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## Molecular sieving behavior of carbonized wood: selective adsorption of toluene from a gas mixture containing $\alpha$ -pinene

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**Abstract** The adsorption properties of wood carbonized at various temperatures were investigated using a mixed gas containing toluene and  $\alpha$ -pinene. Hinoki (*Chamaecyparis obtusa*) samples carbonized at 500–1100°C were exposed to gas mixtures of toluene and  $\alpha$ -pinene at 20°C. The samples carbonized at 500–700°C only adsorbed toluene, whereas those carbonized at 800–1100°C adsorbed both toluene and  $\alpha$ -pinene. Analysis of the surface structure of the carbonized wood by nitrogen adsorption at liquid nitrogen temperature indicated that the sample carbonized at 700°C had micropores mainly 0.6 nm in diameter and few mesopores, whereas the samples carbonized at 900°C and 1100°C had mesopores and micropores larger than 0.8 nm in diameter. With the sample carbonized at 700°C, the flat-shaped toluene molecules could probably penetrate into the narrower pores, 0.8 nm in diameter, whereas the bulky globular-shaped  $\alpha$ -pinene molecules could not. Carbonization at temperatures higher than 900°C probably enlarged the pore size and thereby reduced the selectivity of adsorption. The results revealed that wood carbonized below activation temperature has a unique flat-pore structure that seems to work as a kind of molecular sieving carbon, successfully removing only the harmful volatile organic compound (VOC), toluene, and leaving behind a pleasant aroma of  $\alpha$ -pinene in the atmosphere.

**Key words** Carbonized wood · Molecular sieve · VOC · Surface structure

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### Introduction

Various kinds of substances classified as volatile organic compounds (VOCs) are found in our living environment. Naturally occurring terpenes (essential oil constituents emitted from wood) can also be found, especially in wooden houses and houses equipped with much wooden furniture. Some of these substances bring about various beneficial physiological functions that are desirable for human health, such as improvement of work efficiency,<sup>1,2</sup> anti-ulcer action,<sup>3,4</sup> and cedar pollenosis restraint.<sup>5</sup> Therefore, “forest therapy,” which makes use of these effects in palliative care and rehabilitation, has recently been attracting much attention.<sup>6</sup> On the other hand, some of the VOCs emitted by chemical materials, such as solvents, resins, adhesives, and paints used for building materials and furniture, are known to be a possible cause of the sick building syndrome, producing symptoms such as lassitude, headaches, rashes, dizziness, and respiratory system disease.<sup>7</sup> Because this is a major concern in our living environment, we must take effective action to address this problem. Therefore, it is desirable to effectively remove all harmful petroleum-derived solvent VOCs from indoor air and leave only those useful and natural fragrant substances emitted from wood.

A carbon-based adsorbent can be a useful means of achieving this selective adsorption. Much effort has therefore gone into the design of suitable pore structures for use in the development of various active carbons and carbon molecular sieves (CMS).<sup>8</sup>

In general, active carbon consists of disorganized graphitic micro-planes with slit-shaped pores and variable pore-size distributions. The micropore structure of such carbons is unique because the slit-like apertures and the constrictions of the micropores are similar in size to the molecular dimensions of various adsorbates, allowing these carbon structures to function as a molecule sieve.<sup>9</sup> Moore and Trimm<sup>10</sup> reported experimental evidence for the preferential adsorption of flat molecular probes compared to the nonsorption of spherical molecular probes of similar dimensions. Most studies, however, have only been con-

cerned with the industrial use of CMS prepared from petroleum-derived substances for applications such as gas separation,<sup>11,12</sup> purification,<sup>13</sup> and storage.<sup>14</sup> Carbonized wood is a porous, carbon-based material that can also be used for effective air purification, and there are many reports of its use in toxic substance removal, humidity conditioning, and deodorization.<sup>15</sup> In view of the carbon fixation potential of unused wood resources, it is expected that carbonized wood will be utilized more widely as an “eco-material” because of its adsorption function. Therefore, we investigated whether carbonized wood could be used as a CMS for the improvement of indoor air quality.

Few studies have been carried out on the use of CMS gas adsorption materials derived from wood. Arriagada et al.<sup>9</sup> investigated the influence of carbonization temperature, between 600° and 1100°C, on the preparation of CMS pellets derived from hardwood. The carbonization temperature of wood was found to have a very significant effect on the resulting separation properties of the carbonized wood produced. Some of the carbonized wood obtained showed promise in both CO<sub>2</sub>/CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>/C<sub>3</sub>H<sub>6</sub> gas mixture separation but was not tested on VOCs such as aromatic hydrocarbons (>C<sub>6</sub>) and terpenes (>C<sub>10</sub>). Nakajima et al.<sup>16</sup> investigated the influence of carbonization temperature between 400° and 1100°C on the adsorption capacity of carbonized wood made from Hinoki (*Chamaecyparis obtusa*) and plywood when tested against single-component and multicomponent mixtures of typical indoor pollutant VOCs. The adsorption amounts measured differed for each type of VOC, depending on the temperature at which the wood was carbonized. They suggested that the selective adsorption property of carbonized wood for each type of VOC could be controlled by the carbonization temperature; however, the textural property of prepared carbonized wood has not been revealed yet.

Therefore, we investigated the molecular sieving effect of carbonized woods, made from Hinoki cypress carbonized at various temperatures, on gas mixtures containing both toluene and  $\alpha$ -pinene. The terpene  $\alpha$ -pinene is known as a “relaxation aroma” that hastens fatigue recovery during sleep<sup>17</sup> whereas toluene, a common aromatic hydrocarbon, is a petroleum solvent and a typical VOC found in indoor air.<sup>18</sup> The surface structure of different carbonized woods, and how this related to their selective adsorption properties, was also investigated, taking into consideration the differences in molecular dimensions and the shapes of the test adsorbates.

## Materials and methods

### Carbonized wood preparation

Crushed and sieved Hinoki thinned wood samples were prepared, with a particle size of 1.70–2.38 mm and water content of 42.5%. These 15-g subsamples were placed in a porcelain crucible and carbonized under a stream of nitrogen gas with a flow rate of 2 l/min in a muffle furnace

**Table 1.** Concentration of O<sub>2</sub> in the gas drained from the exhaust duct of the furnace during the heat treatment procedure up to 1100°C

Elapsed time (min)	Temperature (°C)	Concentration of O <sub>2</sub> (%)	
		Empty (blank)	With sample
0	–	7.5	4.9
20	100	5.7	3.6
40	200	4.3	2.5
60	300	3.0	1.6
80	400	2.1	0.9
100	500	1.5	0.3
120	600	1.0	<0.1
140	700	0.7	<0.1
160	800	0.4	<0.1
180	900	0.2	<0.1
200	1000	0.1	<0.1
220	1100	<0.1	<0.1

(Motoyama, Japan), within which the specimen chamber with a volume of 20 l was heated at a rate of 5°C/min and kept at a prescribed temperature between 500° and 1100°C for 1 h.

To estimate the extent of nitrogen gas substitution in this carbonizing system, the O<sub>2</sub> gas drained from the exhaust duct of the furnace was monitored using a SEM102 combustion control tester (Komyo Rikagaku Kogyo, Japan) during the heat treatment procedure (up to 1100°C) (Table 1).

### Structural characterization

The specific surface area (SSA) of the carbonized wood samples was measured using a Flow Sorb II 2300 (Micromeritics) flow absorption apparatus and the single-point BET method (after Brunauer, Emmett, and Teller<sup>19</sup>) involving nitrogen adsorption at 77 K using a gas mixture of 24% N<sub>2</sub> and 76% He. The nitrogen adsorption isotherms of the carbonized wood samples at 77 K were measured using a BELSORP18 (Bel, Japan). The mesopore (2–50 nm diameter) and micropore (<2 nm diameter) size distribution was calculated from the resultant data using the Dollimore-Heal (DH) method<sup>20</sup> and the micropore analysis method (MP method<sup>21</sup>), respectively. The DH method and the MP method were based on assumption of mesopore/cylindrical pores and micropore/slit-like pores, respectively. The same methods were used to calculate the surface area and the volume of each size of pore.

Diffraction was carried out using a RINT2000 (Rigaku, Japan) with a 40 mA/40 kV CuK $\alpha$  beam.

The surface structure was visually examined using an S4000 SEM (Hitachi, Japan).

### Adsorption properties for toluene and $\alpha$ -pinene

The carbonized wood samples were dried at 150°C for 1 h, and 20-mg subsamples were then exposed to 3 l of a gas mixture comprising 10 ppm of both toluene and  $\alpha$ -pinene in a fluorinated resin bag at 20°C to investigate their adsorption properties. The temperature inside the bag was then

sequentially increased to 40°, 60°, and 80°C (at intervals of 24 h) to investigate the desorption behavior of samples carbonized at 500°, 700°, or 900°C. Before moving to each subsequent stage, gas concentrations were measured by the thermal desorption-gas chromatography/mass spectrometry system (TD-GC/MS; Turbo Matrix ATD-Clarus 500 GC/MS, PerkinElmer, USA). The removal efficiency for toluene and  $\alpha$ -pinene was determined by the ratio of the gas concentration at each exposure time to the initial concentrations.

### Molecular modeling of the adsorbates

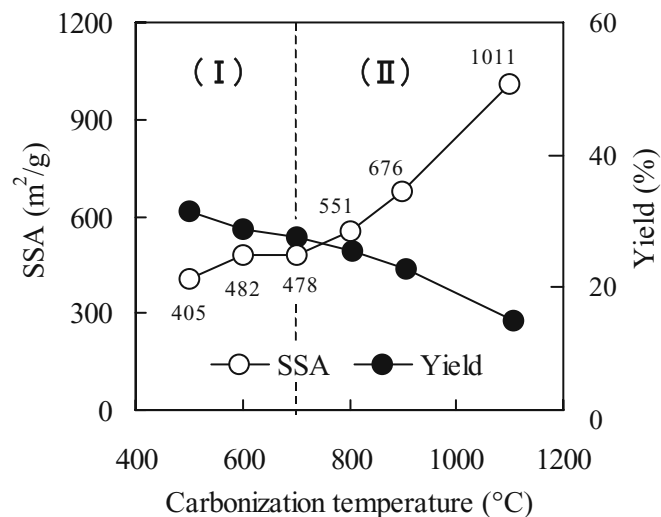
The molecular shapes and dimensions of toluene and  $\alpha$ -pinene were calculated using molecular modeling software, WINMOSTAR (Tencube, Japan). The molecular shapes were based on a calculation result after optimization with MOPAC 6 (AM1). The maximum lengths were then determined, based on calculations of the van der Waals molecular surface.<sup>22</sup> To obtain the minimum dimensions of the modeled molecules, projection views of every 15° rotated along the  $x$ - and  $y$ -axis were snapped and the sizes were compared.

## Results and discussion

### Profiles of prepared carbonized wood samples (yield and SSA)

The yield and specific surface area (SSA), based on the single-point BET of the samples carbonized at 500°–1100°C, are shown in Fig. 1. The SSA increased with rising treatment temperature, in accordance with the decrease in yield.

It is thought that the increase in SSA of the samples carbonized at temperatures below 700°C (referred to as



**Fig. 1.** Specific surface area (SSA) data showing the single-point BET and yield of carbonized wood

stage I) occurred through thermolysis, involving dehydration and deoxidation<sup>23</sup> and the oxidation of the carbon in the wood, in the form of tar, etc.,<sup>24</sup> by the residual air (containing several percent oxygen, as shown in Table 1) in the furnace during the early period of heating. The samples carbonized at temperatures above 700°C (referred to as stage II) showed a rapid increase in SSA, and it is thought that some kind of activator action occurred. This activation might have been caused mainly by the remaining gases generated by the combustion reaction in stage I, and partially by slow release of absorbed air from packaging materials inside the furnace. Studying the effect of carbonizing conditions on the SSA of carbonized wood, Kitamura and Katayama<sup>25</sup> inferred as follows: At temperatures under 700°C, the oxidation reaction of the carbon occurred directly as a result of the action of O<sub>2</sub>, but not employing CO<sub>2</sub>. At temperatures above 700°C, CO<sub>2</sub> activation occurred as a result of the action of originally existing CO<sub>2</sub> and newly generated CO<sub>2</sub> from the O<sub>2</sub> + 2CO reaction. They concluded that SSA of carbonized wood thus increased drastically at temperatures above 700°C. This description agrees well with our results showing SSA increase at stage II.

### Adsorption behavior of toluene and $\alpha$ -pinene

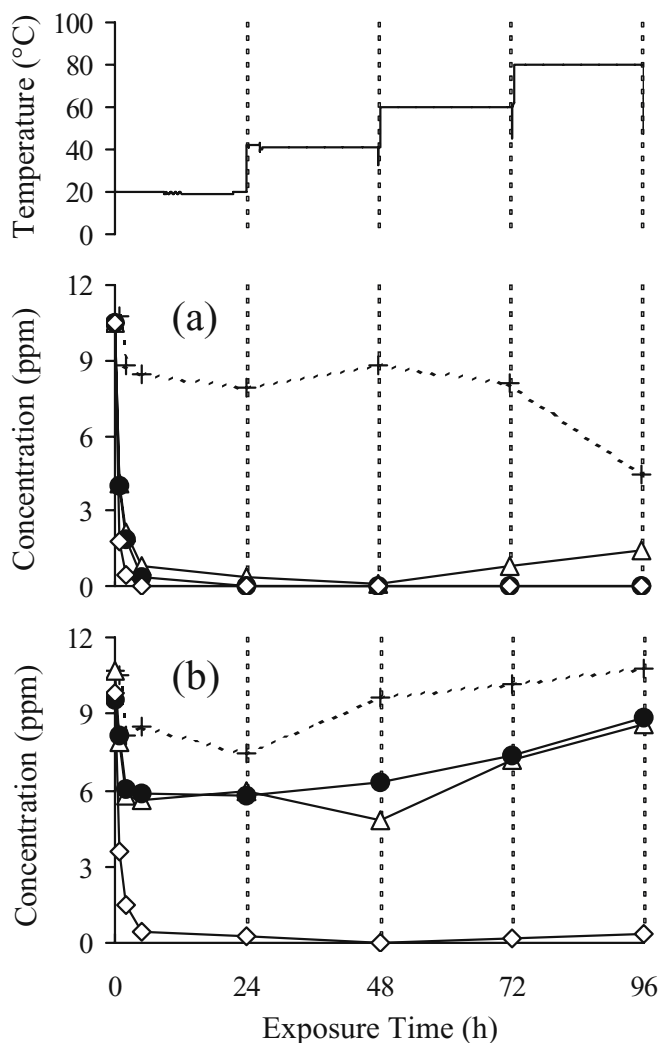
The removal efficiency of toluene and  $\alpha$ -pinene from ambient air by carbonized wood samples heat-treated at 500°–1100°C is shown in Table 2. The samples carbonized at 500°–700°C only adsorbed toluene, whereas those carbonized at 800°–1100°C adsorbed both toluene and  $\alpha$ -pinene. The adsorption of  $\alpha$ -pinene increased dramatically after carbonization at 800°C and above.

The adsorption and desorption behavior of samples carbonized at 500°, 700°, or 900°C were investigated in the mixed gas of toluene and  $\alpha$ -pinene at sequential elevation of the temperature of 20°, 40°, 60°, and 80°C (Fig. 2). Toluene was adsorbed on samples carbonized at 700°C and 900°C, until the temperature reached 40°C, and this level of adsorption was maintained at temperatures up to 60°C and even 80°C. In contrast, toluene began to be desorbed from the samples carbonized at 500°C. By comparison,  $\alpha$ -pinene was adsorbed immediately onto the samples carbonized at 900°C, and this level of adsorption was maintained up to 80°C, with only a very slight amount being desorbed. In contrast, the samples carbonized at 500°C and 700°C only caused a drop in  $\alpha$ -pinene levels of approximately 40%

**Table 2.** Mixed gas removal efficiency of toluene and  $\alpha$ -pinene

Carbonization temperature(°C)	Gas removable efficiency (%) <sup>a</sup>	
	Toluene	$\alpha$ -Pinene
500	97.0	44.5
600	100	13.4
700	99.7	39.5
800	100	92.3
900	100	97.6
1100	100	99.9

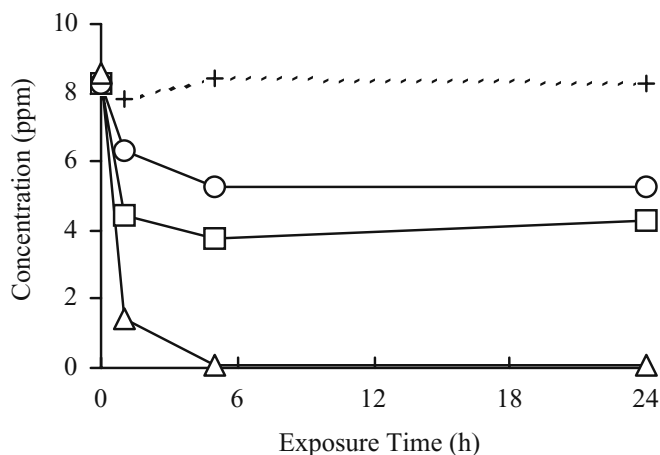
<sup>a</sup>A value in 24 h exposure time



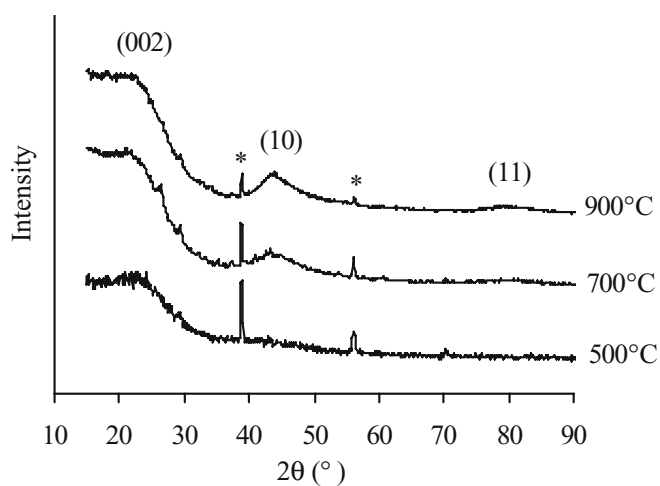
**Fig. 2.** Adsorption and desorption behavior of a gas mixture comprising toluene and  $\alpha$ -pinene exposed to carbonized woods at 20°C, with the temperature sequentially raised to 40°, 60° and 80°C, at intervals of 24 h: **a** toluene; **b**  $\alpha$ -pinene; *plus*, blank experiment; *open squares*, wood carbonized at 500°C; *open circles*, wood carbonized at 700°C; *open triangles*, wood carbonized at 900°C

during the first 2 h, and  $\alpha$ -pinene was then desorbed as the temperature rose. The samples carbonized at 700°C were found to exhibit both highly selective adsorption and high adsorptive ability for toluene but not for  $\alpha$ -pinene. In other words, the samples carbonized at 700°C were able to achieve good toluene/ $\alpha$ -pinene separation, seeming to work as a kind of molecular sieving carbon.

As for the toluene/ $\alpha$ -pinene separation mechanism, there are two possible explanations about the selectivity. (i) Toluene, which is a faster adsorbate than  $\alpha$ -pinene, occupied the adsorption sites of the sample before  $\alpha$ -pinene could reach them. (ii) The formed adsorbing site itself has specificity only for toluene. To define which of these ideas is more probable for our case, the adsorption behavior of a series of samples exposed to a single constituent of  $\alpha$ -pinene gas was investigated (Fig. 3). In this case even the competitive toluene did not exist; the samples carbonized at 500°C and 700°C adsorbed  $\alpha$ -pinene much less than the samples



**Fig. 3.** Adsorption behavior of a gas comprising  $\alpha$ -pinene exposed to carbonized woods at 20°C: *plus*, blank experiment; *open squares*, wood carbonized at 500°C; *open circles*, wood carbonized at 700°C; *open triangles*, wood carbonized at 900°C

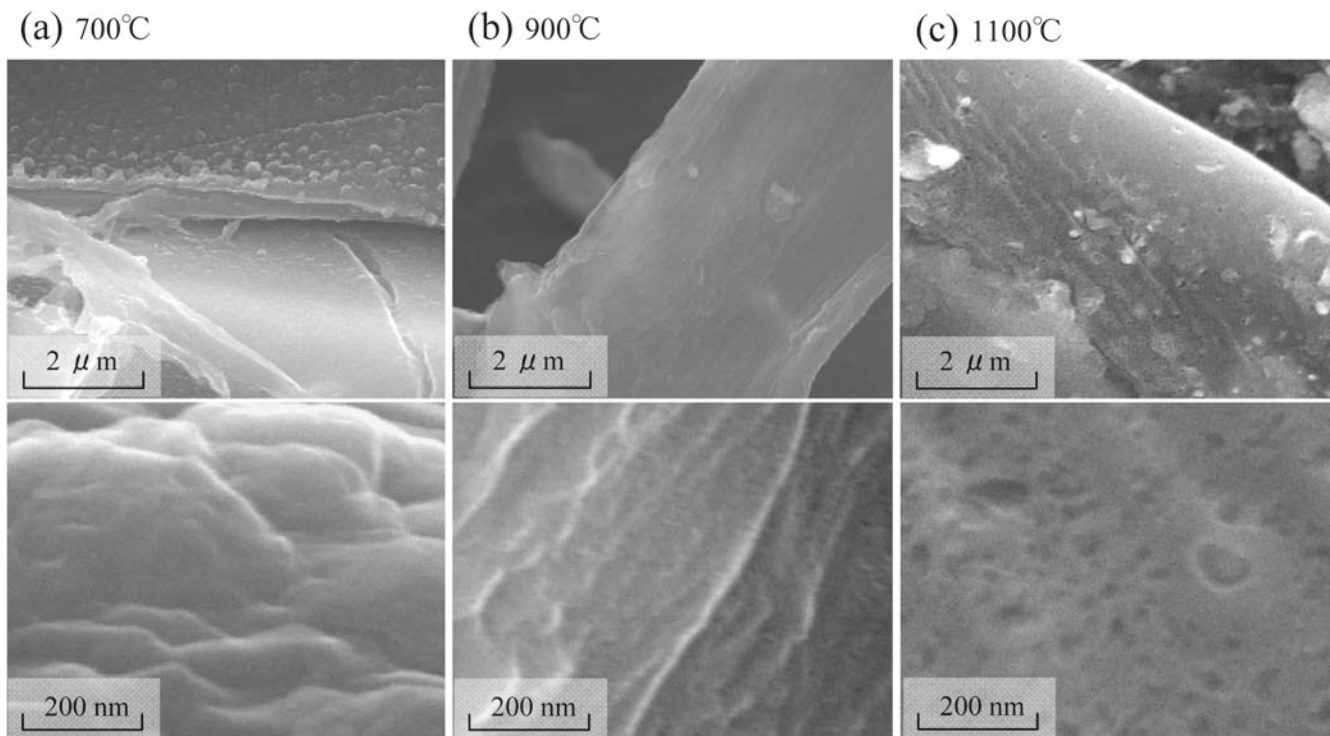


**Fig. 4.** X-ray diffractograms of carbonized wood. From *bottom to top*: wood carbonized at 500°, 700°, and 900°C. (\*), with NaF used for calibration; numbers in parentheses are diffraction index

carbonized at 900°C. This fact indicates that (ii) is more possible, that is to say, the toluene/ $\alpha$ -pinene separation occurred chiefly because the site was specifically adsorbing for toluene only.

#### Structural characterization

The X-ray diffractograms of the samples carbonized at 500°, 700°, and 900°C are shown in Fig. 4. Reflections corresponding to those of graphite, (002), (10) and (11), were observed in the samples carbonized at 700°C but the reflections were broad, indicating the generation of small and disordered particles of stacked carbon layers. These reflections were not found in samples carbonized at 500°C. In their study of the chemical structure of carbonized wood, Nishimiya et al.<sup>23</sup> concluded that dehydration and an increase in the proportion of carbon occurred at tempera-



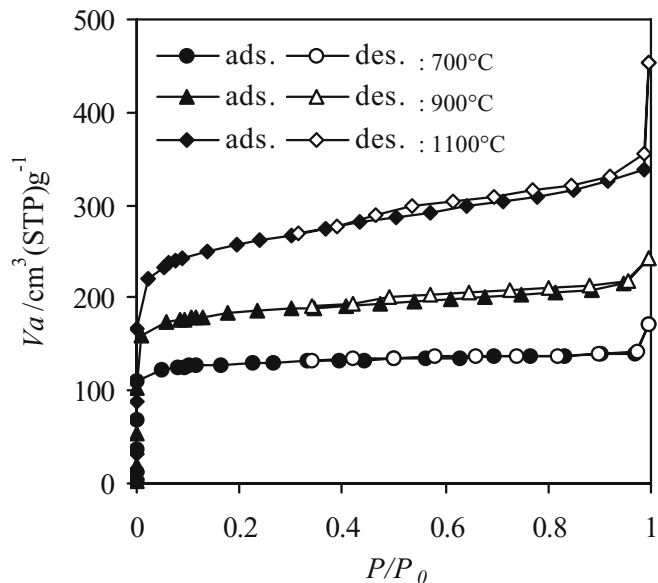
**Fig. 5.** Scanning electron microscopy (SEM) micrographs of carbonized wood at various magnifications: **a** wood carbonized at 700°C; **b** wood carbonized at 900°C; **c** wood carbonized at 1100°C. The images on the *bottom row* are enlargements of those at the top

tures > 600°C, along with a gradual increase in the condensation of aromatic rings. Toluene, with its  $\pi$ -conjugated system of aromatic rings, was therefore presumed to be better adapted to adsorption on the surface structure of the samples carbonized at temperatures above 600°C because of  $\pi$ - $\pi$  interaction. On the other hand, samples carbonized at 500°C had poor porosity and reemitted toluene as the temperature rose because, under 500°C, inadequate carbonization did not produce the same surface structure for adsorbing toluene.

The scanning electron microscopy (SEM) images of the surface structure of the wood samples carbonized at 700°, 900°, and 1100°C are shown in Fig. 5. The samples carbonized at temperatures of 900°C or higher clearly showed the presence of mesopores, several tens of nanometers (nm) in diameter, on the surface. It seems that some activation process occurred during carbonization during 900°C and 1100°C heat treatment. The samples carbonized at 900°C and 1100°C had conspicuous pores whereas at 700°C their presence was unclear. This observation suggests that the increase in SSA of the wood carbonized at temperatures above 700°C is accompanied by new formation of larger pores by an activation process.

The nitrogen adsorption isotherms for samples carbonized at 700°, 900°, and 1100°C are shown in Fig. 6. All samples produced an I-type isotherm (IUPAC) for micropore distribution. However, the samples carbonized at 900°C and 1100°C produced a hysteresis curve for mesopore distribution that was not found at 700°C.

From pore-size distribution analysis, it was found that the sample carbonized at 700°C had micropores mainly



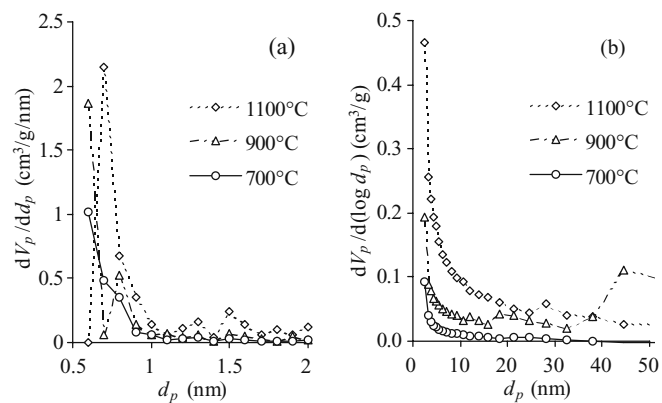
**Fig. 6.** N<sub>2</sub> adsorption isotherms at 77 K for carbonized wood samples: *open and filled circles*, adsorption (*ads.*) and desorption (*des.*) volume of wood carbonized at 700°C; *open and filled triangles*, adsorption and desorption volume of wood carbonized at 900°C; *open and filled diamonds*, adsorption and desorption volume of wood carbonized at 1100°C; *STP*, standard temperature and pressure; *P/P<sub>0</sub>*, relative pressure of nitrogen

0.6 nm in diameter mainly (Fig. 7a) and few mesopores (Fig. 7b), whereas the samples carbonized at 900°C and 1100°C had micropores with a pore size of more than 0.7 nm (Fig. 7a) and more mesopores than the samples carbonized at 700°C (Fig. 7b). The results of mesopore distribution

support the findings of the aforementioned SEM images. The results of micropore distribution suggest that the larger diameter of micropores than those in the samples carbonized at 700°C had been forming as the carbonization temperature was raised.

### Selective adsorption

The relationship between the selective adsorption behavior and the surface structure of carbonized wood was assessed, considering size and shapes for both adsorbates and the pores of the carbonized wood samples. The shapes and dimensions of toluene and  $\alpha$ -pinene molecule of the space-filling model calculated by WINMOSTAR software are shown in Fig. 8. The toluene and  $\alpha$ -pinene molecules are similar in terms of their greatest diameter, but toluene has a minimum diameter that is only half that of  $\alpha$ -pinene and they have contrasting molecular shapes, i.e., flat versus spherical. Toluene, being a flat-shaped molecule (Fig. 8a), can perhaps be adsorbed into the narrower 0.8-nm-diameter pores, whereas the spherical, bulky  $\alpha$ -pinene molecules (Fig. 8b) cannot be adsorbed into pores that size. In the case of a carbon-based adsorbent that has micropores with a slit-shaped pore entrance, the entrance size and the minimum diameter of the adsorbed molecule are also important parameters affecting adsorption behavior. The crucial dimension for toluene is 0.4 nm, which is only about half that of  $\alpha$ -pinene. The generation of mesopores and micropores larger than 0.8 nm is probably related to the adsorption capability for  $\alpha$ -pinene.



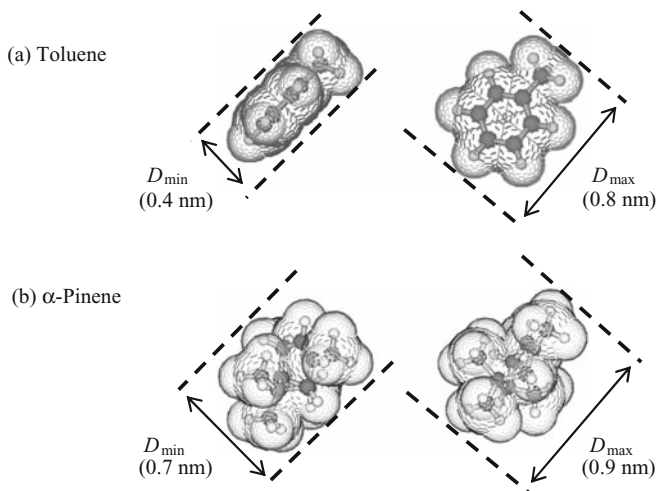
**Fig. 7.** Pore-size distributions of carbonized wood sample: **a** micropore distribution calculated using the micropore analysis (MP) method; **b** mesopore distribution calculated using the Dollimore-Heal (DH) method;  $d_p$ , pore diameter;  $dV_p/dd_p$ , differential pore volume;  $dV_p/d(\log d_p)$ , log differential pore volume

**Table 3.** Results of  $N_2$  adsorption analysis of carbonized woods

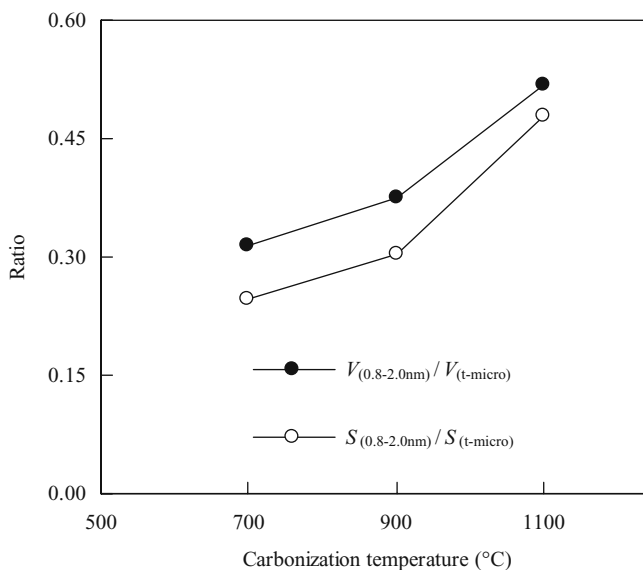
Carbonization temperature (°C)	$S_{(t-micro)}$ ( $m^2/g$ )	$S_{(0.8nm-2.0nm)}$ ( $m^2/g$ )	$V_{(t-micro)}$ ( $cm^3/g$ )	$V_{(0.8nm-2.0nm)}$ ( $cm^3/g$ )	$V_{(meso)}$ ( $cm^3/g$ )
700	623	66	0.22	0.07	0.03
900	873	134	0.31	0.11	0.09
1100	1024	321	0.44	0.23	0.19

$S_{(t-micro)}$ , surface area of total micropores;  $S_{(0.8nm-2.0nm)}$ , surface area of 0.8- to 2.0-nm size pores;  $V_{(t-micro)}$ , volume of total micropores;  $V_{(0.8nm-2.0nm)}$ , volume of 0.8- to 2.0-nm size pores;  $V_{(meso)}$ , volume of mesopores

Table 3 shows the surface area and volume of total micropores,  $S_{(t-micro)}$  and  $V_{(t-micro)}$ , and of micropores with a diameter of 0.8–2.0 nm, which are thought to be responsible for the adsorption of  $\alpha$ -pinene,  $S_{(0.8-2.0\text{ nm})}$  and  $V_{(0.8-2.0\text{ nm})}$ . Figure 9 shows the ratio of 0.8- to 2.0-nm-sized pores to



**Fig. 8.** Molecular shapes and dimensions of toluene **(a)** and  $\alpha$ -pinene **(b)** (space-filling model calculated by WINMOSTAR software).  $D_{max}$ , maximum dimension;  $D_{min}$ , minimum dimension



**Fig. 9.** Ratio of 0.8–2.0 nm pores to total micropores: *open circles*, specific surface area; *filled circles*, pore volume



total micropores. As the carbonization temperature rises, the ratio of micropores larger than 0.8 nm to total micropores rises, and the pore volume of mesopores also increases. The pore development can well explain the loss of toluene selectivity and gain of coadsorptivity of  $\alpha$ -pinene and toluene accompanied with increase of carbonization temperature.

## Conclusions

Carbonized wood adsorption properties for toluene and  $\alpha$ -pinene could be controlled by carbonization temperature. Wood samples carbonized at 700°C were found to have highly selective adsorption properties and high adsorptive ability for toluene. X-ray diffractograms showed that the high adsorption for toluene was generated by condensed aromatic rings. On the other hand, the wood samples carbonized at 700°C did not adsorb  $\alpha$ -pinene, although this selective adsorption ability diminished as the carbonization temperature increased above 900°C. The SEM micrographs suggested that some activation process occurring during carbonization affected the pore structure of the carbonized woods used in this study. Pore-size distribution analysis, using the DH method and the MP method, indicated that the relationship between pore structure generated during carbonization and the molecular form of the adsorbates helped determine this selective adsorption property. Toluene molecules, having a flat shape, could probably be adsorbed into the narrower 0.8-nm pores whereas  $\alpha$ -pinene molecules, having a bulky and globular shape, could not be molecularly adsorbed.

These results suggest that the unique pore structure of wood carbonized at 500°C to 700°C has a selective adsorption property that could be useful in selectively removing harmful VOCs from the living environment, leaving only pleasant aromas.

This characteristic of carbonized wood, which enables it to act as a kind of CMS, is expected to lead to its utilization in room air quality control, contributing to the creation of a healthy and comfortable living environment.

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