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Abstract: Mesoporous silica materials containing microporous cavities provided by surface-bound β-cyclodextrin (CD ICS) were synthesized by co-condensation of a β-CD-functionalized triethoxysilane (CD ICL) with TEOS using dodecylamine, tetradecylamine, or hexadecylamine surfactants as structure directing agents. The incorporation of β-CD within the mesoporous framework was supported by IR, Raman, MALDI TOF MS, 13C solids CP-MAS NMR, and TGA results. Small-angle X-ray diffraction and nitrogen adsorption provide evidence of ordered silica mesostructured frameworks. For materials with similar CD loading, the textural properties (surface area and pore volume) doubled as the surfactant changed from dodecylamine (C12) to hexadecylamine (C16). The textural properties decrease with CD loading (2 to 6%). The sorption capacity of gas phase polar and apolar species (nitrogen and methyl chloride) varies along with the adsorption properties in aqueous solution toward p-nitrophenol according to the CD loading (2–6%) and surfactant template employed. Along with gas adsorption of model compounds, the structural effects relate to the surfactant alkyl chain length due to the structure directing effects of the C12 to C16 surfactants. This study reveals the structural contribution of surface modification and framework incorporation of β-cyclodextrin with mesoporous silica framework materials.

Subjects: Environmental Chemistry; Materials Chemistry; Materials Science

Keywords: mesoporous; silica; surface modification; characterization; β-cyclodextrin
MALDI TOF MS, 13C CP-MAS NMR, TGA, FTIR and Raman spectroscopy

ABOUT THE AUTHORS
Lee D. Wilson and Sarker T. Mahmud are interested in the development of modified biomaterials with tunable physicochemical properties, particularly for technological applications related to adsorption-based phenomena. The incorporation of host compounds such as β-cyclodextrin (β-CD) into framework materials is of considerable interest due to the unique host–guest chemistry of cyclodextrin host compounds. Our research has focused on heterogeneous adsorption processes and the design of polymer adsorbents with improved uptake and selectivity toward waterborne contaminants.

PUBLIC INTEREST STATEMENT
Adsorption-based phenomena are ubiquitous in nature as evidenced in many physical and biological processes. There is a need to develop materials with tunable adsorption properties for a variety of different applications such as chemical separations for industry to the controlled removal of waterborne contaminants for environmental remediation. Silica is an abundant material with unique properties that affords composite formation with carbon-based compounds. The present study aims at the development of hybrid silica materials with surface modification using a well-known biomaterial known as β-cyclodextrin (β-CD). This study reports a facile and versatile method for the preparation and characterization of mesoporous silica materials functionalized with β-CD and the potential utility of such materials for specialized adsorption-based applications.
1. Introduction

Porous materials (Malgras et al., 2015; Morris & Cejka, 2015; Thangaraj, Albert, & Wilhelm, 2012; Xu, Pang, Yu, Huo, & Chen, 2007) are widely used as adsorbents, catalysts, and catalyst supports due to their large surface area and pore volume characteristics. Microporous crystalline aluminosilicate materials (zeolites) have uniform pores in the range of 0.5–2.0 nm with structurally well-defined pores and channels. Zeolites have application as molecular sieves and catalysts for cracking of crude oil (Cejka, Morris, Nachtigall, & Roth, 2014; Davis, 2002; Lehman & Larsen, 2014; Primo & Garcia, 2014; Rangnekar, Mittal, Elyassi, Caro, & Tsapatsis, 2015; Xu et al., 2007; Ying, Wei, Hua, & Steven, 2000), however, the general utility of zeolites is somewhat limited due to their small pore-size distribution. Consequently, the design of zeolite-like materials (Eddaoudi, Sava, Eubank, Adli, & Guillerm, 2015; Ying et al., 2000) with ordered frameworks and larger pores (>2 nm) has been a topic of recent research and development. Hence, the synthesis of mesoporous materials with tailored framework structure that includes pore sizes and shapes has attracted wide attention due to their use as squestrants where selective molecular recognition is required (Qu, 2008). Examples of such applications include adsorption, catalysis, molecular sieving, chemical sensing, and environmental remediation (Bergna & Roberts, 2005; Férey, 2008; Levy & Zayat, 2015; Mitzi, 2008; Rurack & Martinez-Manez, 2010; Valtchev, Mintova, & Tsapatsis, 2011; Yang et al., 2015).

Beck et al. (1992) first reported the synthesis of a new family of ordered mesoporous molecular sieves designated as MCM-41; one member of the family exhibited a hexagonal arrangement of uniform mesopores where the pore dimensions were in the range of 15 Å to greater than 100 Å (Kondawar, Potdar, & Rode, 2015). A variety of ordered mesoporous materials have been reported that employ self-assembly using neutral (Tanev & Pinnavaia, 1995) cationic (Guan, Inagaki, Ohsuna, & Terasaki, 2000), anionic surfactants (Lu et al., 2000), block copolymers (Chen et al., 2005), or β-cyclodextrin (β-CD) (Cepeda et al., 2013; Lu, Chen, & Jiao, 2005) as structure directing templates. Since the discovery of MCM-41 in 1992, considerable effort has been directed toward the incorporation of organic functionality within such ordered mesoporous materials (Rath, Rana, & Parida, 2014). Silica materials with organic surface functionalization are of great interest in environmental remediation and chromatographic separations due to their relatively high surface area and modified hydrophobicity. The incorporation of organic moieties in silica enables tuning of the surface properties by modification of the hydrophilic–lipophilic balance, surface-binding affinity, and the surface reactivity toward oxidation and hydrolytic processes and selective adsorption of heavy metals (Samiey, Cheng, & Wu, 2014).

The incorporation of organic groups in mesostructured silica can be achieved by post synthetic grafting of organic groups onto the channel walls via the pendant –Si–OH groups or by direct co-condensation of symmetric tetraalkoxy-substituted orthosilicate precursors such as TEOS [Si(OEt)4] with asymmetric reagents of the type RSi(OEt)3 (Lim, Blanford, & Stein, 1998; Lim & Stein, 1999) where R is an organic functional group. Both methods have the common disadvantage of non-uniform distribution of the organic functionality in the pores as well as limitations on the extent of organic loading. In order to achieve greater organic loading and uniform surface coverage, several reports relating to the synthesis of periodic mesoporous organosilica (Bergna & Roberts, 2005; Levy & Zayat, 2015; Mitzi, 2008; Rebbin, Rothkirch, Ohta, Hikima, & Funari, 2014; Rurack & Martinez-Manez, 2010; Valtchev, Mintova, & Tsapatsis, 2011) have been reported. The polymerization of bridged silsequioxane monomers, (RO)3Si–B–Si(OR)3, or the copolymerization of TEOS with (RO)Si–B–Si(OR)3, in the presence of surfactant affords MCM-41-related materials, where the organic functionality becomes an integral part of the channel walls. Subsequent removal of the surfactant yields a periodic mesoporous organosilica material, similar to hexagonal mesophasic silica (HMS) without any notable channel blockage (Hatton, Landskron, Whitnall, Perovic, & Ozin, 2005; Levy & Zayat, 2015). Hatton et al. (2005) synthesized periodic mesoporous silica with a variety of bridging groups employing the synthetic methodology described above. Another synthetic pathway was reported by Shimojima and Kuroda (2003) where the direct formation of hexagonally ordered mesoporous silica hybrids without the use of surfactant and any other silica source except a single-branched siloxane–based oligomers as the only precursor. A new family of mesoporous hybrid silica materials with covalently bound cyclodextrin was reported with
relatively high surface area and pore volume (Alam, Al-Jenoobi, & Al-mohizea, 2013; Huq, Mercier, & Kooyman, 2001; Liu, Lambert, & Fu, 2003, 2004; Liu, Naismith, & Economy, 2004; Liu, Wang, & Economy, 2004; Mahmud, 2007; Wilson & Mahmud, 2015; Wilson et al., 2010; Yang, Sun, & Song, 2014). The microporous cavities provided by cyclodextrin in these functionalized mesoporous silica materials are potentially useful as adsorbents for environmental remediation and chromatographic separations.

Cyclodextrins (CDs) (Crini, 2014) represent an important class of cyclic oligosaccharides containing variable numbers (n = 6–8) of D-glucopyranose units connected by α-(1, 4) linkages. The structure of β-cyclodextrin (β-CD; n = 7) is similar to that of a truncated cone with the primary hydroxyl groups (C6–OH) situated at the narrower rim and the secondary groups (C2–OH and C3–OH) at the wider annular rim. The interior of the macrocycle is lipophilic in nature while the exterior surface is hydrophilic due to the numerous polar hydroxyl groups at the macrocycle periphery. Considerable interest in the basic science and technology of CDs is related to the ability of such hosts to form stable inclusion complexes with appropriately sized guests in solution and the gas phase. The formation of inclusion complexes results in changes to the physiochemical properties of the guest molecule: (i) solubility profile, (ii) chemical stability toward heat, light, and oxidizing conditions, and (iii) vapor pressure. Hence, CDs are widely used as carriers and stabilizers in the formulation of pharmaceuticals, food and flavors, cosmetics, packaging, and textiles (Crini, 2014; Morin-Crini & Crini, 2013; van
de Manakker, Vermonden, van Nostrum, & Hennink, 2009). The utility of CDs in polymer materials as adsorbents have been widely reported (Mohamed, Wilson, & Headley, 2010; Mohamed, Wilson, Headley, & Peru, 2015; Morin-Crini & Crini, 2013; Pratt, Wilson, Kozinski, & Mohart, 2010; Udoetok, Dimmick, Wilson, & Headley, 2016; Wilson & Guo, 2012; Wilson, Mohamed, & Headley, 2011, 2014). Similarly, CD-functionalized silica compounds and their adsorbent properties have been reported (Alam et al., 2013; Bibby & Mercier, 2003; Crini & Morcellet, 2002; Mahmud, 2007; Wilson & Mahmud, 2015; Wilson et al., 2010). In particular, surface-modified silica materials containing CDs have improved adsorption properties relative to the unmodified silica materials. The goal of this study was to prepare and characterize a series of modified mesoporous silica materials (cf. Scheme 1 and 2). It will be shown that these materials have relatively high surface area with controlled pore size and the surface modification with β-cyclodextrin onto the silica framework reveals the potential utility of these materials as specialized adsorbents for heterogeneous adsorption processes (Mahmud, 2007; Wilson & Mahmud, 2015; Wilson et al., 2010).

2. Experimental

2.1. Materials

3-Isocyanatopropyltriethoxysilane (ICL) was purchased from Gelest Inc., USA. All other chemicals were purchased from Aldrich Inc., Canada. Pyridine was dried over potassium hydroxide pellets for 24 h. The pyridine decant was collected and distilled from calcium hydroxide at atmospheric pressure and stored over 4 Å sieves in screw-capped bottles. β-CD was dried in an Abderhalden pistol drier (Harwood & Moody, 1990) with acetone as the refluxing solvent.

3. Synthesis of materials

3.1. Preparation of CD-functionalized silane (CD-ICL)

4.95 g (20.0 mmol) of ICL was added to a stirred solution of dried β-CD (5.74 g, 5.0 mmol) in 70 mL of dried pyridine (cf. Scheme 1). The solution was stirred at 70°C under N₂ for 48 h. The solvent was removed under reduced pressure under N₂. The product CD-ICL was obtained as a light yellow solid.

3.2. Preparation of CD-functionalized mesoporous silica (CD-ICS) from CD-ICL

CD-ICL (X mmol where X = 0.61, 1.21, 1.81) was stirred in 10 mL of water for 30 min. The mixture is then added to the surfactant (dodecylamine, tetradecylamine, or hexadecylamine) 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, TMB (6.7 mmol) was added as pore expanding agent. The mixture was then stirred for 24 h and the resulting powder was filtered and washed by ethanol and then by water. The “as-synthesized” material (cf. Scheme 2) was dried overnight under vacuum and was washed by Soxhlet extraction using ethanol for 24 h. The material obtained was labeled as CD ICS Y (Z) where Y = 100X/30.3 or 2, 4, 6, respectively, and Z = number of carbon atoms of the alkyl chain in the neutral surfactant. Here, 2, 4, or 6 represent the molar percentage of β-CD with respect to TEOS, the bracketed values 12, 14, or 16 represent the number of carbon atoms of the hydrophobic chain in the SDA used during synthesis. For example, CD ICS 2 (12) means 2% CD-incorporated mesostructured silica prepared using dodecylamine and CD-ICS 6 (16) represents 6% CD-incorporation within mesostructured silica prepared using hexadecylamine as the SDA. The sample ID for these composite materials and their relative composition (w/w %) is provided in Table 1.

| Surfactant template (SDA) | β-CD loading (2% w/w) | β-CD loading (4% w/w) | β-CD loading (6% w/w) |
|---------------------------|-----------------------|-----------------------|-----------------------|
| Dodecylamine (C12)        | CD ICS 2(12)          | CD ICS 4(12)          | CD ICS 6(12)          |
| Tetradecylamine (C14)     | CD ICS 2(14)          | CD ICS 4(14)          | CD ICS 6(14)          |
| Hexadecylamine (C16)      | CD ICS 2(16)          | CD ICS 4(16)          | CD ICS 6(16)          |
4. Materials characterization

4.1. $^1$H NMR Spectroscopy

$^1$H NMR (Bruker; 500 MHz Avance NMR spectrometer) spectra was obtained with 128 scans using DMSO-$d_6$ as the internal reference for chemical shift measurements at room temperature.

4.2. Small-angle X-ray diffraction

Small-angle X-ray diffraction data were obtained on a Rigaku Miniflex diffractometer using Cu K$_\alpha$ radiation (wavelength 1.5418 Å) from $2\theta = 2^\circ$ to $10^\circ$. A sample of 2 g was dry mounted by pressing on to an aluminum disk sample holder.

4.3. Solid-state $^{13}$C NMR CP MAS

Solid-state $^{13}$C NMR with cross polarization $^{13}$C ($^1$H) magic-angle spinning spectra were run at 150.8 MHz on a Varian Inova 600 spectrometer with rotor size 3.2 mm, spinning rate 16 kHz with a CP ramp pulse program. The chemical shifts were externally referenced to hexamethylbenzene at 16.9 ppm at ambient temperature. Data were processed with a 100 Hz line broadening and left shifting FID (1–2 data points) to correct baseline.

4.4. MALDI-TOF mass spectrometry

MALDI-TOF mass spectra were obtained using a Voyager DE STR MALDI Mass Spectrometer operating in positive ion linear mode, calibrated with angiotensin 1 (m/z 1,296.6853) and spectra were acquired from m/z 700 to m/z 3,000. Approximately, 2 mg of sample was placed in an Eppendorf sample tube and ground with a 200-μL pipette tip. A volume 50 μL of 75% acetonitrile with 0.1% aqueous trifluoroacetic acid was added to the tube. The sample was sonicated for 30 min, followed by addition of 1 μL of the sample slurry plus 1 μL of matrix solution (5 mg/mL alpha-cyano-4-hydroxycinnamic acid) to the MALDI plate with air drying. Milli-Q grade water was used for the preparation of the aqueous solutions.

4.5. DRIFT spectroscopy

Diffuse reflectance FTIR (DRIFT) spectra were obtained in reflectance mode using a Bio RAD FTS-40 spectrophotometer. KBr was used as both the background and matrix over the range of 400–4,000 cm$^{-1}$. Samples were prepared by mixing with pure spectroscopic grade KBr in an approximately equal ratio (KBr:sample ~ 1:1), grinding together in a small crucible, and finally pressing with a spatula onto the sample holder to make a uniform planar upper surface. The spectra were taken at room temperature with a resolution of 4 cm$^{-1}$ with approximately 250 scans.

4.6. Raman spectroscopy

Raman Spectroscopy measurements were obtained using a Renishaw system 2000 with an excitation wavelength of 514 nm using an 180° backscattering geometry at 295 K. The calibration was performed using silicon wafer referenced at 520 cm$^{-1}$.

4.7. Nitrogen adsorption

Nitrogen adsorption–desorption isotherms of the adsorbents were measured at 77 K on a Micromeritics ASAP 2000 SA analyzer. Samples were ground in a small crucible and passed through 40 mesh-size sieve prior to measurement. Each sample was degassed at 110°C at 10$^{-6}$-mm Hg until a stable background vacuum pressure was achieved. Samples were analyzed over a variable relative pressure range (40 mm Hg to 710 mm Hg) of nitrogen at 77 K.

4.8. TGA

TGA analysis of solid samples was performed on TG-DSC-1100 supplied by Setaram Scientific and Industrial Equipment, NJ, USA. 20 to 50 mg of sample was placed onto a microbalance within the analyzer. The sample was heated in flowing Ar gas from 20 to 600°C with a heating rate of 10°C/min.
5. Results and discussion

As outlined above, the incorporation of an organic functional group in a mesoporous silicate framework can be achieved by introduction of an asymmetric orthosilicate through conjugation of β-CD with 3-isocyanatopropytriethoxysilane (CD-ICL). According to Scheme 2, the reaction of TEOS with CD-ICL affords a direct synthesis pathway to obtain surface-modified HMS containing β-CD (cf. Scheme 2), referred to hereafter as CD-ICS materials (Richer, 1998; Richer & Mercier, 2001), as described in Table 1. Related materials were reported by Hu et al. (2001), where cyclodextrin was anchored to the silica framework via cyanoanlur chloride to afford modified HMS.

5.1. 1H NMR results

The 1H NMR spectrum and assignment of 1H nuclei of native β-CD in DMSO-d6 at 295 K (cf. Figure S1; Supporting Information) agree with results reported by Schneider, Hacket, and Rüdiger (1998). The 1H NMR data for the assignment of β-CD are as follows: δ 3.29 (m, 7H, H-2), 3.34 (m, 7H, H-4), 3.55 (m, 7H, H-6), 3.60–3.70 (m, 21H, H-3, H-6 a, b), 4.45 (m, 7H, OH-6), 4.82 (s, 7H, H-1), 5.68 (s, 7H, OH-3), 5.75 (m, 7H, OH-2). The 1H NMR results of ICL in DMSO-d6 (cf. Fig. S2; Supporting Information) are assigned as follows: δ 0.60 (m, 2H, SiCH3), 1.15 (t, 9H, SiOCH2CH3), 1.60 (m, 2H, SiCH2CH2), 3.33 (m, 2H, SiOCH2CH2), 3.75 (q, 6H, SiOCH2CH3).

The chemical shifts of the methylene protons of the propyl moiety of the ICL precursor are as follows: 0.60 (α-), 1.60 (β-), and 3.33 ppm (γ-). After the coupling reaction between ICL and β-CD, the chemical shifts of α-, β-, and γ- protons of the conjugate product are shifted upfield to 0.50, 1.40, and 2.93 ppm, respectively. The measured change in chemical shift differences (Δδ = product–precursor) for α-, β-, and γ- protons are (0.60–0.50) = 0.10, (1.60–1.40) = 0.20 and (3.33–2.93) = 0.40 ppm, respectively. The linker methylene groups (α-, β-, and γ-) are connected to β-CD via the urethane linkage where the γ nuclei are directly coupled to the β-CD macrocycle via the urethane linkage, in agreement with the shielding effects. The β- and α-protons are shielded to a lesser extent with increasing distance from β-CD. Thus, the variable Δδ values are in accordance with the relative position of amide linkage and its known inductive and hydration effects on the adjacent nuclei (Mohamed, Wilson, & Headley, 2011). The H-1 nuclei of β-CD are relatively unaffected in the CD-ICL product. The CH3 nuclei of the triethoxysilane moiety for the CD ICL conjugate represent the terminal nuclei of the β-CD at variable levels of cross-linking (Mohamed et al., 2010).

The results are consistent with the relative reactivity of the various hydroxyl groups and the occurrence of steric effects for large linkers such as ICL. Similar trends in the pattern of substitution were observed for diisocyanate conjugation with β-CD at variable levels of cross-linking (Mohamed et al., 2010).

5.2. Infrared spectra

Figure 2 shows the IR spectra of CD-ICS 2(14), CD-ICS 4(14), and CD-ICS 6(14) as well as the synthetic precursor CD-ICL. IR spectra for the CD-ICS materials reveal a dominant band attributed to Si–O–Si stretching (1,050–1,150 cm⁻¹) that is characteristic of siloxane condensation (Harwood & Moody, 1990; Smith, 1999). The bands observed in the IR spectra of the CD-ICL overlap along with characteristic IR bands of CD-ICS and provide support that grafting of β-CD occurs within the mesopore channels of HMS. A representative
IR spectrum of a CD-ICS material can be assigned, as follows: 3,350 (N–H stretching), 2,971, and 2,924 (C–H stretching), 1,634 (C=O stretching Amide I), 1,560 (N–H bending Amide II), 1,437–1,280 (OCH, HCH, CCH, COH bending of $\beta$-CD), 1,260 (Amide III), 1,150 (C–O stretching of $\beta$-CD) 1,090 (Si–O–C stretching), 870 (C–C anomeric vibration of $\beta$-CD), 947, and 578 cm$^{-1}$ (skeletal vibration of $\alpha$-1,4 linkage of $\beta$-CD).

5.3. Raman scattering of CD ICS

Complementary Raman spectra were obtained for all nine CD ICS materials, as shown in Figure 3. A prominent signature is the O–H (3,650–3,000 cm$^{-1}$) and C–H stretching (3,000–2,800 cm$^{-1}$) bands. The band at 1,100–1,000 cm$^{-1}$ was assigned to Si–O–Si anti-symmetric vibration (Jung, Gupta, Oh, Kim, & Whang, 2005) which provide support for siloxane condensation. As the loading of $\beta$-CD increases from 2 to 6% (w/w), a range of vibrational bands (1,442, 1,398, 1,315, 1,209, 1,125, 933, 841, 641, and 473 cm$^{-1}$) (Ponchel et al., 2004) appear with a corresponding increase in intensity, in agreement with the incorporation of $\beta$-CD within the silica framework.

The uncertainty as to whether the CD hosts are embedded within the mesopore framework or bound to the surface of the silica framework may be addressed using specialized surface techniques (vide infra). According to the conclusions given by Liu et al. (2003), the DS value determines the
position of CD within or on the surface of the silica. The occurrence of cross-linking on each annular face of CD is likely to result in incorporation within the silica matrix. However, if CD polymers are not so extensively cross-linked (Huq et al., 2001) where each CD was attached to 2.8 silicon atoms; DS < 3), polymerization became asymmetric resulting in localization at the mesopore surface. Since, the CD ICS materials were synthesized from CD-ICL that contains four reactive centers, it is more probable that the CD host is incorporated within the silica network to a greater extent, as compared with CD that is grafted solely on the silica surface. However, the present results cannot quantitatively differentiate between surface-bound versus matrix-bound β-CD moieties. In part, the depth profiling of the Raman excitation source (514 nm) is estimated to penetrate the sample surface to 1 μm or more in depth resulting in Raman signal contributions from both structure types.

Figure 4 illustrates the Raman spectra of various types of CD ICS materials and β-CD hydrate. A prominent band at 3,000–2,800 cm\(^{-1}\) due to C–H stretching from β-CD was observed along with other signatures (1,440–1,240 cm\(^{-1}\)) for C–H and O–H bending with reduced intensity. Signatures for C–O–C stretching (1,115 cm\(^{-1}\)), C–OH stretching (1,032 cm\(^{-1}\)), α-1, 4-glycosidic linkages (930 cm\(^{-1}\)), C–H stretching of the anomeric carbon (847 cm\(^{-1}\)), and the skeletal vibration modes of β-CD (473 cm\(^{-1}\)) were reduced or nearly absent in Figure 4.

Figure 3. Raman spectra of (a) β-CD (b) CD-ICS 2(12) and (c) CD-ICS 6(12) at ambient temperature with excitation wavelength 514 nm.

Figure 4. Raman spectra of (a) β-CD (b) CD-ICS 6(14) and (c) CD-ICS 6(16) (d) CD-ICS 4(12) (e) CD-ICS 2(16) and (f) CD-ICS 4(16).
5.4. MALDI-TOF mass spectrometry
The incorporation of β-CD within the mesostructured framework of HMS was supported by MALDI-TOF mass spectrometry due to the surface sensitivity of this method. Due to the desorption of the surface-bound species by laser irradiation, the method affords the direct detection of covalently grafted oligomers onto the silica network (Li et al., 2009; Mullens, Anugu, Gorski, & Bach, 2011; Zhang et al., 2010). Figure 5 illustrates the MALDI-TOF MS results of β-CD hydrate where the two diagnostic fragments at m/z 1,157 and 1,173 are observed. The molecular ions are assigned to non-covalent complexes formed between β-CD and alkali metal ions present in solution, as follows; [β-CD + Na]+ and [β-CD + K]+.

The MALDI-TOF spectra for the CD-ICS materials in Figure 6 show similar features at m/z 1,157 and 1,173 that correspond to the molecular ions described in Figure 5 for β-CD. The fragment ions in Figure 6 that correspond to desorbed adducts ([β-CD + Na]+ and [β-CD + K]+) and their hydrated forms from the surface of CD-ICS upon laser ablation. These results provide strong unequivocal support.
that β-CD is bound within or onto the surface of the mesoporous framework of HMS. Besides these fragment ions, other signatures due to glucose oligomer fragments originating from β-CD and a less-intense peak due to [β-CD + linker + Na]^+ are also observed. Figure 6 illustrates the MALDI-TOF MS of CD-ICS 4(12) where the major peaks were assigned to molecular fragments therein.

A review of the literature for MALDI-TOF MS studies revealed no reports of such studies for surface-modified silica materials (Bauer, Glasel, Decker, et al., 2003; Bauer, Glasel, Hartmann, Bilz, & Mehnert, 2003; Bauer, Glasel, Hartmann, et al., 2003, Bauer et al., 2004; Li et al., 2009; Mullens et al., 2011; Vuluga, Hamaide, Pantiru, & Novat, 2002; Yoo et al., 2006; Zhang et al., 2006, 2010) for such MALDI-TOF MS studies, as reported herein. The results in Figure 6 provide complementary evidence that β-CD is covalently attached to the silica network according to peaks at m/z 1,157 and 1,173 due to [β-CD + Na]^+ and [β-CD + K]^+. Additional MALDI-TOF MS results for the other CD-ICS materials are listed elsewhere (Mahmud, 2007). This study represents one of the first examples that illustrate the utility of MALDI-TOF MS results to confirm the surface- and matrix-level incorporation of β-CD within such mesoporous silica framework materials.

5.5. Solid state 13C NMR CP-MAS spectroscopy

Solid State 13C NMR CP-MAS spectra (Pessine, Calderini, & Alexandrino, 2012) for the various CD-ICS materials were obtained at 150.8 MHz on a Varian Inova 600 spectrometer at a spinning rate of 16 kHz. Figure 7 shows the 13C NMR spectrum for CD-ICS 2(14) in the solid state. The 13C signature of the urethane linkage (OCONH) was observed ca. δ = 160–170 ppm. The 13C lines for the triethoxysilane unit (OCONHCH₂CH₂CH₂Si) are observed ca. δ = 9–50 ppm, upfield from the 13C signatures for β-CD (Brunel, Cauvel, Fajula, & DiRenzo, 1995). The 13C NMR lines for β-CD reside in the central spectral region (ca. δ = 60–110 ppm), in agreement with other results for β-CD materials in the solid state (Gidley & Bociek, 1988; Karoyo et al., 2015; Sfihi, Legrand, Doussot, & Guy, 1996).

In addition to the expected peaks observed in the solid state 13C NMR CP-MAS spectra, the peaks which correspond to the TMB (the pore expander) are observed in the aromatic region (denoted as
b, c, and d). This indicates that the pore expander was not completely removed by Soxhlet extraction with ethanol despite the use of the verbatim procedure reported elsewhere (Huq et al., 2001). The results indicate that the use of a pore expander (TMB) for the synthesis of such composite materials may result in entrapped impurities during the formation of the silica framework. Although β-CD can form relatively stable complexes with such substituted aromatic compounds, it is more likely that the TMB becomes entrapped in the silica network during the condensation process, in a manner similar to the occurrence of surface- vs. matrix-bound β-CD. Support for the latter comes from the use of Soxhlet extraction since adsorbed guests should be displaced from the cavity of β-CD with organic solvents such as ethanol due to the destabilization of complex stability (Crini, 2014; Inoue et al., 1993; Liu & Guo, 1999). The inability to remove TMB after Soxhlet extraction after 72 h of washing supports the idea that TMB is entrapped within the silica framework. Solid state $^{13}$C NMR CP-MAS spectra of other CD-ICS materials reveal $^{13}$C NMR signatures ($\delta = 60$–110 ppm) due to β-CD; whereas, the upfield $^{13}$C signature ($\delta < 60$ ppm) is due to ICL providing support to the covalent attachment of β-CD with the silica framework (Mahmud, 2007).

5.6. Small-angle X-ray diffraction

Figure 8 shows the SAXD patterns of CD-ICS materials prepared at different loadings of β-CD and surfactant templates. The spectra of the surfactant-extracted CD-ICS materials reveal intense and sharp signatures near $2\theta = 2.2^\circ$ that indicated spacings with expected values ($d_{100} = 4.1$ nm) which provide support of an ordered mesoporous silica framework. As the loading of β-CD increases for CD-ICS 4(12) to CD-ICS 6(12), the low-angle diffraction line at $2.2^\circ$ decreases in intensity. A similar trend is observed for CD-ICS 4(16) and CD ICS 6(16). Liu et al. (2003) attributed to a loss of periodicity and intensity that occurs with increased β-CD loading. The SAXD line at $2.2^\circ$ shows an attenuated intensity as the TEOS level decreases from 90 to 50%, where the signature disappears for a lower TEOS content (25%). Greater loading of β-CD is accompanied by a concomitant decrease in the TEOS content. The result is a reduction in the stability of the silica framework, in agreement with the loss of long-range ordering observed in Figure 8.

It should be noted that the low-angle signature is very sharp in intensity for the CD-ICS materials templated with C16-amine as compared with CD ICS materials prepared using the C12-amine. Similar observations were reported elsewhere (Tanev & Pinnavaia, 1996) where superior templation of HMS was noted for non-ionic surfactants with longer alkyl chain lengths relative to surfactant templates with shorter alkyl chain length. Previous results (TEM, nitrogen adsorption and SAXD) indicate that such materials reveal a wormhole morphology in the silica framework with an approximate 40 Å pore size diameter (Huq et al., 2001). No notable PXRD signatures were evident for HMS materials at the highest CD loading (CD-HMS 8%) which was attributed to the contrast matching caused by the
possibility of CD entrapped within the pore channels. The greater pore-size distribution of CD-HMS 8% showed evidence of severe structural perturbation and mechanical instability of the mesoporous framework, as described above for CD-ICS materials.

In a previous report, Liu et al. (2003) reported that mesoporous materials containing β-CD that used C16-trimethylammonium bromide (CTAB) as the surfactant template resulted in cross-linking between β-CD that was completely functionalized with ethoxy silane. In the case of β-CD, up to 42 hydrolysable (7 × 6 OEt groups from triethoxysilane) groups are available, as compared with only four in the case of TEOS. SAXD measurements of the polysilsequioxanes showed no apparent structural order or periodicity. As the proportion of TEOS decreases and the cyclodextrin monomer content increases, the long-range order is lost. A peak at 2.2° decreases in intensity as the percentage of TEOS decreases from 90 to 50% and the low-angle peak at 2.2° is absent when the percentage of TEOS is 25% or less. The same group also reported β-CD hybrid mesoporous silica that used a monomer of CD having an isocyanate carbamate linkage in the absence and presence of added surfactant (CTAB) (Liu, Lambert, et al., 2004; Liu, Naismith, et al., 2004). The preparation of β-CD hybrid mesoporous silica that used a tri-block copolymer as the structure directing template was also reported (Liu, Wang, et al., 2004).

5.7. Thermogravimetric analysis (TGA) results

Figure 9 is a typical thermogram obtained for silica-based materials containing β-CD, HMS (without β-CD), and the CD-ICL precursor. Weight loss events were observed in the low, medium, and high temperature regimes. At low temperatures (<110°C), the CD-ICS materials reveal the loss of bound water from surface sites and micropore domains. In the intermediate temperature region (100–200°C), surfactant-containing materials “as HMS” and “as CD-ICS 6(12),” the accompanying weight loss profile is assigned to the decomposition/loss of the surfactant and/or pore expander (TMB). In the high-temperature region, the thermogram for “as HMS” is compared with “as CD HMS” to show an event ca. 300°C for the “as CD HMS.” In the case of CD ICS materials, CD-ICL reveals a similar event ca. 300°C, in agreement with the decomposition of β-CD (Cunha-Silva & Teixeira-Dias, 2004; Sambasevam, Mohamad, Sarih, & Ismail, 2013).

The temperature derivative of the TGA results (DTG) for CD-ICL and CD-ICS 6(12) is shown in Figure 10. A prominent decomposition event ca. 324°C of β-CD for the CD-ICL moiety, in agreement with covalent attachment of β-CD to the silica network. The decomposition of CD-ICL and CD-ICS 6(12) occurs above 320°C which exceeds the known melting point of β-CD (298–300°C). The offset in temperature (ΔT ≈ 20°C) suggests that β-CD is covalently bound to the silica network because of the greater enhanced thermal stability toward loss of β-CD in such materials.
5.8. Nitrogen adsorption

Figure 11 illustrates a typical nitrogen adsorption–desorption isotherm of CD-ICS materials (cf. Figures S4 and S5; Supporting Information) which generally displays Type IV isotherms with hysteresis loops, characteristic of materials with variable textural porosity (Thommes, 2010). Generally, H4 hysteresis loops are observed which feature parallel and almost horizontal branches which correspond to adsorption–desorption in narrow slit-like pores (Kruk & Jaroniec, 2001) that have narrow pore size distributions.

It is important to define and differentiate the terms textural mesoporosity and framework mesoporosity to clarify the discussion concerning porosity (Tanev & Pinnavaia, 1996). The framework mesoporosity is defined as the porosity due to the uniform channels of the templated framework. The size of the framework-confined mesopore is equal to the diameter of the framework channels. The diameter of the framework-confined mesopore varies with the parent rod-like micelles (template) where it can be increased by an increase in the surfactant alkyl chain length or by the addition of pore expander such as TMB. The porosity arising from two contributions; (i) non-crystalline intra-aggregate voids and (ii) spaces created by contacts between particles contribute textural mesoporosity. The size of the textural mesopore varies with the size, shape, and the number of interfacial contacts within the aggregates.
The presence of framework-confined mesoporosity is indicated by an adsorption step centered at the relative pressure region from 0.05 to 0.3. From the height and slope of the sorption step in this region, a qualitative indicator of the extent and the uniformity of the framework mesoporosity is illustrated. For materials with less CD loading, e.g. CD-ICS 2% or CD ICS 4%, adsorption in the region (0.05–0.3) is greater with a steeper slope (cf. Figures S4 and S5; Supporting Information). The framework-confined mesoporosity of HMS is more well-defined at lower CD loadings and the adsorption in the relative pressure region (0.05–0.3) decreases with a lower slope with increased CD loading. With an increased level of incorporation of β-CD within a mesopore framework, the periodicity of the mesopore framework is degraded. Similar observations were reported by Huq et al. (2001) by observing structural perturbations of the framework caused by entrapment of CD moieties within the silica network.

The presence of textural mesoporosity is verified by well-defined hysteresis loops in the relative pressure range from 0.3 to 1.0. A comparison of the adsorption isotherms of materials prepared using different surfactant systems reveals that CD-ICS materials prepared using templates with shorter alkyl chains have greater textural mesoporosity vs. framework mesoporosity. An opposite trend occurs for surfactants with longer alkyl chains, in agreement with a report by Tanev and Pinnavaia (1996). The textural properties of CD-ICS materials determined from nitrogen adsorption vary as the chain length of the surfactant template varies and as the content of CD varies (cf. Table 2 in Wilson & Mahmud, 2015). The surface area (SA) varies from 2.0 to 6.8 × 10² m²/g, while the pore volume (PV) varies from 0.21–1.2 cm³/g. A general decrease in the PV and SA occurs as the β-CD loading increases for CD-ICS materials prepared with the same surfactant (C12) where a comparison of CD-ICS materials prepared with a CD loading from 2 to 6% show a decrease in SA from 630.3 to 307.0 m²/g with a decrease in PV from 0.67 to 0.21 cm³/g. Similar trends were observed for CD-ICS materials prepared using C14- and C16-amines, and these results further indicate that β-CD incorporation likely occurs in the pore channels. At similar CD loadings, the framework mesoporosity increases as the surfactant alkyl chain length increases. A comparison of CD-ICS 2(12) and CD-ICS 2 (16) shows that the surface area increases (630.3 m²/g to 906.5 m²/g) with an increase in pore volume from 0.67 to 1.18 cm³/g as the surfactant alkyl chain length increases (C12 to C16). Similar trends were observed for other CD loadings for other CD ICS materials.

Among the various types of hybrid mesoporous silica containing β-CD, a general drawback relates to a decrease in the framework mesoporosity, SA, and mechanical instability occurs with increased CD loading. Although an increase in the CD loading may enhance the sorption capacity of these composite materials, the mechanical instability of CD-ICS materials pose limitations. As for the CD-HMS materials reported by Huq et al. the CD loading is lower than that reported by Liu et al. (8% for CD-HMS and 25% for Liu et al.) while the reported PNP sorption capacity for both types materials were observed to be comparable (Huq et al., 2001; Liu et al., 2003). As mentioned above, an increase in CD loading is anticipated to result in greater sorption capacity for CD-based organosilica materials (Zolfaghari, 2015). The effect was not observed by Liu et al. (2003) since greater CD loading resulted in a loss of framework mesoporosity and the surface area decreased due to structural destabilization of the framework. Another consideration is the filling of the pore network at greater CD loading which may result in steric effects that reduce the accessibility of organic dyes such as p-nitrophenol (PNP) along with attenuated pore diffusion due to blockage of the mesopore domains. The general concept, “more cyclodextrin, more adsorption” may not necessarily apply due to changes in the mechanical stability of the framework, potential steric effects due to loading of the CD moiety in the mesopore channels, and limitations on the surface immobilization of β-CD for the synthetic conditions described above. The synthesis of CD-HMS materials using the “one pot method” by Huq et al. (2001) is facile and convenient; however, the cyanoget chloride linker used is sensitive to alkaline hydrolysis of APS MCT. The CD ICS materials that employ the ICL linker herein are less susceptible to hydrolysis, as evidenced by its greater stability in aqueous solution (Wilson et al., 2010). Consequently, the design of CD-ICS materials reported herein offer a facile and efficient synthetic method that solves the problem of CD accessibility and versatile attachment of cyclodextrin to the silica
6. Conclusion

In this study, the synthesis of a new type of mesoporous hybrid silica adsorbent containing covalently bound cyclodextrin was prepared and characterized using a range of material characterization methods. The CD-ICS materials were characterized using FT-IR/Raman spectroscopy, solid state $^{13}$C NMR spectroscopy, and MALDI-TOF mass spectrometry. The uptake properties of CD-ICS materials with gaseous species and in aqueous solution were reported (Wilson & Mahmud, 2015; Wilson et al., 2010). The MALDI-TOF MS characterization and the adsorption results provide corroborating support that $\beta$-CD is incorporated within and onto the surface of the silica framework. The mesoporous silica materials containing $\beta$-CD reported herein will contribute positively to future industrial applications that are related to sorption-based processes and chemical separations involving the removal of organic and inorganic anion species from water (Jadhav et al., 2015; Kusrinì, Sofyan, Suwartha, Yesya, & Priadi, 2015).

Supplementary material

Supplementary material for this article can be accessed here http://dx.doi.org/10.1080/23312009.2015.1132984.

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