Incorporation of Cyclodextrin into Mesostructured Silica

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The incorporation of cyclodextrin (CD) groups inside mesoporous silica frameworks was attempted using two methods: by the grafting of the CD groups into the channels of preformed mesoporous silica hosts and by the direct synthesis of CD-containing mesoporous materials by a one-step process. While the grafting procedure failed to incorporate CD groups inside the pore channels of mesoporous silica substrates, the direct synthesis approach yielded materials whose physical and chemical characteristics (as determined by X-ray diffraction, N_2 sorptometry, transmission electron microscopy, and elemental analysis) were indicative of the presence of CD groups inside the pore channels of the materials. The CD-containing mesoporous materials, denoted as CD-HMS, were prepared by the co-condensation of tetraethoxysilane and a silylated derivative of β-cyclodextrin in the presence of a structure-directing dodecylamine surfactant solution. Materials with CD group loadings up to 0.39 mmol g^{-1} and uniform pore channels with diameters in the range of 38−42 Å were prepared by this method. Preliminary adsorption experiments using aqueous *p*-nitrophenol solutions showed that the CD-HMS materials were promising for the removal of organic compounds from water.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six or more linked D-glucopyranose units. Because of their toroidal shape, these macromolecules contain geometrically well-defined angstrom-scale cavities which are known to form inclusion compounds with organic molecules of suitable geometry and function.[1−17] A potentially important application for cyclodextrins is the removal of toxic organic contaminants in water.[4−7] Moreover, the chiral nature of the cavity in these molecules makes them promising candidates for enantiomeric separation applications.[14] However, the utility of these molecules for any of these goals is curtailed by the high solubility of cyclodextrins in aqueous media. Hence, the conversion of CDs into an insoluble material form is required to make possible their use in practical applications such as environmental remediation and chiral chromatography. Toward this goal, researchers have, in recent years, exploited two principal methods of producing CD-functionalized materials. The first of these involved the cross-linking of CDs into polymers using C−OH linkers such as epichlorohydrin and diisocyanato compounds.[1−7] The second approach utilizes the coating or grafting of CD moieties onto a stationary phase such as organic polymers[8,9] or silica gel.[10−17]

Although CD-containing polymers have proven to be useful for the separation of organic pollutants from water,[4,5] these materials often have somewhat of a low binding affinity with organic molecules.[2] A notable exception to this is the recently reported preparation of a new “nanoporous” CD polymer (denoted β-CD-HDI)[6,7] which proved to be very effective in the removal of small organic molecules from water (binding constants for aromatic molecules on the order of 10^8−10^9 M^{-1}). Although this material can be considered “nanoporous” in the sense that it contains cavities resulting

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(1) Harada, A.; Li, J.; Kamachi, M. *Nature* **1993**, *364*, 516.

(2) Zhu, X. X.; Brizard, F.; Wen, C. C.; Brown. G. R. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 335.

(3) Crini, G.; Cosentino, C.; Bertini, S.; Naggi, A.; Torri, G.; Vecchi, C.; Janus, L.; Morcellet, M. *Carbohydr. Res.* **1998**, *308*, 37.

(4) Crini, G.; Bertini, S.; Torri, G.; Naggi, A.; Sforzini, D.; Vecchi, C.; Janus, L.; Lekchiri, Y.; Morcellet, M. *J. Appl. Polym. Sci.* **1998**, *68*, 1973.

(5) Crini, G.; Janus, L.; Morcellet, M.; Torri, G.; Naggi, A.; Bertini, S.; Vecchi, C. *J. Appl. Polym. Sci.* **1998**, *69*, 1419.

(6) Li, D.; Ma, M. *CHEMTECH* **1999**, *29*, 31.

(7) Ma, M.; Li, D. *Chem. Mater.* **1999**, *11*, 872.

(8) Zhao, X.-B.; He, B.-L. *React. Polym.* **1994**, *24*, 9.

(9) Sreenivasan, K. *J. Appl. Polym. Sci.* **1996**, *60*, 2245.

(10) Tanaka, M.; Yoshinaga, M.; Ito, M.; Ueda, H. *Anal. Sci.* **1995**, *11*, 227.

(11) Ciucanu, I.; König, W. A. *J. Chromatogr., A* **1994**, *685*, 166.

(12) Ciucanu, I. *J. Chromatogr., A* **1996**, *727*, 195.

(13) Crini, G.; Morcellet, M.; Torri, G. *J. Chromatogr. Sci.* **1996**, *34*, 477.

(14) Sébille, B.; Guillaume, M.; Vidal-Madjar, C.; Thuaud, N. *Chromatographia* **1997**, *45*, 383.

(15) Zhang, L.; Wong, Y.; Chen, L.; Ching, C. B.; Ng, S. *Tetrahedron Lett.* **1999**, *40*, 1815.

(16) Phan, T. N. T.; Bacquet, M.; Laureyns, J.; Morcellet, M. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5189.

(17) Crini, G.; Y. Lekchiri; L. Janus; Morcellet, M.; Morin, N. *Chromatographia* **1999**, *50*, 661.

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from the CD molecules, the polymer had a very low surface area (1.7−1.9 m^2 g^{-1})[6] and is thus completely lacking in *framework* nanoporosity. Thus, β-CD-HDI consists of a highly tortuous matrix of tightly packed organic polymer chains through which guest molecules must awkwardly (slowly) diffuse to reach the binding receptor sites. The incomplete loading levels observed for some of the studied organic guest molecules (i.e., toluene = 56−60%) may be related to their inability to access many of the binding sites.

Although processable polymer-based adsorbents such as β-CD-HDI are well-suited for the development of membrane-based treatment technologies, the potentially slow uptake kinetics of these polymers may make these materials incompatible in fixed or fluidized bed treatment systems, in which effluent flow rates can be very high. Moreover, another problem which must be addressed is the susceptibility of organic polymers to biological fouling,[18] an effect which is likely to be especially deleterious for polymers composed of oligosaccharides (i.e., sugars)!

In this work, we demonstrate the preparation of a new class of CD-containing materials possessing uniform *framework* nanoporosity. Our synthetic approach utilizes the concept of surfactant-directed mesostructured oxide assembly to produce hybrid CD−silica composite materials with well-defined nanometer-scale porosity. Because of their large and uniform framework mesoporosity, the new materials will have the potential benefit of having improved access of guest molecules to the binding sites. Furthermore, the location of CD moieties *within* the structure of a siliceous framework may reduce the materials' susceptibility to biological degradation.

The surfactant-directed assembly of mesostructured silica is now a well-established area in the synthesis of inorganic materials.[19−28] Thus, nanoporous silica with uniform framework pore channels, with diameters typically in the range of 1−10 nm, can be prepared using a variety of surfactants, including quaternary alkylammonium ions (forming materials denoted as M41S),[19,20] neutral amines (forming HMS silica),[24−26] and nonionic surfactants (forming MSU-X silica).[27,28] The synthesis of these materials involves the assembly and cross-linking of molecular silica precursors (typically silicate oligomers[19−23] or silicon alkoxides[24−28]) at the interface of aqueous surfactant micelles. The subsequent removal of the surfactant from the resulting mesophases (by calcination or extraction) results in nanoporous materials with pore channels whose dimensions and structures mirror those of the assembly micelles.

Functional derivatives of mesostructured silicas such as MCM-41 and HMS can be formed using a variety of guest inclusion techniques.[29] One of the most common inclusion methods is the *grafting* or *anchoring* of guests onto the Si−OH groups lining the pore channel surface of a preformed mesostructure, typically by condensation reaction with a hydrolyzable organosilane of the type $(RO)_3Si-R'$.[30−33] Another useful method of producing functional mesostructures is by the *direct incorporation* of hydrolyzable organosilane groups into the structure.[34−41] This technique involves the addition of organosilane into the assembly mixture (including surfactant and the silica precursor) and forms a functional mesostructure in a single step of formation.

In this research, we report attempts at preparing CD-functionalized nanoporous silicas by grafting CD moieties into the pore channels of surfactant-assembled mesoporous silica. Also, we investigate a direct incorporation strategy for the inclusion of the macromolecular guests into mesoporous structures. Finally, the effectiveness of promising materials resulting from these synthetic approaches for the adsorption of aromatic molecules will be discussed.

Experimental Section

Materials. All chemicals were purchased from Aldrich, with the exception of monochlorotriazinyl β-cyclodextrin (MCT-β-CD) which was supplied by Wacker Biochemie. The structure of MCT-β-CD consists of β-cyclodextrin to which electrophilic chlorotriazinyl groups (MCT, $-OC_3N_3ClO^-Na^+$) have been attached (with an average of 2.8 MCT groups per β-CD molecule) (Scheme 1). The chemical formula of MCT-β-CD can therefore be expressed as $C_{42}O_{35}H_{53.2}(ClC_3N_3O^-Na^+)_{2.8}$.

Mesostructured silicas, with uniform pore channels of diameters ranging from 4 to 5 nm (hereafter denoted MSU silica), were prepared following previously published procedures.[27,28,36] Likewise, thiol-functionalized mesostructured silicas (hereafter denoted as MSU-SH), with similar pore channel sizes to the MSU silica, were also prepared following reported techniques.[36,41]

Grafting of CD Groups to Mesostructures. The synthesis of CD-incorporated mesostructures was attempted by

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[18] Sheikholeslami, R. *Environ. Prog.* **1999**, *18*, 113.

[19] Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

[20] Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

[21] Monnier, A.; Schuth, F.; Huo, Q.; Kumar, D.; Margolese, D.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.

[22] Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schuth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

[23] Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schuth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176.

[24] Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.

[25] Tanev, P. T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 2068.

[26] Zhang, W.; Pauly, T. R.; Pinnavaia, T. J. *Chem. Mater.* **1997**, *9*, 2491.

[27] Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.

[28] Prouzet, E.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 516.

[29] Moller, K.; Bein, T. *Chem. Mater.* **1998**, *10*, 2950.

[30] Brunel, D.; Cauvel, A.; Fajula, F.; DiRenzo, F. *Stud. Surf. Sci. Catal.* **1995**, *97*, 173.

[31] Cauvel, A.; Brunel, D.; Renzo, F. D.; Fajula, F. *AIP Conf. Proc.* 1996, *354*, 477.

[32] Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* (*Weinheim, Ger.*) **1997**, *9*, 500.

[33] Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923.

[34] Burkett, S. L.; Sims, S. D.; Mann, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1367.

[35] Macquarrie, D. J. *J. Chem. Soc., Chem. Commun.* **1996**, 1961.

[36] Richer, R.; Mercier, L. *J. Chem. Soc., Chem. Commun.* **1998**, 1775.

[37] Lim, M. H.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1998**, *10*, 467.

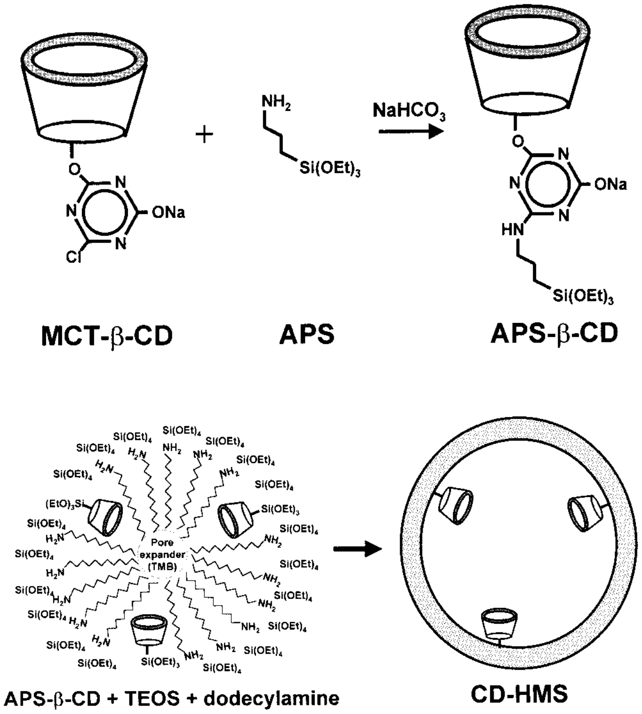
[38] Corriu, R. J. P.; Mehdi, A.; Reyé, C. *C. R. Acad. Sci.* **1999**, *2*, 35.

[39] Bossaert, W. D.; De Vos, D. E.; Van Rhijn, W. M.; Bullen, J.; Grobet, P. J.; Jacobs, P. A. *J. Catal.* **1999**, *182*, 156.

[40] Mercier, L.; Pinnavaia, T. J. *Chem. Mater.* **2000**, *12*, 188.

[41] Richer, R.; Mercier, L. *Chem. Mater.* **2001**, *13*, 2999.

Scheme 1. Representation of CD-HMS Direct Synthesis Process, Depicting the Preparation of the Silylated CD Precursor (Top) and the Surfactant-Directed Assembly of the Final Product (Bottom)[a]



[a] Note that the figures are not shown to atomic scale.

promoting the nucleophilic attachment of MCT-β-CD to presynthesized MSU-SH. The general reaction can be described by the following equation

$$\text{MSU-SH} + \text{Cl-C}_3\text{N}_3\text{-}\beta\text{-CD} \rightarrow \text{MSU-S-C}_3\text{N}_3\text{-}\beta\text{-CD} + \text{HCl} \quad (1)$$

Thus, 20 mg of MSU-SH was stirred at room temperature in 3.4 g of water with 0.34 g of MCT-β-CD and 68 mg of $NaHCO_3$ for 3 days. The suspension was then filtered, washed with water, and air-dried. In another attempt to anchor the CD groups inside the mesoporous host, 100 mg of MSU-SH was refluxed in 5 mL of pyridine with 0.2 g of MCT-CD for 2 days. The material was then filtered, washed (pyridine, acetone, and followed by methanol), and air-dried. Both of these grafting techniques were performed on five different MSU-SH samples with pore diameters in the range of 4−5 nm.

The grafting of CD into the pore channels of the mesoporous silicas was also attempted using an amino-functionalized mesostructure. Thus, amino-functionalized MSU-SH was prepared by refluxing dried samples of MSU-SH with a copious amount of 3-aminopropyltriethoxysilane in anhydrous toluene for 48 h. The resulting product (hereafter denoted as MSU-NH_2) was filtered, washed with toluene and ethanol, and dried. MSU-NH_2 was then reacted with MCT-β-CD following the previously described protocols. The reaction of this process can be described by the following equation

$$\text{MSU-NH}_2 + \text{Cl-C}_3\text{N}_3\text{-}\beta\text{-CD} \rightarrow \text{MSU-NH-C}_3\text{N}_3\text{-}\beta\text{-CD} + \text{HCl} \quad (2)$$

Direct Synthesis of CD-Functionalized Mesostructures. In a typical synthesis, MCT-β-CD (X mmol, where X = 0, 0.61, 1.21, 1.81, or 2.42) and 3-aminopropyltriethoxysilane (APS) (2.8X mmol) were stirred in 10 mL of water for 30 min. This mixture was then added to a dodecylamine solution (6.7 mmol in 10 mL of ethanol and 90 mL of water) and stirred for 30 s, after which TEOS (30.3X mmol) was added. After the mixture was further stirred for 30 s, 1,3,5-trimethylbenzene (6.7 mmol) was added as a pore-expanding agent.[20,25,32] The mixture was then stirred for 24 h, and the resulting powder was filtered and washed by Soxhlet extraction over ethanol for 24 h. The materials thus obtained are hereafter labeled as CD-HMS-Z%, where Z reflects the molar percentage of APS-CD with respect to the total amount of Si present in the synthesis mixture (i.e., $Z = 100\ X/30.3$, or 0, 2, 4, 6, and 8, respectively).

Characterization of Materials. Transmission electron microscopy (TEM) was performed using a Philips CM 30 T electron microscope (National Centre for HREM, Delft, The Netherlands) with an LaB_6 filament as the source of electrons operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.

Powder X-ray diffraction patterns were measured on a Rigaku Rotaflex diffractometer equipped with a rotating anode using Cu Kα radiation (Ontario Geoscience Laboratories, Sudbury, Ontario, Canada).

FTIR spectra of the mesostructures were obtained from KBr pressed pellets (0.5% sample by weight) using a Perkin-Elmer Paragon 1000 FTIR spectrometer.

N_2 adsorption isotherms of the adsorbents were measured at −196 °C on a Micromeritics ASAP 2010 sorptometer. Prior to measurement, all samples were outgassed at 110 °C at 10^{-6} mmHg. BET surface areas were measured from the linear part of the BET plot ($0.05 < P/P_0 < 0.25$). Pore size distributions were calculated from the isotherm data using the Broekhoff−deBoer (BdB) method.[42] Mesopore volumes (V_{mp}) were assumed to be equal to the liquid volume of adsorbed nitrogen below $P/P_0 = 0.7$, while the textural pore volumes (V_{tp}) were assumed to be equal to the liquid volume of adsorbed nitrogen between $0.7 < P/P_0 < 1.0$.[43]

C, H, and N analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Adsorption of Aromatic Molecules by CD-HMS Materials. For each CD-HMS composition prepared, 5 mg samples were stirred with 25 mL of aqueous solutions of *p*-nitrophenol (pNP) for 5 h. The suspension was then centrifuged, and the residual pNP concentration in the supernatant was measured using UV−vis spectroscopy. The amount of pNP adsorbed by the CD-HMS was then determined by subtracting the pNP concentration in the supernatant from that of the untreated pNP solution. In this way, the treatment of a dilute solution of pNP (130 ppb) and a more concentrated one (29.5 ppm) with the CD-HMS adsorbents was investigated.

Results and Discussion

CD Grafting in Mesostructures. For the pure MCT-β-CD, the FTIR spectrum exhibited sharp IR bands at 1297, 1358, 1409, 1471, and 1573 cm^{-1}. Since the bands observed in the FTIR spectra of the parent thiol- or amino-functionalized mesostructures used for the grafting reactions did not overlap with the characteristic bands of MCT-β-CD, the presence or absence of bands in this region of the spectrum was used to determine whether successful inclusion of the CD moieties within the mesostructures occurred. Despite all the attempts at grafting the MCT-β-CD groups inside the mesostructures, none of the characteristic IR bands of these groups could be observed in any of the resulting

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(42) Broekhoff, J. C. P.; de Boer, J. H. *J. Catal.* **1968**, *10*, 377.

(43) Prouzet, E.; Cot, F.; Nabias, G.; Larbot, A.; Kooyman, P.; Pinnavaia, T. J. *Chem. Mater.* **1999**, *11*, 1498.

Table 1. A Comparison of the Theoretical and Experimental Compositions of CD-HMS Materials

	theoretical composition			experimental composition			
material	%C	%N	CD content (mmol g^{-1})	%C	%N	CD content based on N assay (mmol g^{-1})	CD content based on C assay (mmol g^{-1})
HMS	0	0	0	0.59	n.d.		
CD-HMS-2%	15.0	3.34	0.21	10.0	2.52	0.16	0.14
CD-HMS-4%	22.1	4.91	0.31	22.6	5.34	0.34	0.32
CD-HMS-6%	26.3	5.85	0.37	23.6	5.61	0.35	0.33
CD-HMS-8%	29.0	6.44	0.41	27.8	6.74	0.43	0.39

materials. Moreover, the N_2 adsorption isotherms for the grafted materials were identical to those of the parent thiol- or amino-functionalized mesostructures. It was thus concluded that the grafting methods did not succeed in incorporating CD moieties into the mesoporous structures. Although the diameter of the pore channels of the inorganic hosts (4−5 nm) should have been sufficiently large to accommodate the CD moieties (dimensions 15.3 × 7.8 Å), these were nonetheless unable to react with the anchoring sites (-SH or -NH_2) inside the mesostructure pore channels. It can be postulated that the large and bulky CD groups graft at the openings of the pore channels, thus preventing further penetration of CD moieties deeper within the pore channels where the majority of the anchoring sites are located.

Recently, the grafting of CD moieties onto a mesoporous silica gel was investigated.[16] The silica gel used in the study possessed a bimodal distribution of mesopores, centered at about 50 and 65 Å, respectively. While the authors of this research found that the grafting process reduced the size of the larger diameter pore channels (>60 Å) of the silica gel, the volume of the 50 Å pores remained largely unaffected by the grafting process.[16] This suggested that the smaller mesopores (<60 Å) were not accessible for grafting with large moieties such as CDs. Moreover, the surface areas of the CD-grafted silica gels (231−241 $m^2\ g^{-1}$) were only slightly smaller than that of the parent support (270 $m^2\ g^{-1}$).[16] Thus, it can be inferred that the CD groups were grafted only to the external surface area of the silica gel particles and the walls of the larger pores (>60 Å) of the silica gels but not inside the more restrictive pore channels with diameters <60 Å. The absence of CD group inclusion into the 40−50 Å pore channels of the mesostructured silica studied in the present work thus concurs with the results obtained by other researchers.

Direct Incorporation of CD into Mesostructures: Chemical Composition of CD-HMS Materials. Unlike the failed inclusion attempts using the grafting methods, the CD-incorporated mesostructures prepared by the direct synthesis method (CD-HMS) all featured the characteristic FTIR bands of the MCT-β-CD groups, qualitatively denoting the successful inclusion of these groups into the silica frameworks. The presence of significant amounts of C and N inside these materials (as measured by elemental analysis, Table 1) further demonstrated the successful inclusion of CD groups. A comparison of the theoretical elemental compositions of the CD-HMS materials with those obtained by elemental analysis is shown in Table 1. Following the reaction process described by eqs 3 and 4 below and depicted in Scheme 1, it was assumed that the nucleophilic attachment of APS to MCT-β-CD was complete (eq 3) and that the subsequent cross-linking of TEOS and APS-β-CD produced the hybrid material in 100% yield (eq 4).

$$2.8\ \underset{\underline{\mathbf{APS}}}{\mathrm{Si(OEt)_3C_3H_6NH_2}} + \underset{\underline{\mathbf{MCT\text{-}\beta\text{-}CD}}}{\mathrm{(ClC_3N_3O^-Na^+)_{2.8}\text{-}C_{42}O_{35}H_{53.2}}} \rightarrow$$

$$\underset{\underline{\mathbf{APS\text{-}\beta\text{-}CD}}}{\mathrm{(Si(OEt)_3C_3H_6NH\text{-}C_3N_3O^-Na^+)_{2.8}\text{-}C_{42}O_{35}H_{53.2}}} + 2.8\ \mathrm{HCl} \tag{3}$$

$$\mathrm{n}\ \underset{\underline{\mathbf{APS\text{-}\beta\text{-}CD}}}{\mathrm{(Si(OEt)_3C_3H_6NH\text{-}C_3N_3O^-Na^+)_{2.8}\text{-}C_{42}O_{35}H_{53.2}}} + (1\text{-}\mathrm{n})\ \underset{\underline{\mathbf{TEOS}}}{\mathrm{Si(OEt)_4}} \rightarrow$$

$$\mathrm{[(SiO_{1.5}C_3H_6NH\text{-}C_3N_3O^-Na^+)_{2.8}\text{-}C_{42}O_{35}H_{53.2}]_n[SiO_2]_{1\text{-}n}} + (4{+}4.4\mathrm{n})\ \mathrm{EtOH} \tag{4}$$

$$\underline{\mathbf{CD\text{-}HMS\text{-}\mathit{Z}\%}}\ (Z = 100\ \mathrm{n},\ \text{where n=0, 0.02, 0.04, 0.06 and 0.08})$$

Thus, the theoretical compositions of the CD-HMS materials were determined on the basis of the formula given in eq 4. Generally, the correlation between the experimental and the theoretical compositions was very good (Table 1), and the CD group loadings (expressed in mmol g^{-1}) calculated on the basis of the independent C and N measurements were very consistent with each other and were, generally, in close agreement with the expected theoretical values. The CD loadings calculated on the basis of N content, however, were all slightly higher than those determined based on C content. This minor discrepancy may be explained by the presence of a small amount of unreacted aminopropylsilane groups within the materials resulting from the slightly incomplete reaction of APS with MCT-β-CD (eq 3). Therefore, the CD group loadings in the materials that were determined on the basis of the C content in the materials can be considered a more accurate reflection of the true quantity of CD moieties incorporated within the CD-HMS materials.

Compared to CD-grafted silica gels, significantly higher CD group loadings can be achieved using the direct incorporation approach used in this research. Whereas CD-HMS materials have been prepared with CD group contents up to 0.39 mmol g^{-1} (Table 1), loadings of not more than 0.187 mmol g^{-1} [11,12] and usually well below 0.15 mmol g^{-1} [10,16] have been reported for CD-grafted silica gels.

Structural Characterization of CD-HMS Materials. SEM micrographs of the CD-HMS materials showed that the materials largely consisted of relatively large coarse particles with diameters typically in the 50−300 μm range (Figure 1). The CD-HMS-2% sample possessed a spongy macroporous morphology clearly visible by SEM (Figure 1a). Likewise, the TEM images of this material (Figure 2a) showed that CD-HMS-2% contained hollow macrovoids with diameters in the range of 200−400 nm. Although CD-HMS-4% was also found to contain a significant amount of similar macrovoids (Figure 1b), CD-HMS-6% and CD-HMS-8% appeared mostly devoid of these (parts c and d of Figures 1 and 2). Although CD-HMS-4% was also found to contain a

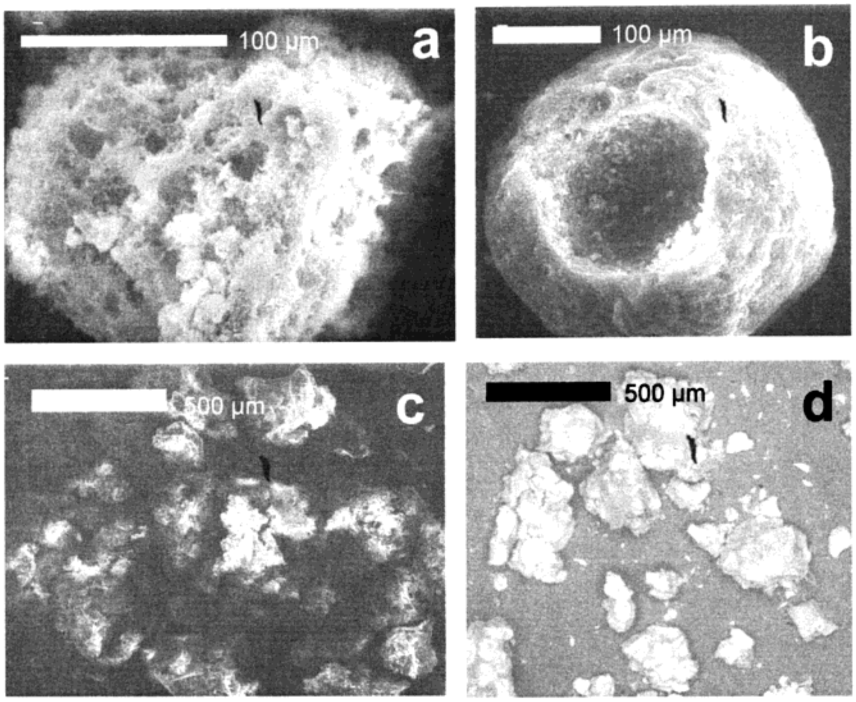

Figure 1. SEM images of representative samples of CD-incorporated mesoporous silicas: (a) CD-HMS-2%; (b) CD-HMS-4%; (c) CD-HMS-6%; (d) CD-HMS-8%.

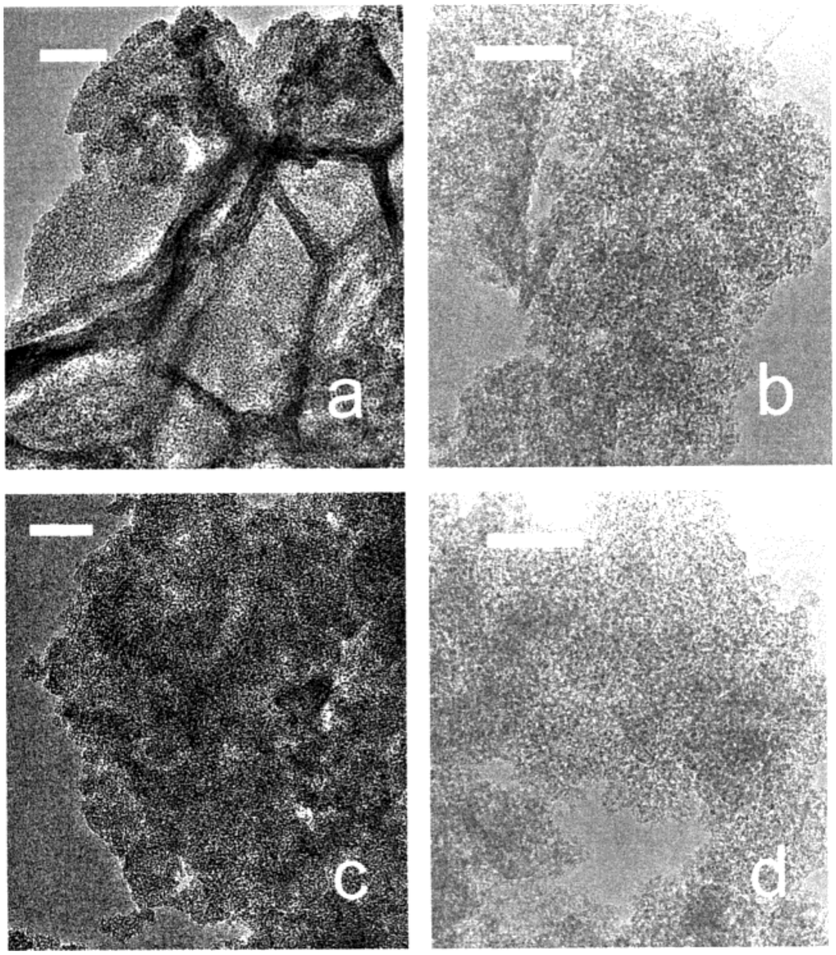

Figure 2. TEM images of representative samples of CD-incorporated mesoporous silicas: (a) CD-HMS-2%; (b) CD-HMS-4%; (c) CD-HMS-6%; (d) CD-HMS-8%. The scale bar in each image represents 100 nm.

significant amount of similar macrovoids, CD-HMS-6% and CD-HMS-8% appeared mostly devoid of these, as attested by the TEM images shown in Figure 2b. It can be speculated that the presence of small amounts of the CD moieties in the synthesis mixture may result in emulsion formation, producing materials with distinc-

Table 2. Physical and Surface Properties of CD-HMS Materials

material	d spacing (Å)	surface area ($m^2\ g^{-1}$)	mesopore volume, V_{mp} ($cm^3\ g^{-1}$)	textural pore volume, V_{tp} ($cm^3\ g^{-1}$)	mesopore diameter (Å)
HMS	43	1199	0.86	0.22	28
CD-HMS-2%	*a*	547	0.51	0.42	38
CD-HMS-4%	52	319	0.26	0.33	39
CD-HMS-6%	47	197	0.21	0.11	40
CD-HMS-8%	n.d.[b]	235	0.27	0.16	42

[a] Although a diffraction signal was evident for this material, the presence of an unusually high background signal prevented the accurate determination of its d spacing. [b] No XRD signal detected.

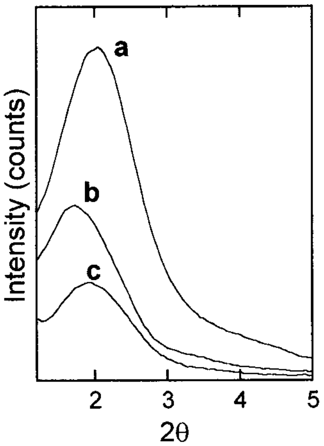

Figure 3. Powder X-ray diffraction patterns for (a) HMS silica, (b) CD-HMS-4%, and (c) CD-HMS-6%.

tive macrocellular morphologies. In contrast, when an excessive amount of CD is added to the surfactant solution (or if none is put in at all), no emulsion is formed and the mesostructures do not assemble into macroporous foamlike structures.

The TEM images of representative CD-HMS samples (Figure 2) were typical of those obtained for HMS and MSU-X mesostructures, featuring a random network of wormhole-motif pore structures.[24−27] Although little long range order can be observed in the images, the pore channels generally appear to be quite uniform in size. A close inspection of the images shows that the pore channels are approximately 3−4 nm in diameter and typical pore center-to-pore center distances are about 4−5 nm. An extensive TEM examination of the samples revealed that the wormhole-motif mesoporous phase predominated over any amorphous phases in the samples. The CD-HMS materials can thus be considered compositionally pure HMS-type mesostructured materials.

Table 2 displays the crystallographic and surface properties of the CD-HMS materials obtained from their XRD patterns (Figure 3) and N_2 isotherms (Figure 4), respectively. In accordance with the features observed in the TEM images, the single broad XRD signals obtained for the CD-HMS materials (Figure 3) are indicative of the wormhole-motif nature of alkylamine-assembled mesoporous frameworks,[24−26] which exhibit some degree of structural correlation because of the uniformity of the pore channel diameters. The lattice spacings measured from the XRD patterns (Table 2) ranged from 4.3 to 5.2 nm, which are values that are consistent with the pore center-to-pore center distances estimated from the TEM images (Figure 2).

In comparison with pristine HMS silica, however, the XRD reflections of the CD-HMS materials are shifted to lower diffraction angles (Figure 3), denoting an expansion of the framework d spacing upon CD inclusion (Table 2). The presence of the large CD groups in the assembly mixture thus appears to effectively act as a swelling agent toward the structure-directing micelles, resulting in materials with significantly higher lattice spacings than that of pristine HMS silica. The observed systematic decrease in XRD signal intensity upon increasing the CD group loading (Figure 3) can be attributed to contrast matching resulting from the presence of the organic groups inside the pore channels of the materials, a phenomenon which is commonly observed in mesostructure inclusion compounds.[32,40,41] No XRD reflection was observed for CD-HMS-8%, the material with the highest CD loading studied, possibly as a result of extreme contrast matching caused by the very high organic group loading in the pore channels.

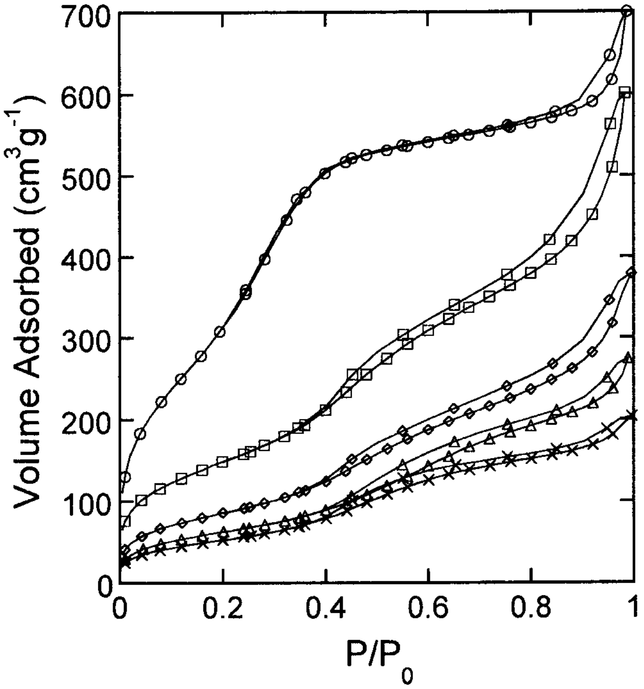

Figure 4. N_2 adsorption−desorption isotherms for pristine HMS silica (○), CD-HMS-2% (□), CD-HMS-4% (◇), CD-HMS-6% (×), and CD-HMS-8% (△).

Surface and Pore Characterization of CD-HMS Materials. The N_2 isotherm of pristine HMS silica (Figure 4) was typical of previously reported results,[24−26,40] featuring a type IV adsorption curve with an inflection at P/P_0 of about 0.3 (corresponding to a BdB pore diameter of 28 Å, Figure 5), and a second inflection at P/P_0 close to 1 which displayed hysteresis in the desorption branch of the isotherm. This latter feature is characteristic of textural porosity within the particles of the materials, a common feature of HMS

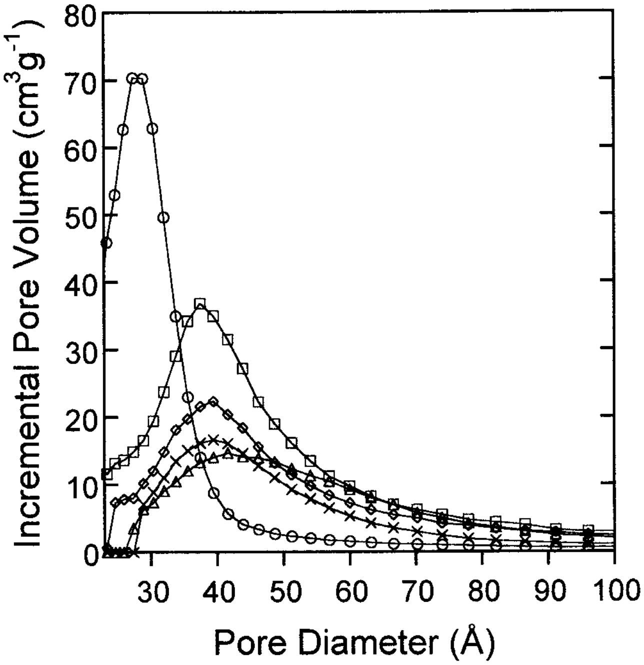

Figure 5. Pore size distributions for pristine HMS silica (○), CD-HMS-2% (□), CD-HMS-4% (◇), CD-HMS-6% (×), and CD-HMS-8% (△). The pore sizes were calculated from the N_2 adsorption isotherms using the Broekhoff–deBoer model.[42]

silicas.[24–26] From the isotherm data, a very high surface area (1199 m^2 g^{-1}) and pore volume (0.85 cm^3 g^{-1}) were determined, both being characteristic of HMS silica.[24–26] In contrast, the surface areas and pore volumes of the CD-HMS materials decreased as a function of CD loading (Table 2), denoting the presence of the large moieties within the pore channels of the materials. An anomaly in this trend exists for CD-HMS-8%; despite its higher CD loading, this material has a pore volume and surface area which are *larger* than those of CD-HMS-6%. CD-HMS-8% had a much broader pore size distribution than the others, centered at 42 Å but skewed toward larger pore diameters (Figure 5). This broadening in pore distribution denotes the severe structural perturbation of the framework caused by the inclusion of an excessive amount of CD moieties in the HMS framework, as evidenced by the absence of an XRD signal in this sample. Hence, the average pore size of CD-HMS-8% is somewhat greater than that of CD-HMS-6%, resulting in a slightly higher pore volume.

As previously mentioned, the presence of textural porosity is a common feature of HMS silica. CD-HMS-2%, however, possesses an unusually high degree of textural porosity (0.41 cm^3 g^{-1}, Table 2) compared to pristine HMS silica and the other CD-HMS materials (0.11–0.33 cm^3 g^{-1}, Table 2), as attested by this compound's highly sloping N_2 adsorption isotherm (Figure 4). This feature is likely to be the result of nitrogen adsorption into the macrovoids present in CD-HMS-2% (Figure 1).

Another indication of the presence of CD groups within the pore channels of the mesoporous materials is that every one of the CD-HMS N_2 isotherms exhibited shallow but distinct desorption hysteresis loops which rejoined the adsorption isotherm only at P/P_0 of about 0.4 (Figure 4). This extended hysteresis is not seen in the isotherm of pristine HMS silica. The presence of this hysteresis in the CD-HMS samples can plausibly be attributed to the bottlenecking of the pore channels resulting from the presence of the rather large CD moieties dispersed within.

Table 3. *p*-Nitrophenol (pNP) Adsorption Properties for CD-HMS Materials

adsorbent/CD group content	pNP concn before treatment	pNP concn after treatment	pNP adsorbed (mmol g^{-1})
CD-HMS-2%	130 ppb	43 ppb	0.0033
(0.14 mmol g^{-1})	29.5 ppm	25.5 ppm	0.13
CD-HMS-4%	130 ppb	72 ppb	0.0021
(0.32 mmol g^{-1})	29.5 ppm	22.3 ppm	0.21
CD-HMS-6%	130 ppb	14 ppb	0.0034
(0.33 mmol g^{-1})	29.5 ppm	20.7 ppm	0.30
CD-HMS-8%	130 ppb	<1 ppb	0.0033
(0.39 mmol g^{-1})	29.5 ppm	16.8 ppm	0.33

[a] The adsorption experiments were carried out using 25 mL of pNP solution and 5 mg of adsorbent.

Previous studies have focused on the inclusion of comparatively small functional organosilane groups (such as butyl, propyl, phenyl, mercaptopropyl, and octyl) within the framework of HMS silica.[40] It was demonstrated that the pore diameters of these materials decreased as a function of increased organic group loading (namely, a result of the increasing "coating" of the pore channels with the organic moieties), while their d spacings remain virtually identical regardless of the nature and amount of the incorporated organosilanes.[40] In the present study, however, the incorporation of CD groups within HMS resulted in materials with *larger* pore diameters than that of pristine HMS silica (Table 2, Figure 5). This observation concurs with the previously discussed suggestion that the CD groups act as micelle swelling agents, augmenting both the d spacings and the pore diameters of the hybrid mesostructures.

Although the inclusion of CD groups within the HMS framework resulted in an abrupt increase in pore diameter compared to that of pristine HMS, the pore sizes of all CD-HMS materials are virtually the same (38–42 Å) regardless of CD loading, while surface areas and pore volume drastically diminish as a function of incorporation (Table 2). These changes in surface properties (namely, reduction in pore volume and surface area but retention of pore diameter as a function of inclusion) are consistent with the presence of large, clusterlike moieties (such as CD) within the pore channels. In contrast, the coating of the mesostructure pore channels with small moieties is expected to result in a simultaneous reduction of surface area, pore volume, and pore diameter.[40]

Thus, the combined evidence provided by the chemical, structural, and surface characterization data of the CD-HMS materials all indicate that the large CD moieties are indeed present inside the channels of the silica frameworks, following the process depicted in Scheme 1.

Adsorption of Organic Molecules by CD-HMS. Table 3 shows the adsorption data of pNP with the CD-HMS materials. The treatment of pNP solution of high concentration (29.4 ppm) with the adsorbents (i.e., under conditions where the molar amount of CD groups present in the adsorbent samples used was *greatly inferior* to that of the pNP in solution) resulted in significant residual pNP concentrations after treatment, indicating that the maximum adsorption capacity of each adsorbent was exceeded (Table 3). At this adsorbate concentration, the pNP adsorption capacities for these materials were found to approach their CD group content (as determined from C analysis, Table 1), denoting saturation of the adsorbents with the aromatic guests. No pNP adsorption was found when pristine HMS silica was used to treat the pNP solutions under identical experimental conditions. Thus, the apparent equivalence between the pNP adsorption capacities and the CD group contents of the CD-HMS materials (Table 3) is evidence that the adsorption of the aromatic molecules is driven by the noncovalent interaction of these guest species with the CD groups in the adsorbent hosts. Moreover, the correspondence between the pNP adsorption capacity and the CD group content denotes that a majority of the CD groups in the CD-HMS materials are accessible for binding with the adsorbate molecules. The uniformity and mesoscale diameter of the pore channels in the CD-HMS materials are thus conducive for the complete access of the binding sites for the target pNP molecules. Similar conclusions have been documented for mesostructure-based metal ion adsorbents, where total access to binding sites by the metal ions was observed only for adsorbents with uniform mesoscale nanoporosity.[32,33]

When solutions containing a low concentration of pNP (130 ppb) were treated by the materials (i.e., under conditions where the molar amount of CD groups present in the adsorbent samples used was *greatly superior* to that of the pNP in solution), significant reduction of the organic molecules was observed for the more highly CD-loaded adsorbents (CD-HMS-6% and CD-HMS-8%) (Table 3). In particular, treatment of this solution by CD-HMS-8% resulted in the removal of pNP to below the detection limit (1 ppb) of the analytical method used to quantitate pNP. On the other hand, the adsorbents with lower CD content (CD-HMS-2% and CD-HMS-4%) were not as effective in removing pNP, since only 45−67% of the aromatic compound was adsorbed from the solution (Table 3). The poor adsorptivity expressed by CD-HMS-2% and CD-HMS-4% can be related to the inherently weak interaction between the aromatic guest molecules and the CD moieties. Since the CD group content in these latter adsorbents is relatively low, it can be presumed that these are quite dispersed within the mesopore channels of the HMS frameworks. This may result in the hindrance of access of the aqueous-phase pNP molecules to the CD groups of the adsorbents, particularly to those sites located deep within the adsorbent particles. Likewise, the improved performance of the more highly CD-loaded CD-HMS-6% and CD-HMS-8% may be attributed to the greater abundance of the CD binding sites within the pore channels, providing a greater number of readily accessible binding sites for the pNP molecules.

Conclusions

The synthesis and characterization of a new class of materials, denoted as CD-HMS, with uniform mesopore channels in which CD groups have been incorporated has been demonstrated. It is anticipated that these new materials will have improved properties over other reported CD-containing materials (including polymers and coated silica), including higher adsorption capacities toward organic compounds, faster adsorption diffusion kinetics, and improved biostability. Preliminary adsorption experiments have shown these materials to be potentially useful for the removal of aromatic molecules such as *p*-nitrophenol from water. This may make CD-HMS and related materials useful for a wide variety of applications requiring the selective adsorption of small organic molecules from aqueous media, including chromatographic separations and environmental remediation. A more detailed investigation on the adsorptive properties of CD-HMS materials for organic compounds is currently in progress.

The results from this research also emphasize the importance of direct (one-step) synthesis for the successful preparation of functional nanoporous materials, since all attempts to incorporate CD groups inside the pore channels of preformed mesoporous substrates by grafting have failed. Therefore, in addition to being less time and reagent consuming, direct synthesis has been shown to be the most suitable means of incorporating large functional groups such as CDs into inorganic mesoporous host structures. Direct synthesis can therefore be considered useful as a general synthesis method for the preparation of nanoporous materials in which very large functional groups need to be incorporated (such as clusters, bulky organometallic complexes, enzymes, and macromolecules), since this method can succeed where postsynthesis grafting often fails.

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