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Adsorption of Organic Solvents' Vapors by Porous Carbon Materials Synthesized by Template Method

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Several specimens of porous carbon materials, whose pore size distributions were controlled by template method, have been synthesized from 2-Furanmethanol (Furfuryl alcohol). Porous materials such as silica gel and natural soils or clays and minerals have been used as templates in the synthesis of the specimens in this research. Some of the specimens show superior adsorbability of several organic solvents' vapors, which are usually generated in work places, as compared with a conventional adsorbent material: common activated carbon (N_2-BET specific surface area: $1310 m^2/g$) from the viewpoints of adsorption rate and quantity.

In addition, a specimen synthesized from commercial vermiculite as template shows remarkable selectivity in adsorption of the vapors. We will also examine a relation between pore size distributions in the specimens and adsorption.

Keywords: Porous carbon materials; Carbonization; Adsorption; BET surface area; Application of natural resources.

1. INTRODUCTION

At the present days, many kinds of organic solvents have been used in various work places for diverse industrial applications. Most of the solvents have some harmfulness to worker's health, and it is very important to remove vapors of them appropriately. In order to prevent workers from poisoning caused by inhalation of the vapors, activated carbons have been mainly used for adsorption of them as gas mask or exhaust until now.

Activated carbons are excellent adsorbents in the point that they can adsorb many kinds of organic substances (including vapors). However, an activated carbon has different adsorbability for vapor of each organic solvent. Further, there are also differences among kinds of activated carbons in their adsorption character to some extent. So it is desirable to use suitable one for the solvents used in each working.

Adsorption character by porous materials is largely affected by porous growths and pore size distributions of them. Activated carbons on the market for adsorption of organic solvents' vapors or organic gases have several values of surface area respectively. However, their pore size distributions are not quite different especially in micro porous region (radius of pores; $r < 1.0$nm). In contrast to this, synthesis of porous carbon materials by template technique can easily realize various specimens [1-17], whose pore size distributions or pore structures are unique for each template and raw substance of carbon [1, 2, 12, 14-17].

We have paid attention that this peculiarity can lead to preparation of more effective adsorbent without chemical additive, whose safety is ambiguous in some cases. Assuming that a specimen prepared by the method shows effective adsorbability of vapor of a very harmful organic solvent clearly, it has a real significance for improvement of air purification in work places.

From the above viewpoint, we have prepared some porous carbon materials by the method with silica gel and natural soils or clays and minerals, which are comparative low-priced template materials, and investigated possibility of their application in adsorption of several organic solvents' vapors.

2. EXPERIMENTAL

2.1. Sample Preparation

In this research, we have used a silica gel (Medium Granular, grain size: 1.70~4.00mm, product of Wako pure chemical Industries Inc.) and 3 types of natural materials (some kinds of volcanic ash soils or clays and minerals which are usually used for horticulture in Japan, products of SEIWA PRO Co., Osaka, Japan) as templates in synthesis of porous carbon materials.

Procedure of the synthesis of the carbon materials is as follows. About 10g of well-dried the template material is soaked in 20ml of 2-Furanmethanol (Wako pure chemical industries Inc.) in a glass bottle capped tightly, for 7days. After this soaking, the material is separated by filtration, and moved into a melting pot.

The material in the pot is heated at T=383K for 30min. in air within a muffle furnace (FP100, Yamato Scientific Co.), and then it is carbonized at T=973K for 30min. with N_2 flow (about 2.5~5.0L/min.) in the furnace. After cooling to room temperature, the material is grinded, and dealt with hydrofluoric acid or sodium hydroxide aqueous solution to dissolve the template. Finally, the carbon material is washed with ultra pure water several times, and dried at T=353K for about 24hours in a drying oven.

N_2-BET specific surface area and pore size distribution 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 Co.) with He gas (≥99.9995%). In addition, elemental analysis (CHN) has been carried out by FISIONS Instruments EA1108.

The surface features of the specimens have been observed with HITACHI S-4700 type scanning electron microscope (SEM), and we have also confirmed XRD (X-ray diffraction) patterns of the samples with RIGAKU RINT 2200 which is equipped with Cu K_α monochrometer. The XRD measurements were carried out in the step scan mode with a 2θ step width of 0.02°-0.25°.

2.2. Measurement of adsorption

Adsorption character of the specimens has been evaluated by an apparatus drawing upon the system stated by JIS K 1474 (Japanese Industrial Standard K 1474, Test methods for activated carbon) [18, 19]. Each measurement has been performed upon about 100mg of the specimen, which is settled into the glass column (ϕ =8mm), at room temperature (T≒298K), and amount of adsorption by each specimen is measured as increase of weight of the column. We have confirmed that temperature was kept almost constant in each measurement. Vapors of the solvents are made by bubbling of dry air. The air flow is sent at the rate of 0.1L/min. by the mini pump (MP-Σ30, SIBATA Scientific Technology Ltd.) into the glass bottle, which has each solvent. All of the solvents used in this research are products of Wako pure chemical industries Inc., and the mini pump can realize automatic control of flow volume adequately. Before measurements, the vapors are purged for a few minutes to secure stability. Conventional common activated carbon (N_2-BET specific surface area; 1310m^2/g), which has comparative high surface area as an adsorbent of organic vapors or gases, is used as a reference in this research.

The above measurements are enough useful and appropriate to evaluate adsorbability of the specimens, for practical utility in work places [19]. In this research, we have measured adsorption character of each specimen for vapor of each single solvent. Evaluation of adsorption character under coexistence of plural different solvents' vapors or water vapor is future subjects after this research.

3. RESULTS AND DISCUSSION

3.1. Properties of samples

Fig.1 shows relations between N_2-BET specific surface area and pore size distribution calculated by MP method in several kinds of conventional common activated carbons, which were produced for adsorption of organic solvents' vapors in general industrial or sanitary application. Activated carbons have several values of surface area (Fig.1 (a)). On the other hand, their pore size distributions, which are especially in micro porous region, are almost overlapped in Fig.1 (b). Among the activated carbons (A1-A5), we have used A1, which is expected to be most superior in adsorption character, as reference for each measurement in this research.

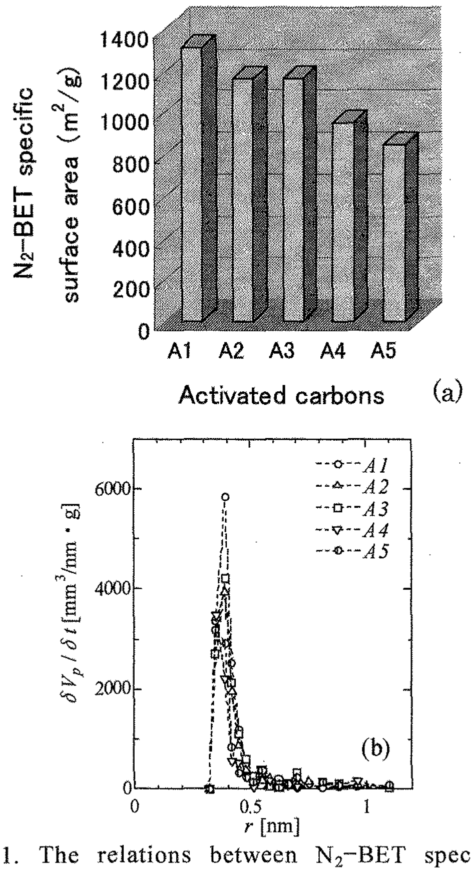

Fig.1. The relations between N_2-BET specific surface area (a) and pore size distribution calculated by MP method (b) in several kinds of activated carbons.

Properties of templates and carbon materials in this research are shown in Table Ⅰ. The templates T1, T2, T3 and T4 correspond to the carbon specimens C1, C2, C3 and C4 in this order. In the templates, T1 is silica gel and T2-T4 are natural soils or clays and minerals. Fig.2 shows images of template materials T2, T3 and T4. T2 and T3 have

Table Ⅰ. Properties of templates and carbon materials in this research. V_{micro} was pore volume calculated by MP method, and V_{meso} was that calculated by D−H method.

SAMPLE	T1	T2	T3	T4
N_2-BET specific surface area (m^2/g)	685.5	134.9	205.7	6.55
Density (g/cm^3)	2.152(4)	1.892(2)	2.153(1)	2.050(5)
V_{micro} (ml/g)	0.37	0.057	0.0326	0.001
V_{meso} (ml/g)	0.1561	0.0806	0.1857	0.0152

SAMPLE	Reference (Activated carbon)	C1	C2	C3	C4
N_2-BET specific surface area (m^2/g)	1310	985.2	883.2	715.6	365.9
Density (g/cm^3)	2.059(2)	1.631(5)	1.915(6)	1.665(2)	1.673(4)
V_{micro} (ml/g)	0.574	0.527	0.418	0.483	0.145
V_{meso} (ml/g)	0.0618	0.5215	0.3897	0.387	0.0817

irregular shaped and sized granules; T2 has grain size about ϕ =10mm, and T3 has the size about ϕ =2−10mm. T4 has square-like shaped grains, which have also a layer structure, and it is within a diameter of about 3−5mm.

3 types of natural soils (T2, T3 and T4) are comparatively lack in physical uniformity, as compared with artificial industrial porous materials (for example; silica gel, zeolite or other ceramic materials). However, as priority in this research, we have investigated pore size distributions and adsorbability of each carbon material, which is finally synthesized by the method. From the point of view, we have confirmed that the specimens have enough evaluation for reproducibility in the preparation.

Fig.3 shows SEM photographs of the specimens (×2.00K). From the photographs, surface feature of the carbon materials are different each other obviously. C2 has a sponge-like complicated surface structure (Fig.3 (b)). On the other hand, surface of C3 has numerous elliptic pores (Fig.3 (c)). Further, SEM image of C4 is different from those of the other specimens considerably; numbers of irregular-sized layers are piled (Fig.3 (d)).

Fig.4 shows pore size distributions in the specimens calculated by MP method. The distributions in the carbon materials are almost reflected those of each template. The figures indicate that carbon materials C1−C3 have distributions of pores in the region which activated carbon has extreme few pores (in short, larger size in micro porous region: r≒0.5−1nm). Furthermore, their porous growths surpass that of the reference in meso porous region (radius of pores; 1.0nm <R_p<15nm) (Fig.5). The latter property is expected to bring about good effect on adsorption rate. In contrast to this, the specimen C4, which has been synthesized from commercial vermiculite produced by firing of vermiculite or weathered biotite minerals, has prominent limited pore size distribution (Fig.5 (d)). In the distribution, only a steep peak is found especially in micro porous

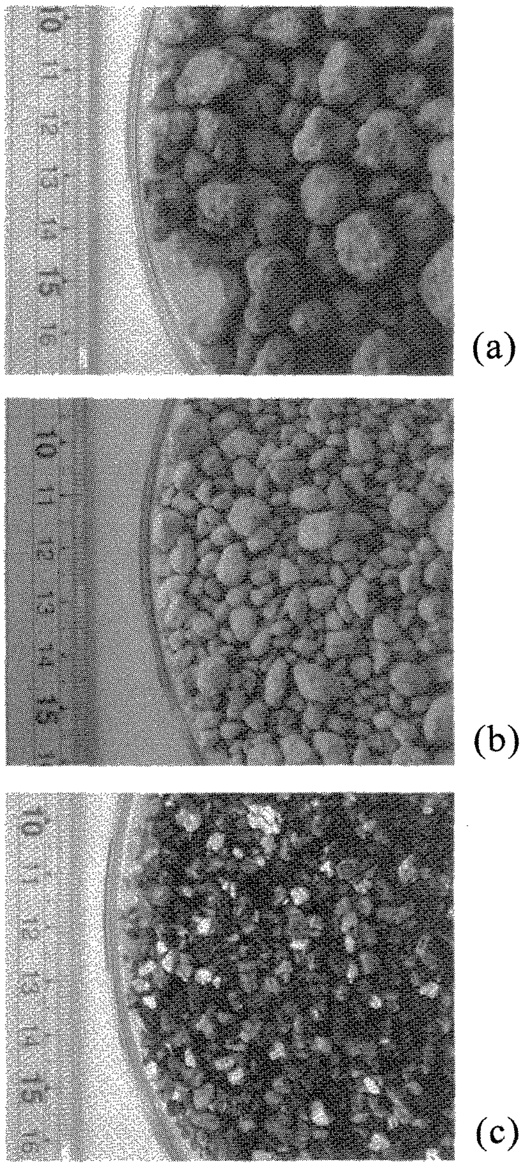

Fig.2. Photo images of the template materials; T2 (a), T3 (b) and T4 (c). Scale unit in the images is cm.

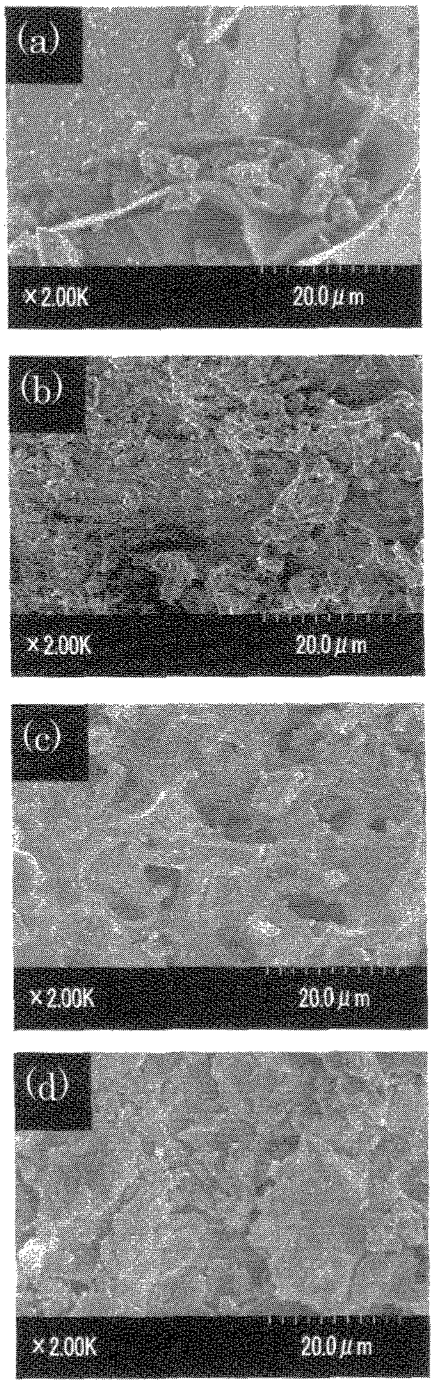

Fig.3. SEM photographs of the template carbon materials; C1 (a), C2 (b), C3 (c) and C4 (d).

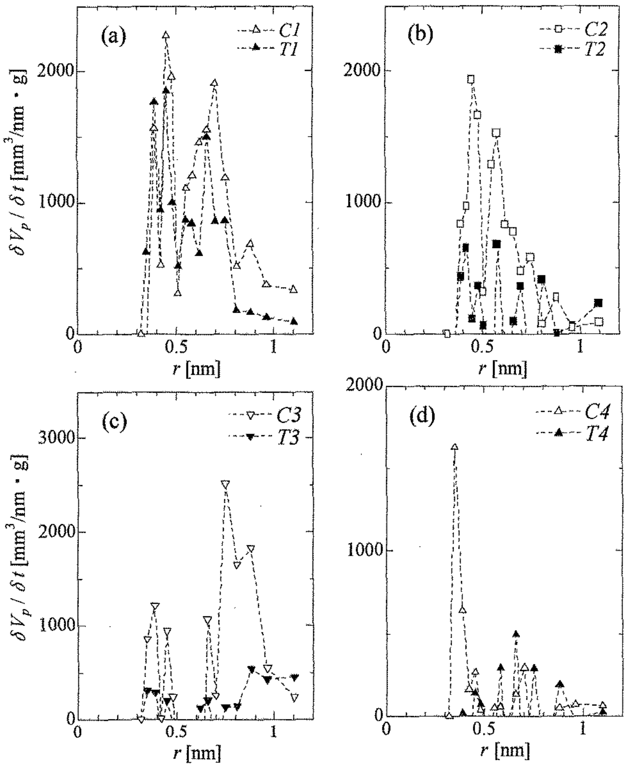

Fig.4. Pore size distributions of the specimens and their template materials calculated by MP method; C1 and T1(a), C2 and T2 (b), C3 and T3 (c) and C4 and T4 (d).

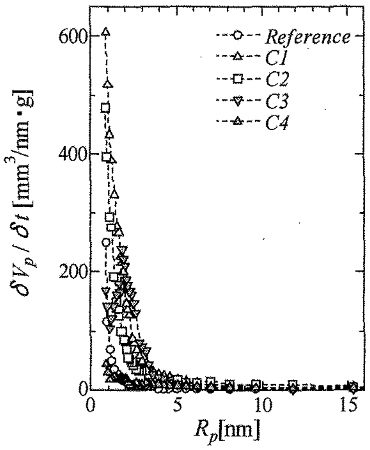

Fig.5. Comparison of pore size distributions calculated by Dollimore−Heal method of the reference and the specimens.

region, and it is located at smaller size (r≒0.35−0.39nm), compared with the peak in the data of the reference (Fig.1 (b)).

XRD patterns of the specimens are shown in Fig.6 (They are shifted to the direction of intensity, for clearness of expression.). In the figure, specimens C1−C3 show typical pattern of non crystal carbon. However, especially in the profiles of C2 and C3, some small peaks correspond to template materials are found. This result indicates that template materials were not dissolved completely in C2 and C3; assuming that they are dissolved perfectly, the specimens have higher specific surface area, moreover, higher adsorbability. In a strict sense, the specimens in this research are complexes of carbon and template materials.

The sample C4 has several comparative sharp peaks in its XRD pattern. From the peaks, the structure is well understood as hexagonal; lattice parameters calculated by least square refinement: a =7.3239(273) Å and c =15.7503(652) Å. We have also confirmed that the sharp peaks originate from a layer structure of un-dissolved template

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
C1	89.2	1.6	0.0
C2	51.1	1.1	0.1
C3	80.3	1.7	0.0
C4	60.7	2.2	0.0

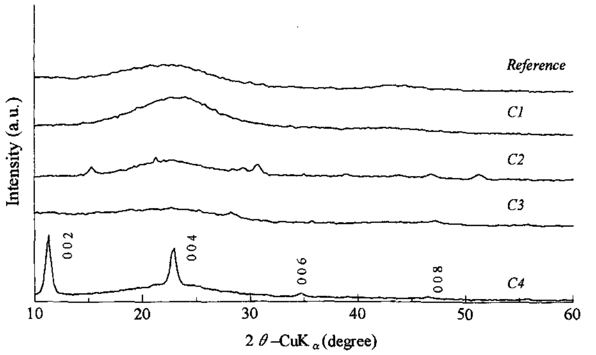

Fig.6. XRD patterns of the reference and the specimens in this research. They are shifted to the directions of intensity, for clarity of expression.

material (commercial vermiculite) in the specimen.

Table II shows the results of elemental analysis (CHN) of the specimens. As compared with the reference, rate of content of carbon in the specimens, particularly C2 and C4, is clearly low. These results also support the above remark concerning possibility for further improvement. In addition, among the templates, 3 types of natural soils (T2, T3 and T4) are expected to contain small quantity of some organic components, and they seem to have some effects on carbonization.

3.2. Adsorption by samples

The specimens synthesized in this research have various pore size distributions, which are different from those of conventional activated carbons, so it is expected that each carbon material has a unique adsorption character for organic solvents' vapors.

Fig.7 shows adsorption of several organic solvents' vapors by the reference. The reference is excellent in adsorption of vapor of cyclohexane and several chain compounds (hydrocarbons). Activated carbon is certainly excellent adsorbent especially from the viewpoint of cost. Here, we have paid attention to several organic solvents' vapors, which are shown comparative weak or slow adsorption by activated carbon, in measurements of adsorption character of template carbon materials in this research.

Fig.8 shows adsorption of vapors of several organic solvents by the reference and the specimens C1–C3. As a result, some of the specimens show superior (or approximately equal) adsorption of several organic solvents' vapors as amount or rate in increase of weight of the column, as compared with the reference.

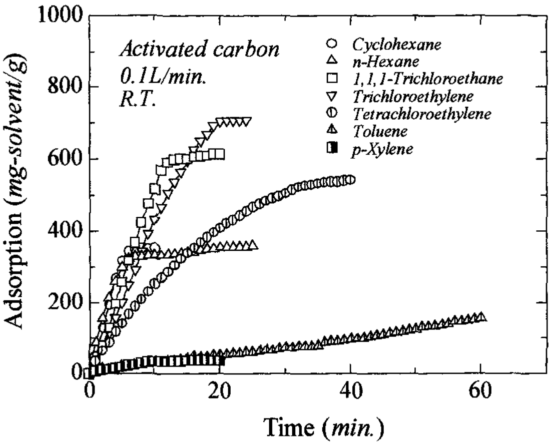

Fig.7. Adsorption of several organic solvents' vapors by the reference (activated carbon).

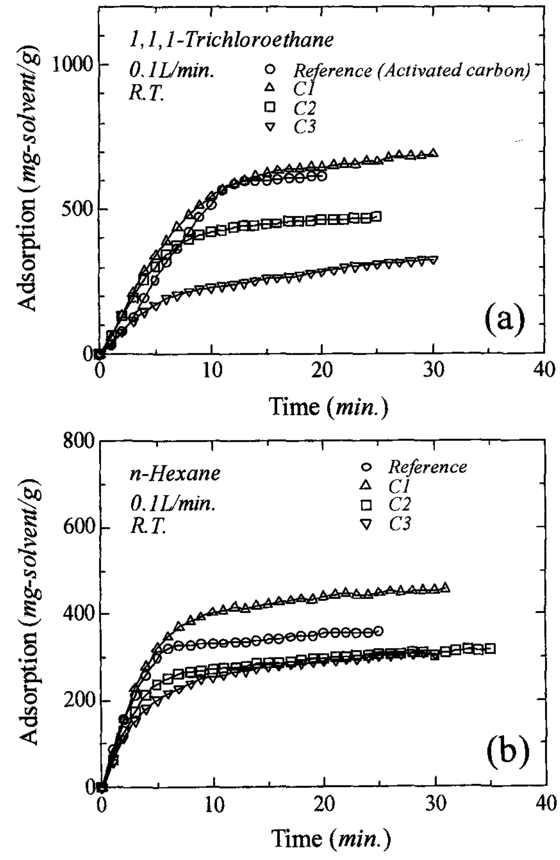

Fig.8. Adsorption of several organic solvents' vapors by the reference and the specimens (C1–C3); (a) 1, 1, 1- Trichloroethane, (b) n-Hexane, (c) Methanol, (d) Toluene.

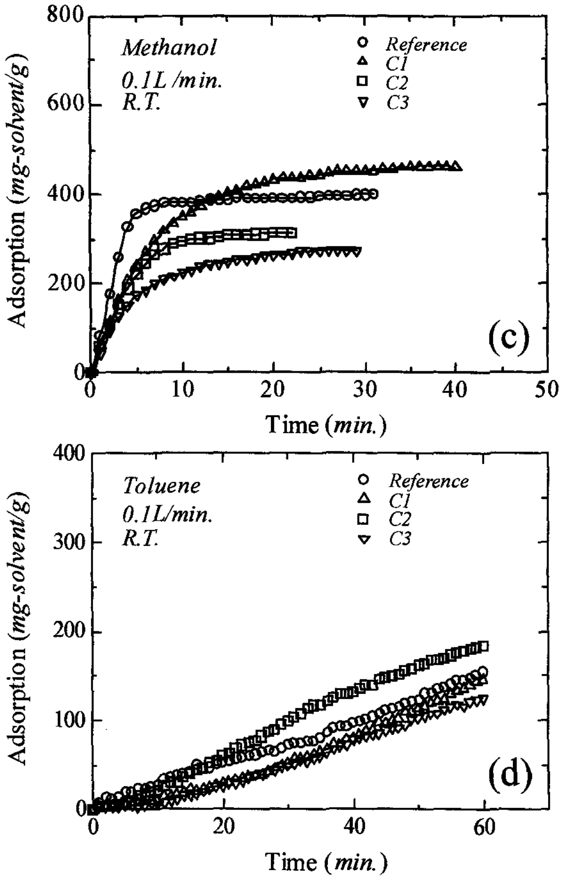

Fig.8. (*Continued.*)

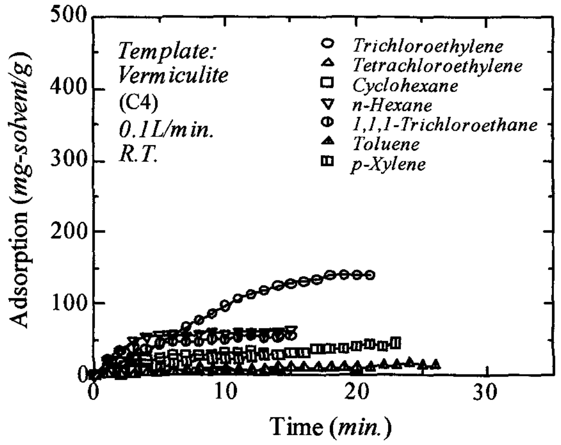

Fig.9. Selectivity in adsorption of organic solvents' vapors by C4 sample.

Previously, T.Kyotani *et al.* have reported that a carbon material which was prepared from furfuryl alcohol and lamellae saponite shows quite large amount of absorption and swelling ratio for various organic solvents (liquid) in comparison with a popular activated carbon [5]. The results in our research do not conflict their report. Especially, in adsorption of vapors of 1, 1, 1-Trichloroethane, C1 and C2 show effective result in the beginning time zone (0−5min.) as compared with the reference. This is attributed to the growth of pore structure in meso porous region, that is, their porous growths surpass that of the reference obviously (Fig.5). C1 also exceeds the reference in amount of adsorption as a consequence here. Further, in adsorption of n-Hexane (Fig.8 (b)), C1 exceeds in amount of adsorption more than that of the reference, in the time zone after 3min. passes. On the other hand, in adsorption of methanol (Fig.8 (c)) which has a small-sized chain type molecule, C1 is inferior to the reference at the beginning time zone. However, it is superior to the reference in amount of adsorption after 14 min. passes. Contribution by growth of meso pores in C1 or C2 is not found in adsorption of methanol.

C1 has shown effective adsorptions for vapors of several kinds of chain compounds. In contrast to this, C2 adsorb several vapors of aromatic compounds effectively. Fig.8 (d) describes the results for vapor of Toluene. In adsorption of Toluene, C2 surpasses the reference in amount of adsorption after 20 min. passes. On the other hand, C1 and C3 are inferior to the reference obviously.

This result can not be explained by only growth of pore structures in the specimens, because the growth in C1 surpasses that of C2 in wide region of pore size as Fig.4. It seems that there is some difference in surface chemical effect between C1 and C2. We will continue investigation concerning this point in a following research.

In addition, C4, which is a specimen prepared from commercial vermiculite as template, shows remarkable selectivity (Trichloroethylene) in adsorption of organic solvents' vapors in this research (Fig.9). C4 has never shown substantial adsorption of Tetrachloroethylene. This property of the specimen is seemed to be mainly originated from its very narrow pore size distribution, and it is expected to lead application of the material as a sensor for vapor of particular organic solvent. Assuming that various narrow pore size distributions in specimens are realized by using other natural soils or clays and minerals as templates, objective organic compound in selectivity is also expected to be changed.

Of course, the specimens in this research are still imperfect for practical application and utility yet. At first, procedure of synthesis of the specimens is still insufficient; removal of the template materials after carbonization. Improvements of this point will bring about template carbon materials which have superior adsorbability, compared with the specimens at present. In addition, form of the specimens except for C4 is small powder, so some appropriate shaping or granulation is preferable for handling.

However, as a result, porous carbon materials synthesized by template method have enough potentiality for realization of safe and more effective adsorbents of organic solvents' vapors, and materials which contribute to detection for specified organic solvent's vapor in work places.

4. CONCLUSIONS

Several porous carbon materials have been prepared by template method from 2-Furanmethanol in order to evaluate their property as adsorbent materials for vapors of organic solvents, which are used in work places. Silica gel and natural soils or clays and minerals have been used as templates in the synthesis of the carbon specimens in this research.

The specimens have various pore size distributions, which are different from those of conventional activated carbons, and some of the specimens show superior adsorbability of several organic solvents' vapors, as compared with a common activated carbon (N_2-BET specific surface area: 1310m^2/g). Besides, the specimen synthesized from commercial vermiculite shows remarkable selectivity (Trichloroethylene) in adsorption of the vapors.

These results indicate that synthesis of porous carbon materials by template method can be useful for improvement of air purification and detection of specified organic solvent's vapor for environment evaluation in work places.

5. ACKNOWLEDGEMENTS

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