Reaction of the Si₈O₂₀(SnMe₃)₈ Building Block with Silyl Chlorides: A New Synthetic Methodology for Preparing Nanostructured Building Block Solids

Jason C. Clark and Craig E. Barnes*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

Received January 6, 2007. Revised Manuscript Received April 3, 2007

A series of silicate based "building block" (bb) materials has been synthesized via the reaction of the cubic, spherosilicate $Si_8O_{20}(SnMe_3)_8$ with the chlorosilanes $HSiCl_3$, Me_2SiCl_2, and $SiCl_4$. The resulting materials are amorphous, porous, high surface area matrices composed of intact Si_8O_{20} building blocks that are cross-linked together through a series of siloxane linkages formed from the reaction of trimethyltin groups on the spherosilicate precursor and the silyl chloride groups. These siloxane-based linkages provide chemically robust, covalent connections between building blocks. The distribution of chemically distinct linking groups may be influenced by manipulating initial stoichiometries, changing solvents, varying temperature, and using different linking silyl chlorides. General procedures for preparing silicate platforms having linking groups with specific connectivities to surrounding building blocks in the matrix are described. The synthetic strategy for preparing the building block matrices described here forms the basis for preparing a wide range of nanostructured solids in which the identity and distribution of linking groups can be controlled by design. Applications to heterogeneous catalysts are discussed.

Introduction

The notion of nanostructuring in solid-state chemistry and materials science refers to different aspects or properties of a material depending on the context or intended application. Nanometer sized balls,[1−3] dots,[4−6] tubes,[7−12] and wires[13−18] are examples of discrete objects that exhibit different forms of nanostructuring. Zeolites, templated sol-gels, and porous carbons are other examples of materials that exhibit nanost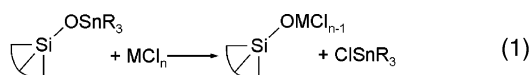ructuring based on their porosity.[19−26] These materials are currently of great interest because of their applicability in the areas of separations and solid-state science and as catalyst supports.[19,21,22,27−30]

The use of nanostructured porous materials in catalysis relies upon control of surface structure or the ability to create a well defined array of identical sites on their surfaces. This poses the challenge of developing a simple, well understood synthetic methodology which can be used to prepare targeted nanostructured architectures on the internal and external surfaces of solid-state materials. The dispersion and structure of the catalytically active sites are important because high temperature reaction conditions can result in coalescence or aggregation of the active centers producing new species with variable activities and/or selectivities. Thus, maintaining site dispersion is important to ensure the catalytic centers remain single-site in nature. Site homogeneity is also critical to correlating activity and selectivity to a specific site. Once established, this structure−reactivity relationship can be used to optimize catalytic performance.

(1) Uthirakumar, P.; Lee, Y. S.; Suh, E. K.; Hong, C. H. *Phys. Lett. A* **2006**, *359*, 223.
(2) Ghosh, S.; Mukherjee, P. S. *J. Org. Chem.* **2006**, *71*, 8412.
(3) Wang, J.; Zhu, Y. J.; Wu, Y. J.; Wu, C. J.; Xu, D. F.; Zhang, Z. *Mod. Phys. Lett. B* **2006**, *20*, 549.
(4) Zhou, H.; Narayan, J. *J. Nanopart. Res.* **2006**, *8*, 595.
(5) Teo, B. K. *Coord. Chem. Rev.* **2003**, *246*, 229.
(6) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 8410.
(7) Fan, J. Y.; Wu, X. L.; Chu, P. K. *Prog. Mater. Sci.* **2006**, *51*, 983.
(8) Scholes, G. D.; Rumbles, G. *Nat. Mater.* **2006**, *5*, 683.
(9) Zhao, X. J.; Zhang, S. G. *Chem. Soc. Rev.* **2006**, *35*, 1105.
(10) Bell, M. S.; Lacerda, R. G.; Teo, K. B. K.; Milne, W. I. Characterisation of the growth mechanism during PECVD of multiwalled carbon nanotubes. In *Carbon: the Future Material for Advanced Technology Applications*; Springer: Berlin, 2006; Vol. 100, p 77.
(11) Britz, D. A.; Khlobystov, A. N. *Chem. Soc. Rev.* **2006**, *35*, 637.
(12) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105.
(13) Thiaville, A.; Nakatani, Y. Domain-wall dynamics in nanowires and nanostrips. In *Spin Dynamics in Confined Magnetic Structures*; Springer: Berlin, 2006; Vol. 101, p 161.
(14) Kline, T. R.; Tian, M. L.; Wang, J. G.; Sen, A.; Chan, M. W. H.; Mallouk, T. E. *Inorg. Chem.* **2006**, *45*, 7555.
(15) Condon, A. *Nat. Rev. Genet.* **2006**, *7*, 565.
(16) Wang, Y.; Cao, G. Z. *Chem. Mater.* **2006**, *18*, 2787.
(17) Goldberger, J.; Fan, R.; Yang, P. D. *Acc. Chem. Res.* **2006**, *39*, 239.
(18) Hu, J. T.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435.
(19) Zhai, S.; Wei, L.; Yang, D.; Wu, D.; Sun, Y. *Prog. Chem.* **2006**, *18*, 1330.
(20) Cai, X.; Zhu, G. S.; Zhang, W. W.; Zhao, H. Y.; Wang, C.; Qiu, S. L.; Wei, Y. *Eur. J. Inorg. Chem.* **2006**, 3641.
(21) Lee, J.; Kim, J.; Hyeon, T. *Adv. Mater.* **2006**, *18*, 2073.
(22) Lu, A. H.; Schuth, F. *Adv. Mater.* **2006**, *18*, 1793.
(23) Tao, Y. S.; Kanoh, H.; Abrams, L.; Kaneko, K. *Chem. Rev.* **2006**, *106*, 896.
(24) Schuth, F. *Annu. Rev. Mater. Res.* **2005**, *35*, 209.
(25) Cundy, C. S.; Cox, P. A. *Microporous Mesoporous Mater.* **2005**, *82*, 1.
(26) Minoofar, P. N.; Dunn, B. S.; Zink, J. I. *J. Am. Chem. Soc.* **2005**, *127*, 2656.
(27) Logar, N. Z.; Kaucic, V. *Acta Chim. Slov.* **2006**, *53*, 117.
(28) Ma, Y.; Tong, W.; Zhou, H.; Suib, S. L. *Microporous Mesoporous Mater.* **2000**, *37*, 243.
(29) Cheetham, A. K.; Ferey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.
(30) Brunel, D.; Bellocq, N.; Sutra, P.; Cauvel, A.; Lasperas, M.; Moreau, P.; Di Renzo, F.; Galarneau, A.; Fajula, F. *Coord. Chem. Rev.* **1998**, *180*, 1085.

Current challenges in the field of heterogeneous catalysis involve the development of novel synthetic methodologies to prepare next generation, "ultraselective"[31,32] catalysts in the areas of oxidation–reduction and acid catalysis.[33,34] The main requirements for producing such catalysts are a knowledge of what the active catalyst is, a method of *selectively* preparing the active catalyst on a support, and the ability to prepare high densities of the active catalyst while maintaining site isolation and open access to substrates. We are currently developing a new synthetic methodology to address these goals which does not begin with a preexisting support surface. In this approach, the different parts of what will ultimately become the catalytically active site should be present and take on a structure-directing role as the matrix is formed. This strategy is similar to molecular imprinting techniques[35,36] that have been developed recently in the fields of molecular recognition[37–41] and chromatography.[42] However, in the methods described here, templates are not utilized and thus solvent extraction or high-temperature treatments are not necessary to remove structure directing agents to open up the binding site for substrate recognition. Second, rather than build the matrix atom-by-atom, rigid, preformed, molecular building blocks (bb's) will make up the majority of the matrix. Rigid bb's help in developing procedures to predict and control how the matrix grows while bb's greater than or equal to 1 nm make it easier to ensure that catalysis sites remain chemically isolated from one another and noninteracting. This synthetic paradigm of linking groups that become catalyst sites surrounded by nanometer sized bb's also requires that a convenient chemical linking chemistry exist to put the matrix together. We have chosen a simple metathesis reaction (eq 1) first reported by Feher et al.[43,44] as the critical linking reaction to build our solids.

$$\overset{OSnR_3}{\underset{Si}{\diagdown}} + MCl_n \longrightarrow \overset{OMCl_{n-1}}{\underset{Si}{\diagdown}} + ClSnR_3 \qquad (1)$$

From the perspective of materials synthesis, this type of reaction has several advantages over traditional syntheses of mixed metal oxides. It is broadly applicable to high valent metal and main group chloride complexes including those containing Al, Si, P, Ti, V, Fe, W, and Sn.[44,45] In contrast to hydrothermal or sol–gel technologies, the linking reaction must be conducted with the complete exclusion of water to prevent the formation of hydroxides and complicating condensation reactions. Avoiding these reactions is of great importance because of the well-known problem of phase segregation in mixed metal hydrolysis systems.[46,47] Complementary functional groups on each condensing entity (SnMe₃ on the bb; chlorine on the linker) also ensure that linking entities remain atomically dispersed throughout the solid because self-condensation cannot occur. Finally, nonaqueous, bb syntheses of metal oxide materials represent a novel but simple approach to materials synthesis which has not been studied in great detail.[48–51]

Herein we report on model studies of the reactions between the octa(trimethyltin) cubooctomeric spherosilicate, Si₈O₂₀-(SnMe₃)₈ (herein referred to as the "tin cube") and several silane chloride reagents. We will describe and illustrate a simple synthetic strategy to place specific linking groups into a silicate matrix made up of Si₈O₂₀ bb's. Chlorosilane linking reagents represent models for the reactions of other transition metal chlorides as well as robust connecting groups that stabilize the matrix. The silane linking groups are, however, easily characterized in these matrices via solid state ²⁹Si NMR. This approach to preparing "nanostructured" solids is applicable to a wide variety of other metals and thus addresses one of the fundamental current challenges in catalysis science.

Experimental Section

General Details. As a result of the moisture sensitivity of the chlorosilane reagents several steps were taken to exclude all sources of water from reactants and solvents as well as any hydroxyl groups present on glassware used in reactions. All Schlenk reaction vessels were treated with chlorotrimethylsilane/triethylamine prior to use. Hexanes and toluene (Fisher Scientific) were dried using sodium–potassium alloy and distilled. Si₈O₂₀(SnMe₃)₈, was heated overnight at 100 °C under vacuum to remove waters of hydration in the crystal.[52] *Caution: Trimethyltin containing compounds can be extremely toxic and should be handled properly to avoid contact while manipulating them.* All silyl chlorides were distilled, degassed, and stored under vacuum in Schlenk vessels equipped with high vacuum Teflon stop cocks. All solvents and silanes were delivered into reaction vessels using vapor transfer methods.

²⁹Si solid-state NMR (SSNMR) experiments were acquired at 79.43 MHz at spin rates of 3.56–5.56 kHz on a Varian Inova spectrometer. Samples were placed in 5 mm pencil rotors in a N₂ dry box and sealed using paraffin wax. Normal one pulse magic angle spinning (MAS) and cross polarization (CP) MAS spectra were collected as described in the text. A 30° pulse and relaxation delays of 30 s were used for all one pulse experiments while 10 s relaxation delays were used for CPMAS experiments.

(31) Neurock, M. *J. Catal.* **2003**, *216*, 73.
(32) Somorjai, G. A.; McCrea, K. R.; Zhu, J. *Top. Catal.* **2002**, *18*, 157.
(33) Gorte, R. J. *Handb. Porous Solids* **2002**, *1*, 432.
(34) Hodnett, B. K. *Heterogeneous Catalytic Oxidation*; Wiley: New York, 2000; p 348.
(35) Becker, J. J.; Gagne, M. R. *Acc. Chem. Res.* **2004**, *37*, 798.
(36) Davis, M. E.; Katz, A.; Ahmad, W. R. *Chem. Mater.* **1996**, *8*, 1820.
(37) Marty, J. D.; Mauzac, M. Molecular imprinting: State of the art and perspectives. In *Microlithography - Molecular Imprinting*; Springer: Berlin, 2005; Vol. 172, p 1.
(38) Diaz-Garcia, M. E.; Laino, R. B. *Microchim. Acta* **2005**, *149*, 19.
(39) Lisichkin, G. V.; Novotortsev, R. Y.; Bernadyuk, S. Z. *Colloid J.* **2004**, *66*, 387.
(40) Asanuma, H.; Hishiya, T.; Komiyama, M. *Adv. Mater.* **2000**, *12*, 1019.
(41) Collinson, M. M. *Crit. Rev. Anal. Chem.* **1999**, *29*, 289.
(42) Quaglia, M.; Sellergren, B.; De Lorenzi, E. *J. Chromatogr., A* **2004**, *1044*, 53.
(43) Feher, F. J.; Weller, K. J. *Inorg. Chem.* **1991**, *30*, 880.
(44) Feher, F. J.; Weller, K. J. *Chem. Mater.* **1994**, *6*, 7.
(45) Ghosh, N. N.; Clark, J. C.; Eldridge, G. T.; Barnes, C. E. *Chem. Commun.* **2004**, 856.

(46) Sanchez, C.; Ribot, F.; Doeuff, S. Transition Metal Oxo Polymers Synthesized Via Sol-Gel Chemistry. In *Inorganic and Organometallic Polymers with Special Properties*; Laine, R. M., Ed.; Kluwer: Dordrecht 1992; p 267.
(47) Schottner, G. *Chem. Mater.* **2001**, *13*, 3422.
(48) Vioux, P. A. *Chem. Mater.* **1997**, *9*, 2292.
(49) Apperley, D.; Hay, J. N.; Raval, H. M. *Chem. Mater.* **2002**, *14*, 983.
(50) Yan, W.; Mahurin, S. M.; Overbury, S. H.; Dai, S. *Chem. Mater.* **2005**, *17*, 1923.
(51) Lorret, O.; Lafond, V.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **2006**, *18*, 4707.
(52) Clark, J. C.; Saengkerdsub, S.; Eldridge, G. T.; Campana, C.; Barnes, C. E. *J. Organomet. Chem.* **2006**, *691*, 3213.

BET nitrogen adsorption–desorption surface area analyses were performed using a Quanta Chrome Nova 1000 instrument.

General Procedure for the Preparation of Cross-Linked Solids. In a typical reaction, 1.00 g (0.539 mmol) of Si_8O_{12}-$(OSnMe_3)_8$ in a Schlenk vessel was heated at 100 °C overnight to remove waters of hydration in the crystal.[52] The dry tin cube was dissolved in 40 mL of solvent, and 0.732 g (4.31 mmol) of $SiCl_4$ (8:1 $SiCl_4/Si_8O_{12}(OSnMe_3)_8$; 4:1 Cl/SnMe$_3$) was vapor transferred into the reaction at −78 °C. The solution was refluxed under static vacuum for ∼2 days whereupon all volatiles were removed under dynamic vacuum.

Tailoring the Matrix: The Method of Sequential Additions. In a typical reaction to synthesize silicate matrices containing silyl linking units having no residual chloride groups, an initial dose of 0.051 g (0.373 mmol) of $HSiCl_3$, for example, was added to approximately 1 g (0.539 mmol) of $Si_8O_{20}(SnMe_3)_8$ dissolved in 40 mL of solvent and allowed to stir for 2 days while refluxing under static vacuum. A second cross-linking dose of 0.458 g (2.69 mmol) of $SiCl_4$ was added, and the reaction was refluxed for 2 additional days under static vacuum after which a clear gel was observed. All volatiles were removed, and an off-white powder was obtained. This powder was then exposed to an excess of $SiCl_4$ in the gas phase. All volatiles were removed, and the resulting white powder was heated overnight at 100 °C under dynamic vacuum. A similar procedure was used to synthesize analogous materials containing dimethylsilyl linking units.

A slightly different synthetic approach was utilized to obtain a bb platform having singly connected (capping) dichlorohydridosilyl or chlorodimethylsilyl groups on the surface of the cross-linked silicate matrix. A solid bb matrix was synthesized by dissolving 1.00 g of $Si_8O_{20}(SnMe_3)_8$ in toluene and adding 0.274 g (1.62 mmol) $SiCl_4$ at −78 °C. This mixture was refluxed under static vacuum for 2 days. All volatiles were removed, and the remaining white powder was exposed to 0.458 g (2.70 mmol) of $HSiCl_3$ vapor overnight. All volatiles were removed, and the final product was heated under dynamic vacuum at 100 °C overnight. A similar procedure was used to synthesize an analogous material containing chlorodimethylsilyl groups.

Results and Discussion

The synthesis and characterization of nanostructured, silicate materials having centers with identical immediate environments was achieved for a series of reactions of Si_8O_{20}-$(SnMe_3)_8$ with $SiCl_4$, $HSiCl_3$, and Me_2SiCl_2. These reactions involve linking together Si_8O_{20} silicate building units via metathesis reactions where silyl chloride groups replace the trimethyltin groups around the tin cube to form new siloxane linkages and trimethyltin chloride. Under the nonaqueous conditions utilized for these reactions, the silylchloride linkers will *only* react with functional groups on the bb (eq 1) preventing the formation of domains of interconnected linking groups within the resulting solid matrices. This linking together of preformed molecular precursors is referred to as a "building block" approach to materials synthesis.

The conditions utilized to produce cross-linked bb materials are generally mild enough such that disruption of the Si_8O_{20} bb does not occur. Under these conditions, the linking reactions are also irreversible and lead to random substitution patterns of links around the eight positions on the cubic spherosilicate bb and random distributions of linking groups in the matrix. Thus, these materials are expected to be
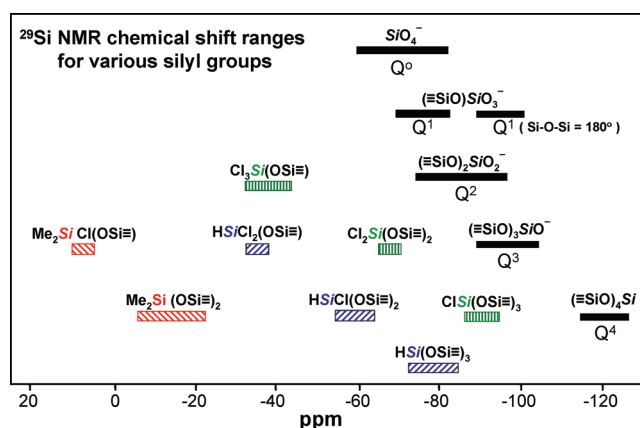

Figure 1. ^{29}Si SSNMR chemical shift ranges for the linking groups involved in the bb matrices described in these investigations.

amorphous, porous glasses as a result of inexact fitting of bb's in the matrix.[53,54]

The amorphous nature of these materials makes traditional diffraction methods inapplicable for structural characterization. However, ^{29}Si SSNMR provides a powerful tool to obtain information about the structure of these materials via chemical shift and CP behavior. Figure 1 summarizes the chemical shift ranges that have been reported in the literature for ^{29}Si nuclei in silicates as well as empirically derived chemical shift ranges found for silyl chloride linking groups described in this study.[55]

The ease with which information can be obtained from chemical shift analysis of ^{29}Si SSNMR spectra makes silyl chloride linkers good candidates for model studies to develop the methods ultimately needed to produce single site heterogeneous catalysts by design (vide infra). Few metals having potential catalytic properties can be as easily observed using SSNMR.[56,57]

Despite the information gained from SSNMR, there are limitations to its application in this setting. Deeply embedded $Si(OSi\equiv)_4$ Q^4 silicon nuclei in silicates have few effective spin–lattice relaxation mechanisms available to them, and thus relaxation of these nuclei can be extremely long.[58] Consequently, quantitative information obtained from integrated signal intensities is generally not reliable because of variable saturation of NMR transitions. Attempts to address this problem with long relaxation delays (60 s) to obtain quantitative relative integrations were unsuccessful in our studies given the instrument time available to us.

Another experiment available in SSNMR spectroscopy utilizes the dipolar interactions of ^{29}Si nuclei with hydrogen nuclei present in the matrix. This interaction can be exploited to observe and assign signals using CP pulse sequences.[55] CP enhancements can also be used advantageously to observe signals from ^{29}Si nuclei close to hydrogen atoms that are not prominent in MAS experiments because of low concen-

(53) Eckert, H. *NMR Basic Principles Prog.* **1994**, *33*, 125.
(54) Baldus, H.-P.; Jansen, M. *Angew. Chem., Int. Ed.* **1997**, *36*, 328.
(55) Engelhardt, G.; Michel, D. General aspects of ^{29}Si and ^{27}Al NMR of the silicate and aluminosilicate framework solids. *High Resolution SSNMR of Silicates and Zeolites*; Wiley: New York, 1987; p 106.
(56) Smith, M. E. *Nucl. Magn. Reson.* **2000**, *29*, 251.
(57) Gervais, C.; Smith, M. E.; Pottier, A.; Jolivet, J. P.; Babonneau, F. *Chem. Mater.* **2001**, *13*, 462.
(58) Larsen, F. H.; Farnan, I. *Chem. Phys. Lett.* **2002**, *357*, 403.
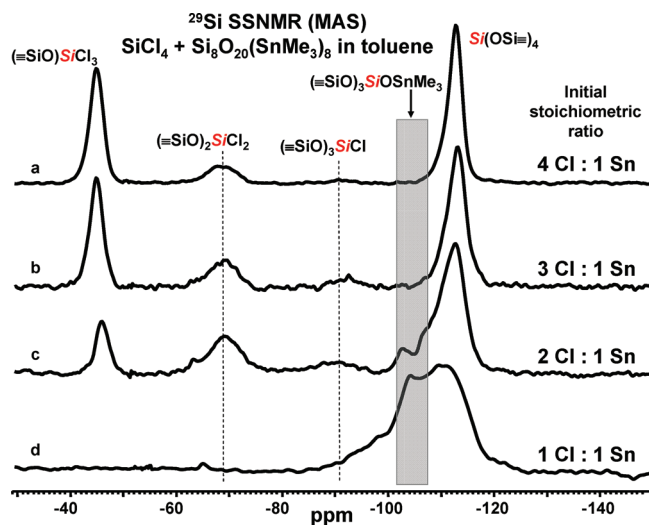
Figure 2. ^{29}Si SSNMR traces for the glasses isolated starting with different stoichiometric ratios of SiCl₄ and Si₈O₂₀(SnMe₃)₈ in toluene. Conditions: 80−90 °C, 1−2 days.

Figure 3. ^{29}Si SSNMR traces for the glasses isolated starting with different stoichiometric ratios of SiCl₄ and Si₈O₂₀(SnMe₃)₈ in hexane. Conditions: 60−70 °C, 1−2 days.

trations. Examples of ^{29}Si signals that are expected to show large enhancements for linking species used in these investigations are dimethylsilyl (=SiMe₂) and hydrido silyl (≡SiH) groups. Si₈O₂₀ cage silicon atoms bearing these linking groups as well as cage silicon bearing trimethyltin groups are also expected to show small signal enhancements due to longer range dipolar interactions in CPMAS experiments but, as will be shown below, not nearly as large as for the two groups mentioned above.

Constructing Cross-Linked Building Block Networks− General Synthetic Considerations. As a preface to preparing tailored solids, we briefly explored several of the basic synthesis parameters which affect how cross-linking occurs and the properties of the final resulting bb matrices that were formed. These parameters were (1) the ratio of linker to bb; (2) the specific type of chlorosilane reagent used to cross-link bb's; (3) the solvent; and (4) the temperature used for cross-linking. The growth of these materials is expected to occur by first forming small, soluble oligomeric species consisting of only a few linked bb's. As the reaction proceeds, these oligomeric species should also become linked to one another until they reach a critical molecular weight which causes phase separation.

The first chlorosilane reagent studied to monitor this process was silicon tetrachloride. Four ratios of SiCl₄ per trimethyltin group on Si₈O₂₀(SnMe₃)₈ were used to investigate the effects of initial stoichiometry on the extent of cross-linking that is present in the solid products. The range of stoichiometric ratios studied ranged from one Si−Cl per trimethyltin group (2 SiCl₄/cube) to four Si−Cl per trimethyltin group (8 SiCl₄/cube). If all Si−Cl groups present in silicon tetrachloride remain active throughout the cross-linking process, then a maximum of four Si₈O₂₀ cubes can become connected to the linking silicon (i.e., a four-connected center).

Figure 2 shows the ^{29}Si MAS SSNMR for the products of this series of reactions run in toluene at 80−90 °C. When an excess of SiCl₄ is reacted with the tin cube, the presence of capping groups (−45 ppm) and dichlorosilyl linking
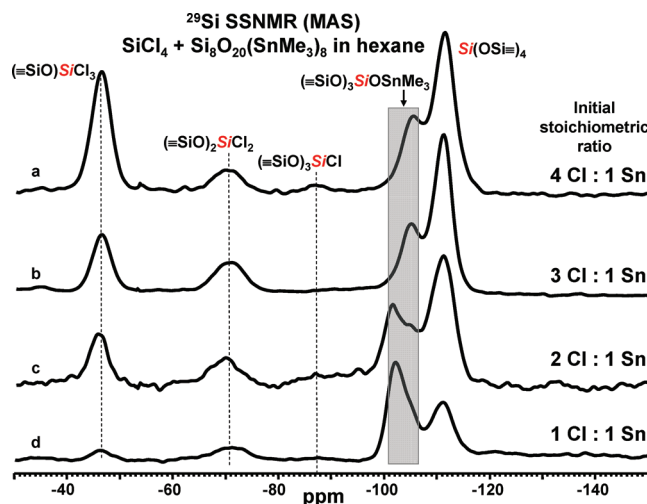
groups (−68 ppm) connecting two bb's and possibly a small signal assigned to three-connected Cl−Si(O-cube)₃ groups (−90 ppm) are observed (traces c and d). The absence of a signal between −99 and −104 ppm in spectrum a indicates that all trimethyltin groups have been lost from the matrix in this sample. X-ray fluorescence analyses of these materials confirm that virtually all tin (<0.1 wt %) is removed by this procedure. The complete removal of trimethyltin groups in this and other samples containing excess linking reagent is important in that it indicates that all SnMe₃ groups remain accessible to reaction throughout the various phases of matrix growth. NMR analyses of the tin byproducts indicate that trimethyltin chloride is the only volatile compound formed in the reaction.

As the stoichiometric amount of SiCl₄ is decreased, the distribution of linking groups shifts toward higher cross-linking and an increase in the number of residual trimethyltin groups is observed. At the lowest stoichiometric ratio of SiCl₄ to cube (trace d), only siloxane signals assignable to linkages connecting three and four bb's are observed along with a large signal assigned to residual trimethyltin groups in the matrix. The ^{29}Si MAS NMR spectrum of this highly cross-linked material also shows a broadening of the Q⁴ signal in the spectrum assigned to both four-connected linking silicon atoms and cage silicon atoms. These two distinct types of silicon environments cannot be distinguished via their ^{29}Si signals because both are of the same general form, Si(OSi≡)₄. The broadening of this signal is consistent with the development of an increasing number of local environments around pseudo-tetrahedral Q⁴ type silicon atoms in the sample which results from extensive cross-linking. When a similar set of reactions were run in hexane at 50 °C, the degree of cross-linking again increases as the concentration of SiCl₄ decreases (Figure 3). However, when the same initial stoichiometries are compared, the spectra from the reactions run in toluene at higher temperatures generally display a greater degree of cross-linking than those run in hexane. Furthermore, in the lower temperature reactions, residual SnMe₃ groups are present in all instances. These observations are consistent with the rate of reaction of individual Si−Cl

Table 1. BET Surface Area Analysis of the Solids Resulting from the Reaction of SiCl$_4$ + Si$_8$O$_{20}$(SnMe$_3$)$_8$ under the Conditions Given^a

conditions	Cl:Sn	surface area (m^2/g)	total pore volume (cm^3/g)	average pore radius (Å)
toluene, 80–90 °C, 2 days	4:1	203	0.165	17
toluene, 80–90 °C, 2 days	3:1	258	0.180	14
toluene, 80–90 °C, 2 days	2:1	570	0.385	13
toluene, 80–90 °C, 2 days	1:1	590	0.423	14
hexanes, 50 °C, overnight	4:1	low^b	low	low
hexanes, 50 °C, overnight	3:1	low^b	low	low
hexanes, 50 °C, overnight	2:1	low^b	low	low
hexanes, 50 °C, overnight	1:1	low^b	low	low

^{a} Absorption Gas: nitrogen. Pore size distributions calculated using standard BJH equations. ^{b} Surface area estimated to be <5 m^2/g.
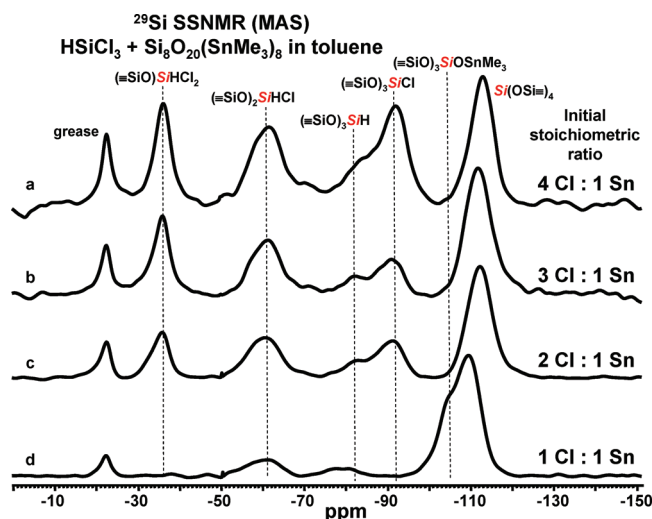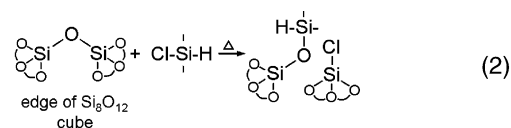

Figure 4. ^{29}Si SSNMR traces for the glasses isolated starting with different stoichiometric ratios of HSiCl$_3$ and Si$_8$O$_{20}$(SnMe$_3$)$_8$ in toluene. Conditions: 80–90 °C, 1–2 days.

groups present on the linker decreasing as each subsequent silylchloride group reacts.

Comparison of BET surface area measurements for the products of the SiCl$_4$ reactions described above clearly shows that products from reactions in hexane are not high surface area materials (Table 1). The dramatic difference in surface area between the two families of samples is consistent with the initial formation of small oligomeric species in hexane made up of only a few cross-linked Si$_8$O$_{20}$ bb's while higher surface area samples result from the formation of extended, cross-linked silicate matrices with open pores. Precipitation of the oligomers at an earlier stage of matrix growth when hexane is used as the solvent appears to inhibit further cross-linking.

Similar correlations were observed between the initial reaction stoichiometry and the degree of cross-linking in reactions involving HSiCl$_3$ or Me$_2$SiCl$_2$ with the tin cube (Supporting Information). In the case of trichlorosilane HSiCl$_3$, however, evidence for disruption of the Si$_8$O$_{20}$ core was observed in one instance. When large excesses of HSiCl$_3$ are heated with the tin cube at high temperature in toluene, a significant signal at ~−90 ppm is observed in the ^{29}Si SSNMR (Figure 4, traces a–c). On the basis of chemical shift and no observable enhancement in CPMAS spectra relative to signals assigned to groups containing the Si−H moiety (vide infra), we assign this peak to chlorosiloxane groups of the form (≡SiO)$_3$SiCl. An explanation for the

development of chlorosiloxane groups in the matrix is chlorine transfer from the linker to silicon atoms associated with the cube core as illustrated in eq 2.

$$(2)$$

This is the only case where evidence for attack on the cube has been observed in our investigations. Spectrum d in Figure 4 shows that when lower stoichiometric amounts of the linker are used, no evidence for disruption of the cube is observed. Finally, parallel experiments with trichlorosilane using hexane as the solvent at lower temperature showed no evidence for disruption of the cube for any of the stoichiometries investigated (Supporting Information).

Comparison of surface area measurements for different linkers and different stoichiometric ratios shows that the overall surface area in these bb matrices is a sensitive function of the cross-linking that develops. When large excesses of linker are used initially, the major product in the reaction with trimethyltin groups is the one-connected, capping group. Matrices that have mostly capping groups and low numbers of multiply connected linkers give rise to products with low surface areas. The average connectivity of linkers in a matrix may be increased by decreasing the stoichiometric ratio of linking reagent to bb. These conditions, together with higher reaction temperatures, generally yield porous solids with high surface area that are divided between micro- and a broad distribution of mesopores (Supporting Information).

Another noteworthy observation from these experiments is that even at intermediate linker-to-bb ratios (Cl/SnMe$_3$ ~ 0.5−1.5), significant numbers of unreacted SnMe$_3$ groups remain in the solid products. This fact, together with the previous discussion, allows us to present a qualitative picture of the microstructure of these bb matrices as they evolve and grow into macromolecular solids. The high numbers of capping groups that develop with excess linking reagent and presence of residual tin groups at intermediate ratios of linker-to-bb indicate that the rate of reaction of a chloride containing linker slows as it cross-links more cubes. This can arise from a number of factors. Electronically, more highly oxygenated silicon linking centers are expected to have lower reactivity than polychloro centers. Furthermore, as linking centers become "embedded" in the matrix, steric access to them for further reaction is expected to be more hindered and thus slower. Finally, as the Si$_8$O$_{20}$ matrix becomes more highly cross-linked, it also becomes more rigid. Residual trimethyltin groups should become spacially isolated from one another and react with additional linking reagent to form capping siloxane groups.

The simultaneous observation of both Si−Cl and −SnMe$_3$ groups in several of the final products is also important. Depending on the solubility of the oligomers that develop, phase separation of these intermediates impacts the rate at which SnMe$_3$ groups react. If phase separation occurs too soon (i.e., at the stage of small oligomers), then low surface area products are obtained which contain a significant

number of trimethyltin groups. Additionally, as bb's become locked into the developing matrix, unreacted trimethyltin groups will become spatially isolated from Si−Cl groups and thus unable to react.

This model relating microstructure and macroscopic properties of bb solids may be reconstituted into a methodology by which tailored, silicate materials can be prepared by design. Tailoring in this context refers to preparing cross-linked bb matrices containing specific, unique types of linking groups. For example, we would like to be able to prepare samples that contain only embedded, dimethylsilyl linking groups connecting two bb's and no other group derived from Cl$_2$SiMe$_2$.

Nanostructured Solids. We refer to the strategy introduced above as the *method of sequential additions* because it relies on both the sequence and the size of doses of different cross-linking reagents in tailoring the distribution of such groups in the matrix. The two types of groups that we focus on here are "embedded" cross-linking groups wherein maximum connectivity to the matrix is achieved and "surface" groups which do not cross-link bb's at all but are singly connected to isolated corners of immobilized building blocks in the matrix.

To obtain embedded silyl units within a silicate bb matrix, a limiting initial dose of a linking reagent is added to a solution of the tin cube. This should result in complete reaction of silyl chloride groups and thus 100% cross-linking around these linking moieties. The reaction mixture at this point should contain a number of small, oligomeric species and possibly unreacted bb's. Exposure of this mixture to a second dose of a different linking reagent will serve to link oligomers and reduce the number of unreacted trimethyltin groups on the bb's. The correct amounts of doses could be determined analytically via an understanding of the relative rates of coupling as a function of connectivity or empirically through a few trial reactions.

To obtain an extended matrix having only "surface" groups, the sequence of doses must be reversed and adjusted to first produce a bb "platform" composed of rigid, cross-linked bb's in which some unreacted tin groups are still present. If the bb's are indeed rigidly held in the matrix, then few trimethyltin groups will be close enough together on the platform to form additional cross-links when a second reagent is delivered, regardless of the size of the dose. Reaction with tin groups then leads to isolated, one-connected surface groups derived from the second linking reagent. The main elements of the sequential addition strategy are illustrated schematically in Figure 5.

Matrices Containing Embedded Cross-Linking Groups. The first example of this strategy involved preparing a matrix that has only three-connected trichlorosilane derived linking groups. A limiting dose of HSiCl$_3$ added to the tin cube in toluene (see Experimental Section) followed by several doses of silicon tetrachloride gave rise to a white, water sensitive solid whose ^{29}Si SSNMR (MAS) is shown in Figure 6. On the basis of our previous assignments, signals for a distribution of capping and cross-linking groups derived from SiCl$_4$ are readily seen as well as the expected Q^4 silicate signal. Signals for any groups containing the H−Si≡ moiety are
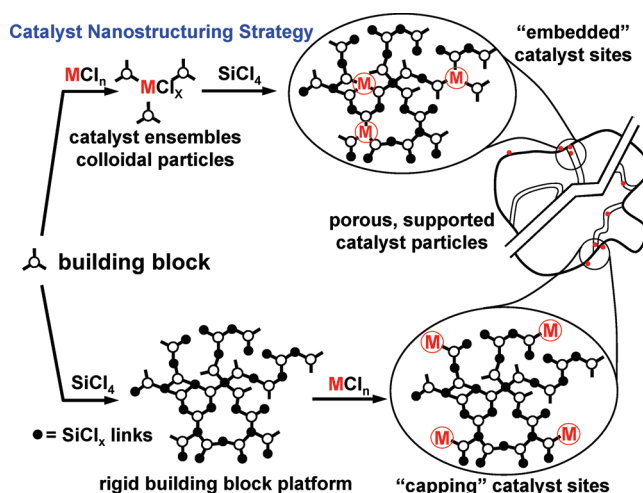

Figure 5. Schematic illustration of sequential addition strategy leading to nanostructured bb matrices
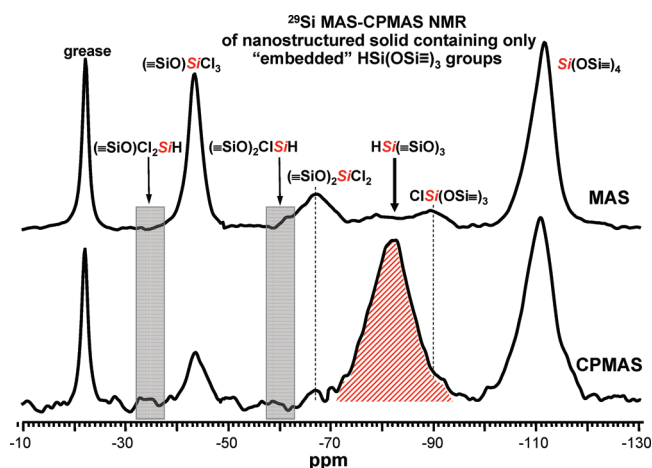

Figure 6. SSNMR experiments (MAS and CPMAS) illustrating a linking group distribution tailored for "embedded" HSi(OSi)$_3$ groups in a bb solid.

not obvious. A second SSNMR spectrum taken combining MAS and CP shows a large new peak at −83 ppm which may be assigned to the presence of three-connected (≡SiO)$_3$Si−H groups in the sample. Just as important is the lack of any recognizable signals in the CPMAS spectrum at chemical shifts which could be assigned to either two-connected or capping Si−H-containing groups. This sample represents the successful synthesis of a tailored matrix of cross-linked Si$_8$O$_{20}$ bb's containing only three-connected Si−H linking groups interspersed with a distribution of linking groups derived from silicon tetrachloride. The total surface area measured for this sample was 513 m^2/g.

Following a similar procedure but using a combination of dichlorodimethylsilane and silicon tetrachloride gives rise to the MAS and CPMAS ^{29}Si SSNMR spectra (Supporting Information) which clearly confirms the presence of the two-connected dimethylsiloxane linker while showing no sign of the analogous capping group. The surface area for this sample was found to be 740 m^2/g.

Matrices Containing Surface or Capping Silane Groups. Reversing the addition sequence leads to materials wherein the trichloro- and dimethylsilane linking precursors end up exclusively as "capping" groups connected to the matrix by only one Si−O-silane bond. Figure 7 shows the MAS and
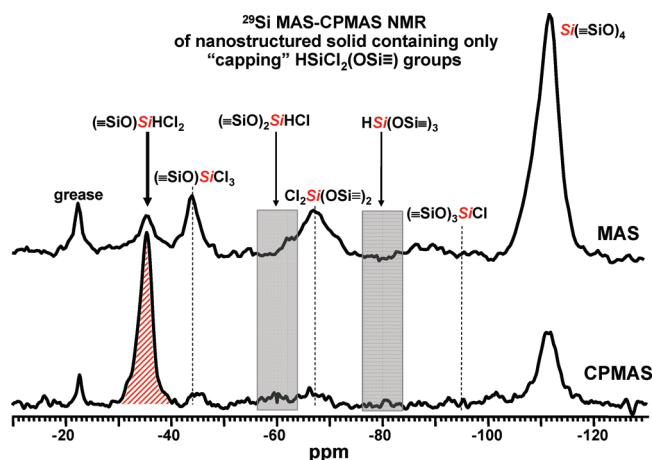
Figure 7. SSNMR experiments (MAS and CPMAS) illustrating a linking group distribution tailored for "surface" $HSiCl_2(OSi)$ groups in a bb solid.

^{29}Si SSNMR spectra for a support in which initial cross-linking with $SiCl_4$ created a platform Si_8O_{20} cubes containing some unreacted $SnMe_3$ left on the surface. Consistent with the rigidity of the matrix, when the matrix is exposed to an excess of $HSiCl_3$, only one-connected "capping" groups are seen in the NMR. A similar result is obtained for a sequence of $SiCl_4$ followed by Me_2SiCl_2 wherein only one-connected Me_2SiCl groups are observed in the NMR (Supporting Information)

Summary and Conclusions

The reactions of the trimethyltin substituted cubic spherosilicate, $Si_8O_{12}(OSnMe_3)_8$, with several silyl chloride linking reagents to form bb solids are described. An initial round of investigations probing the effects of initial stoichiometry, solvent, and temperature gave rise to a model for how these matrices grow and evolve as a function of cross-linking. The major steps in constructing porous, high surface area cross-linked solid materials are the following: (1) Initial fast reaction of Si−Cl and trimethyltin groups forms capping siloxane moieties on the corners of the cube with loss of $ClSnMe_3$. (2) Subsequent reactions of Si−Cl groups are slower such that if an excess of the linker is present, a high number of capping siloxane groups are formed with low cross-linking in the matrix. If lower amounts of the linking silyl chloride reagent are present, then Si−Cl groups on the capping siloxane moieties will react further to form linking groups with higher connectivities to cubes in the matrix. (3) Solvation (i.e., solubility) of the growing bb oligomers influences growth of the matrix by determining when phase separation occurs. (4) Trimethyltin groups on the growing matrix remain accessible to linking reagent throughout growth of the matrix. At higher levels of cross-linking,

however, tin groups become spatially isolated from one another on the rigid matrix such that reactions with silyl chloride reagents at the later stages of matrix growth yield only capping groups.

This model for cross-linking and evolution of these matrices can be used to prepare nanostructured bb solids by design. The method of sequential additions involves exposing solutions of the tin cube to measured doses of linking reagents at prescribed time intervals. The basic premise is simply that a limiting amount of cross-linking reagent will form links subject to the factors discussed above until a maximum connectivity is achieved. The collection of oligomers formed will be uniform from the standpoint of all linking units having the same connectivity. Subsequent doses of other linking reagents will serve to continue cross-linking until a macromolecular solid is formed. This sequence of additions yields a specific type of "embedded" site in the matrix. Reversing the order of linking reagents and adjusting the dose equivalents will ultimately give rise to a matrix of cross-linked cubes in which a silane group can be placed exclusively in "surface" positions connected to cubes in the matrix by only one siloxane bond. This methodology is demonstrated here for trichlorosilane and dimethyldichlorosilane linking reagents in which either can be inserted into the growing matrix either in embedded or in surface positions.

The method of sequential additions is quite general and can be applied to numerous metal and main group chloride reagents such as $AlCl_3$, $SnCl_4$, $TiCl_4$, $VOCl_3$, VCl_4, and WCl_6. All of these reagents have been tested in our laboratories and found to react with the tin cube in a manner similar to that of the silyl chlorides reported on here. This methodology thus appears to address a long standing challenge in the fields of catalysis and materials science of preparing site isolated, atomically dispersed metals in and on metal oxide matrices in which all the metal sites are identical. Studies with the linking reagents listed above will be described in the near future.

Supporting Information Available: SSNMR [29]Si spectra for varying initial stoichiometries of linking reagents $HSiCl_3$ and Me_2SiCl_2 and the cube, $Si_8O_{20}(SnMe_3)_8$, representative pore size distribution for high surface area solids investigated here, and summaries of surface areas and pore size distributions for $HSiCl_3$ and Me_2SiCl_2 derived building block solids (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM070038B