Microporous inorganic/organic hybrids via oxysilylation of a cubic symmetry nanobuilding block 
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[(\text{HMe}_2\text{SiOSiO}_{1.5})_8] \text{ with } \text{R}_x\text{Si(OEt)}_{4-x}
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The B(C_6F_5)_3 catalyzed Piers-Rubinsztajn (oxysilylation) reaction of the cubic symmetry Q-cage \([(\text{HMe}_2\text{SiOSiO}_{1.5})_8]\) with ethoxysilanes in hexane forms microporous 3-D networks coincident with ethane evolution. Slow drying provides monoliths whereas fast drying provides powders. The reaction is most efficient if initiated at 60°C for 5 min and then allowed to progress at ambient. The products offer high specific surface areas [SSAs > 700 m^2/g, e.g. with Si(OEt)_4], with micropores of 0.6–2.0 nm, mesopores of 2–40 nm, total pore volumes \(\approx 0.5\) cc/g, and thermal stabilities to 320°C. Changes in reaction conditions (times, solvent volumes, catalyst concentrations) do not significantly change product properties pointing to rapid and complete reaction as evidenced by the near absence of residual Si-H under all conditions for 1:1 Si-H:Si-OEt ratios. RSi(OEt)_3 gives similar 3-D microporous gels. Smaller R groups give higher SSAs than those with large R groups; however, R = n-octyl is not porous. Rigid, bridged compounds [(EO)_xSi–R–Si(EO)_y] (R = phenyl, biphenyl) offer high SSAs whereas flexible bridges (R = (CH_2)_x or x) give reduced SSAs. All materials were characterized by FTIR, TGA, XRD and BET. XRD studies show periodicities suggesting some long range ordering as might be expected for reactions with cubic symmetry Q_8 cages. However, the fast reaction rates likely generate kinetic rather than thermodynamic products that cannot be expected to exhibit high degrees of ordering. Gel affinities for specific organics were studied showing some preferential ability to absorb specific solvents for example the 1:1 OHS:vinylSi(OEt)_3 gels were more selective for toluene than the 1:1 OHS:TEOS gels.

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1. Introduction

Micro- (pore sizes <2 nm) and meso-porous (pores 2–50 nm) materials have been subjects of great interest for more than half a century because they offer many distinct properties of potential utility to diverse fields ranging from catalyst substrates, to biosorbents, to drug storage and delivery, to remediation systems, to living cell containers, to gas sieving, to nano-reactors, to gas storage and vacuum insulation panel core materials.\(^1\)-\(^3\)\(^9\)

Over this period of time, researchers have developed diverse synthetic routes to micro- and meso-porous materials in the general categories of amorphous inorganics, amorphous organics and crystalline analogs including zeolites, metal organic framework (MOFs), and covalent organic framework (COFs) materials. Most of these syntheses are aqueous in nature and many require strongly basic environments, elevated temperatures and relatively long reaction times. Only a small fraction of the reported synthetic methods rely on the formation of covalent bonds to build highly symmetrical 3-D porous structures.\(^17\)-\(^39\)

Most high surface area materials containing silicon are made via sol–gel polymerization of tri- and tetraalkoxysilanes.\(^40\)-\(^42\) These materials are made by acid or base catalysis through controlled hydrolysis and condensation to form highly cross-linked xero- or aerogels depending on the drying method. Surface areas of >1000 m^2/g have been achieved by these methods, however the long reaction times necessary and the use of aqueous/polar solvent systems to make these materials by sol–gel processing has prompted exploration of simple alternative synthetic methods to high surface area materials, especially those that avoid aqueous solutions, use low catalyst loadings (<10 mol%), and can be made within minutes rather than hours or days.

Functionalized silsesquioxanes have been of considerable interest for developing high surface area materials due to their ordered 3D structures, which position crosslinks in specific positions in Cartesian space with excellent spatial orientation and uniform porosity. Silsesquioxide based high SSA materials have been synthesized by Friedel–Crafts,\(^43\)-\(^45\) cross-coupling,\(^41\)-\(^46\)-\(^48\) thiol-ene,\(^49\) radical polymerization,\(^50\) polyesters/polyimides,\(^51\)-\(^52\) and hydroisilylation.\(^42\)-\(^53\) The best of these materials made by Friedel–Crafts reaction was reported by Chaikittisilp et al., in which they have achieved 2500 m^2/g.\(^53\) However most methods are limited due to their multistep reactions, and use of expensive or large amounts of catalyst.

We report a new, very general method of synthesizing micro/mesoporous hybrid materials based on Q-type siloxanes with 3-dimensional ordering using the Piers-Rubinsztajn reaction, which we refer to here as oxysilylation, reaction (1).\(^54\)-\(^60\) In oxysilylation, an Si–H bond is reacted with an alkoxysilane in the presence of catalytic amounts of (C_6F_5)_3B, generating a volatile compound and releasing ethane. The synthetic approach is extremely fast, highly selective, and facile. The method produces fully ordered nanostructured materials that can be tailored by changing reaction conditions such as temperature, solvent, and catalyst loadings. Continuous control of reaction conditions offers the potential to produce unique functional materials via a simple reaction process.
alkane and a new Si–O–Si linkage. The suggested mechanism is shown in reaction (2).58)–61)

Scheme 1. General oxysilylation reaction using two alkoxy silanes.

Scheme 1 provides a general synthesis of the micro-/mesoporous materials we have learned to prepare using two types of alkoxy silane precursors. The key to the efficacy of this reaction (5–40 min at 60°C) is the use of micromolar amounts of catalyst [(C₆F₅)₃B]. A further advantage is that the only leaving group is an alkane. Finally, the reactions can be run in low boiling solvents that are easily removed to give microporous powders or monoliths.

If one component is used in excess, e.g. OHS, then the resulting gel will contain reactive sites for the introduction of secondary and tertiary functional groups providing a simple route to multiple types of materials for diverse applications.

2. Experimental

2.1 Materials

Chemicals and solvents were obtained from commercial suppliers and used without further purification, unless otherwise indicated. Octakis(dimethylsiloxy)octasilsesquioxane, [HSiOSiO₁.₅]₈ (OHS) and tris(pentafluorophenyl)boron [B(C₆F₅)₃] were supplied by Mayatierials Inc. and Oakwood Chemicals, respectively. Hexane and dichloromethane (CH₂Cl₂) were purchased from Fisher Scientific. CH₂Cl₂ was distilled from CaH₂ under N₂ prior to use. All other chemicals were purchased from Sigma Aldrich or Gelest Inc. and used as received.

2.2 Synthetic methods

2.2.1 Copolymerization of OHS with TEOS

1:1 molar equivalents of OHS:TEOS (SiH/SiOEt) were used. OHS (0.500 g, 3.94 mmol of Si–H) was dissolved in 15 mL of hexane in a 25 mL round-bottom flask equipped with a magnetic stirrer. Alternately a 20 mL glass vial can be used. TEOS (0.206 g, 3.94 mmol of OEt) was added to the solution. The solution was stirred at 60°C in a thermostatted silicone oil bath. After 5 min, B(C₆F₅)₃ (3 mg, 6 μmol) dissolved in 500 μL of CH₂Cl₂, was added using a micropipette. The solution was then either heated for a period of only 5 min or several hours and then removed from the oil bath. A gel forms 1–2 min after addition of B(C₆F₅)₃. Samples removed from the oil bath after 5 min show progressive gelation from the bottom up and a gel front forms with time.

Gels were also formed from at 60°C, at ambient and below using 1:1 molar equivalents of OHS:TEOS (SiH/SiOEt). OHS (0.500 g, 3.94 mmol of Si–H) was dissolved in 15 mL of hexane in a 20 mL glass vial. TEOS (0.206 g, 3.94 mmol of OEt) was added to the solution. B(C₆F₅)₃ (3 mg, 6 μmol) dissolved in 500 μL of CH₂Cl₂, was added using a micropipette. The solution was then either heated for a period of only 5 min or several hours and then removed from the oil bath. A gel forms 1–2 min after addition of B(C₆F₅)₃. Samples removed from the oil bath after 5 min show progressive gelation from the bottom up and a gel front forms with time.

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Thereafter the resulting gel was dried at ambient. The neck of the round-bottom flask or vial was then covered with aluminum foil with a single hole perforated using a syringe needle (0.7 mm dia.) to control drying rates. The gel dries at 20°C in 72–240 h. Significant shrinkage occurs on drying resulting in single piece, glassy solids. Faster drying rates provide powders.

2.2.2 General copolymerization of OHS with RSi–(OEt)₃ where R = Ph, vinyl, CH₃, (CH₂)₃Cl, (CH₂)₂CF₃, (CH₃)₂H

1:1 molar equivalents of OHS:RSi(OEt)₃ (Si–H/Si–OEt) were used to prepare the gels. OHS (0.500 g, 3.94 mmol of Si–H) was dissolved in 15 mL of hexane in a 25 mL round-bottom flask.
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\[\text{RSi(OEt)}_3\] (3.94 mmol of OEt) was added to the flask. The solution was stirred at 60°C for 5 min. B(C\(_6\)F\(_5\))\(_3\) (3 mg, 7 \(\mu\)mol) was dissolved in 500 \(\mu\)L of CH\(_2\)Cl\(_2\) then added to the resulting solution. Further reactions and drying were run as above.

2.2.3 General copolymerization of OHS with (OEIp)\(_2\)Si–R–Si(OEIp)\(_3\) where R = Ph, biphenyl, (CH\(_2\))\(_2\), (CH\(_3\))\(_2\)

1:1 molar equivalents of Si–H/Si–OEt were used to prepare the gels. OHS (0.500 g, 3.94 mmol of Si–H) was dissolved in 15 mL of hexane in a 25 mL round-bottom flask equipped with a magnetic stirrer. (OEIp)\(_2\)Si–R–Si(OEIp)\(_3\) (3.94 mmol of OEt) was added to the flask. The solution was stirred at 60°C for 5 min. B(C\(_6\)F\(_5\))\(_3\) (3 mg, 7 \(\mu\)mol) was dissolved in 500 \(\mu\)L of CH\(_2\)Cl\(_2\) then added to the resulting solution. Resulting gels were further reacted and dried as described above.

2.3 Analytical methods

2.3.1 Fourier–transform infrared spectroscopy (FTIR)

Diffuse reflectance Fourier transform (DRIFT) spectra were obtained using a Nicolet 6700 Series FTIR spectrometer (Thermo Fisher Scientific, Inc., Madison, WI). Optical grade KBr (International Crystal Laboratories, Garfield, NJ) was ground with 1.0 wt% of the sample to be analyzed. The ground powder was packed into a sample holder and leveled off with a glass plate to give a smooth surface. The FTIR sample chamber was purged continuously with N\(_2\) prior to data acquisition. 64 scans were averaged for each spectrum in the range 4000–400 cm\(^{-1}\) with a precision of \(\pm 1\) cm\(^{-1}\).

2.3.2 Specific surface area (SSA) and porosity analyses

Were carried out using an ASAP 2020 sorption analyzer (Micromeritics Inc., Norcross, GA). Samples (200 mg) were degassed at 150°C/8 h. Each analysis was run at 196°C (77 K) with \(N_2\). The SSAs were determined by the BET multipoint method using ten data points at relative pressures (p/p\(_0\)) of 0.05–0.30. The micropore size distribution was determined by the Horvath-Kawazoe method. Data points were collected with low pressure incremental dose mode at 0 < p/p\(_0\) < 0.1. Mesopore size distributions were calculated using the BJH method from data points collected at 0 < p/p\(_0\) < 1.0.

2.3.3 Thermal gravimetric analysis (TGA)

Thermal stabilities of materials under synthetic air were measured on a Q600 simultaneous TGA-DSC Instrument (TA Instruments, Inc., New Castle, DE). Before analysis, samples were ground into a powder and 15–25 mg were placed into alumina pans and then ramped from 25 to 1000°C (10°C/min). The air-flow was 60 mL/min.

2.3.4 X-ray diffraction (XRD)

Patterns were collected on a Rigaku Rotating Anode Goniometer (Rigaku Denki, LTD., Tokyo, Japan). The Jade Program 2010 (Version 1.1.5 Materials Data, Inc., Livermore CA) was used to determine the presence of crystalllographic phases. XRD scans were made from 5 to 40° 2\(\theta\), using a scan rate of 0.5° min\(^{-1}\) in 0.01° increments (2\(\theta\) min\(^{-1}\) for those in SI) and Cu K\(\alpha\) radiation (1.541\(\text{Å}\)) operating at 40 kV and 100 mA.

2.3.5 Solvent impregnation studies

Gels (500–600 mg) were ground into powders and dried in air for 30 min at 100°C. Powders were cooled to ambient and weighed. Powders were then placed in a clean beaker and covered with 20 mL of reagent grade solvent for 30 min. The mixture was then gravity filtered and the powders patted dry with a Kimwipe\(^{65}\) and air-dried for 10 min before weighing. Solvent mass retention was calculated from the difference between wet and dry mass using the following formula: \[\frac{\text{mass}_{\text{wet}} - \text{mass}_{\text{dry}}}{\text{mass}_{\text{wet}}} \times 100\% = \text{mass gain}.\]

3. Results and discussion

In this initial work, our objectives have been to undertake a simple survey beginning with the basic nanobuilding block OHS shown in Scheme 1, and study its oxysilylation reactions first with Si(OEt)\(_3\) to explore the range of conditions that can be used to produce microporous gels. Thereafter, we replaced Si(OEt)\(_3\) with selected RSi(OEt)\(_3\) and (EtO)\(_2\)Si–R–Si(OEIP)\(_3\) systems to identify sets of materials with a range of properties.

This work is considered a prelude to using excess vinyl and/or OSI\(_{\text{Me}}\)H groups in oxysilylation leaving these functionalities available for the introduction via hydrosilylation, oxysilylation, or other catalytic cross-coupling reactions of second and tertiary functional groups. However, given that OSI\(_{\text{Me}}\)H groups are also potential points of reduction, it should also be possible to form catalyst particles within these microporous gels. Hence, the work described here establishes groundwork for further, more complex studies.

We begin with a detailed analysis of oxysilylation in a OHS: Si(OEt)\(_4\) system with a 1 Si–H: SiOEt ratio that results in micro/mesoporous gels and then introduce OHS:RSi(OEt)\(_3\) systems with 1 Si–H: 1 SiOEt ratios. These gels were characterized by FTIR, TGA, \(N_2\) absorption and XRD. Then we assessed their physical properties with respect to solvent affinity.

Generally, reactions were run in 15 mL of hexane to which was added \(\approx 5 \mu\)mol (C\(_6\)F\(_5\))\(_3\)B as a dichloromethane solution. Reactions were heated to 60°C and either kept at that temperature or removed after 5 min and allowed to proceed at ambient. Initiation was typically observed within a few minutes as evidenced by the evolution of ethane bubbles. In all instances, the yields appear to be quantitative. Caution should be used as these reactions can evolve gas violently especially if the alkoxy group is MeO.

The resulting materials are similar with roughly the same SSAs and average pore sizes, without consequence to solvent volumes, catalyst concentrations or temperature as suggested by the data recorded in Table 1. These results suggest almost complete crosslinking as suggested by the FTIR studies below. Thus, solvent appears to have no influence on the reaction rate or the extent to which the reaction reaches completion under these conditions.

Note that the reactions can also be run in CH\(_2\)Cl\(_2\) albeit, the reaction temperature must be limited to the boiling point, 40°C. Reactions run in THF or EtOH are much slower as they are mild Lewis acids and the reaction is difficult to drive to completion. However, the intermediate stages lead to materials that can be used to form coatings.\(^{66}\)

The recovered gels are hydrophobic as formed and remain so on careful drying. Slowly dried samples retain the vessel shape, Fig. 1; whereas, rapid drying leads to cracking driven by changes in osmotic pressure.

3.1 FTIR analyses

Figure 2 compares the FTIR of OHS with the reaction product obtained from the stoichiometric reaction of all the Si–H groups with an equal amount of Si–OEt at 60°C in hexane. The key features of the product are the complete absence of vSi–H and the appearance of a new vSi–O band at 1040 cm\(^{-1}\) with retention of the original cage vSi–O band at 1120 cm\(^{-1}\). Indeed the FTIR spectra with the exception of the new vSi–O band at 1040 cm\(^{-1}\)
are identical to a typical FTIR spectrum of polydimethylsiloxane.\textsuperscript{52) Also worth noting is that no $\bar{\text{Si}}\text{-OH}$ bands are observed showing that there is no cleavage of $\bar{\text{Si}}\text{-O}$ bonds during this reaction, which is important for maintaining structural orientation. These results are in keeping with the TGA ceramic yields discussed below which are quite high and in keeping with complete reaction. Detailed FTIR data for the majority of the gels is given in Table S1.

| #  | Solvent Vol. (ml) | Catalyst (mg)/(μmol) | Temp. (°C) | CY (wt%) | SSA (m²/g) | Micropores (<2 nm) | Mesopores (>2 nm) | Micro + Meso (cm³/g) | Cum. pore vol. (cm³/g) | Peak pore dia. (Å) |
|----|------------------|----------------------|------------|----------|------------|---------------------|-------------------|---------------------|---------------------|---------------|
| 1  | 5 (2.5)(4.88)    | 60°C                 | 84.71      | 785      | n/a        | n/a                 | n/a               | n/a                 | n/a                 | n/a           |
| 2  | 10 (2.5)(4.88)   | 60°C                 | 86.42      | 768      | 0.28       | 7.5                | n/a               | n/a                 | n/a                 | n/a           |
| 3  | 15 (2.5)(4.88)   | 80°C                 | 87.00      | 770      | 0.28       | 7.0                | 0.35              | 0.63                | n/a                 | n/a           |
| 4  | 20 (2.5)(4.88)   | 60°C                 | 87.23      | 750      | 0.27       | 7.3                | 0.30              | 0.57                | n/a                 | n/a           |
| 5  | 10 (1.3)(2.44)   | 60°C                 | 85.68      | 520      | 0.17       | 7.0                | 0.31              | 0.48                | n/a                 | n/a           |
| 6  | 10 (5.0)(9.76)   | 60°C                 | 87.51      | 778      | n/a        | n/a               | n/a               | n/a                 | n/a                 | n/a           |
| 7  | 15 (2.5)(4.88)   | –5°C                 | 86.63      | 754      | 0.27       | 7.5                | 0.37              | 0.64                | n/a                 | n/a           |
| 8  | 15 (2.5)(4.88)   | 20°C                 | 86.50      | 756      | 0.27       | 7.5                | 0.32              | 0.59                | n/a                 | n/a           |
| 9  | 20 (2.5)(4.88)   | 60°C                 | 87.13      | 755      | n/a        | n/a               | n/a               | n/a                 | n/a                 | n/a           |
| 10 | 30 (2.5)(4.88)   | 60°C                 | 85.79      | 702      | 0.26       | 7.1                | 0.25              | 0.51                | n/a                 | n/a           |
| 11 | 40 (2.5)(4.88)   | 60°C                 | 86.68      | 713      | n/a        | n/a               | n/a               | n/a                 | n/a                 | n/a           |
| 12 | 50 (2.5)(4.88)   | 60°C                 | 82.96      | 663      | 0.25       | 7.2                | 0.23              | 0.48                | n/a                 | n/a           |

3.2 Thermal analysis (TGA/DTA) of the 1:1 OHS:TEOS dry gel

Table 1 records the ceramic yields (CY) for the sets of experiments undertaken to explore the effects of reaction conditions on the final products. The ceramic yields recorded average 85 ± 3 wt%. The theoretical ceramic yield for this system is calculated to be 94.5 wt%. Figure 3 shows a typical TGA/DTA of the 1:1 reaction product presenting a mass loss onset at ≈320°C. The mass loss is associated with an exotherm likely oxidation of residual Si-H and Si-Me groups.

Note that the mass loss in air continues to at least 800°C. This type of decomposition pattern is typical of hybrid materials that decompose with partitioning of the products into gaseous fragments and char. The char then slowly oxidizes at higher temperatures in air but remains relatively stable if heated in nitrogen.\textsuperscript{53,67)}

Several reasons can be cited for why the ceramic yield is lower than theory. One reason is that some of the starting reagents might be lost to sublimation in the TGA, e.g. OHS sublimes at 280°C in air. Alternately and typically, fragments of the gel polymer may also leave as volatiles for example, O(SiMe₂H)₂ which can be envisioned as a gaseous decomposition fragmentation product. However, the reproducibility of the reaction as determined by FTIR and TGA suggest complete reaction. There is no indication of residual Si-H groups in these materials.
although in the reactions discussed below some residual Si–H groups are seen suggesting less perfect conversions.

3.3 X-ray diffraction (XRD) of materials

Figure 4(b) provides a typical XRD and suggests a material that has significant periodicity as evidenced by peaks at 7.2, 17, and 23 °2θ. Compared to OHS, with peak locations at 8.3, 18.9 and 24.4 °2θ representing periodic distances of 1.1, 0.5 and 0.3 nm as shown in Fig. 4(a), peaks are greatly broadened and slightly shifted to the left. Peak intensities are very weak as evidenced by the noiser pattern. It appears the cross-linking of OHS:TEOS material synthesized here may be described as a cubic system like OHS, although it is difficult to clearly identify due to low crystallinity.

Peaks in Fig. 4(b) are tentatively assigned to the (100) or (010), (120), and (112) planes, respectively based on the literature. Thus, the broad peak at ≈ 7.2 °2θ suggests a larger unit cell of ≈ 1.3 nm that arises from the addition of Si–O units to the original OHS cell. The peak centered near 17 °2θ corresponds to the cage that is now expanded with the addition of 8 Si–O bonds and suggests a distance closer to 0.6–0.7 nm as might be expected. The peak at ≈ 24 °2θ corresponds to the separation between cage faces. In toto, it appears that there is some extended periodicity in the formed gel that again is not influenced by concentration effects. The XRDs of the other products look very similar as seen in Fig. S1–S7 and no further comments seem to be required to elucidate any unique structural correlations.

One may argue that these materials are not particularly crystalline and further efforts might be made to form materials with higher degrees of periodicity such as found for zeolites. Highly periodic materials such as zeolites are typically prepared using hydrothermal conditions wherein an equilibrium is established that allows defects to dissolve out and be replaced by uniform structures over a longer period of time. In contrast, the oxysilylation products reported here are kinetic products with structures that form in minutes, even at or below room temperature. The evolution of byproduct ethane removes the potential to form an equilibrium; thus, defects that form are retained and there are no mechanisms to anneal out defects. Hence the periodic structures will only show short range order as seen here and in porous cage systems with other types of tethers between cages.

Efforts to identify species forming during the course of the reaction by mass spectral analysis were unsuccessful, likely due to the rapidity of the polymerization reaction.

3.4 Specific surface areas and porosities

The micropore distribution for all gels had peak pore diameters of 6–7 Å (Tables 1–3). Figure 5 provides a typical plot. Super-critical processing does not appear to be necessary to retain high specific surface areas (SSAs), which equates to avoiding extensive pore collapse.

| Table 2. Selected properties for various gels, 1:1 OHS:RSi(OEt)3 (Si–H/Si–OEt) |
|----------------|----------------|----------------|
| **R**          | **Density* (g/cm³) ± 5–10%** | **SSA (m²/g) ± 8** | **Micropores** | **Mesopores** | **Found CY (%)** | **Theor. CY (%)** |
| OCH₂CH₃       | 0.89            | 766             | 0.28 7.2 | 0.35 85.5 | 90.6 |
| CH₃           | 1.05            | 579             | 0.22 6.3 | 0.21 88.9 | 89.5 |
| Ph            | 1.03            | 452             | 0.18 5.9 | 0.24 75.6 | 79.1 |
| (CH₂)₂CF₃    | 1.15            | 141             | N/A   N/A | 0.07 74.0 | 76.2 |
| Vinyl         | 1.09            | 485             | 0.19 7.1 | 0.17 85.4 | 87.5 |
| (CH₂)₂Cl     | 1.17            | 112             | N/A   N/A | 0.07 77.9 | 79.0 |
| (CH₂)₃H      | N/A             | 6               | N/A   N/A | 0.02 71.4 | 74.1 |

*The values represent the average of three runs (n = 3).

| Table 3. Selected properties for various gels, 1:1 OHS:RSi(OEt)₃ (Si–H/Si–OEt) |
|----------------|----------------|----------------|
| **R**          | **Density* (g/cm³) ± 5%** | **SSA (m²/g) ± 12** | **Micropores** | **Mesopores** | **Found CY (%)** | **Theor. CY (%)** |
| Phenyl         | 0.91            | 710             | 0.27 5.5 | 0.28 81.4 | 83.8 |
| Biphenyl       | 0.96            | 655             | 0.25 6.0 | 0.26 76.8 | 79.2 |
| H(CH₂)₃       | 0.94            | 668             | 0.19 6.2 | 0.22 86.3 | 89.7 |
| H(CH₂)₆       | 1.07            | 422             | 0.17 7.0 | 0.13 79.3 | 78.2 |

*The values represent the average of three runs (n = 3).
Highly porous materials with pore widths in both micro- and mesoporous ranges will exhibit hysteresis during gas adsorption experiments. Interconnected pore systems combined with pore blockages cause a lag in desorption of adsorbent from the material, see Fig. 6, in agreement with literature. Thus porosity measurements are taken from the adsorption stage which are minimally affected by hysteresis. Typical pore size distribution in mesopore range is shown in Fig. 7.

Understanding these distributions and how they are affected by reaction conditions and different functional groups is important for future experiments where these materials may be used for separations efforts and or as catalyst substrates. Thus, the above lays the groundwork for practical efforts.

For the R–Si(OEt)3:OHS systems studied (see Table 2), SSAs ranged from 6–665 m2/g. Trends in porosity and SSAs appear to depend on R group size and flexibility. SSAs for gels with non-flexible functional groups (e.g. R = Me, vinyl) had SSAs > 450 m2/g. Thus, R = Me system gave the highest SSAs observed of 580 ± 7 m2/g and for R = vinyl, the SSA was 485 ± 7 m2/g. SSAs decrease as the chain length increases from C1 to C8. Thus, R = (CH3)2H offered the lowest SSA of 6 m2/g.

One secondary objective of the current studies was to assess the effects of different bistriethoxysilane [(EtO)3Si–R–Si(OEt)3] spacers. Table 3 records these studies with SSAs ranging from 400–700 m2/g. Trends in porosity and SSA are, as expected, dependent on spacer length and flexibility. Thus rigid spacers gave systems with SSAs > 650 m2/g in contrast to flexible spacers where the C8 spacer gave lower but still quite respectable SSAs. These results agree with the work by Oviatt et al., but contrast with work done by Corriu et al., where the flexibility of the linker did not appear to be a factor in gel porosities.

The phenyl and biphenyl bistriethoxy precursors provide gels with rigid spacers and are the only materials to offer some slight differences in average pore sizes and may suggest with more detailed studies that it is possible to carefully manipulate pore sizes.

3.5 Solvent impregnation studies

The gels produced here can be considered to be a form of modified silica with octahedral (cubic symmetry) units bridged by tetrahedral linkers. In all cases, the linkers consist of Me2SiOSiO1.5 units, which are expected to confer hydrophobicity to the gels. However, the large content of silica-like building blocks suggests the potential for other types of affinities for both solvents and gases. Thus, we attempted to briefly ascertain solvent affinities using a very simple impregnation test (see experimental section).

Table 4 provides sets of solvent retention data for selected gels produced above. One goal here was to contrast solvent affinities of the simple 1:1 gel with gels with varying vinyl contents as a test case for future studies. The results suggest that even though the simple gels have higher SSAs with approximately the same surface areas and microporosities of the resulting gels. Generally, small and/or rigid structural elements lead to high surface area gels. All of the resulting gels show, by XRD, short-range periodicity indicative of 3-D ordering. Surprisingly, there is very little difference in the micropore sizes ranging between 5 and 20 Å with peak pore sizes primarily in the 6–7 Å range. Mesopores are all relatively similar at 2–40 nm range. With the exception of the rigid spacer systems, these results are to be expected given that almost all the pores are built around a rigid 3-D cage joined primarily by Si–O–Si linkages.

Changes in solvent, solvent volume, and catalyst concentrations had essentially no effect on the final product suggesting that the reaction goes to completion with great facility.

These results suggest the potential to design gels with different affinities for solvents, gases and other more valuable or more toxic species. One simple set of solvent impregnation tests was...
improve solvent af
run to demonstrate the potential to modify gel structures to
other af
work was inspired by studies from the Brook group.48)

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Fig. 7. Typical mesoporosimetry plot for a 1:1 OHS:TEOS reaction at 0 ≤ p/p0 ≤ 1 a. differential pore volumes b. cumulative pore volume.

| Gel Composition | SiHO:Et | SiHO:Et:Vinyl | SiHO:Et:Vinyl | SiHO:Et:Vinyl |
|-----------------|---------|---------------|---------------|---------------|
|                  | (1:1)   | (1:0.5:0.5)   | (1:0.25:0.75) | (1:1)         |
|                  | % avg. mass gain | % avg. mass gain | % avg. mass gain | % avg. mass gain |
| Acetonitrile [5.8] | 26      | 30             | 44             | 44             |
| Methanol [5.1]   | 29      | 38             | 39             | 39             |
| Tetrahydrofuran [4.0] | 34     | 32             | 34             | 45             |
| Toluene [2.4]    | 31      | 26             | 57             | 65             |
| Hexanes [0.0]    | 3       | 10             | 17             | 12             |
| SSAs (m2/g)      | 806     | 659            | 580            | 485            |

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