁻¹	772.8	759.8	829.0	799.7	812.8
V _{micro} / ml g ⁻¹	0.374	0.29	0.415	0.354	0.379
V _{meso} / ml g ⁻¹	0.3735	0.5234	0.3711	0.3955	0.4400
YIELD CONSTANT (SAMPLE / TEMPLATE)	0.267	0.182	0.162	0.201	0.208

SAMPLE	SB1	SB2	SB3	SB4
TEMPLATE	T2	T2	T2	T2
RAW SUBSTANCE	Furfuryl alcohol	Furfuryl alcohol	Furfuryl alcohol	Furfuryl alcohol
SOAKING PERIOD	10 d	22 d	10 d + 15 d	10 d + 2 d
FILL PRESSURE / kPa	Normal	Normal	Normal	80
CARBONIZATION TEMPERATURE / K	973	973	973	973
N ₂ -BET specific surface area / m ² g ⁻¹	698	397.9	569.7	653.2
V _{micro} / ml g ⁻¹	0.453	0.167	0.374	0.306
V _{meso} / ml g ⁻¹	0.3878	0.3716	0.3222	0.333
YIELD CONSTANT (SAMPLE / TEMPLATE)	0.504	0.558	0.553	0.461

SAMPLE	SC1	SC2	SC3	SC4	SC5
TEMPLATE	T2	T2	T2	T2	T2
RAW SUBSTANCE	Glucose	Glucose	Glucose	Glucose	Glucose
SOAKING PERIOD	6 d × 2	3 d + 11 d + 2 d	8 d + 4 d	5 d + 6 d	5 d
FILL PRESSURE / kPa	42	40	25.7	3.1	2.8
CARBONIZATION TEMPERATURE / K	1173	1173	1173	1173	1173
N ₂ -BET specific surface area / m ² g ⁻¹	1000	720.6	870	975.3	911.4
V _{micro} / ml g ⁻¹	0.801	0.603	0.712	0.505	0.738
V _{meso} / ml g ⁻¹	0.8134	0.5961	0.7454	0.7296	0.7286
YIELD CONSTANT (SAMPLE / TEMPLATE)	0.130	0.201	0.155	0.178	0.115

SAMPLE	SD1	SD2	SD3
TEMPLATE	T1	T1	T2
RAW SUBSTANCE	Glucose	Sucrose	Sucrose
SOAKING PERIOD	7 d + 6 d	5 d + 3 d	5 d + 3 d
FILL PRESSURE / kPa	49	68	69
CARBONIZATION TEMPERATURE / K	1173	1173	1173
N ₂ -BET specific surface area / m ² g ⁻¹	551	724.1	867.9
V _{micro} / ml g ⁻¹	0.233	0.353	0.680
V _{meso} / ml g ⁻¹	0.3461	0.4159	0.6274
YIELD CONSTANT (SAMPLE / TEMPLATE)	0.110	0.099	0.103

or T2 and different carbon ingredients. The ingredients are furfuryl alcohol, sucrose, and glucose (in the order corresponding to their hydrophobicity). In the results, we have found that T1 and T2 have opposite patterns in specific surface area. T1 shows most preferable result in the specimen synthesized from furfuryl alcohol (SA1). In contrast to this, T2 have most high specific surface area in the specimen synthesized from glucose (SC1). These results are also expected to be caused by hydrophobicity of T1 and hydrophilicity of T2. As a matter of course, in the synthesis of porous carbons, examination of yield point or yield constant is another significant matter from viewpoints of their practical application. Figure 5 (b) shows comparison of yield constants of carbon specimens synthesized from each carbon ingredient and template T1 or T2. In yield constants, furfuryl alcohol shows prominent results as compared with other carbon ingredients. On that regard, further improvement of synthesis procedure by the use of sucrose or glucose is desirable.

N_2 -BET specific surface areas and yield constants of several groups of the carbon specimens are plotted in Figure 6.

Specimens SA have been synthesized from furfuryl alcohol and the template T1 (Figure 6 (a)). In the specimens, soaking period in carbon ingredient possesses significance for porosity, and specific surface area increases with the soaking period obviously. On the other hand, yield constant seems to decrease with the soaking period. In synthesis of porous carbon materials, advancement of porosity generally leads to decrease of yield constant or yield point of carbon specimens. This contrariety makes difficulty in synthesis of new porous carbon materials, and the circumstance is same applies to the synthesis of the carbon specimens in this research.

The specimens SA4 and SA5 have been synthesized by impregnation process under reduced pressure. From their results in porosity, this decompression does not seem to have remarkable effect on advancement of surface areas for the group SA, and impregnation at normal pressure can be enough synthesis procedure for the combination of furfuryl alcohol and the template T1. Complicated artifice is not much required in synthesis of the specimens SA, and this is a good point for practical use of the specimens.

Specimens SB have been synthesized from furfuryl alcohol and the template T2. In the specimens, SB1 and SB2 have been synthesized by impregnation at normal pressure. On the other hand, SB3 and SB4 have been synthesized by the process under reduced pressure. In the specimens, yield constant increases with soaking period (Figure 6 (b)), and specific surface area of the specimens decreases with the period. It is attractive that these dependences are opposite of them by the group SA. These features are expected to be caused by difference of

hydrophobicity of T1 and T2. Further, repeat of impregnation procedure seems to produce a reduction in descent of specific surface area caused by rising of yield constant (SB3 and SB4). On that regard, the specimens SB leave place for further improvement on porosity.

Figure 6 (c) shows specific surface areas and yield constants of specimens SC, which have been synthesized from glucose and the template T2. In the figure, specific surface area increases with soaking period, similarly in the case of the specimens group SB. On the other hand, their specific surface area's transition is not uniformity, and their dependence on fill pressure (SC1 and SC2: approx. $P=40$ kPa, SC3: approx. $P=25$ kPa, SC4 and SC5: approx. $P=3$ kPa) is not confirmed clearly from the results. Effect of soaking period on porosity is assumed to have a peak at relatively short time (approximation of the degree of 11 d). In addition, number of times of filling does not show sufficient effect in the specimens SC.

The specimens SC are insufficient in yield constant as compared with other specimens groups, which are synthesized from furfuryl alcohol. However, their preferable specific surface areas are noteworthy, and the carbon ingredient used for the specimens SC is more safety as compared with furfuryl alcohol. This point is significant from viewpoint of their practical application, particularly for industrial or occupational hygiene as adsorptive materials.

Figure 7 shows pore developments of several carbon specimens and their template materials in mainly mesoporous region. In the developments, carbon specimens by the use of T1 differ only slightly, and their pore developments reflect the development of T1 very well (Figure 7 (a) (b)). All of the carbon specimens prepared by the use of T2 are conform in the point that they have a peak at $R_p \approx 2$ nm (Figure 7 (c) (d) (e)). However, they have also some difference in large pore size region ($R_p > 2$ nm). Particularly, the specimens SC, which are prepared from glucose, have obvious decrease in their pore developments at $R_p = 3-5$ nm. Seeking into pore development of the template T2, we have found that the prominent decrease by the carbon specimens is fine reflection of pore development of T2. The feature is also expected to contribute to preferable specific surface area of the specimens SC.

As mentioned above, the synthesis of template carbon materials depend markedly on combinations of template material and carbon ingredient, and synthesis conditions. In this regard, most of them have some tendency for porous properties or yield constant of carbon specimens, and they can be useful reference for improvement of carbon specimens' porosity as adsorbent materials. Particularly, in synthesis of porous carbons, advancement of porosity and yield constant are difficult to be in keeping each other, and the above investigations are useful and important to inquiry most appropriate synthesis

Table IV
Results of elemental analysis of the carbon specimens.

SAMPLE	Content / mass %		
	C	H	N
SA1	57.1	1.5	0.3
SA2	59.9	2.6	0.5
SA3	70.3	2.5	0.5
SA4	79.5	2.8	0.4
SA5	71.4	2.5	0.4

SAMPLE	Content / mass %		
	C	H	N
SB1	81.3	2.2	0.2
SB2	81.4	2.5	0.1
SB3	78.5	2.2	0.2
SB4	84.2	2.3	0.1

SAMPLE	Content / mass %		
	C	H	N
SC1	86.4	1.5	0.9
SC2	88.1	1.2	0.1
SC3	80.6	1.3	0.3
SC4	83.0	1.3	0.1
SC5	80.7	1.6	0.3

SAMPLE	Content / mass %		
	C	H	N
SD1	56.3	1.7	0.6
SD2	67.4	1.7	0.7
SD3	87.3	1.1	0.2

SAMPLE	Content / mass %		
	C	H	N
ST1	40.5	0.9	0.5
ST2	82.3	1.8	0.3

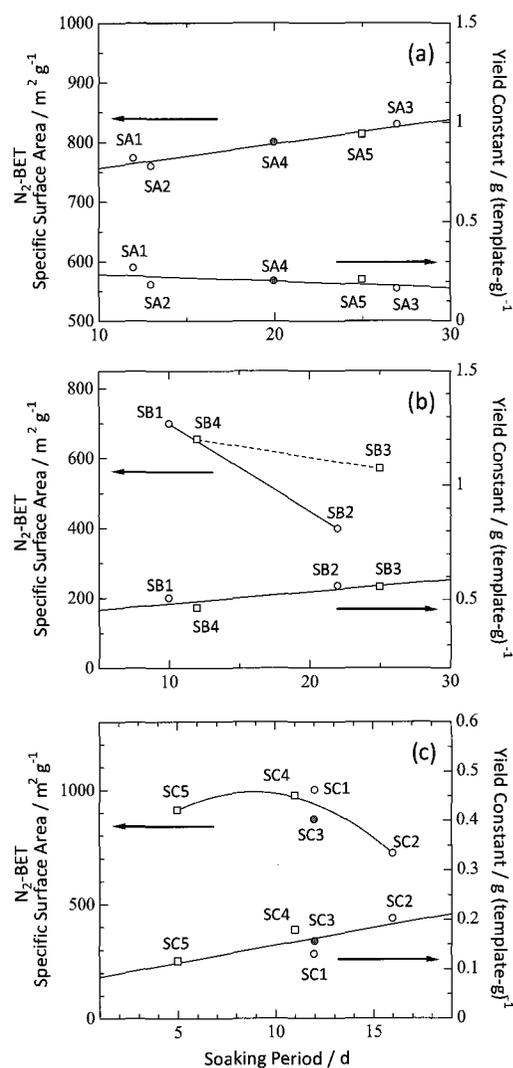


Fig.6. N₂-BET specific surface areas and yield constants of several groups of the carbon specimens.

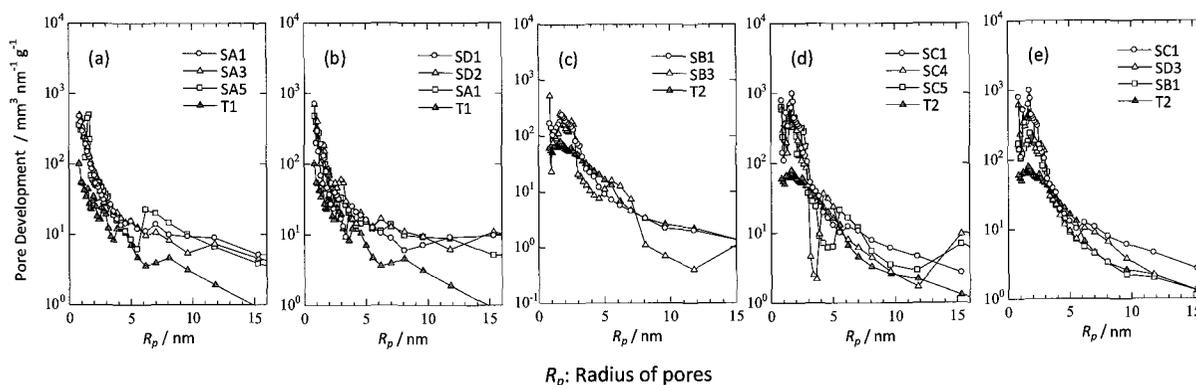


Fig.7. Pore size distributions in mesoporous region of the carbon specimens calculated by D-H method.

method and its condition. The dependence is also attractive from viewpoints of materials chemistry.

4. CONCLUSIONS

We have prepared several kinds of porous carbon materials by template technique, and investigated effects of some synthesis conditions and starting materials or ingredients on porosity of the specimens.

The impregnation state of carbon ingredients into templates is an important factor for the synthesis, and the state markedly depends on properties of template materials. The template which has high hydrophilicity shows more effective results by the use of water solubility of glucose or sucrose for carbon ingredient. However, we have confirmed that furfuryl alcohol is effective by and large on yield constant for the both template materials used in this research.

Soaking period of the templates in carbon ingredient has also pronounced effect on porosity of the specimens, and this effect is changed by combinations of template and carbon ingredient. In this regard, repeating the impregnation procedure does not seem to have a drastic effect on the porosity and yield constant of the specimens.

Properties of template materials commencing with pore development and chemical properties give an indication pointer for synthesis process of template carbons. Intimate investigation of template materials is useful for effective synthesis and practical applications of new porous carbons by template method.

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