

Synthesis of Extremely Large Mesoporous Activated Carbon and Its Unique Adsorption for Giant Molecules

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The steam invigoration of pitches (softening points 85 and 280 °C) homogenized with 1–3 wt % of organo rare-earth metal complexes such as $\text{Ln}(\text{C}_5\text{H}_5)_3$ or $\text{Ln}(\text{acac})$ ($\text{Ln} = \text{Y}, \text{Yb}$) at 930 °C provided activated carbons with an extremely high mesopore ratio, >70%. The resulted activated carbon selectively adsorbs giant molecules such as vitamin B_{12} , blue acid 90 dye, dextran, nystatin, and humic acid, reflecting their large mesopore volumes. To understand what kind of carbon skeleton in pitch is suited for generation of high mesopore ratio, the steam invigoration of a series of condensed polynuclear aromatics (COPNA) resins prepared from naphthalene, anthracene, phenanthrene, pyrene, or perylene and *p*-xylene- α, α' -diol were conducted in the presence of rare-earth metal complexes. As a result, COPNA resins containing phenanthrene, perylene, and pyrene generated large mesopore volume.

Introduction

Activated carbon is the general term of carbonaceous materials obtained by steam or alkali-metal-assisted invigoration of polyacrylonitrile, poly(vinyl chloride), pitch, rayon, wood, etc. In general these compounds exhibit a microporous structure (pore diameter <20 Å, BET surface area 1000–3000 m^2) and these are useful as adsorbents for various substrates such as trihalomethane in city water and impurity in sugars in addition to toxic substances. In contrast, carbonaceous materials bearing larger pore sizes such as mesopore (diameter 20–500 Å) or macropore (>500 Å) are scarcely reported so far (Figure 1). Only the macroporous carbon (pore size 200–1000 Å) obtained by heat treatment of a propane–butane mixture on the carbon black is reported.¹ This paper deals with the formation of extremely large mesoporous activated carbon attained for the first time by steam invigoration of pitches mixed with rare-earth metal complexes such as $\text{Ln}(\text{C}_5\text{H}_5)_3$ and $\text{Ln}(\text{acac})_3$ ($\text{Ln} = \text{Sm}, \text{Y}, \text{Yb}, \text{Lu}$) in 1–3 wt % loading level. Such a large mesoporous carbon was not obtained by pyrolysis of poly(furfural/acetylferrocene),^{2,3} poly(vinylferrocene/divinylbenzene),⁴ polymer blends of inorganic compounds^{5,6} or pitch/organometallics blends,^{7–9}

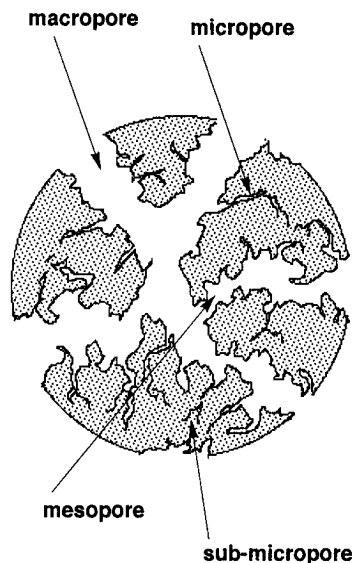


Figure 1. Conceptions of various pores.

although ultrafine metal particles or ultrafine iron carbide particles were formed in the resulting carbon matrixes. Boron doping on the polycrystalline graphite showed a higher Young's modulus and a lower thermal expansivity, but the increase of mesopore ratio was not observed.¹⁰

Experimental Section

Materials. $\text{Ln}(\text{C}_5\text{H}_5)_3$ ($\text{Ln} = \text{Y}, \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Er}, \text{Yb}, \text{Lu}$),¹¹ $(\text{C}_5\text{H}_5)_2\text{Co}$,¹² $\text{TiCl}_2(\text{C}_5\text{H}_5)_2$,¹³ $\text{ZrCl}_2(\text{C}_5\text{H}_5)_2$,¹⁴ $[(\text{C}_8\text{H}_{12})\text{RhCl}]_2$,¹⁵ $(\text{C}_8\text{H}_{12})_2\text{PdCl}_2$,¹⁶ $(\text{C}_5\text{H}_5)_2\text{YbCl}$,¹⁷ and (C_5H_5) -

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(1) (a) Likhonolov, V. A.; Fenelonov, V. B.; Okkel, L. G.; Gonocharova, O. V.; Avdeeva, L. B.; Zaikovskii, V. I.; Kuvshinov, G. G.; Semikolenov, V. A.; Duplyakin, V. K.; Plaxin, G. V. *React. Kinet. Catal. Lett.* **1995**, *54*, 381. (b) Surovikin, V. F.; Plaxin, G. V.; Semikolenov, V. A.; Likhonolov, V. A.; Tiuniva, I. U.S. Patent 4,978,649, 1990.

(2) Yajima, S.; Omori, M. *Chem. Lett.* **1972**, 843.

(3) Yajima, S.; Hasegawa, H.; Hayashi, I.; Imura, M. *J. Mater. Sci.* **1978**, *13*, 2569.

(4) Hirano, S.; Yogo, Y.; Suzuki, H.; Naka, S. *J. Mater. Sci.* **1983**, *18*, 2811.

(5) Ohya, A.; Marsh, H. *J. Mater. Sci.* **1982**, *17*, 309.

(6) Marsh, H.; Dachille, F.; Melvin, J.; Walker, P. L. *Carbon* **1971**, *9*, 155.

(7) Yasuda, H.; Miyanaga, S.; Nakamura, A.; Sakai, H. *J. Inorg. Organomet. Polym.* **1991**, *1*, 135.

(8) Yasuda, H.; Hiwara, A.; Nakamura, A.; Sakai, H. *J. Inorg. Organomet. Polym.* **1991**, *1*, 239.

(9) Miyanaga, S.; Yasuda, H.; Hiwara, A.; Nakamura, A.; Sakai, H. *J. Macromol. Sci., Chem. Ed.* **1990**, *A27*, 1347.

(10) Wagner, P.; Dickinson, J. M. *Carbon* **1970**, *8*, 313.

(11) (a) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42. (b) Fisher, E. O.; Fisher, H. *J. Organomet. Chem.* **1965**, *3*, 181.

(c) Raid, A. F.; Wailes, D. C. *Inorg. Chem.* **1966**, *5*, 1213.

(12) Wilkinson, G.; Cotton, F. A.; Birmingham, J. M. *J. Inorg. Nucl. Chem.* **1956**, *2*, 96.

(13) Summers, L.; Uloth, R. H.; Holmes, A. *J. Am. Chem. Soc.* **1955**, *77*, 3604.

(14) Reid, A. F.; Wailes, P. C. *Aust. J. Chem.* **1966**, *19*, 309.

YbCl_2^{18} were prepared with the established methods. Commercial samples of $\text{Mn}(\text{acac})_3$, Ph_4Sn , CaI_2 , $\text{Y}(\text{O}i\text{Pr})_3$, $\text{Y}(\text{O}_2\text{-CC}_{10}\text{H}_7)_3$, $\text{Sm}(\text{acac})_3$, $\text{Sm}(\text{O}i\text{Pr})_3$, Y_2O_3 , and Yb_2O_3 were purchased from Strem Chemicals Inc. F400 (Filtrisorb 400) activated carbon was purchased from Toyo Cargone (BET surface area, $946 \text{ m}^2/\text{g}$, mesopore ratio 9.7%, averaged pore size 24.0 \AA , powder size $0.9\text{--}1.1 \text{ mm}$; its origin is bituminous coal). Kimco-activated carbon obtained from coconut husk shows the BET surface area of $726 \text{ m}^2/\text{g}$, mesopore ratio of 6.5%, and averaged pore size of 23.2 \AA .

Measurements. BET surface area, mesopore ratio, and pore size are measured by Autosorb-6 (Quanta Chrome) using nitrogen gas, and mercury porosimetry was measured by a porosimeter, Autopore 9220 (Shimadzu). XRD investigations were performed on a Rigaku RDA-1B diffractometer using $\text{Cu K}\alpha$ radiation at 40 kV , 30 mA . Thermogravimetric analyses were carried out on a Shimadzu TGA-50 thermogravimetric analyzer. SEM micrographs were obtained on a Hitachi S-2150 scanning electron microscope operated at 200 kV . XPS measurements were conducted with a Perkin-Elmer PHI5400 spectrometer using a magnesium anode. Adsorption on activated carbons was measured by a Tohsco SC-8010 high-speed liquid chromatograph.

Steam Invigoration of the Precursor. Petroleum pitch (4 g) possessing a softening point of 85°C (elemental analysis C 93.2, H 4.7, N 1.2, O 0.4, and S 0.5%) was dissolved in THF (50 mL) and rare-earth metal complexes such as $\text{Y}(\text{acac})_3$ or $\text{Ln}(\text{C}_5\text{H}_5)_3$ (1–3 wt % of pitch) were mixed with the petroleum pitch. Then the solvent was removed by flash distillation under vacuum and the product was mixed with powdered hard pitch (4 g) whose softening point was 280°C (elemental analysis C 94.0, H 3.5, N 1.1, O 1.0, S 0.4%). Homogenization of pitch was made by pulverizing and kneading the mixture at ambient temperature and heating to 360°C every 30 min four times. Then air oxidation of the mixture was carried out at 360°C for 40 min–1 h using a crucible (alumina > 99.5%, Nippon Kagaku Togyo) in Kantal combustion furnace (Motoyama MTKW-11-1040, 200 V , 3.7 kW). Steam invigoration was applied to the mixture at 930°C for 1–6 min. The temperature was controlled by a digital program (Chino KP-1131) coupled with a thyristor unit (Sansa Elec. Co. VP1-2020) and was monitored by sheathed thermocouple (type R; Pt/Pt–Rh). Blank carbon was obtained by the same procedure as described above, but the rare-earth metal compound was not mixed in this case. The reproducibility of the resulting mesopore ratio and the BET surface area is >95%. Thermogravimetric analysis of the pitch possessing a soft point of 85°C reveals the beginning of the decomposition at ca. 200°C , and weight loss of 60% was achieved at 700°C , while the pitch possessing a soft point of 280°C begins the decomposition at ca. 290°C and weight loss of 14% was observed at 700°C .

Adsorption of Dyes on the Activated Carbon. Acid orange 7, basic blue 9, and basic violet 3 were purchased from Wako Pure Chemical Ind. Acid blue 90 was purchased from Tokyo Chemical Industry Co. Ltd. The adsorbate (10 mg) was diluted with water (100 mL). An activated carbon (10 mg) was dissolved in an adsorbate solution (10 mL) placed in a test tube, and the mixture was rotated (8 rpm) with a rotor (RT-50, Taitec). After the delay of 2 h, the activated carbon was removed from the solution by centrifugation (3000 rpm, 10 min) and the concentration of adsorbate in the resulting solution was analyzed by a high-performance liquid chromatograph (HPLC, Tohsco-SC 8010 fitted with a column, TSK gel ODS-80nTm). A mixture of $\text{CH}_3\text{CN}/20 \text{ mM}$ phosphate buffer = $7/3$ was employed as elution using the UV (254 nm) detector.

Adsorption of Vitamins on the Activated Carbon. Vitamin B₁, vitamin B₂, vitamin B₆, and vitamin B₁₂ were purchased from Wako Pure Chemical Industry. The adsorbate (10 mg) was diluted with distilled water (100 mL) and an

Table 1. Specific Surface Area of Activated Carbon Obtained from $\text{Ln}(\text{C}_5\text{H}_5)_3/\text{Pitch}$ Precursor^a

organo-metallics	carbonization yield/%	metal content/%	BET surface area/ $\text{m}^2 \text{ g}^{-1}$	mesopore ratio/%	pore size/ \AA
$\text{Y}(\text{C}_5\text{H}_5)_3$	35.1	2.5	210	66.3	49.0
$\text{La}(\text{C}_5\text{H}_5)_3$	29.9	2.5	191	65.5	57.6
$\text{Nd}(\text{C}_5\text{H}_5)_3$	29.0	2.5	183	68.8	54.6
$\text{Sm}(\text{C}_5\text{H}_5)_3$	26.2	2.5	194	73.3	56.6
$\text{Gd}(\text{C}_5\text{H}_5)_3$	25.5	2.5	260	71.3	53.3
$\text{Tb}(\text{C}_5\text{H}_5)_3$	29.7	2.5	212	81.3	57.6
$\text{Er}(\text{C}_5\text{H}_5)_3$	26.8	2.5	198	71.8	53.2
$\text{Yb}(\text{C}_5\text{H}_5)_3$	36.2	2.5	261	74.1	56.8
$\text{Lu}(\text{C}_5\text{H}_5)_3$	35.6	2.5	191	73.8	49.0
none	39.7	0	240	5.7	24.2

^a Steam invigoration, 930°C for 7 min.

activated carbon (10 mg) was mixed with the adsorbate solution (10 mL). The rotation (8 rpm) of a mixture was continued for a fixed time, and then the activated carbon was removed by centrifugation (3000 rpm, 10 min). The concentration of the adsorbate in the aqueous solution was determined by a high-performance liquid chromatograph.

Adsorption of Dextran, Nystatin, and Humic Acid on Activated Carbon. Dextran 10, 20, and 80 were purchased from Pharmacia LKB Biotechnology AB Uppsala. Nystatin and humic acid were obtained from Wako Pure Chemical Ind. The concentration of these compounds in an aqueous solution was analyzed by the same method as described above.

Preparation of COPNA Resin. *p*-Toluenesulfonic acid (5 wt % of aromatics) was added to a 1:1 mixture of naphthalene, anthracene, pyrene, or perylene and *p*-xylene- α,α' -diol (PXD, 10 mL) in dry THF (100 mL), and then THF was removed by flash distillation under vacuum. The resulting mixture was heated to 160°C with stirring and maintained there for 3–30 min. Resulting polymer was poured into excess MeOH in order to remove unreacted materials, and the precipitate was dried in vacuum.

Steam Invigoration of COPNA Resins with Rare-Earth Metal Complexes. A COPNA resin (5 g) was mixed with rare-earth metal complexes (metal content, 1–2 wt % of the pitch) such as $\text{Y}(\text{C}_5\text{H}_5)_3$ or $\text{Yb}(\text{C}_5\text{H}_5)_3$ in THF (50 mL) and then the THF was removed by flash distillation under vacuum. Air oxidation of the product was performed at 360°C for 40 min, and steam invigoration was carried out at 930°C for 1–6 min. Carbonizing yields are 15–25%.

Results and Discussion

1. Formation of Mesoporous Carbon Materials.

Petroleum pitch bearing a softening point of 85°C was mixed with various organometallics (1–3 wt %) in THF, and then the solvent was evaporated to dryness to produce the carbon precursor homogenized with organometallics. The resulting carbon precursor was further mixed with hard pitch bearing a softening point of 280°C in 1:1 weight ratio without solvent. Air oxidation of the mixture was carried out at 360°C for 40 min–1 h, and then the steam invigoration was applied at 930°C for 1–10 min by introducing saturated steam (steam 8.3 g/min) heated to 95°C with nitrogen gas at a rate of 3 L/min . The sample was placed in a ceramics boat in a combustion tube attached to an electric furnace. When the steam invigoration of a mixture of $\text{Ln}(\text{C}_5\text{H}_5)_3$ and pitch was conducted, a carbonaceous product with a high mesopore surface area was obtained (Table 1). All of the mesopore ratios ($\sim 70\%$) and pore sizes ($\sim 200 \text{ m}^2$) are equal within experimental error irrespective of the metal used, which shows the largest ionic radius (1.17 \AA) in the case of La metal and smallest ionic radius (1.00 \AA) in the case of Lu. However, BET surface area can be valid up to $>1000 \text{ m}^2$ (carbonization yield 20–30%) when the steam invigoration was carried out in

(15) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

(16) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 52.

(17) Maginn, R. E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1985**, *85*, 672.

(18) Manastyrskyj, S.; Maginn, R. E.; Dubeck, M. *Inorg. Chem.* **1963**, *2*, 904.

Table 2. Specific Surface Area of Activated Carbon Obtained from Organometallics/Pitch Precursor^a

organo-metallics	carbonization yield/%	metal content/%	BET surface area/m ² g ⁻¹	mesopore ratio/%	pore size/Å
Co(C ₅ H ₅) ₂	33.1	2.5	241	7.6	28.3
<i>t</i> -BuMgBr	41.7	2.5	191	6.4	24.6
Mn(acac) ₃	36.9	2.5	203	35.8	38.4
Ti(C ₅ H ₅) ₂ Cl ₂	49.4	2.5	105	17.2	32.2
Ph ₄ Sn	21.0	2.5	174	15.6	27.5
[RhCl(COD)] ₂	38.0	2.5	153	9.9	35.0
PdCl ₂ (COD)	39.7	2.5	145	6.9	26.7
CaI ₂	10.1	2.5	10	62.2	48.0
none	39.7	0.0	240	5.7	24.2

^a Steam invigoration, 930 °C for 7 min.**Table 3. Specific Surface Area of Activated Carbon Obtained from Organolanthanide/Pitch^a**

organo-lanthanides	carbonization yield/%	metal content/%	BET surface area/m ² g ⁻¹	mesopore ratio/%	pore size/Å
Y(OiPr) ₃ ^b	30.3	2.5	305	76.3	50.6
Y(OiPr) ₃ ^b	27.4	1.0	263	61.1	44.8
Y(naphthoate) ₃	26.6	2.5	242	80.8	52.4
Y(naphthoate) ₃	38.8	1.0	141	47.2	37.6
Y(acac) ₃	23.0	2.5	356	81.8	51.0
Y(acac) ₃	39.8	1.0	198	55.7	42.0
Sm(OiPr) ₃	42.6	2.5	203	20.4	28.2
Sm(acac) ₃	24.1	2.5	226	15.6	29.6

^a Steam invigoration, 930 °C for 7 min. ^b Actually, this compound is composed of Y₅(OiPr)₁₃O.

the form of carbon fiber (diameter 30–50 μm). The steam invigoration at 930 °C gave the maximum mesopore ratio, while steam invigoration at 800 or 1100 °C resulted in a lower mesopore ratio, i.e., in the case of Sm(C₅H₅)₃, mesopore ratios of 55% and 47% were obtained, respectively. Heat treatment in the absence of steam invigoration also resulted in the formation of a very low mesopore ratio (5–7%). Of course, such a high mesopore ratio was not obtained by steam invigoration of a mixture of pitch and ligands such as C₅H₆ or acetylacetone. The addition of several organometallics such as Co(C₅H₅)₂, *t*-BuMgBr, Mn(acac)₃, Ti(C₅H₅)₂Cl₂, [RhCl(COD)]₂, or PdCl₂(COD) (2.5 wt % as metal) were ineffective for formation of mesoporous carbon (Table 2), although these organometallics exhibit good solubility in the present pitch. In the case of addition of CaI₂, a large mesopore ratio was observed instead of a very small BET surface area. Thus the addition of late rare earth metal compounds (Sm, Gd, Tb, Er, Yb, Lu) to pitch in 2.5 wt % loading level was very effective for the formation of relatively large mesopore surface area and large mesopore ratio (ratio of mesopore surface area to BET surface area). The BET surface area is 191–260 m²/g and mesopore ratio ranges 65–81% for carbonaceous products obtained in 26–36% yield. The addition of other rare-earth metal compounds such as rare-earth alkoxides, rare-earth acetylacetonate, and rare-earth naphthoate are also effective for the formation of a large mesopore ratio, i.e., 76–81% with pore size of 50–52 Å in the cases of Y(OiPr)₃, Y(naphthoate)₃, and Y(acac)₃ (Table 3). In contrast, the addition of rare-earth chloride and rare-earth oxide is ineffective for the formation of a large mesopore ratio (Table 4). This should be ascribed to the insolubility of these compounds toward the pitch, which makes it very difficult to mix these compounds with pitch homogeneously in the molecular level.

Table 4. Specific Surface Area of Activated Carbon Obtained from Lanthanide Chloride or Lanthanide Oxide/Pitch Precursor^a

lanthanides	carbonization yield/%	BET surface area/m ² g ⁻¹	mesopore ratio/%	pore size/Å
YCl ₃	42.0	237	16.9	33.8
LaCl ₃	40.5	190	13.8	27.2
NdCl ₃	39.7	194	13.5	26.7
SmCl ₃	53.5	193	12.6	30.8
GdCl ₃	40.5	204	11.3	29.8
TbCl ₃	42.2	187	17.3	33.6
ErCl ₃	36.0	274	15.5	28.2
YbCl ₃	38.9	238	12.9	30.6
LuCl ₃	41.9	212	19.9	33.3
Y ₂ O ₃	32.3	332	5.3	23.4
Yb ₂ O ₃	33.8	356	5.5	23.8

^a Lanthanide dichloride and lanthanide oxide, 5 wt % of pitch. Steam invigoration, 930 °C for 7 min.

The mechanical property of mesoporous carbons (prepared from pitch/Y(acac)₃, mesopore ratio 81.1%) is relatively high, although these values are lower than those of typical carbon fibers, i.e., tensile modulus 457–515 kg/mm², tensile strength 14–16 kg/mm², elongation 2–3%, while typical carbon fibers show tensile modulus of 700–800 kg/mm², tensile strength of 25–35 kg/mm² and elongation of 2%. The apparent density of the present mesoporous carbon is 1.73 g/cm³.

Mercury porosimetry was also measured to find the exact pore diameter. As a result, the activated carbon obtained from pitch/Y(acac)₃ (steam invigoration at 900 °C for 15 min, mesopore ratio 63%) shows ca. 48 Å pore size (intrusion volume 0.8 mm³/g), and the macropore was observed in the 100–1000 Å diameter region (intrusion volume ca. 0.3 mL/g), while the blank carbon (mesopore ratio, 6.8%) shows the pore size of 35 Å (intrusion volume 0.4 mL/g) and practically no macropore was observed in the 100–1000 Å region. The activated carbon obtained from pitch/Y(acac)₃ (steam invigoration, 900 °C for 9 min, mesopore ratio 45%) showed the intermediate values between the activated carbon (steam invigoration 900 °C for 15 min) and blank carbon.

To understand the effect of the number of C₅H₅ ligands attached to the metal on the mesopore ratio, the addition of YbCl(C₅H₅)₂ (THF) and YbCl₂(C₅H₅)(THF)₃ (2 wt %) was also tested. As a result, the addition of YbCl(C₅H₅)₂(THF) resulted in the formation of a BET surface area of 250 m²/g (mesopore ratio 62.6%) at a carbonization yield of 28.6%, while the addition of YbCl₂(C₅H₅)(THF)₃ resulted in the formation of BET surface area of 218 m²/g (mesopore ratio 16.1%) at the carbonization yield of 32.3%. Thus the mesopore ratio increased by the addition of organometallic rare-earth complexes in the order Yb(C₅H₅)₃ > YbCl(C₅H₅)₂(THF) > YbCl₂(C₅H₅)(THF)₃ > YbCl₃.

The XPS spectrum of carbons obtained by steam invigoration of pitch/Y(acac)₃ showed the peak of Y3d_{5/2} at 159.9 eV and the peak of Y3d_{3/2} at 161.9 eV to indicate the formation of Y₂O₃. This result was also supported by the measurement of powder XRD, where (222), (400), and (440) signals were observed at 28.8°, 38.7°, and 49.0° (2θ) to indicate the presence of Y₂O₃. In a similar manner, the XRD patterns of the carbonaceous product obtained by steam invigoration of *t*-BuMgBr/pitch, Pd(COD)₂Cl₂/pitch, and [Rh(COD)Cl]₂ show the presence of MgO [42.3° (200), 61.2° (220), and 78.1° (222)], Pd [39.9° (111), 47.1° (200), 68.2° (220),

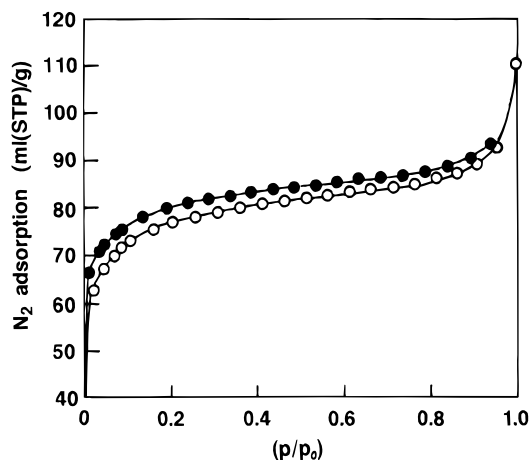


Figure 2. Langmuir type adsorption isotherm for the activated carbon obtained from $\text{Co}(\text{C}_5\text{H}_5)_2/\text{pitch}$. Metal content 2.5 wt %; steam invigoration was carried out at 930 °C for 7 min.

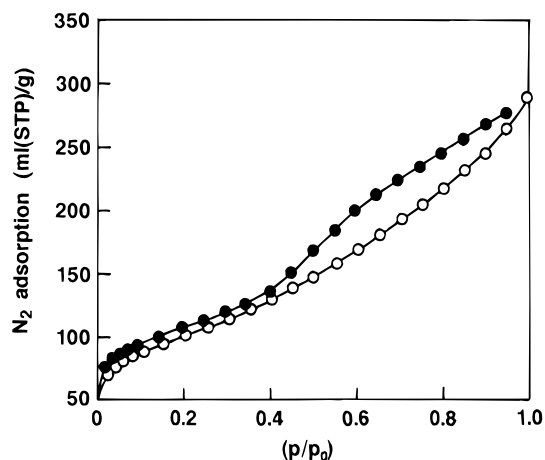


Figure 3. Adsorption isotherm for the activated carbon obtained from $\text{Y}(\text{acac})_3/\text{pitch}$. Metal content 2.5 wt %; steam invigoration was carried out at 930 °C for 7 min.

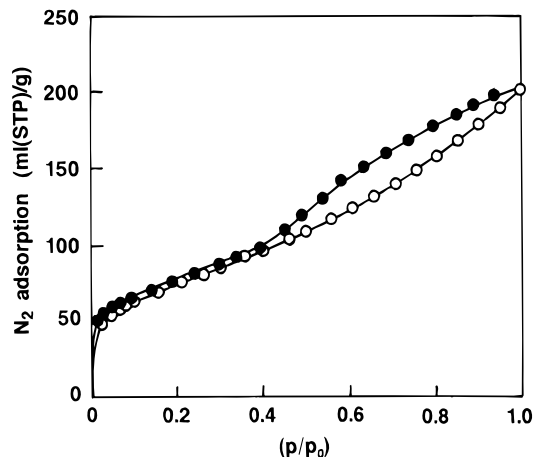


Figure 4. Adsorption isotherm for the activated carbon obtained from $\text{Y}(\text{C}_5\text{H}_5)_3/\text{pitch}$. Metal content 2.5 wt %; steam invigoration was performed at 930 °C for 7 min.

82.1° (311)], and Rh [41.1° (111), 47.8° (200), 70.0° (220), 84.5° (311)], respectively, in the carbon matrixes.

Figures 2–4 show the adsorption isotherms of N_2 gas on the resulting carbon materials. Figure 2 shows the Langmuir type adsorption isotherm for the activated carbon obtained by steam invigoration of a mixture of $\text{Co}(\text{C}_5\text{H}_5)_2$ with pitch. By contrast, Figures 3 and 4 show

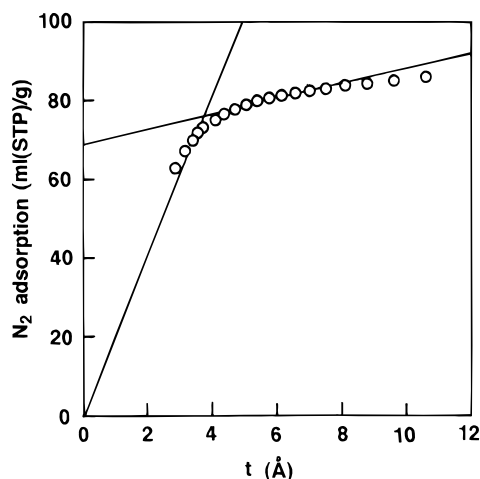


Figure 5. t -plot for the activated carbon obtained from $\text{Co}(\text{C}_5\text{H}_5)_2/\text{pitch}$. Metal content 2.5 wt %; steam invigoration was performed at 930 °C for 7 min.

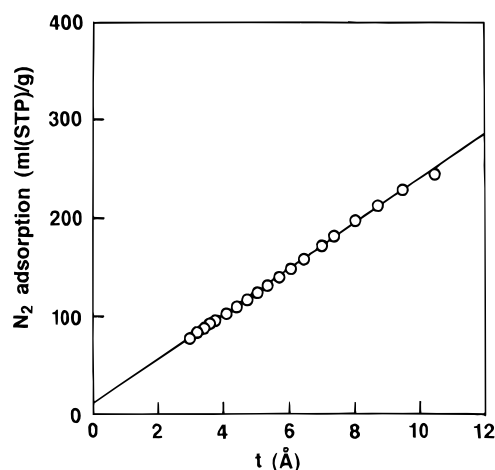


Figure 6. t -plot for the activated carbon obtained from $\text{Y}(\text{acac})_3/\text{pitch}$. Metal content 2.5 wt %; steam invigoration was performed at 930 °C for 7 min.

the adsorption isotherms for the activated carbon obtained from a mixture of $\text{Y}(\text{acac})_3/\text{pitch}$ and $\text{Yb}(\text{C}_5\text{H}_5)_3/\text{pitch}$, respectively, which indicate the presence of slit or syringal type mesopore on the resultant carbon materials.

In an attempt to observe the resulting mesopore directly, the SEM measurement of carbonaceous product obtained from $\text{Y}(\text{acac})_3/\text{pitch}$ was carried out. However, the mesopore was not observed in the SEM photograph. Only the slit type macropore was observed. Even in the TEM measurement ($\times 50\,000$), we have failed to observe the resulting mesopore directly.

To evaluate the pore size, the t -plot of N_2 adsorption proposed by de Boer is often applied for the carbon materials. Figure 5 shows the t -plot for the carbon material obtained from a pitch/ $\text{Co}(\text{C}_5\text{H}_5)_2$ mixture. In this case all the data do not follow the straight line passing through the starting point because of the presence of micropore. For the first step at around <4 Å, all the N_2 adsorbs as single layer, while at around >4 Å N_2 adsorbs as multilayer. By contrast Figure 6 shows the t -plot for the activated carbon obtained from organolanthanide/pitch precursor. In this case all the data follow the straight line passing through the starting point because of the presence of a high mesopore ratio.

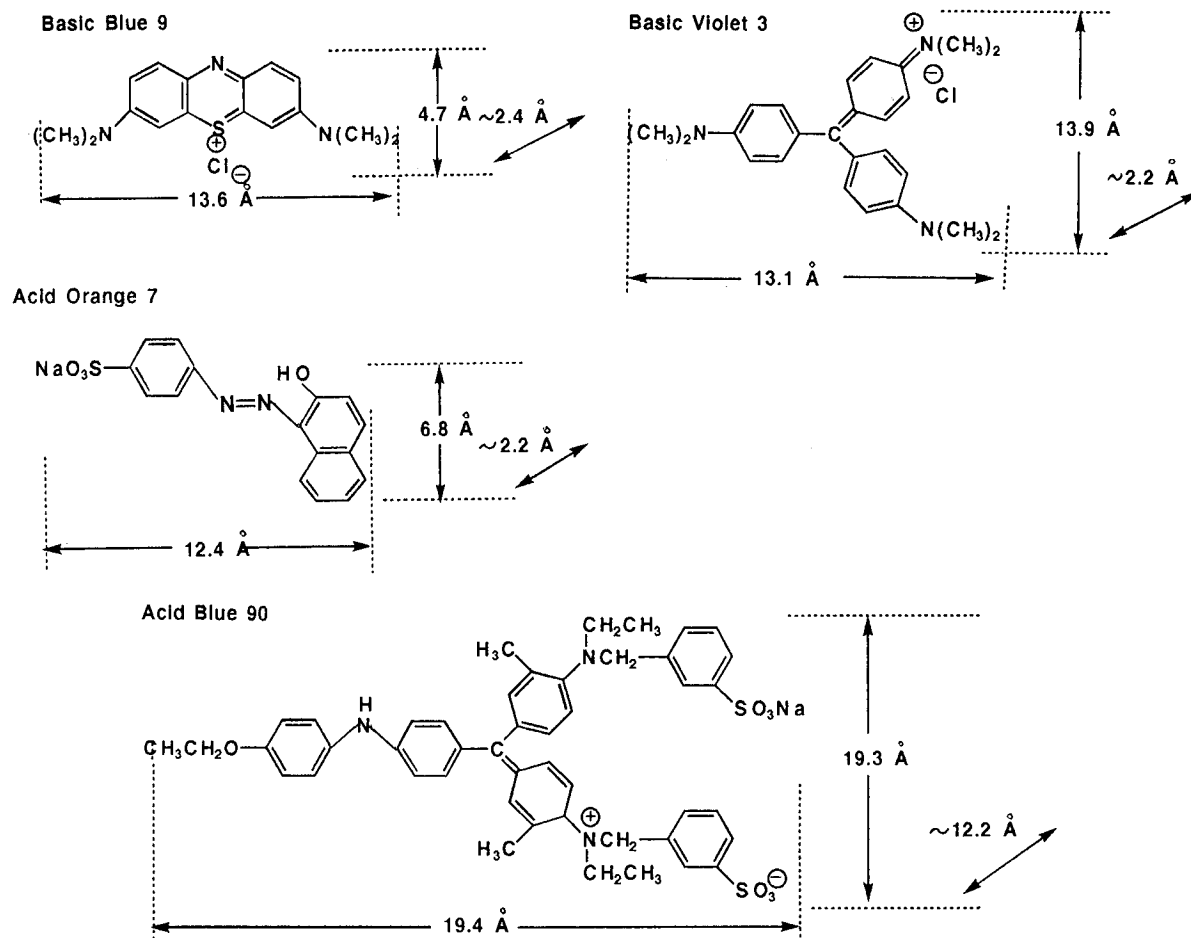


Figure 7. Estimated molecular sizes of basic and acidic dyes.

Table 5. Adsorption of Dyes on Activated Carbons (mg/g)

adsorbate	adsorbent				
	Y(naphthoate) ₃ /AC ^a	Y(OiPr) ₃ /AC ^a	F400	Kimco	blank
basic violet 3	53	62	180	31	23
basic blue 9	49	52	176	66	33
acid orange 7	64	83	193	53	21
acid blue 90	63	69	22	16	5

^a Activated carbon; organometallics, 2 wt % of pitch.

2. Unique Adsorption Behavior of Activated Carbon with a High Mesopore Ratio. The activated carbon was found to have a large mesopore surface area, and therefore giant molecules should be adsorbed on that carbon. The adsorption of basic or acid dyes of different molecular weight was examined here by using various carbon matrixes with large mesopore ratio, i.e., granular activated carbon F400 (Toyo Cargon Co.), Kimco carbon and activated carbons obtained from organolanthanide/pitch composites (Table 5). F400 adsorbs well relatively small basic or acid dyes (basic violet 3, basic blue 9, acid orange 7 with long axis <14 Å)¹⁹ but the activated carbons obtained from pitch/Y(naphthoate)₃ or pitch/Y(OiPr)₃ adsorb a large molecular weight acid dye, acid blue 90 (long axis 20 Å), selectively (Figure 7).²⁰ The adsorption isotherm of acid blue 90 indicates that the adsorption saturates at the concen-

tration of 1 g/L and saturates in the reaction period of 2 h by using mesoporous carbon. Especially noteworthy is that the present material possesses fiber-forming ability and therefore these materials should be useful as a water purifying agent, while such a transformation is impossible for the granular activated carbon, F400.

The adsorption of water soluble vitamins such as vitamin B₁,²⁰ B₂,¹⁹ B₆,²¹ B₁₂²² (Figure 8), and vitamin C to the resulting carbon was studied, while adsorption of vitamin A, D₂, E, and K₁ was not measured because these are insoluble in water. As a result, vitamin B₁ and vitamin B₆ with relatively small diameter adsorb well on F400 and Kimco activated carbons, but mesoporous carbons showed the large adsorption regarding the giant molecule, vitamin B₁₂ (Table 6). The adsorption of vitamin C was measured several times, but the reproducibility of the adsorption is very poor because of the rapid degradation by autooxidation in water. Therefore, we have given up the idea of measuring the adsorption of vitamin C on the activated carbons.

The activated carbons have long been used in the purification of sugars, especially in decoloration of sugars. Therefore the present activated carbons were tested here to examine the adsorption of dextran.¹⁹ Dextran is composed of poly(D-glucopyranose) connected with α-1,6 bonding (Figure 9). Adsorption of dextrans

(19) The size was estimated by computer using Nemesis software applied for Power Macintosh 7100/80AV.

(20) Suh, H. H.; Kim, Y. J. *Rep. R. I. Chem. Spect. Chungnam* **1982**, 3, 36.

(21) (a) Longo, J.; Franklin, K. J.; Richardson, M. F. *Acta Crystallogr. Sect. B* **1982**, 38, 2721. (b) Savinov, V. Kh.; Struchkov, Yu. T.; Batsanov, A. S.; Azizov, M. A. *Koord. Khim.* **1982**, 8, 1623.

(22) Shoemaker, C. B.; Cruckshank, D. W. J.; Hodgkin, C.; Kamper, M. J.; Pilling, D. *Proc. R. Soc. London, Ser. A* **1964**, 278, 1.

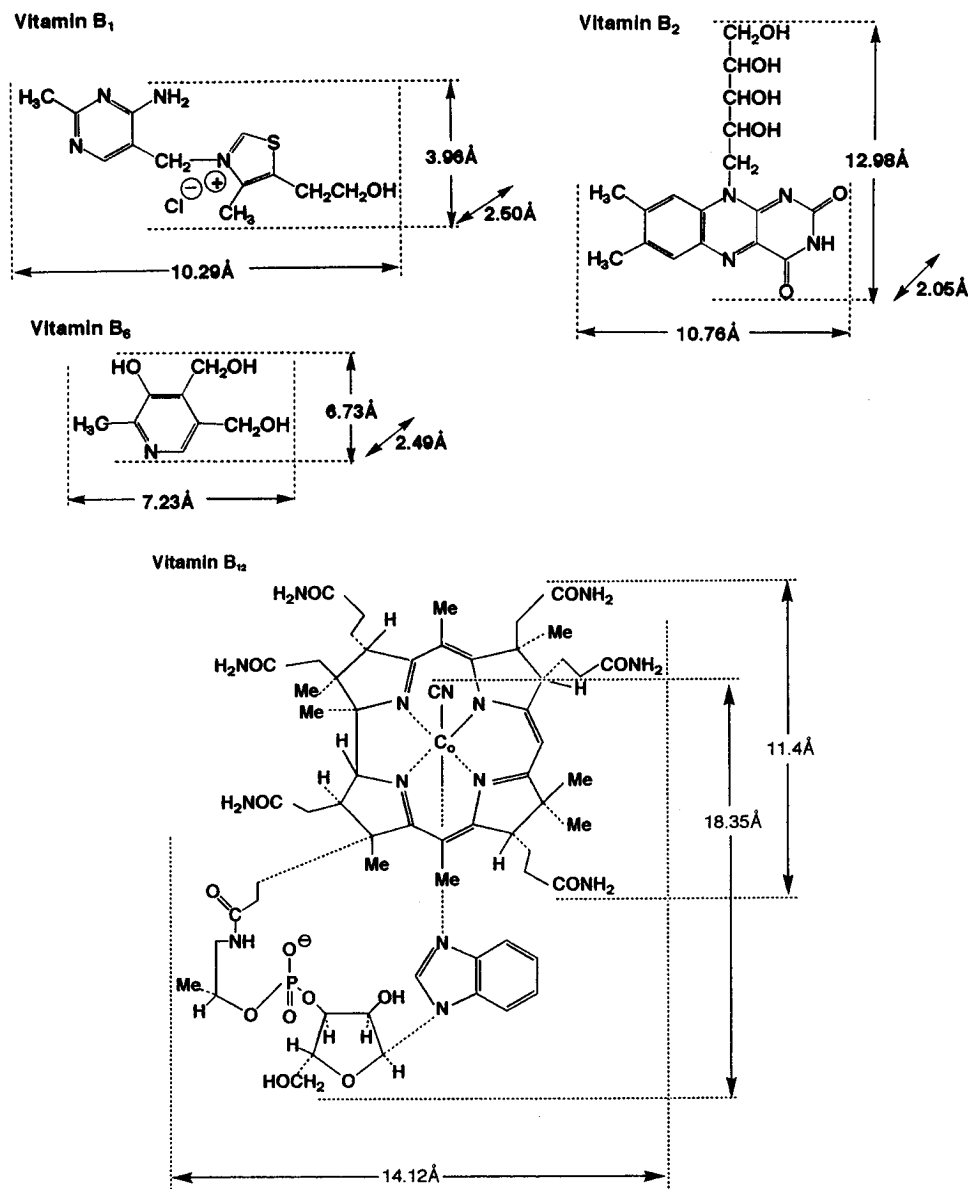


Figure 8. Molecular sizes of vitamins B₁, B₆, and B₁₂.

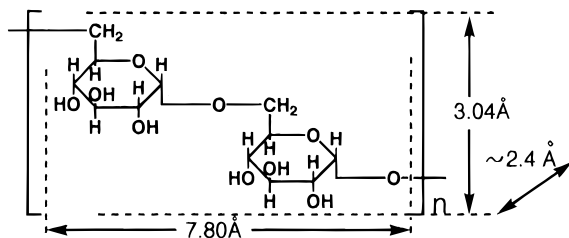


Figure 9. Molecular size of dextrans.

Table 6. Adsorption of Vitamins on Activated Carbons (mg/g)^a

adsorbate	adsorbent				
	Y(naphthoate) ₃ /AC	Y(OiPr) ₃ /AC	F400	Kimco	blank
vitamin B ₆	20	27	79	85	22
vitamin B ₁	24	26	68	71	14
vitamin B ₂	57	63	99	42	31
vitamin B ₁₂	65	70	48	6	9

^a The values measured after 2 h at 25 °C are shown.

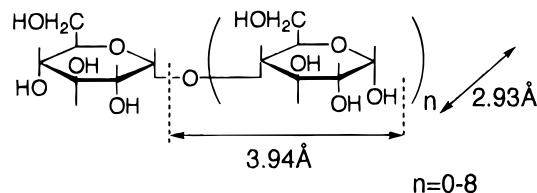
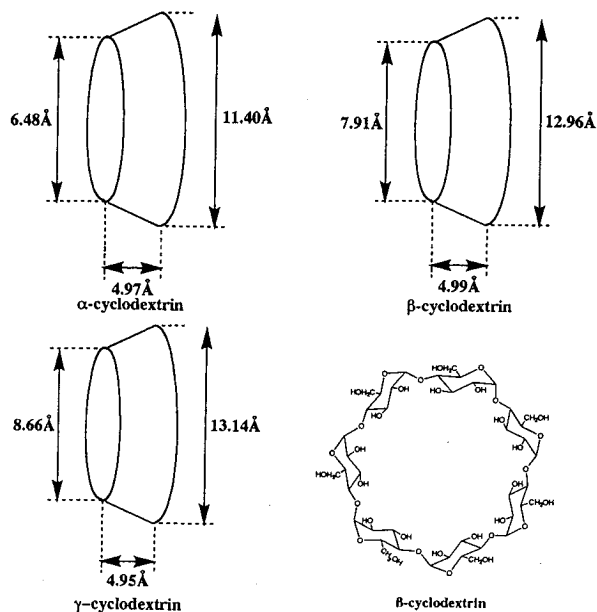
such as dextran 10 ($M_w = 11\,200$), dextran 20 ($M_w = 20\,000$), and dextran 80 ($M_w = 92\,000$) were tested (Table 7). The activated carbon obtained from pitch/

Table 7. Adsorption of Dextrans on Activated Carbons (mg/g)^a

adsorbate	adsorbent				
	Y(acac) ₃ /AC	Y(C ₅ H ₅) ₃ /AC	F400	Kimco	blank
dextran 10	99	56	44	4	0
dextran 20	65	32	25	2	0
dextran 80	35	28	0	0	0

^a The values measured after 2 h at 25 °C are shown.

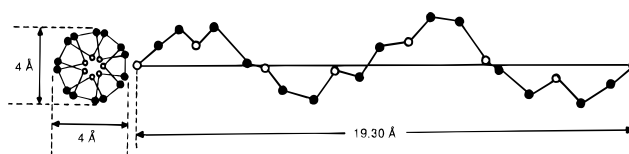
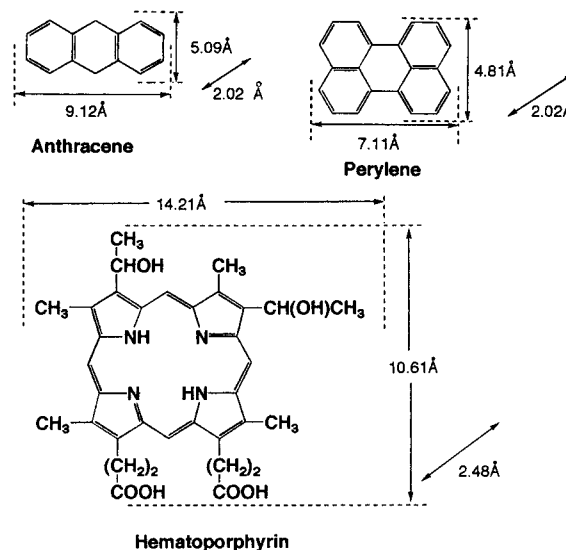
Y(acac)₃ showed relatively large adsorption for dextran 10, 20, and 80, while the activated carbon obtained from pitch/Y(C₅H₅)₃ and F400 showed rather low adsorption. Kimco and blank carbon showed much lower adsorption. The adsorption of the lower molecular weight polysaccharide was also tested here. The maltooligosaccharides used here are listed in Table 8 (Figure 10). Kimco carbon adsorbs maltose and maltotriose selectively, while the activated carbon obtained from pitch/Y(acac)₃ or pitch/Y(C₅H₅)₃ shows an adsorption maximum in the case of maltoheptaose and maltononaose. As an extension of this research, adsorption of α ,²³ β ,²⁴ or γ -cyclodextrin,²⁵ [cyclic poly(D-glucopyranose) connected with 1,4- α -glycoside linkage] was also studied (Figure 11).

**Figure 10.** Molecular size of maltooligosaccharides.**Figure 11.** Molecular sizes of cyclodextrins.**Table 8. Adsorption of Maltoligosaccharides and Cyclodextrins on Activated Carbons (mg/g)**

adsorbate	adsorbent			
	Y(acac) ₃ /AC	Y(C ₅ H ₅) ₃ /AC	Kimco	blank
dextrose	0	0	10	0
maltose	12	0	93	0
maltotriose	36	17	71	14
maltotetraose	41	25	42	14
maltopentaose	46	27	26	12
maltohexaose	58	37	21	12
maltoheptaose	76	37	15	11
maltononaose	66	42	14	15
α-cyclodextrin	38	35	9	7
β-cyclodextrin	42	45	14	3
γ-cyclodextrin	49	49	0	3

Mesoporous activated carbon obtained by steam invigoration of Y(acac)₃/pitch or Y(C₅H₅)₃/pitch shows fairly good adsorption while Kimco carbon as well as blank carbon shows very little adsorption. The diameter of cyclodextrin is <15 Å. Therefore the generated pore (50–60 Å) is much larger than the diameter of cyclodextrins, and hence we cannot see good adsorption on these materials.

Adsorption of various poly(ethylene glycol) was also examined because we can choose an arbitrary chain length (Figure 12). As a result, F400 and Kimco

**Figure 12.** Molecular size of poly(ethylene glycol).**Figure 13.** Molecular sizes of anthracene, perylene, and hematoporphyrin.

activated carbon adsorb high molecular weight poly(ethylene glycol) such as $M_n = 8500$ or 10 000 (105 and 150 mg/g, 87 and 144 mg/g, respectively, for F400 and Kimco carbon) while activated carbon obtained from Y(acac)₃/pitch (45 mg/g) and blank carbon showed less adsorption (37 mg/g) for the poly(ethylene glycol) of $M_n = 10\,000$. Naito et al.²⁶ reported that the critical pore size for adsorption of poly(ethylene glycol) is ca. 18 Å irrespective of molecular weight. Therefore, the pore size of 18–20 Å is suited for the adsorption of poly(ethylene glycol). The higher adsorption of poly(ethylene glycol) in proportion to the molecular weight is attributable to the increased hydrophilicity of the adsorbate. The micropore volume for F400, Kimco and activated carbon obtained from Y(acac)₃/pitch are 0.447, 0.35, and 0.041 mL/g, respectively. These data also support the above estimation.

Giant molecules such as hematoporphyrin²⁷ and nystatin¹⁹ also adsorb well on the mesopore activated carbon (Figure 13). F400 as well as activated carbon obtained from Y(acac)₃/pitch and Y(C₅H₅)₃/pitch adsorb 60–61 mg/g of hematoporphyrin while the blank carbon adsorbs only 8 mg/g of hematoporphyrin. The present mesoporous carbons are ineffective for adsorption of rather small aromatics such as benzene, anthracene,²⁸ and perylene.²⁹ For example, F400 and Kimco carbons adsorb 118–120 mg/g perylene, while mesoporous carbons obtained from Y(C₅H₅)₃/pitch or Yb(C₅H₅)₃/pitch

(23) (a) Klar, B.; Hingerty, B.; Saenger, W. *Acta Crystallogr., Sect. B* **1980**, *36*, 1154. (b) Noltemeyer, M.; Saenger, W. *J. Am. Chem. Soc.* **1980**, *102*, 2710. (c) Nocolis, I.; Viullain, F.; Coleman, A. W.; Rango, C. *Supramol. Chem.* **1994**, *3*, 251.

(24) (a) Steiner, T.; Koellner, G. *J. Am. Chem. Soc.* **1994**, *116*, 5122. (b) Hirotsu, K.; Higuchi, T.; Fujita, K.; Ueda, T.; Shinoda, A.; Imoto, T.; Tabushi, I. *J. Org. Chem.* **1982**, *47*, 1143. (c) Stezowski, J. J.; Czugler, M.; Eckle, E. *Proc. I. S. Cyclodextrins* **1981**, 151.

(25) (a) Harata, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2763. (b) Ding, J.; Steiner, T.; Saenger, W. *Acta Crystallogr., Sect. B* **1991**, *47*, 731.

(26) Kasaoka, N.; Tanaka, E.; Sakata, Y.; Naito, R. *Nippon Kagaku Kaishi* **1987**, *12*, 2260.

(27) (a) Polyakova, I. N.; Strikova, Z. A.; Faeeva, O. A. *Kristallografiya* **1991**, *36*, 1167. (b) Damaschke, O. *Kristallografiya* **1942**, *104*, 114.

(28) (a) Mason, R. *Acta Crystallogr.* **1964**, *17*, 547. (b) Brock, C. P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1990**, *46*, 795.

(29) (a) Ikemoto, I.; Yakushi, K.; Kuroda, H. *Acta Crystallogr., Sect. B* **1970**, *26*, 800. (b) Yamochi, H.; Saito, G.; Sugano, T.; Kinoshita, M.; Katayama, C.; Tanaka, J. *Chem. Lett.* **1986**, 1303.

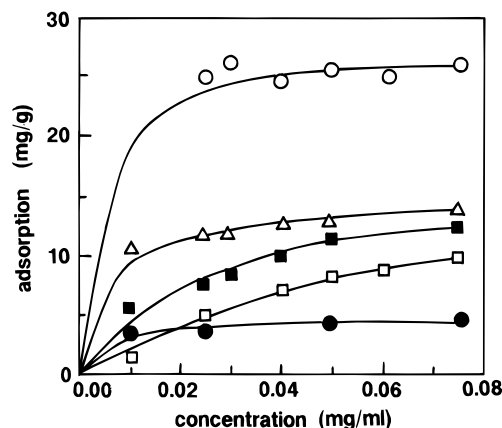


Figure 14. Adsorption isotherm of humic acid on activated carbons obtained from $\text{Y}(\text{acac})_3/\text{pitch}$ (\circ), $\text{Y}(\text{OiPr})_3/\text{pitch}$ (\triangle), and $\text{La}(\text{C}_5\text{H}_5)_3/\text{pitch}$ (\blacksquare), and those on F-400 (\square) and blank carbon (\bullet).

show low adsorption, 20–25 mg/g. Nystatin, an antibiotic substance belonging to polyene system, also adsorbs on the mesoporous activated carbon in 156–162 mg/g. In contrast, F400 and Kimco carbons are unsuited for adsorption of nystatin. These carbons adsorb nystatin at only 85 or 38 mg/g, respectively. Thus variety of flat giant molecules adsorb well on the resulted activated carbons, reflecting their large mesoporous structure.

Purification of city water is made by either direct removal of trihalomethane from water or removal of humic acid,^{19,30} a precursor of trihalomethane, from the water. Here we have attempted the adsorption of humic acid (crystallite dimensions of ca. $(5\text{--}15) \times (10\text{--}14)$ Å) by mesoporous activated carbons. The activated carbon obtained from $\text{Y}(\text{acac})_3/\text{pitch}$ showed largest adsorption (28 mg/g) and activated carbons obtained from $\text{Y}(\text{OiPr})_3/\text{pitch}$ (12 mg/g) or $\text{La}(\text{C}_5\text{H}_5)_3/\text{pitch}$ (10 mg/g) showed moderate adsorption (Figure 14). By contrast, F400 or blank carbons showed very low adsorption toward humic acid (2–5 mg/g). The mesopore volume for the activated carbons obtained from $\text{Y}(\text{acac})_3/\text{pitch}$, $\text{Y}(\text{OiPr})_3/\text{pitch}$, $\text{La}(\text{C}_5\text{H}_5)_3/\text{pitch}$, and F400 and blank carbons are 0.406, 0.251, 0.147, 0.160, and 0.023 mL/g, respectively. Thus adsorption increases with increase of mesopore volume.

To evaluate the effect of Ln_2O_3 obtained from $\text{Y}(\text{acac})_3$ (2.5 wt %) on the adsorption, the metal component was washed away with 6 N HCl or 6 N HNO_3 . The removal ratio of the metal component is 59–76% by 6 N HCl and 73–86% by 6 N HNO_3 , and the resulting carbon exhibits a mesopore ratio of 78.4 or 79.1%, respectively (81.8% before acid treatment). The adsorption of various substrates with these metal-free activated carbon (metal content diminished significantly at least in the contact surface) is approximately the same with the adsorption with the carbon containing Y_2O_3 . For example, mesoporous carbon obtained from $\text{Y}(\text{acac})_3/\text{pitch}$ after acid treatment adsorbs vitamin B_{12} (69 mg/g), acid blue 90 (52 mg/g), and γ -cyclodextrin (42 mg/g), while that before acid treatment shows the adsorption of vitamin B_{12} (66 mg/g), acid blue 90 (52 mg/g), and γ -cyclodextrin (44 mg/g). Thus the adsorption of giant molecules is ascribed to the large mesopore volume.

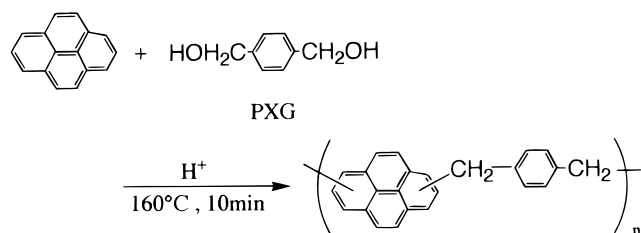


Figure 15. COPNA resin obtained from pyrene and *p*-xylene- α,α' -diol.

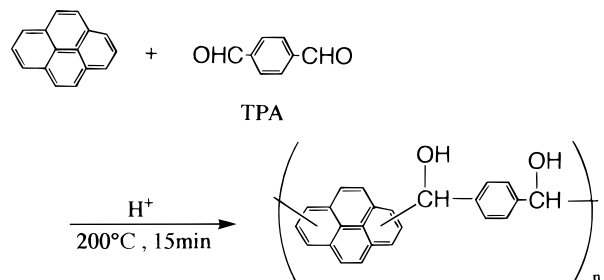


Figure 16. COPNA resin obtained from pyrene and terephthalaldehyde.

3. Model Reaction of Pitch Using COPNA Resin.

Petroleum pitches were led to mesoporous activated carbon by steam invigoration of a mixture of pitch and rare-earth metal complexes (1–3 wt % of pitch). In general petroleum pitch is composed of key building blocks such as benzene, naphthalene, anthracene, phenanthrene, pyrene, perylene unit, etc. Therefore, a great deal of our insight into the mechanism for formation of mesoporous activated carbon should be collected by direct steam invigoration of a mixture of $\text{Ln}(\text{C}_5\text{H}_5)_3$ ($\text{Ln} = \text{Y}, \text{Yb}$) and each individual aromatic. However these volatile aromatics themselves were distilled away during heat treatment when the steam invigoration was performed at 930 °C, while naphthalene can be transformed by heat treatment under pressure to highly graphitized carbon.³¹ Therefore steam invigoration of nonvolatile COPNA (condensed polynuclear aromatics) resins containing these aromatics were tested at 930 °C for 3–10 min. The COPNA resins were prepared by heating the 1:1 mixture of individual aromatic compound and *p*-xylene- α,α' -diol (PXG) at 160 °C for 10 min to result in the formation of polymeric materials with $M_n < 2000\text{--}3000$ (Figure 15). Resulting COPNA resins containing naphthalene,³² anthracene,^{33,34} and pyrene were mixed with rare-earth metal complexes (1–3 wt % of pitch) and oxidized at 360 °C for 40–80 min, and then steam invigoration was conducted at 930 °C. The result of steam invigoration of COPNA resins containing pyrene, phenanthrene, and perylene is shown in Table 9, while the steam invigoration of the corresponding resins containing anthracene and naphthalene showed extremely low mesopore ratio (Table 10). Thus among various aromatic components, especially pyrene, phenanthrene and perylene derivatives serve as a good precursor for highly mesoporous activated carbons. These

(31) Lewis, I. C. *Proc. Int. Symp. Carbon, Tsukuba, Japan* **1990**, 2.

(32) Ohta, M.; Ohtani, S.; Ohta, E.; Kojima, A. *Nippon Kagaku Kaishi* **1988**, 106.

(33) Kaneko, T.; Ohta, E.; Kanazawa, M. Ohtani, S. *Nippon Kagaku Kaishi* **1987**, 1047.

(34) Ohtani, S.; Kobayashi, Y.; Inoue, H.; Ohta, E.; Raskovic, V.; Hongan, Y.; Ohta, M. *Nippon Kagaku Kaishi*, **1986**, 1220. Ohta, M.; Ohtani, S.; Igarashi, M. *Chem. Lett.* **1989**, 1183.

(30) Pollack, S. S.; Lenz, H.; Ziechmann, W. *Soil Sci.* **1971**, 112, 318.

Table 9. Specific Surface Area of Activated Carbon Obtained from COPNA Resin (PXD System) Containing LnCp₃^a

resin	steam invigoration time, min	carbonizing yield, %	BET surface area, m ² /g	mesopore ratio, %
COPNA(pyrene)/Y(C ₅ H ₅) ₃ (2 wt %)	3.0	16	1026	83.5
COPNA(pyrene)/Yb(C ₅ H ₅) ₃ (2 wt %)	3.0	25	687	37.8
COPNA (pyrene)	3.0	34	441	2.4
COPNA(phenanthrene)/Y(C ₅ H ₅) ₃ (2 wt %)	3.0	14	448	76.9
COPNA(phenanthrene)/Yb(C ₅ H ₅) ₃ (2 wt %)	3.0	12	501	55.5
COPNA(phenanthrene)	3.0	31	471	1.9
COPNA(perylene)/Y(C ₅ H ₅) ₃ (2 wt %)	3.0	22	665	30.4
COPNA(perylene)/Yb(C ₅ H ₅) ₃ (2 wt %)	3.0	24	608	33.7
COPNA(perylene)	3.0	34	529	0.8

^a Steam invigoration was performed at 930 °C.**Table 10. Specific Surface Area of Activated Carbon Obtained from COPNA Resin (PXD System) Containing LnCp₃^a**

resin	steam invigoration time, min	carbonizing yield, %	BET surface area, m ² /g	mesopore ratio, %
COPNA(naphthalene)/Y(C ₅ H ₅) ₃ (2 wt %)	0.5	24	267	6.0
COPNA(naphthalene)/Y(C ₅ H ₅) ₃ (4 wt %)	0.5	25	364	3.5
	1.0	20	473	8.0
COPNA(naphthalene)	1.0	40	283	2.2
	3.0	33	498	1.2
COPNA(anthracene)/Y(C ₅ H ₅) ₃ (2 wt %)	3.0	30	505	10.5
COPNA(anthracene)/Yb(C ₅ H ₅) ₃ (2 wt %)	3.0	28	606	5.2
COPNA(anthracene)	3.0	29	490	2.1

^a Steam invigoration was performed at 930 °C.**Table 11. Specific Surface Area of Activated Carbon Obtained from COPNA Resin (TPA System) Containing LnCp₃^a**

resin	steam invigoration time, min	carbonizing yield, %	BET surface area, m ² /g	mesopore ratio, %
COPNA(anthracene)/Y(C ₅ H ₅) ₃ (2 wt %)	6.0	28	747	24.5
COPNA(anthracene)/Yb(C ₅ H ₅) ₃ (2 wt %)	6.0	31	901	20.9
COPNA(anthracene)	6.0	43	497	1.3
COPNA(pyrene)/Y(C ₅ H ₅) ₃ (2 wt %)	6.0	16	1026	83.5
COPNA(pyrene)/Yb(C ₅ H ₅) ₃ (2 wt %)	6.0	24	687	38.5
COPNA(pyrene)	6.0	34	134	5.9

^a Steam invigoration was performed at 930 °C.

aromatics should react with rare-earth metal complexes to form the 1:1 adduct at elevated temperature. In fact, anthracene was reported to react with a divalent samarium complex, Sm(C₅Me₅)₂, at the 4,10 and 8,9 positions to produce [Sm(C₅Me₅)₂] μ - η^3 : η^3 -(C₁₄H₁₀)].³⁵ Pyrene also reacts with Sm(C₅Me₅)₂ at the 3,4 and 5,6 positions to give [Sm(C₅Me₅)₂] μ - η^3 : η^3 -(C₁₆H₁₀)].³⁵ Further pyrolysis of the 1:1 adduct should generate the ultrafine rare-earth metal particles releasing CO₂ and H₂ and the generated metal (or metal hydroxide) should coordinate again to other aromatic molecules. Thus the metal particles shaves the pitch wall to result in the formation of mesoporous carbon.

COPNA resins prepared from terephthalaldehyde (TPA) and pyrene (1:1) by the catalytic action of *p*-toluenesulfuric acid (200–220 °C for 15 min) again showed a relatively large mesopore ratio when the steam invigoration was conducted on the resin at 930 °C, while steam invigoration of the corresponding product obtained from terephthalaldehyde and an-

thracene (1:1) showed a relatively small mesopore ratio. As a model compound for the pitch carbon skeleton, poly(divinylbenzene) and poly(styrene) were also tested. These polymers were mixed with Y(C₅H₅)₃ and Y(acac)₃ (metal content, 2.3 \times 10⁻⁴ mol/g), and steam invigoration was conducted. However generation of mesopore on the resulting carbon was negligible in these cases. Only the mesopore ratio is 2.4–2.5% even in carbonization yield of 10–12%, i.e., depolymerization of poly(styrene) or poly(divinylbenzene) proceeds preferentially in these cases. The addition of Co(acac)₃ or Ni(acac)₂ to the poly(divinylbenzene) again resulted in the formation of small mesopore ratio.

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(35) Evans, W. J.; Gonzales, S. L.; Ziller, W. *J. Am. Chem. Soc.* **1994**, *116*, 2600.