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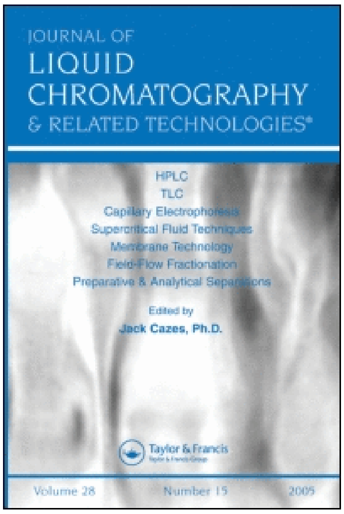

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Liquid Chromatographic Separation of Geometrical Isomers Using Spherical Carbon Packings Prepared from Spherical Cellulose Particles

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LIQUID CHROMATOGRAPHIC SEPARATION OF GEOMETRICAL ISOMERS USING SPHERICAL CARBON PACKINGS PREPARED FROM SPHERICAL CELLULOSE PARTICLES

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ABSTRACT

The packings of spherical carbon beads were prepared by graphitizing the spherical cellulose particles. A types of carbon spherical packings were obtained by various degrees of graphitization. These packings were characterized by examining their chromatographic properties. The higher the degree of graphitization is, the higher the π-electron recognition became, although there was no change in the selection for a methylene group. The mechanism for recognizing the π-electron and the steric selectivity is described and discussed.

INTRODUCTION

In 1984, we developed a gel which could easily be prepared from cellulose (1, 2) and this gel is currently available as Cellulofine (Chisso Co., Ltd.) for a size-exclusion chromatography (SEC). The sphering and reticulating of the cellulose material is easily

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carried out by the *suspension evaporation* method. In addition, this packing is much harder than the standard dextran gels and it has a high flow rate resistance, which is a property which is currently being marked for in the use with aqueous SEC.

On the other hand, we prepared new graphitized carbon microbeads ($d_p < 5$ μm) from spherical cellulose particles without cohesion and conglutination among the microbeads (3). They show no excessive retention even for electron-rich compounds or hydrophobic compounds, and they do not contain residual silica, metal impurities and silanol groups because the packings are prepared from particles composed solely of cellulose. We previously reported that the specific separation of geometrical isomers has been achieved with poly(γ-methyl L-glutamate) (PMG) spheres (4) and silica-supported comb-shaped polymers (5). The retention mechanism of the PMG spheres is based on the formation of a molecular slit which is derived from the rigidity of the PMG main chain. The retention mechanism of silica-supported comb-shaped polymers is related to the highly oriented structures of an immobilized phase.

On the other hand, the carbon packings obtained can separate geometrical isomers by the charge-transfer interaction mechanism. The excellent selection process for geometrical isomers seems to be related to the surface property derived from the layered structures of the surface graphite. This paper gives some results on the study of the relationship between the chromatographic properties and the structure or surface properties of types of carbon packings, differing on the graphitization degree.

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EXPERIMENTAL

Preparation of graphitized carbon microbeads

Spherical cellulose particles (Cellulofine GC-15 uf) the starting material, had a mean particle diameter of 4.77 μm, an exclusion limit of Da. 6200 and porosity 73 % in aqueous SEC. Using this cellulose spherical particles as a starting material, the carbon microbead was prepared by the method previously reported without conglutination among the microbeads due to adsorbed water and coal tar. The microbeads carbonized at 1000 °C were heated up to 2800 °C at heating rate of 10 °C min^{-1}, and in order to vary the degree of graphitization, respectively allowed to stand for 1.0, 2.5 and 4.5 h at the temperature and cooled. According to these procedures, the three kinds of carbon packings were prepared.

Chromatography

A slurry of 2.5 g of the beads in 25 ml of dioxane-paraffin (20 : 80) was packed into a stainless steel column (50~150 x 4.6 mm I. D.). As a reference column, Inertsil ODS (150 x 4.6 mm I. D.) were purchased from GL Science Co., Ltd.. TONEN Carbonex were also purchased. The chromatograph included a JASCO 880-PU pump, an UV-VIS Shimadzu photodiode array SPD-M6A and a Shodex refract monitor SE-51. A 5 ml portion of the sample dissolved in an eluent (1.0 mg ml^{-1}) was injected through a Rheodyne Model 7125 injector. All chromatography was carried out at 25°C.

Other measurements

Surface area analysis of the particles was carried out by Brunau-Emmet-Teller (BET) method using a Shimadzu 2205 measurement of surface area analysis. Scanning electron micrographs of the beads were obtained using a JEOL JSM-T20, and X-ray diffraction was carried out using a Geiger flex RAD-IB.

RESULTS AND DISCUSSION

Characterization

TABLE 1 lists the abbreviations and the results of the elemental analysis of the microbeads obtained in each process. All of the carbon contents reached almost 100 %.

FIGURE 1 shows the X-ray diffraction patterns of the carbon microbeads obtained. The diffuse reflections for Carbon-0 indicate that their structures are turbostratic, that is, the graphite-like layer in the structure is small two-dimensionally, in addition, it is disordered three-dimensionally. In terms of the heating treatment at 2800 °C, the hk0 and 00l reflections increase as the hkl reflection becomes sharp. In addition, the d_{001} reflection gradually appeared. This indicated that the degree of graphitization increased, that is, the sheets of the graphite-like layers expanded two-dimensionally. The d_{002} reflection for Carbon-1.0, -2.5 and -4.5 was split into two reflections at 25.9° and 26.3°. The d_{002} reflection at 26.3° should be associated with the needle-like structure, as reported by Knox et. al.[6] In addition, the

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TABLE 1 Abbreviations and elemental analysis of beads obtained in each process

Time of graphitization (h)	Beads	Elemental analysis	
		C%	H%
	Starting materials (Cellulose)	43.0	6.3
0	Carbon-0	96.3	0.6
1.0	Carbon-1.0	99.7	-
2.5	Carbon-2.5	99.6	-
4.5	Carbon-4.5	99.8	-

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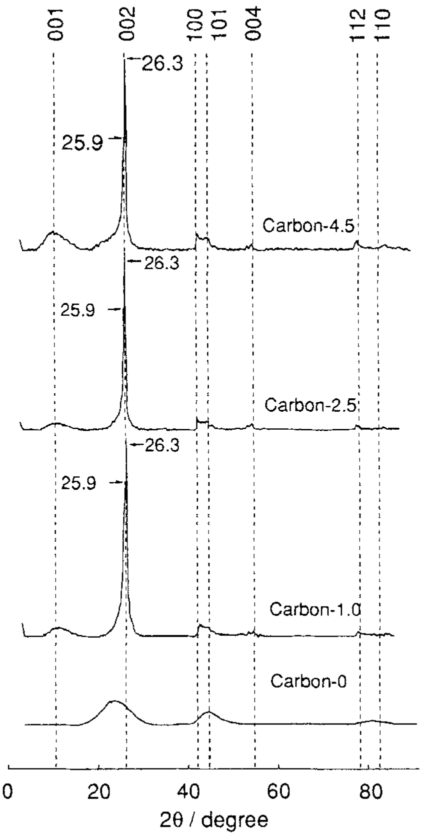

FIGURE 1 X-ray diffractgrams of Carbon-0, -1.0, -2.5 and -4.5.

longer the time of graphitization is, the bigger the increase of the d_{002} reflection is at 26.3° than at 25.9°. This suggests that the Warren structure of the two-dimensional turbostratic graphites, with no layer registration, are converted into three-dimensional graphites with layer registration (6).

FIGURE 2 shows the scanning electron micrographs. In spite of the heat-treatment at high temperatures, microbeads, after carbonization or graphitization, maitained a completely spherical shape. The amount of the needle-like structure increased in the order of Carbon-0, Carbon-1.0, -2.5 and -4.5 with the progress of graphitization. This corresponded to the results of the X-ray diffraction patterns, as shown in FIGURE 1. The surface area of the

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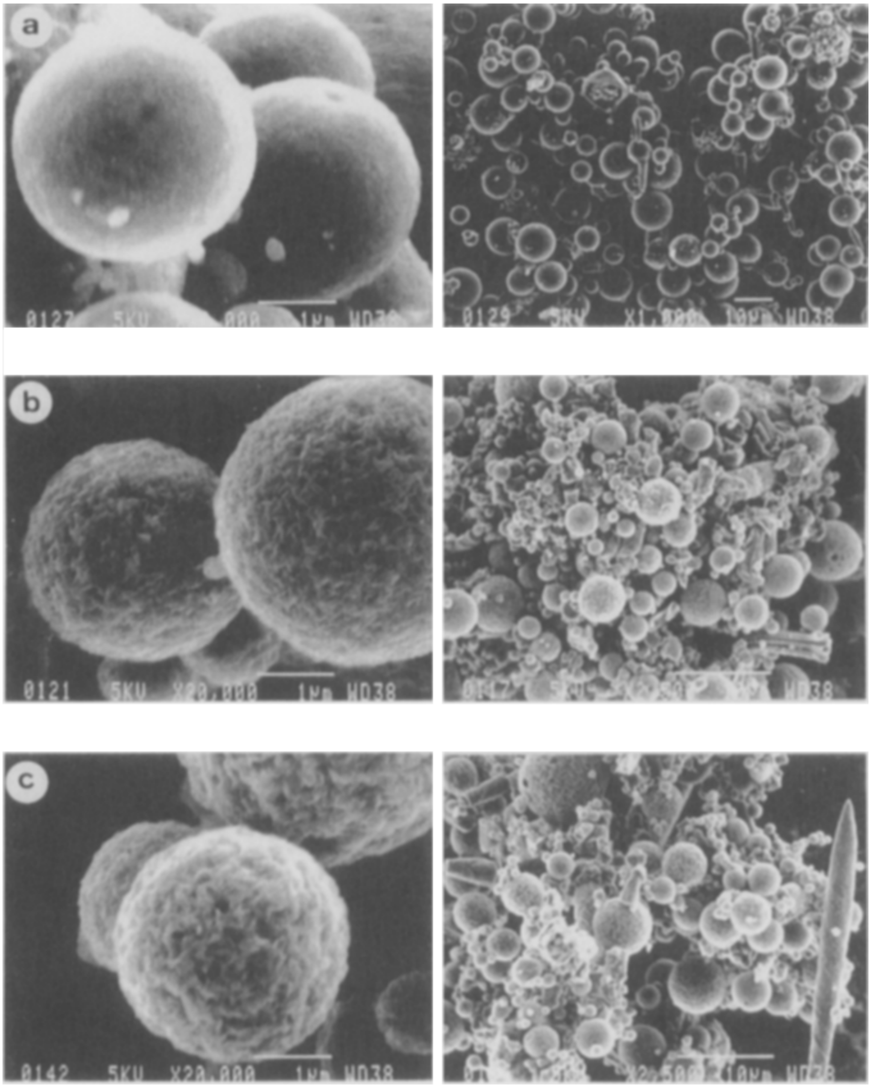

FIGURE 2 Scanning electron micrographs of Carbon-1.0 (a), Carbon-2.5 (b) and Carbon-4.5 (c).

microbeads obtained in each process was measured by the BET method. The microbead surface areas were 216, 2.6, 2.8 and 5.8 ($m^2\ g^{-1}$), respectively for Carbon-0, Carbon-1.0, Carbon-2.5 and Carbon-4.5.

Chromatography

Charge-transfer interaction

Non-graphitized carbon, the Carbon-0, showed the adsorption for all solutes owing to turbostratic structural carbon surface of the high surface area. In contrast, as shown in FIGURE 3, a close correlation between the k' value and the carbon number of methyl alkanates was observed similarly in the, Carbon-1.0, Carbon-2.5 and Carbon-4.5 columns. The retention capacity factors of all the graphitized carbon packing types increased with the increase of the alkyl chain lengths. The longer the time of graphitization is in the Carbon-1.0, -2.5 and -4.5 columns, the more the retentions for methyl alkanates increases. The capacity and separation factors for each series of solutes with all of the carbon packing types are listed in TABLE 2. Although the retention of methyl alkanates increased, no change in the separation factors occurred. Accordingly, these results seem to be related to the surface area of the carbon packings. In contrast, the separation factors, $k'_{p\text{-hydroxyalkylbenzoate}}/k'_{\text{alkylbenzoate}}$ and $k'_{\text{alkylbenzoate}}/k'_{\text{alkylbenzene}}$ gradually increased, with the progress of the graphitization degree in the Carbon-1.0, Carbon-2.5 and Carbon-4.5 columns. These attributes are derived from the increase of the charge-transfer interaction between the lone pair electrons of the solute and the π-electron of the carbon surface, because the degree of graphitization increased, that is, the sheets of the graphite-like layers expanded two-dimensionally, in addition, the π-electron seemed to transfer regularly, as the two-dimensional turbostratic graphites are converted into three-dimensional graphites.

Steric selectivity

As shown in FIGURE 4 and 5, the carbon packings gave a excellent mixture of geometrical isomers which were separated, although the ODS showed a low selectivity process for geometrical isomers. The specificity of the carbon packings was emphasized by examining the relationship between their separation factors and surface properties.

TABLE 3 lists the separation factors of the *E*- and *Z*- isomers of the stilbene for Carbon-i.0, 2.5, -and 4.5. The larger retention of the *E*-isomer can be explained by the fact that the *E*-isomer, which is more planar (7), has a larger area for contact with the carbon phase than the Z-isomer, as shown in FIGURE 6. This assumption can be explained by the significant preference for the planar compound, triphenylene than for a non-planar compound, *o*-terphenyl, as shown in TABLE 3. In addition, this interaction is derived from the π-electron of the sheets of the graphite-like layers, which can work as electron-accepting

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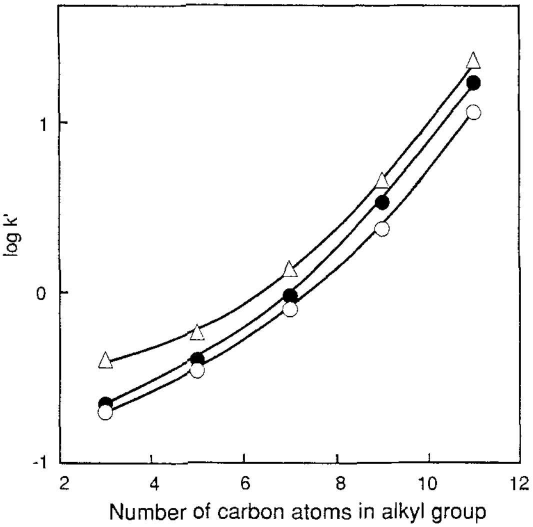

FIGURE 3 Relationships between the capacity and carbon number of methyl alkanoates for Carbon-1.0 (a), -2.5 (b) and -4.5 (c). Solute: methyl butanoate, methyl hexanoate, methyl octanoate, methyl decanoate, methyl dodecanoate. Eluent: acetonitrile-water (60 : 40).

TABLE 2 Selectivity of solutes with Carbon-1.0, -2.5 and -4.5

Solute	Carbon-1.0		Carbon-2.5		Carbon-4.5	
	k'	α	k'	α	k'	α
Methyl *n*-Decanoate	2.4		3.4		4.7	
		4.7		4.9		4.9
Methyl *n*-Dodecanoate	11.3		16.8		22.9	
n-Butylbenzene	1.3		1.3		1.9	
n-Butylbenzoate	1.7	1.4	2.0	1.8	3.0	2.3
		1.0		1.2		1.5
n-Butyl *p*-hydroxybenzoate	1.8		2.3		4.3	

Eluent: acetonitrile-H_2O (60 : 40)

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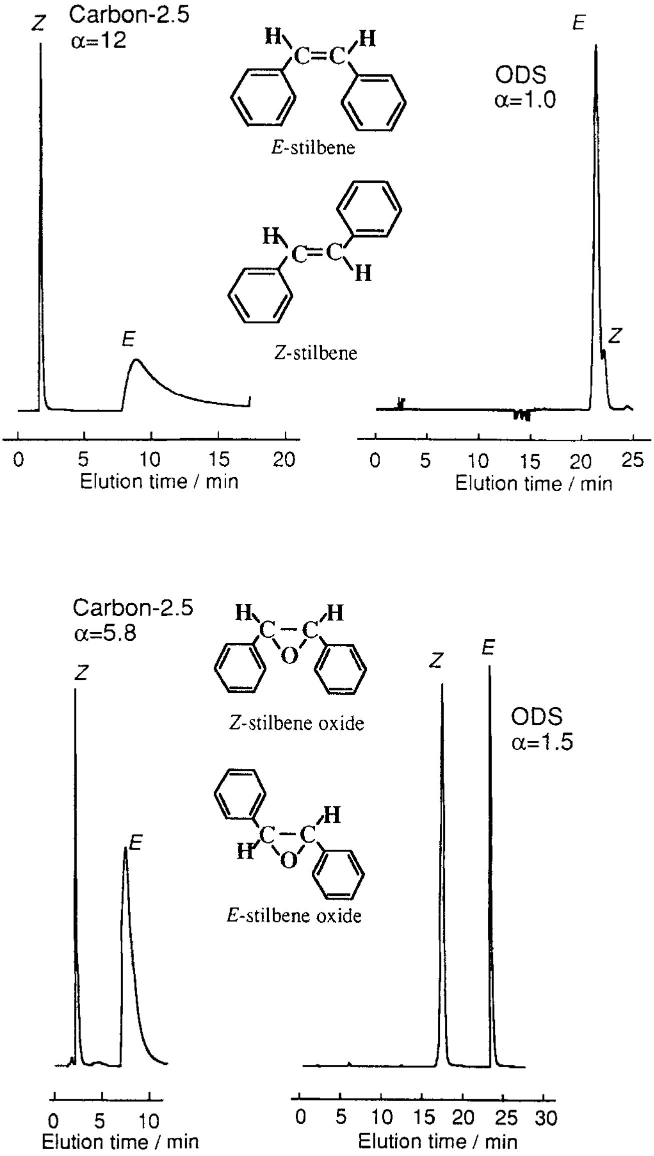

FIGURE 4 Chromatograms of *E* / *Z*-stilbene and *E* / *Z*-stilbene oxide isomers with Carbon-2.5 and ODS. Eluent, acetonitrile for Carbon-2.5, acetonitrile-water (50 : 50) for ODS in the cases of *E* / *Z*-stilbene, acetonitrile-water (60 : 40) in the cases of *E* / *Z*-stilbene oxide, respectively. Flow rate, 0.5 ml min^{-1}.

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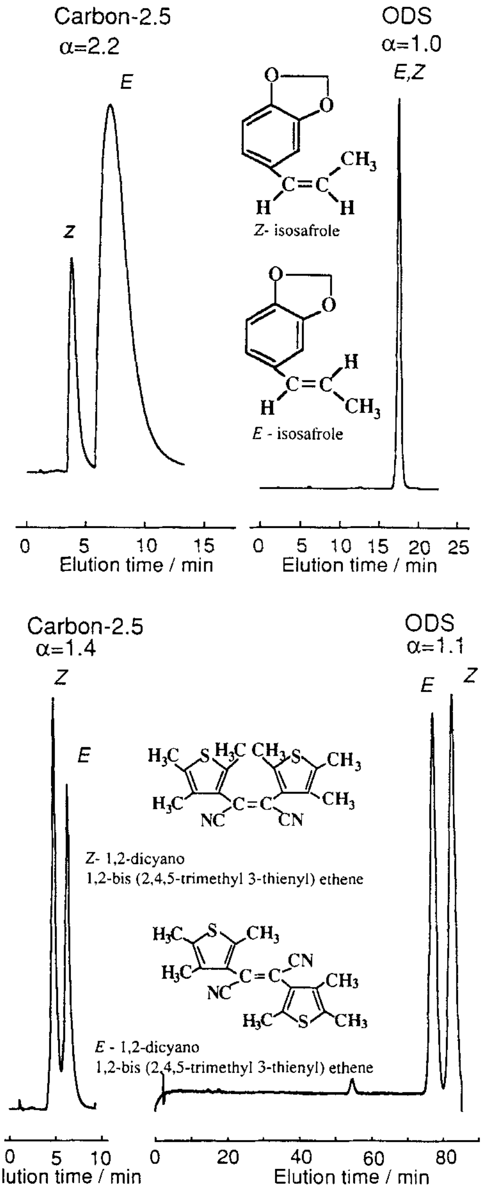

FIGURE 5 Chromatograms of *E* / *Z*-isosafrole and *E* / *Z*-1,2-dicyano 1,2-bis (2,4,5-trimethyl 3-thienyl) ethene isomers with Carbon-2.5 and ODS. Eluent, acetonitrile-water (60 : 40), Flow rate, 0.5 ml min^{-1}.

TABLE 3 Selectivity of *E* / *Z*- isomers for each column

Solute	Carbon-1.0		Carbon-2.5		Carbon-4.5		ODS	
	k'	α	k'	α	k'	α	k'	α
Z-Stilbene	1.2^{a}		0.6^{a}		1.7^{a}		8.3^{b}	
		4.5		12				1.1
E-Stilbene	5.5^{a}		7.0^{a}		adsorption^{a}		8.1^{b}	
o-Terphenyl	0.1^{c}		0.1^{c}		0.2^{c}			
		80.4		259		318		
Triphenylene	9.2^{c}		19.0^{c}		63.2^{c}			
Z-1,4-Dichloro 2-butene	1.3^{d}		1.6^{d}		2.1^{d}		5.0^{b}	
		1.0		1.1		1.1		1.0
E-1,4-Dichloro 2-butene	1.4^{d}		1.8^{d}		2.3^{d}		5.0^{b}	

a: acetonitrile, b: acetonitrile-H_2O (50 : 50), c: tetrahydrofuran, d: acetonitrile-H_2O (30 : 70)

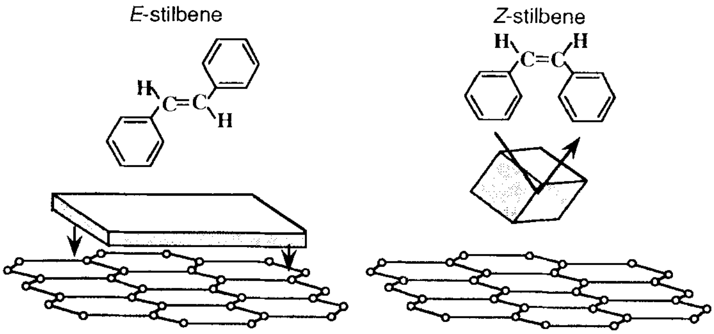

FIGURE 6 Schematic illustration of adsorption of planer and non-planer compounds on the surface of carbon beads.

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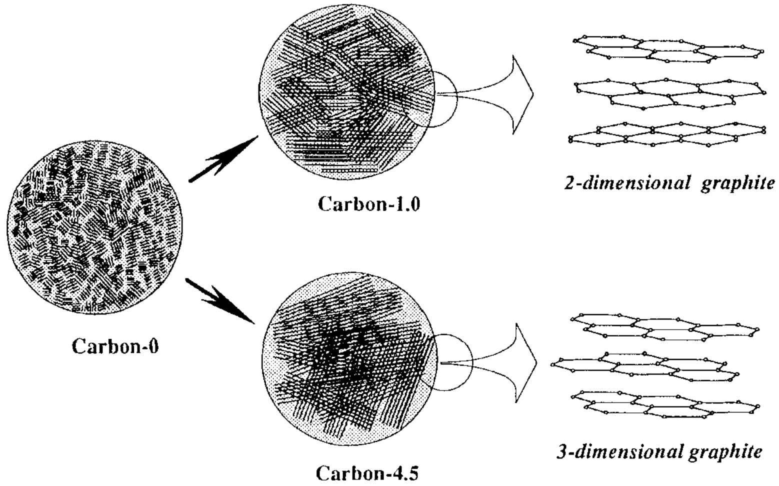

FIGURE 7 Schematic illustration of structural changes of graphite-like layer with progressing of graphitization.

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groups. This assumption is supported by the following facts, from calculating the energy level of the HOMO (highest occupied molecular orbital) in stilbene, we found that the *E*-isomer is more of an electron donating isomer (-8.63 eV) than the Z-isomer (-9.06 eV), as calculated by one of our members (8). However, the carbon packings showed almost no selectivity for geometrical isomers of 1,4-dichloro-2-butene, although their retention increased with the progress of graphitization. Geometrical isomerism of 1,4-dichloro-2-butene for 1,4-dichloro-2-butene which had non-conjugating substituent groups provided no difference in the energy level of the HOMOs (*E*-isomer: -10.035 eV Z-isomer: -10.102 eV) (9). This indicated the the contribution of the steric effect, that is, the contribution of the slit-like structure (10) of surface was small. According to these results, the separation mechanism of the geometrical isomers was derived mainly from the π- electron of the carbon bead surface.

In conclusion, it was assumed that the carbon packings which were obtained that their sheets of graphite-like layers expanded two-dimensionally, and that the Warren structure of two-dimensional turbostratic graphites with no change in layer registration were converted into three-dimensional graphites with layer registration, that is, a pyrolytic deposition of carbon needles takes place, presumably from organic vapors which were released just above 1000 °C, with the progress of graphitization. Therefore, we assume that the carbon packings obtained in our study developed structural changes when graphitizing occurred, as schematically illustrated in FIGURE 7. It is considered that the increase in the charge-transfer interaction between the lone pair of electrons from the solute and the π-electron from the carbon beads surface are derived from these structural changes. As the results electron-rich compounds are retained more on the carbon beads surface.

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