

Fabrication of New Nanoporous Carbons through Silica Templates and Their Application to the Adsorption of Bulky Dyes

Sangjin Han, Kwonnam Sohn, and Taeghwan Hyeon*

School of Chemical Engineering and Institute of Chemical Processes, Seoul National University, Seoul 151-744, Korea

Received February 8, 2000. Revised Manuscript Received July 18, 2000

New nanoporous carbons with extremely high mesopore volumes and surface areas have been produced using silica nanoparticles as templates. The polymerization of resorcinol and formaldehyde (RF) in the presence of silica sol particles generated RF gel-silica nanocomposites. Carbonization followed by HF etching of silica templates generated nanoporous carbons with pore sizes predominantly in the range of 10–100 nm. These carbons exhibited very high pore volumes of $>4 \text{ cm}^3/\text{g}$ and high surface areas of $\sim 1000 \text{ m}^2/\text{g}$. These nanoporous carbons exhibited excellent adsorption capacities for bulky dyes. In the best case, the adsorption capacity of the nanoporous carbon is over 10 times higher than that of commercial activated carbon.

Introduction

Activated carbons have been extensively utilized in various industrial adsorption and separation processes. These porous carbons are usually prepared by the carbonization of various raw materials followed by physical or chemical activation.¹ Many different carbonaceous precursors, such as wood, coal, lignite, coconut shell, and peat, have been used in the preparation.¹ Many polymeric precursors including polyacrylonitrile, poly(furfuryl alcohol), poly(vinylidene chloride), and phenol resin have been applied as porous carbon precursors. Pekala and co-workers developed carbon aerogel materials using resorcinol–formaldehyde (RF) gel as precursor.^{2–4}

Activated carbons are generally microporous, and the production of mesoporous carbons is desirable for the separation and adsorption of bulky organic materials.⁵ Recently, Yasuda and co-workers developed new mesoporous carbons from the steam invigoration of pitches homogenized with $\sim 3 \text{ wt } \%$ organo-rare-earth metal complexes.^{5,6} These mesoporous activated carbons selectively adsorbed giant molecules such as dyes and humic substances; the adsorption capacities of these carbons for dyes, however, were moderate.^{6,7}

One of the most extensively studied areas in materials chemistry is the fabrication of nanoporous materials through template approaches.⁸ After the preparation of mesoporous M41S silica materials by the Mobil researchers in 1992, many different inorganic mesoporous materials have been synthesized. Self-assemblies of surfactants and block copolymers have been frequently applied as templates in the synthesis. Our group and other group have synthesized mesoporous carbon materials with regular three-dimensionally interconnected pore arrangements by using mesoporous silica materials as templates.^{9,10} These mesoporous carbons exhibited very interesting electrochemical performance in their application as supercapacitors.⁹

Colloidal crystals have been utilized as templates for the synthesis of many porous materials with close-packed pore arrangements.¹¹ Organic templates such as uniform polymer latex spheres have been applied as templates for the preparation of inorganic porous materials.¹² Polymers and carbons with closed-packed pores have been prepared using colloidal silica crystals as templates. Zakhidov et al. reported the synthesis of

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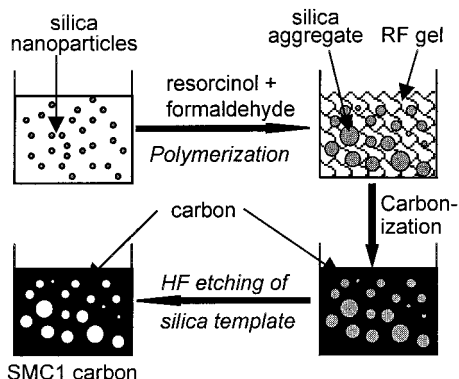


Figure 1. Schematics for the synthesis of nanoporous SMC1 carbons: (1) polymerization of resorcinol and formaldehyde (RF) in the presence of silica nanoparticles; (2) carbonization of RF gel-silica composite at 850 °C to get a carbon-silica composite; (3) HF etching of silica aggregates to get nanoporous SMC1 carbons.

various carbons with close-packed ~100 nm pores using synthetic opal templates.¹³

Recently, we have developed a new synthetic method to produce nanoporous carbons with high mesopore volumes using commercial silica sol particles as templates.^{14,15} In this report, we would like to present the detailed characterization of these nanoporous carbons and their application to the adsorption of bulky dyes.

Experimental Section

Preparation of Porous Carbons. The overall synthetic scheme is shown in Figure 1. The aqueous colloidal silica sol solution, Ludox HS-40 (40 wt % silica in water, average particle size ~12 nm) was purchased from the Aldrich Chemicals Co. Resorcinol (99%, ACS reagent) and formaldehyde (37 wt % aqueous solution, ACS reagent) were polymerized in the presence of silica sol particles to generate silica-RF gel composites. Carbonization followed by HF etching of the composites produced porous carbons. In a typical synthesis, a 1:2 mixture of resorcinol and formaldehyde was added to the Ludox HS-40 silica sol solution. The reaction mixture after adjusting the initial pH was aged at 85 °C for 1 week to get a composite of silica and resorcinol-formaldehyde gel (RF gel). To evaporate off residual water, the resulting silica-RF gel composites were heated at 85 °C for 2 days in open air. For carbonization, the composite was heated under nitrogen atmosphere from room temperature to 850 °C with a heating rate of 5 °C/min and was held at that temperature for 3 h. The resulting silica-carbon composite was stirred in a 48 wt % aqueous HF solution (J. T. Baker) for 12 h. The carbon materials were retrieved by filtration and were washed exhaustively with deionized water until the pH of the filtrate reached 7. The carbon materials produced were designated as SMC1 (silica-sol-mediated synthesized carbon one).

Characterization of Carbons. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2000 system. Surface areas and pore volumes were determined using the BET equation and the BJH (Barrett, Joyner, and Halenda) method. The pore size distribution curve was obtained from the analysis of the adsorption branch of the nitrogen isotherm using the BJH method.¹⁶ S_{BET} is the surface area calculated by the BET method. S_{BJH} is the cumulative adsorption surface area in the pore ranges of 1.7–300 nm calculated by the BJH method. V_{TOTAL} is the single point total pore volume of pores <~150 nm. V_{BJH} is the cumulative adsorption pore volume in the pore ranges of 1.7–300 nm calculated by the BJH method. Mesoporosities were calculated from the ratio of S_{BJH} to S_{BET} . D_{BET} is the average pore diameter calculated from the equation $4V_{\text{TOTAL}}/S_{\text{BET}}$.

Scanning electron micrographs have been obtained on a JEOL JSM 840-A microscope. Thermal analysis was performed under both nitrogen and oxygen atmospheres with a heating rate of 10 °C/min using a Perkin-Elmer TGA7 thermal analyzer.

Dye Adsorption Experiments. Acid green 20 dye (molecular weight of 586.5, $\lambda_{\text{max}} = 604$ nm) and Direct blue 78 dye (molecular weight of 959.9, $\lambda_{\text{max}} = 604$ nm) were purchased from Clariant Chemicals Co. Acid blue 45 (molecular weight of 474.3, $\lambda_{\text{max}} = 595$ nm) and Acid violet 17 (molecular weight of 761.9, $\lambda_{\text{max}} = 545$ nm) were purchased from Aldrich Chemicals Co. The commercial activated carbons were purchased from Junsei Chemicals Co, Calgon Carbon Corp., and Norit Corp. The dimensions of dyes were estimated by the energy minimization method using the Sybyl force field.

For the dye adsorption experiments, 10 mg of carbon was added into 10 mL of the aqueous dye stock solution and the resulting mixtures were stirred at room temperature. The stirring time was taken long enough to reach adsorption equilibrium (either 3 or 4 h, the time dependence of the Direct blue 78 dye adsorption is supplied in the Supporting Information). The mixture was centrifuged (3800 rpm) to remove treated carbon samples. The upper clear portion of the solution was taken for the UV/vis spectroscopic measurement (Beckman DU-65 spectrophotometer).

Results and Discussion

Synthesis of Carbons under Various Initial pH Values. Nanoporous SMC1 carbons were synthesized under various initial solution pH's. The reaction composition was fixed at 1:2:7.5:86 = resorcinol:formaldehyde:SiO₂:H₂O (molar ratio). The pH of the Ludox HS-40 silica sol solution was 9. The addition of resorcinol decreased the pH of the solution to 8. Additional adjustment of the solution pH was performed by adding either 1 N NaOH or 1 N HNO₃ aqueous solution. The plot of the surface areas and total pore volumes of carbons versus the initial reaction pH is shown in Figure 2. Carbons prepared in acidic media exhibited very low surface area. For example, the BET surface area of carbon prepared at pH 4.3 was 125 m²/g. It is well known that the silica sol stability decreases significantly in the acidic medium and extensive aggregation occurs as a result.¹⁷ These aggregated silica particles might not act as effective templates for the carbon synthesis. Carbons produced in neutral or weakly basic media were mesoporous with very high pore volume and high surface area. The best result was obtained for the carbon prepared in pH 8, producing the highest pore

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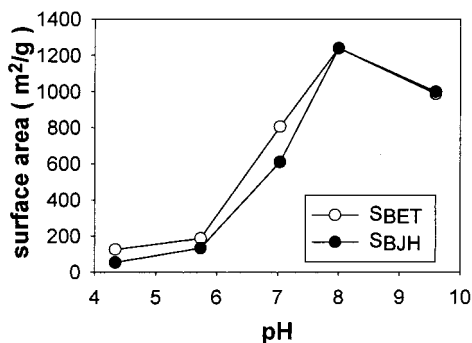
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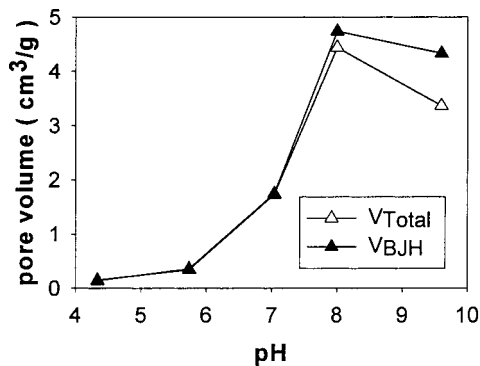
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(a)



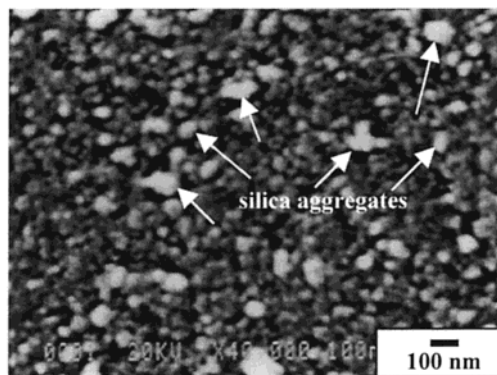
(b)

Figure 2. Plots of (a) surface areas and (b) pore volumes of SMC1 carbons synthesized at the various initial pH's of the reaction mixture. The reaction composition was fixed as 1:2:7.5:86 resorcinol:formaldehyde:SiO₂:H₂O.

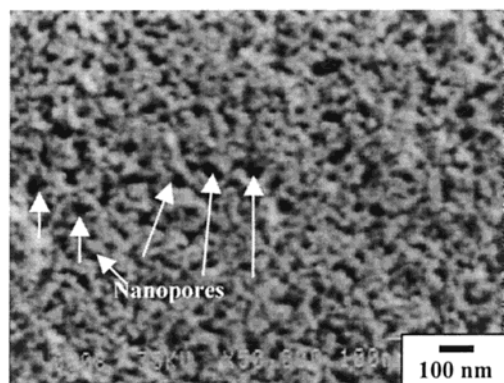
volume. The nearly identical BET and BJH surface areas of the carbon produced at that pH showed that the carbon was meso- and macroporous. The surface area and pore volume of carbon prepared at pH 9.6 decreased because of the partial dissolution of silica particles.

Lin and Ritter studied the effect of the pH on the structure of carbon xerogels produced from the resorcinol-formaldehyde (RF) gel.¹⁸ They reported that a nearly nonporous material was obtained at the initial pH > 7. The surface areas of carbons prepared at pH 7.0–5.7 were kept constant, and the carbons were predominantly microporous. Our results are, at first, seemingly contradictory to their report. On the contrary, our data confirms the true templating role of silica particles. When silica particles were removed from the RF-silica composite prior to carbonization, nearly nonporous carbon with low surface area was obtained. The carbon xerogel derived from the sol-gel polymerization of resorcinol-formaldehyde (RF) at pH 8 without silica templates was nearly nonporous, which is consistent with the results by Lin and Ritter.¹⁸ These results clearly demonstrate the templating role of silica particles.

Considering the average silica particle size of ~12 nm,¹⁹ a single silica particle is not responsible for the



(a)



(b)

Figure 3. Scanning electron micrographs (SEM) of (a) SMC1-7.5-carbon/SiO₂ composite and (b) SMC1-7.5 carbon. The micrographs have been obtained on a JEOL JSM 840-A electron microscope.

Table 1. Pore Characteristics of the SMC1 Carbons Prepared with Various SiO₂/Resorcinol Molar Ratios and the Commercial Activated Carbons

sample name ^a	S _{BET} (m ² /g) ^b	S _{BJH} (m ² /g) ^c	V _{Total} (cm ³ /g) ^d	V _{BJH} (cm ³ /g) ^e	meso-porosity ^f	D _{BET} (nm) ^g
SMC1-1.5	653	487	1.21	1.18	0.75	7.4
SMC1-4.5	1228	949	1.57	1.63	0.77	5.1
SMC1-7.5	950	910	5.46	4.82	0.96	23
SMC1-10.5	982	957	2.61	4.12	0.97	10.6
SMC1-15	737	713	1.49	1.95	0.97	8.1
Junsei	1275	204	0.66	0.18	0.16	2.1
Norit-HDH	465	215	0.43	0.33	0.46	2.8
Calgon	744	260	0.51	0.29	0.35	2.0

^a Sample name: SMC1-X (X = SiO₂/resorcinol/SiO₂ molar ratio). ^b S_{BET} is the surface area calculated by the BET method. ^c S_{BJH} is the cumulative adsorption surface area (pores 1.7–300 nm) calculated by the BJH method. ^d V_{TOTAL} is the single point total pore volume (pores < 150 nm). ^e V_{BJH} is the cumulative adsorption pore volume calculated by the BJH method (pores, 1.7–300 nm). ^f Mesoporosity is defined as the ratio S_{BJH}/S_{BET}. ^g Average pore size (D_{BET}) is calculated by the equation 4V_{TOTAL}/S_{BET}.

formation of mesopores; instead the silica aggregates act as templates. The aggregates of silica particles were observed in the scanning electron micrograph (SEM) of carbon-silica composites (Figure 3a). The SEM of SMC1-7.5 carbon (Figure 3b) showed pores ranging 10–100 nm.

Synthesis of Nanoporous Carbons in Various Precursor-to-Silica Ratios. To find out the optimum reaction conditions, we have synthesized SMC1 carbons

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Table 2. Adsorption of Dyes on Carbons (mg/g)^a

dyes	carbons							
	SMC1-1.5	SMC1-4.5	SMC1-7.5	SMC1-10.5	SMC1-15	Norit-HDH	Junsei	Calgon
Acid blue 45 ^b	134	376	358	369	231	176	213	219
Acid green 20 ^c	312	604	991	639	321	116	221	223
Acid violet 17 ^d	82	724	748	738	514	126	33	82
Direct blue 78 ^e	116	661	880	878	506	69	30	85

^a The adsorption capacities have been obtained after stirring a mixture containing 10 mg of carbon in 10 mL of aqueous stock solution.

^b Initial dye concentration: 9.9×10^{-4} M with 3 h of stirring. ^c Initial dye concentration: 4.0×10^{-3} M with 4 h of stirring. ^d Initial dye concentration: 1.0×10^{-3} M with 3 h of stirring. ^e Initial dye concentration: 9.8×10^{-4} M with 3 h of stirring.

by varying the SiO₂/resorcinol ratio. In the synthesis, the molar ratio of resorcinol to formaldehyde was fixed at 1:2 and the initial pH of the reaction mixture was kept at 8. The precursor-to-silica ratios were varied by increasing the amount of silica sol at a fixed amount of precursors.

The sample codes are designated as SMC1-*X*, where SMC1 stand for silica-sol-mediated synthesized carbon and *X* is the molar SiO₂/resorcinol ratio of the starting reaction mixture.

The carbon content of SMC1 carbons was over 91 wt %. The molar carbon to hydrogen (C/H) ratios of SMC-1 carbons were 4.6–8.2. Thermogravimetric analysis (TGA) conducted at the temperature range of 30–1000 °C under an oxygen atmosphere of the SMC1-5 carbon exhibited 2.6 wt % residue. These results demonstrate that most of the silica template was successfully removed by HF etching. The carbonization yield of SMC1-7.5 carbon calculated from the ratio of the amount of carbon to the amount of RF gel-SiO₂ composite was found to be around 15 wt %. Obviously, the carbonization yield is strongly dependent on the ratio of SiO₂/precursor.

Table 1 shows the pore characteristics of SMC1 carbons produced at various silica/precursor molar ratios. With increasing silica sol contents, the resulting carbons exhibited higher surface area and pore volume. The excessive addition of silica sol, however, reduced the surface area and pore volume of the carbons. The mesoporosities of SMC1 carbons, calculated from the ratio of *S*_{BJH} to *S*_{BET}, turned out to be higher than 0.7, demonstrating that they are predominantly mesoporous. The highest total pore volume and mesopore volume was obtained with SMC1-7.5 carbon. The total pore volume of the carbon was as high as 5.46 cm³/g, and the BJH pore volume was also very high (4.82 cm³/g). The nearly identical BET and BJH surface areas of the SMC1 carbons prepared at the high SiO₂/resorcinol molar ratio demonstrated the predominant meso- and macroporous character of the carbon.

The relatively lower BJH surface area (pores in the range of 1.7–300 nm) compared to the BET surface area of the carbons prepared from the lower amount of silica revealed that they possess some micropore fractions. The formation of these micropores resulted from the carbonization of the RF gel itself and was not related to the silica template.

The N₂ adsorption-desorption isotherms and the corresponding pore size distributions of SMC1 carbons prepared with various precursor-to-template ratios are shown in Figure 4. The hysteresis at the high pressure of N₂ adsorption-desorption isotherms of all these carbons strongly suggests the presence of mesopores. The pore size distribution of SMC1-1.5 was quite narrow with a mean pore dimension of 14 nm, which is

similar to the dimension of the isolated Ludox HS-40 silica nanoparticle (12 nm). The result demonstrated that isolated silica particles act as templates in the synthesis. As we described in the previous report, when the surfactant stabilized Ludox silica sol particles have been utilized as templates for the carbon synthesis, nearly uniform mesoporous carbons with pore dimensions similar to the corresponding silica sol particles sizes were prepared.¹⁵ The pore size distributions of SMC1-7.5 and SMC1-10.5 carbons, on the other hand, were very broad, demonstrating that the silica particles are agglomerated.

Dye Adsorption Studies for SMC1 Carbons.

Porous carbons have been extensively applied as adsorbents for the treatment of drinking and waste water. The most commonly applied carbons are activated carbons with high surface areas, and they are mostly microporous. They have been extensively applied as adsorbents for the removal of water pollutants such as trihalomethanes in drinking water. For the adsorption of bulky pollutants such as dyes and humic substances, mesoporous carbons with high pore volumes are more desirable. As mentioned in the Introduction, Yasuda and co-workers synthesized new mesoporous carbons from the steam invigoration of carbon precursors impregnated with organo-rare-earth metal complexes and these mesoporous carbons exhibited moderate adsorption capacities for bulky dyes.^{6,7} In the best case, the adsorption capacity of their mesoporous carbon for a bulky dye was 3 times higher than that of commercial activated carbon. For a small size dye, the adsorption capacity of the mesoporous carbon was even smaller than that of commercial activated carbons.

As shown in the previous section, some of the SMC1 carbons are predominantly mesoporous and exhibited extremely high mesopore volumes along with quite high surface areas. These SMC1 carbons can be excellent adsorbents for bulky organic materials, and we have conducted adsorption experiments on SMC1 carbons for dyes of various sizes. For comparison, the adsorption test were conducted for the commercial activated carbons (Junsei, Norit, and Calgon) that are frequently applied as adsorbents for water treatment. The pore characteristics of these commercial activated carbons are shown in Table 1.²⁰ We have chosen four dyes with different sizes. The adsorption capacities of the SMC1 carbons and commercial activated carbons for four dyes

(20) To check the effect of HF treatment, the three commercial carbons were stirred in a 48 wt % aqueous HF solution for 12 h under conditions similar to those for the synthesis of SMC1 carbons. The pore characteristics and adsorption capacities of these carbons changed after the HF treatment. The adsorption capacities of the HF-treated commercial carbons, however, are still much lower than those of SMC1 carbons. The detailed results are supplied in the Supporting Information.

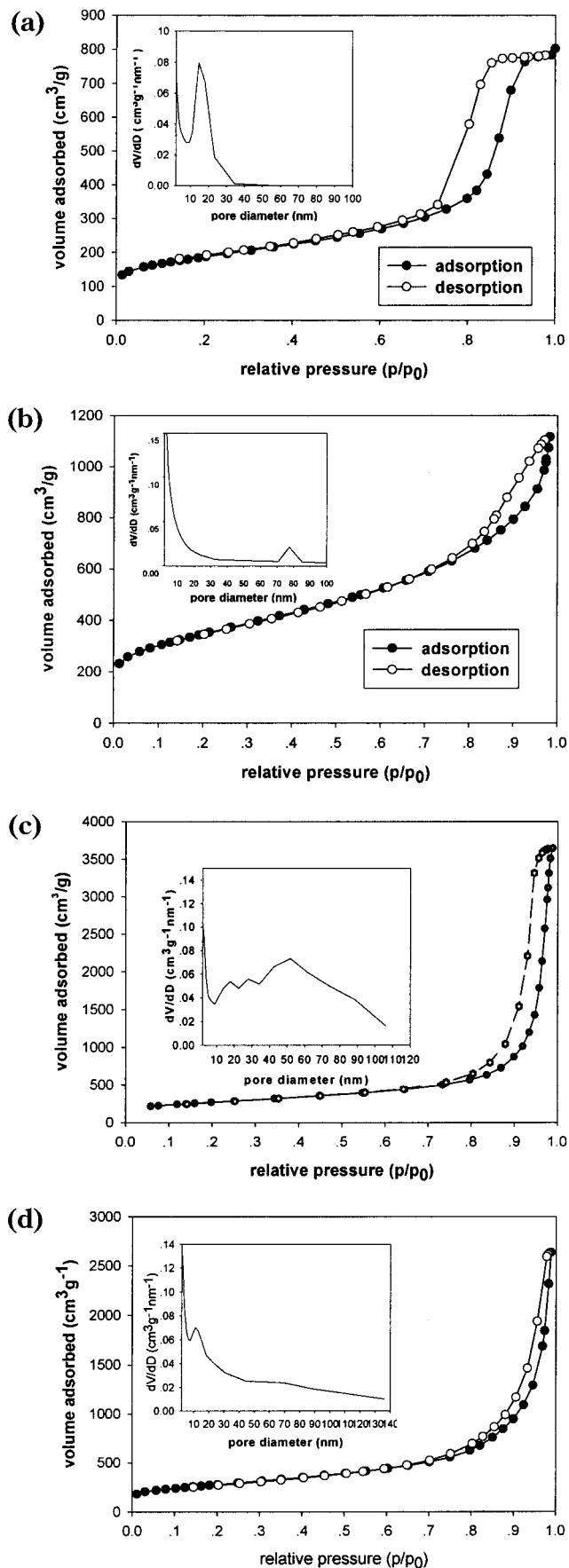


Figure 4. N_2 adsorption-desorption isotherms and the corresponding pore size distribution calculated from the adsorption branch of the nitrogen isotherm by the BJH method of (a) SMC1-1.5, (b) SMC1-4.5, (c) SMC1-7.5, and (d) SMC1-10.5 carbons.

are summarized in Table 2.²⁰ The adsorption capacities of the carbons were strongly dependent on the size of the dyes. For the adsorption of small size Acid blue 45 dye [molecular dimension: 3.8 Å (radius) \times 13 Å (length)], the SMC1 carbons and commercial activated carbon showed similar adsorption capacities. The results showed that the small-sized dye can penetrate and adsorb easily onto both micropores and mesopores.

For the adsorption of the slightly bigger-sized Acid green 20 dye [molecular dimension: 12 Å (radius) \times 19 Å (length)], the predominantly mesoporous SMC1-4.5 and SMC1-10.5 carbons exhibited about 3 times higher adsorption capacities compared to the commercial activated carbon. The best result was obtained with SMC1-7.5, exhibiting 4.5 times higher capacity than that of the Calgon carbon. When Acid violet 17 [molecular dimension: 8 Å (radius) \times 21 Å (length)] was tested for the adsorption, the adsorption capacities of SMC1-7.5 carbon were 6 times higher than that of the best commercial carbon (Norit-HDH). The biggest difference in the dye adsorption capacity of carbons have been obtained with the adsorption experiment for the largest sized Direct blue 78 [molecular dimension: 15 Å (radius) \times 28 Å (length)]. The adsorption capacity of SMC1-7.5 was found to over 10 times higher than that of the best commercial carbon (Calgon).

These results clearly demonstrate the superior adsorptive behavior of predominantly mesoporous SMC1 carbons. The bulky dyes can be effectively adsorbed on large mesopores, whereas they cannot penetrate into micropores. Most of the surface of the mesoporous SMC1 carbons can be effectively utilized as the adsorption sites for bulky dyes.

Summary and Conclusions

Silica-RF gel composites were generated from the sol-gel polymerization of resorcinol and formaldehyde in the presence of silica sol aggregates. The composite was carbonized and etched with HF solution to produce high surface area nanoporous carbons (SMC1) with high mesopore volumes of >4 cm^3/g . The optimum initial pH for the reaction mixture turned out to be around 8. The SMC1 carbon synthesized with the precursor to silica template molar ratio of 1:7.5 exhibited the highest total pore volume (5.5 cm^3/g) and mesopore volume (4.8 cm^3/g).

These SMC1 nanoporous carbons exhibited extremely high adsorption capacities for dyes. For example, the adsorption capacities of the SMC1-7.5 carbon for a bulky Direct blue 78 dye was over 10 times higher than that of the commercial activated carbon. The adsorption capacities of SMC1 carbons for a small size dye are comparable to that of the commercial activated carbon.

Acknowledgment. We thank the Korea Research Foundation through the Brain-Korea 21 project and the Korea Science and Engineering Foundation (Basic Research Program No. 98-05-02-03-01-3) for the financial support.

Supporting Information Available: Tables providing a comparison of the pore characteristics and adsorption capacities (mg/g) of the commercial carbons before and after HF treatment and a plot of the time dependence of the Direct blue 78 adsorption on various carbons. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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