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Adsorption Properties of Woodceramics

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ABSTRACT

Gas adsorption properties of wood and woodceramics were evaluated by specific surface area (SSA), adsorption capacity for oxygen and nitrogen, and by the rapid measuring method for volatile organic compounds (VOCs).

Woodceramics showed different preferences on the adsorption for gases and perfumery materials depending on the starting material, irrespective for the SSA. Furthermore, the gas adsorption properties as evaluated by the rapid VOC evaluation method differed depending on the particle size. In particular, cedar-based woodceramics 1.0-1.7 mm in size showed strong adsorption power for citral, and coarsest particles (>4.0 mm in size) for geraniol, in which more than 99.9% of the compounds were adsorbed. About 99.7-99.8% of pulegone and menthone, and 99.0% of nerol were adsorbed by the cedar-based woodceramics 4.0 mm or larger in particle size.

Key words: adsorption, woodceramics, perfumery materials, pore, c/c composite

1. INTRODUCTION

Wood-based materials are attracting attention because they are good absorbers of volatile organic compounds (VOCs). Woodceramics are carbon/carbon composite materials consisting of plant-originated amorphous carbon reinforced by glassy carbon generated from phenol resin. Woodceramics can be produced by impregnating wood-based (lignocellulosic) materials, such as hiba, cedar, pine, medium density fiber (MDF) boards, waste paper, apple wastes, etc., with phenol resin, and by then calcining the resulting material. Thus, they are porous materials having Brunauer-Emmett-Teller (BET) specific surface area of about 500 m^2g^{-1}, and have potential as adsorbents.

Woodceramics are also advantageous because they are environmentally friendly materials in that they can be produced from lignocellulosic industrial wastes, such as waste paper [1], olive pomace and olive stones [2], and apple pomace [3]. Woodceramics are advantageous in that they not only make use of wastes, but also are stronger and resistant to higher temperatures than the original carbonaceous material, and other functions can be imparted thereto. For instance, Woodceramics prepared from apple pomace showed potential for gas adsorbents [3]. Although woodceramics produced from apple pomace typically has a small BET specific surface area lower than 0.5 m^2g^{-1} (nitrogen), they show oxygen and nitrogen gas adsorption capacities well comparable to molecular sieve carbon (MSC). Other attempts have been made to produce woodceramics from carbonaceous materials [4]. Similarly, since broiler litter generally contains about 40 mass% (dry basis) carbon [5,6], an attempt of producing woodceramics from biomass based on chicken wastes has been made [7]. As compared with carbonized chicken wastes, the product (woodceramics) is advantageous in that it is free of unfavorable smell [8].

Thus, the gas adsorption properties of woodceramics were investigated and evaluated from the viewpoint of acquiring information on the gas adsorption mechanism and of evaluating adsorption power on different type of perfumery compounds (essential oil components).

2. EXPERIMENTAL

Samples

The following samples were prepared and used in the experiment. For comparison, carbonized tree (wood charcoal; see Fig. 1(a)) was used.

1. CE-Woodceramics prepared from cedar. Saw waste of cedar crushed to particles 0.1 mm in size was mixed at a weight ratio of 6:4 with phenolic resin (BELLPEARL S890, a product of Kanebo, Ltd.), and the resulting product was sintered at 800°C in a rotary continuous heating kiln while flowing gaseous nitrogen.
2. AP-Apple fiber (product of Nichiro Corp.) was mixed at a weight ratio of 6:4 with phenolic resin (BELLPEARL S890), and the resulting product was sintered at 800°C in the same manner as CE (See Fig, 1(b)).

Other raw wood materials were also used as comparative samples where necessary.

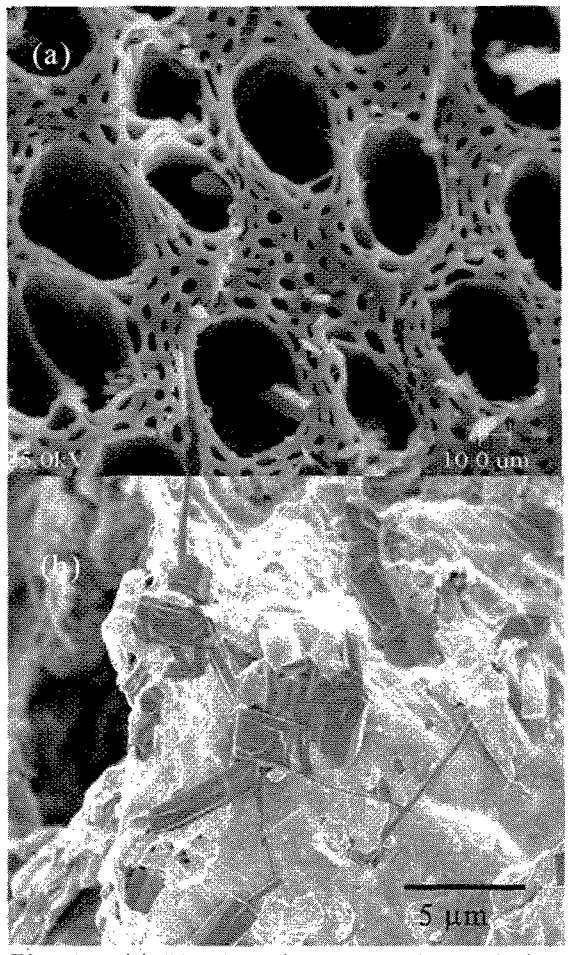

Fig. 1. **(a)** FE-SEM photograph of a typical carbonized tree. Charcoal has macro-pores 1-50 μm in diameter. **(b)** FE-SEM photograph of woodceramics made from apple-waste.

Specific Surface Area (SSA)

Adsorption isotherms and SSA (Multipoint Brunauer-Emmett-Teller (BET) method) were obtained using nitrogen gas as adsorbate at 77 K (Autosorb 1, Quantachrome Instruments) and where necessary, gaseous CO_2 as adsorbate at 195 K (BELSORP-mini, BEL Japan).

Oxygen and Nitrogen Gas Adsorption Properties

Figure 2 shows the system for measuring basic gas adsorption capacity of the sample. The gas adsorption capacity of the sample is calculated in the following manner. Under applied pressure, the limited system 1 to 3 is so controlled to satisfy the following equation (1):

$$P_c V_{c1} = n_0 RT \quad (1)$$

where, P_c (2.7 kgf cm^{-2} in the present case) is the controlled constant pressure;

V_{c1} is the controlled constant volume;

n_0 is the total amount (mol) of gas introduced into the system;

R is the gas constant; and

T is absolute temperature in Kelvin.

By opening the valve 3 and introducing gas into the sample chamber 4, the closed system 1 to 4 obeys the following equation (2):

$$P_{obs} \times (V_{c2} - V_x) = n_1 RT \quad (2)$$

where, P_{obs} is the observed pressure;

V_{c2} is the total volume of the system;

V_x is the sample volume; and

n_1 is the amount (mol) of free gas.

The gas adsorption capacity q_{O2} (mg g^{-1}) (for oxygen) can be obtained by:

$$q_{O2}\ (\text{mg g}^{-1}) = (n_0 - n_1) \times mw_{O2}/sw \times 1000 \quad (3)$$

where,

mw_{O2} is the molecular weight of oxygen (32g); and

sw is the sample mass (g).

Thus, equation (3) can be rewritten as:

$$q_{O2}\ (\text{mg g}^{-1}) = \left(\frac{P_c V_{c1}}{RT} - P_{obs} \times \frac{V_{c2} - V_x}{RT}\right) \times \frac{mw_{O2}}{sw} \times 1000 \quad (4)$$

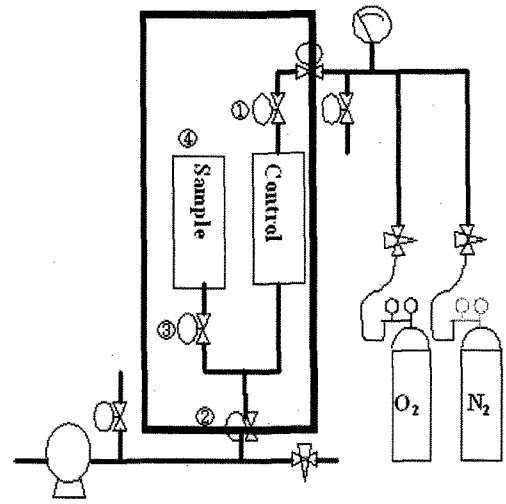

Fig 2. Basic gas adsorption capacity measuring system.

The nitrogen gas adsorption capacity q_{N2} (mg g^{-1})(for nitrogen) can be obtained by analogy to the case of oxygen gas adsorption equation (4), except for substituting mw_{N2} (28g) for mw_{O2}.

Rapid measuring method for volatile organic compounds (VOCs)

The adsorption properties of Woodceramics were evaluated by using the rapid measuring method for volatile organic compounds (VOCs) evolved from wood materials recently developed by Nishimoto et al[9]. This method had been developed by using thermogravimetry (TG) and gas chromatography (GC), based on the findings that the sum of the peak areas obtained in a predetermined duration of time in the chromatogram is directly related to the amount of gas species evolved from the sample.

Thus, as shown in Fig, 3, a small amount (50mg) of the sample was sealed in a vial with the adsorbates, and they were kept at a certain temperature (383 K) for 1 hour. Then, 1 ml of the gas phase was taken and measured by GC

(HP6890, equipped with HP6890 FID and DB-1 capillary column) using He as the carrier gas. In this manner, adsorption power of woodceramics for carvone, pulegone, geraniol, citronellol, menthone, nerol, and citral was evaluated.

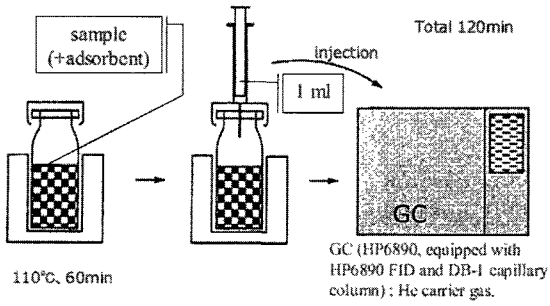

Fig. 3 Schematically shown process of the rapid measurement for evaluating adsorption power of volatile compounds.

3. RESULTS AND DISCUSSION

The SSA of the samples are shown in Table 1.

Table 1 SSA of the samples and comparative samples.

Samples		SSA $m^2 g^{-1}$
Samples	BELLPEARL S890	2
	CE	555
	AP	3
Comparative	BELLFINE	1687
	FLUKA 05120	913
	Cedar	500

From the results above, and from the texture shown, it can be understood that woodceramics greatly differs in SSA depending on the starting material, and none could yield an SSA as high as the commercial products.

Figs. 4(a) and 4(b) show oxygen and nitrogen gas adsorption profiles for CE and AP, respectively.

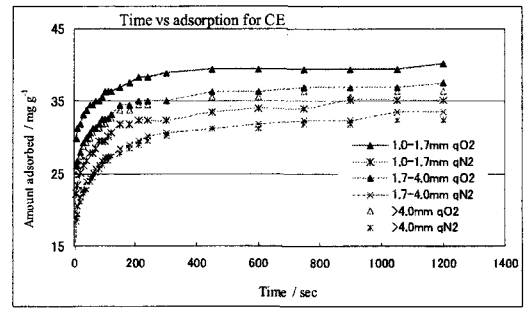

Fig. 4(a) Oxygen (triangles) and nitrogen (crosses) gas adsorption curves for CE differing in particle size; solid line: particle size 1.0-1.7 mm; no lines: particle size 1.7-4.0 mm; broken lines: particle size greater than 4.0 mm.

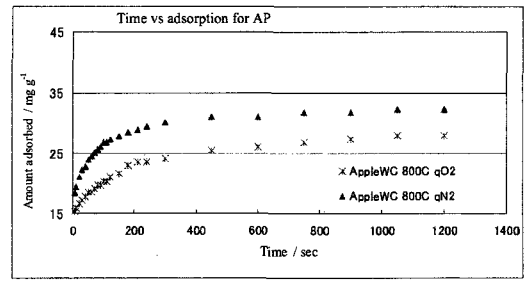

Fig. 4(b) Oxygen (triangles) and nitrogen (crosses) gas adsorption curves for AP obtained by carbonizing at 800 °C

Since BET is directly related with the physisorption attributed to van del Waals force, the large BET SSA of CE indicates that physical gas adsorption is dominant for CE. AP also shows high adsorption, however, the low SSA suggests that adsorption of AP occur mainly by chemical adsorption. Thus, as shown in Fig. 4(a), CE takes up nitrogen and oxygen gases in a similar manner in the initial stage of adsorption. On the other hand, as shown in Fig. 4(b), AP preferentially takes up oxygen as shown by the adsorption curve with steep tangent in the initial stage of adsorption curve.

In order to evaluate the selectivity of the gases, the following parameter, time constant, τ, was defined[10]. Fig. 5 is a graph showing the time constant τ values obtained from oxygen and nitrogen adsorption curves, plotted on the abscissa and the ordinate, respectively. The bold straight line connects points on which the time constant is equal for oxygen and nitrogen. The steeper the gradient of the line connecting to the origin, the better is the selectivity for nitrogen. It can be seen that CE samples have no selectivity on gas species, whereas AP shows some selectivity on nitrogen than on oxygen.

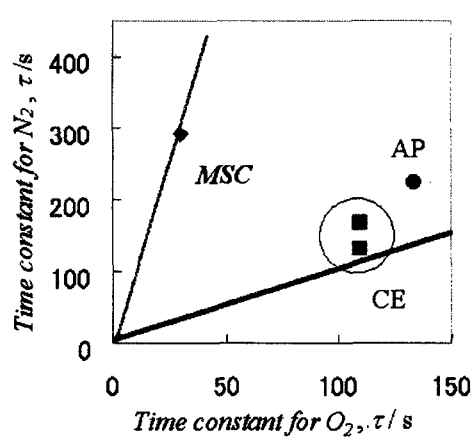

Fig. 5 Evaluation of gas adsorption selectivity. The bold straight line indicates that the time constant is equal for oxygen and nitrogen. MSC is for commercially available molecular sieve carbon. The steeper the gradient of the line connecting to the origin, the better is the selectivity for nitrogen.

Table 2 shows the results obtained by the rapid measuring method for volatile organic compounds (VOCs). The lower the value, the higher is the adsorption power for the perfumery substances. The adsorption capacity of CE differing in particle size is also compared; CE(1) consists of particles with size range of 1.0~1.7mm, CE(2) 1.7~4.0mm, and CE(3) above 4.0mm. It can be seen that coarser particles of CE.adsorb more perfumery substances, but depending on the material. Particularly high adsorption power was exhibited on geraniol (coarsest particles) and citral (finer particles), in which more than 99.9% of the compounds were adsorbed. However, in cases of pulegone, citronellol, and menthone lower adsorption power was obtained for finer particles.

4. CONCLUSIONS

Gas adsorption properties of wood and woodceramics were evaluated by specific surface area(SSA), adsorption capacity for oxygen and nitrogen, and by the rapid measuring method for VOCs. Adsorption selectivity on oxygen and nitrogen differed depending on the starting material. In general, Woodceramics showed higher adsorption power for perfumery materials, but the power depended on the particle size and the perfumery compound species.

5. REFERENCES

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Table 2 Adsorption capacity for perfumes. (in *TVOC* /nL; n=3)

	perfume only 0.1 mL	with CE(1)* (0.05g)	with CE(2)* (0.05g)	with CE(3)* (0.05g)	with cedar wood (1.0g)	with bamboo charcoal (0.2g)	with cedar charcoal (0.05g)
Menthone	111.4	16.9	2.5	0.3	0.4	24.3	9.8
Pulegone	124.5	22.7	3.2	0.4	2.9	5.7	12.9
Citronellol	81.9	11.5	5.1	4.9	7.0	10.5	18.0
Nerol	96.6	7.8	2.6	1.0	7.4	17.6	17.6
Citral	176.8	0.1	2.6	3.4	6.9	7.0	15.9
Geraniol	80.5	3.3	2.3	0.1	3.2	10.2	30.8
Carvone	106.9	0.3	1.2	2.2	1.4	33	6.4

(1) particle size 1.0~1.7mm, (2) 1.7~4.0mm, (3) above 4.0m

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