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Synthesis of Microporous Carbon Materials by the use of Perlite for Activation

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Several microporous carbon materials have been synthesized from some kinds of raw substances for carbon, by the use of granules or powder of a Perlite product. Perlite is an inexpensive mineral, which has a small value of surface area (≑5 m^2/g; N_2-Langmuir surface area) and few micro and meso pores. In contrast, the carbon materials synthesized in this research show significant growth of micropores, and they have comparative high specific surface area (≑515-756 m^2/g). This is attributed to an activation effect by H_2O comprised in the Perlite product from the result of thermal analysis, and the porous growth by Perlite powder is more remarkable than that by Perlite granules. These results are expected to be useful for development of porous materials including adsorbents of harmful substances for hygienic applications.

Keywords: activation, application of natural resources, carbon, microporous materials, occupational hygiene.

1. INTRODUCTION

Currently, various carbon materials have attracted much attention in their industrial practical availability for electrodes of lithium ion battery and fuel cell. Especially, carbons which have layered, spherical or porous structure attract strong interest, and there are many studies of their industrial applications and scientific properties at the present day [1]. In addition, in occupational or industrial hygiene, porous carbon materials as typified by activated carbons serve a very important role for adsorbents of harmful substances; organic solvents' vapors, organic gases, and several liquid substances [2,3]. Moreover, the porous carbons surpass other artificial porous materials in safety, stability and levity. From the above reasons, further application and development of porous carbons for environmental improvement are anticipated in the days ahead.

In the previous reports, we have prepared several porous carbon materials from polyfurfuryl alcohol by template technique, and we have used several kinds of natural soils or clays and minerals for templates in the synthesis [4,5]. The carbon specimens have certain unique porous growth, and some of them show more effective adsorbability of several organic solvents' vapors (especially several kinds of aromatic vapors) compared with a common activated carbon [5]. We expect that these results can be useful for improvement in air purification of work places.

Adsorption character of porous materials is affected markedly by their pore size distributions. Therefore, control of the porous character in adsorbent materials is extremely important, and it has been a matter of concern from the standpoints of industrial and scientific study. Realization of more effective and less expensive method of building up arbitrary micro and meso pores in porous materials leads to development of more effective and treatable adsorbents for hygiene. At this point, in pore size distributions of porous materials, micro porous region (radius of pores; $r<1.0$ nm) is assumed to influence on adsorption quantity because the region corresponds to sizes of most of chemical substances' molecules.

In this report, we have prepared several microporous carbon materials from mixtures of a Perlite product and several kinds of raw substances of carbon, by a simple method. We have found that the carbon specimens have significant growth of micro pores and high surface areas, as compared with the initial Perlite product. Further, the Perlite product has been used in the forms of granules or powder in the synthesis. In extent of micropores' growth, obvious difference is found between the both carbon specimens, which were prepared by each form of Perlite. We have examined the activation effect by Perlite, and also discussed its possibility for application in development of porous materials.

2. EXPERIMENTAL

2.1 Sample Preparation

Perlite is a light natural mineral which is almost composed of SiO_2, K_2O and Al_2O_3. The amorphous mineral has air permeability and fire resistance, and it is used generally for ameliorants and building materials at the present day [6]. The mineral is quite inexpensive, and it is easy to procure its on-market products in large quantity. In this research, we have used a Perlite product, which is wholesaled by KOHJIYA Corp. (Hitachinaka, Ibaraki, Japan) in the synthesis of porous carbon materials. The initial state of the Perlite product is granular; grain size approximately ϕ =3–5 mm (Fig. 1), and it is a popular form of Perlite in the market. In the synthesis of the carbon specimens, we have used the product in the form of the granules and powder. Perlite powder is prepared by ball mill crushing of the granules, and particle size of the powder is approximately ϕ =30–50 μm (confirmed by SEM photographs).

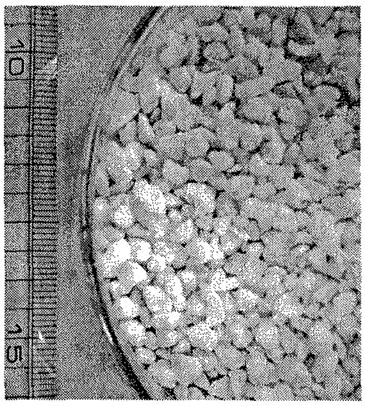

Fig. 1 Photo image of Perlite granules. Scale unit in the image is cm.

All of test reagents used in the synthesis are products of Wako pure chemical industries Inc., and raw substances of carbon for the specimens are polyfurfurylalcohol (2–Franmethanol), phenol resin (phenol and formaldehyde solution; the molar ratio of phenol and formaldehyde is approximately 1:1), glucose (D(+)–glucose, anhydrous) and sucrose.

Synthesis procedures of the specimens from polyfurfurylalcohol and phenol resin are according to the previous report [4]. Approximately 3.5 g of well-dried the Perlite product is soaked in a sufficient quantity of each fluid in a glass bottle sealed up tightly, for 1 week.

On the other hand, glucose and sucrose are used as saturated aqueous solutions at room temperature (T≒298K). The saturated aqueous solutions are impregnated into commensurate Perlite under reduced pressure (approximately 50 kPa) for 40min., and the soaking as previously noted is carried out. 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=383K for 1 hour in air within a muffle furnace (FP100, Yamato Scientific Corp.). These procedures are repeated twice.

After the impregnations of raw substances, they are carbonized at T=973K (polyfurfurylalcohol and phenol resin) or 1173K (glucose and sucrose) for 30 min. with CO_2 flow (5.0–6.0 L/min.) in the furnace. 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 several times, and dried at T=323K for 1 day in a drying oven.

2.2 Characterization of the samples

N_2–Langmuir surface areas and pore size distributions of the carbon materials have been measured (by BELSORP 36, BEL JAPAN Inc.) with N_2 gas (≥99.9995%), and density of each specimen has been measured (by Micromeritics multivolume pycnometer 1305, SHIMADZU Corp.) with He gas (≥99.99995%).

The surface features of the specimens have been observed with SEM (S–4700 type scanning electron microscope, HITACHI High Technologies Corp.), and we have confirmed XRD (X–ray diffraction) patterns of the samples (with RIGAKU RINT 2200) for affirmation of sufficient dissolution of Perlite. In addition, elemental analysis (CHN) has been carried out (by FISONS Instruments EA1108 in Materials and Interfaces Research Lab., Institute of Industrial Science, The University of Tokyo or PerkinElmer 2400 II CHNS/O Analyzer).

We have also performed XRF (X–ray Fluorimetry) measurements (by RIGAKU RIX 2000) and thermal (TG–DTA) analysis (by RIGAKU Thermoflex TAS300 system) on the Perlite product.

3. RESULTS AND DISCUSSION

In this research, we have prepared carbon specimens by the use of Perlite granules from polyfurfuryl alcohol (S1), phenol resin (S2), sucrose (S3) and glucose (S4). In addition, a specimen by the use of Perlite powder has been prepared from glucose (S5).

Figure 2 shows isotherms (at 77K) of some of the specimens in this research and the referential common activated carbon (≒ 1607 m^2/g; N_2–Langmuir surface area), which is a representative high-performance microporous carbon in practical utility. The isotherms can be classified to Type I , which is characteristic curve indicating microporous materials, and all of the specimens show isotherms of Type I .

Figure 3 shows that the specimens have a pore size distribution which is similar to that of activated carbon. They have micro pores intensively, and few meso pores (radius of pores; 1.0 nm $<R_p<$ 15 nm) in their pore size distribution. The feature is especially prominent in S1 and S2 (Table I).

Table I Properties of Perlite granules and powder, the reference and carbon specimens in this research. V_{micro} is pore volume calculated by MP method, and V_{meso} is that calculated by D–H method.

SAMPLE	Reference (activated carbon)	P1 (Perlite granules)	P2 (Perlite powder)
N_2–Langmuir surface area (m^2/g)	1607	4.971	6.276
Density (g/cm^3)	2.059(5)	1.533(8)	2.354(5)
V_{micro} (ml/g)	0.574	0.006	0.0888
V_{meso} (ml/g)	0.0618	0.01	0.0141

SAMPLE	S1 (polyfurfurly alcohol, P1)	S2 (phenol resin, P1)	S3 (sucrose, P1)	S4 (glucose, P1)	S5 (glucose, P2)
N_2–Langmuir surface area (m^2/g)	515.3	668.1	582.8	603.3	755.8
Density (g/cm^3)	1.821(7)	1.614(5)	1.679(5)	1.780(5)	2.067(8)
V_{micro} (ml/g)	0.181	0.259	0.197	0.176	0.193
V_{meso} (ml/g)	0.0557	0.0422	0.1037	0.1402	0.2803

Table II The results of elemental analysis of the reference and the specimens.

	C (wt %)	H (wt %)	N (wt %)
Reference (activated carbon)	91.1	0.4	0.2
S1	79.5	2.6	0.2
S2	79.5	2.4	0.1
S3	72.5	2.9	0.5
S4	73.9	2.3	0.4
S5	70.8	2.9	0.4

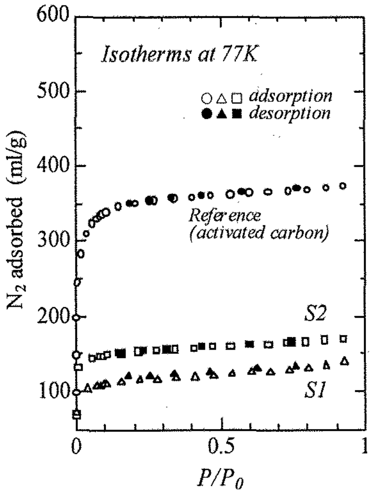

Fig. 2 N_2 adsorption and desorption isotherms at 77K of the reference and the specimen S1 and S2.

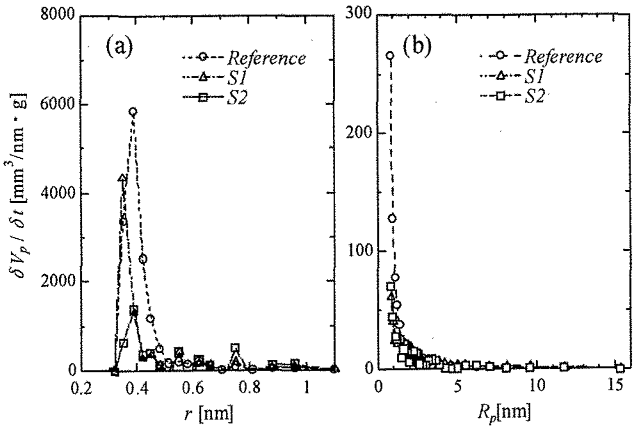

Fig. 3 Pore size distributions of the reference and the specimen S1 and S2 calculated by MP (a) and Dollimore–Heal (b) method.

Moreover, the specimens show significant growth of surface areas more than those of common template carbon materials. Template carbons generally have surface areas which are several dozens times of those of template materials, and similar pore size distributions compared with templates [7–12]. In this regard, the Perlite product has limited surface area (≑5 m^2/g; N_2–Langmuir surface area), so it is supposed to be insufficient for template material in synthesis of porous carbons.

However, each specimen in this research has a certain degree of surface area, and some of the specimens have surface area which is more than 100 times of that of the original Perlite product. This result is also outstanding more than the case of synthesis by the use of vermiculite [4]. Therefore, porous growth in the specimens does not stand on the scheme of porous carbon materials by template technique.

We have carried out XRF measurements on the initial state Perlite and Perlite heat-treated at 1173K. The result of quantitative analysis on the initial Perlite is in accordance with the reference data [6]. As a consequence, almost constant results are available on the both measurements (Fig. 4).

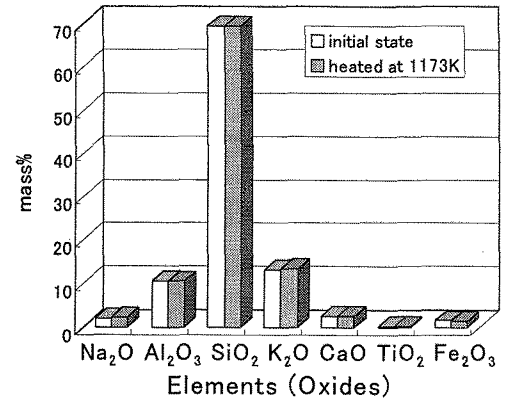

Fig. 4 The result of quantitative analysis by XRF on the initial state Perlite and Perlite heat-treated at 1173K.

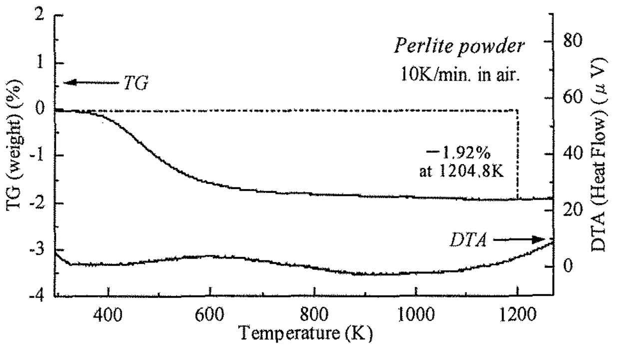

Fig. 5 The result of TG–DTA analysis on Perlite powder in this research.

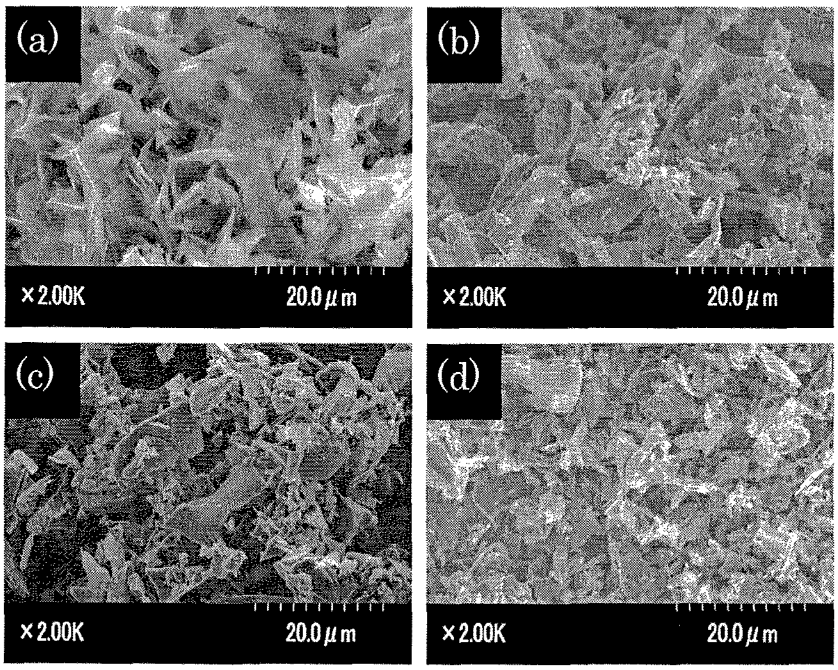

Fig. 6 SEM photographs of the carbon specimens; S1 (a), S2 (b), S3 (c) and S5 (d).

Figure 5 shows the result of thermal analysis (TG–DTA) by TAS300 system on the Perlite product (powder). The measurement has been carried out at the rate of temperature rising of 10K/min. and within the temperature region from R.T. (T≑293K) to 1273K in air. The TG curve in the figure shows extreme gentle decrease from 373K to around 1173K. In the DTA curve, no obvious peak is found. This result is almost invariable in the case of granules of the Perlite product. The gentle decrease in the TG curve from 373K is largely corresponding to desorption of H_2O in the Perlite. (The decrease in the curve is also appropriate to content of crystallization water in Perlite by the reference data [6].) This phenomenon is supposed to originate a kind of activation effect for micro porous growth in the carbon specimens.

The specimens (S3–S5), which are synthesized from glucose or sucrose, excel in porous growth in mesoporous region or surface area. The carbon specimens in this research have different specific surface areas by each raw substance of carbon, and the specimen which has higher surface area clearly shows more fine structure in SEM photographs (Fig. 6). As a result of elemental analysis, rate of content of carbon differs little among the specimens (Table II), and this result suggests that activation effect by Perlite differs in each raw substance.

Furthermore, the specimen synthesized from Perlite powder obviously has large surface area more than those of the specimens from Perlite granules. That is, pulverization of the Perlite product increases surface areas of the specimens efficiently. This result is preferable in the point

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that a simple artifice can improve the specimens' capability.

The specimens in this research have large surface areas to some extent. On the other hand, they also have few meso pores, so they are expected to be lack in adsorption rate in the case that they are used for adsorbents of some harmful substances. Of course, they are clearly inferior to common activated carbons made from coconut shells. Therefore, they can not be used for practical utility in current themselves.

However, it is attractive that the synthesis of porous carbon materials by the use of Perlite can realize concentrative microporous growth in carbon materials by a simple method. In contrast, conventional template technique for synthesis of new porous carbon materials mainly achieves an effect on meso porous growth by availing of meso porous structure of template materials [7–22]. That is, addition of Perlite powder in synthesis procedure of conventional template carbons has prospects of bringing about desirable both micro and meso porous growth in the specimens, and more effective porous materials for adsorbents and several other industrial products. Schemes of porous growth in carbon by Perlite and template method are different, and their multiplier effect can be expected. We will investigate further effective application of Perlite for synthesis of porous materials in a following research.

4. CONCLUSION

Perlite has a certain type of activation effect for synthesis of microporous carbons from several kinds of raw substances. As a result, a carbon specimen from glucose shows preferable porous growth and specific surface areas among the specimens in this research. In addition, the activation effect becomes more prominent when Perlite is used in the form of fine powder. The activation effect originates concentrative porous growth in micro porous region in the carbon specimens, and this attractive effect is expected to be useful in development of more effective porous adsorbent materials in combination with conventional template method.

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