

Hybrid TiO₂–SiO₂ Organic/Inorganic Gels: Preparation, Characterization, and Temperature-Programmed Pyrolysis and Oxidation Studies

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Permethylated cyclooligosiloxane rings, tetraethylortosilicate (TEOS), and Ti(*i*Pr)₂Cl₂ were used to prepare hybrid TiO₂–SiO₂ xerogels. A number of solvents were ineffective for leaching the organic silicon from the samples at 336 K after several hours. The nitrogen desorption isotherms of these materials reveal that microporous structures with broad pore size distributions are generated upon gelation. Characterization of the samples by means of ²⁹Si CP/MAS NMR shows incorporation of the “organic silicon” into the amorphous structure and also suggests a great extent of homogeneity in the proton distribution around all tetrahedral silicate centers. The thermal stability of these hybrid TiO₂–SiO₂ materials was studied under flowing nitrogen and air by means of temperature-programmed (TP) techniques, and in situ diffuse reflectance infrared spectroscopy (DRIFTS). The stability of the Si–C bond in the absence of oxygen is hardly influenced by the presence of Ti. All Ti-containing samples undergo high-temperature pyrolytic decomposition of the Si–C bond, even when oxygen was present. In the presence of oxygen, the Ti function catalyzes the complete oxidation of the remaining alkoxide groups, rather than Si–C bond oxidation. The thermal stability of the latter and the decomposition of alkoxide groups into olefins are confirmed by both TP methods and DRIFTS.

Introduction

Hybrid organic/inorganic gels have attracted considerable attention as materials and catalysts.^{1–9} In particular, aerogels produced via supercritical drying of the wet gels are typically high surface area materials with open pore structures. On the other hand, conventional drying techniques produce xerogels, which may possess relatively high surface areas, but large pores are lost upon water evaporation due to shrinkage caused by capillary forces. There are several reasons why hybrid gels may yield commercially attractive materials. First, hydrophobicity is generally viewed as a desirable property, since this should in principle enhance the adsorption of organic species. Second, this property may also impart stability in the presence of moisture, which has been identified as one of the major hurdles that prevent their use as microfilters, supercapacitors for electric cars, and adsorbents.¹⁰ In addition, since each organic hanging group (Si–C bond) results in one less

point of cross-linking, it should be a priori possible to prepare relatively flexible, open pore structures upon conventional drying.

In this contribution, we report on the preparation, characterization, and pyrolytic and oxidative stability of TiO₂–SiO₂ hybrid gels prepared by using permethylated cyclooligosiloxanes as the “organic silicon” source, tetraethylortosilicate as the “inorganic silicon” precursor, and Ti(*i*-PrOH)₂Cl₂ as the titanium source. The alcogel state was characterized by means of ²⁹Si magic angle spinning (MAS), cross-polarization (CP)/MAS nuclear magnetic resonance (NMR), and nitrogen adsorption and chemical tests. In situ diffuse reflectance infrared spectroscopy (DRIFTS) and temperature-programmed pyrolysis and oxidation (TPP and TPO) techniques with mass spectrometric detection were used to monitor the thermal stability of these materials. Our short-term goal is to produce hybrid gels with low-temperature partial oxidation catalytic properties. Our long-term objective is to produce hybrid materials with moderately flexible networks that may be suitable for molecular imprinting leading to selective adsorption and catalysis applications.¹¹

Experimental Section

Sample Preparation, Adsorption Measurements, and Chemical Tests. The preparation of hybrid TiO₂–SiO₂ gels

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- (1) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, 1007.
- (2) Schubert, U. *New J. Chem.* **1994**, 18, 1049.
- (3) Diré, S.; Babonneau, F.; Carturan, G.; Livage, J. *J. Non-Cryst. Sol.* **1992**, 147/148, 62.
- (4) Brunet, F.; Lux, P.; Virlet, J. *New J. Chem.* **1994**, 18, 1059.
- (5) Loy, D. A.; Jamison, G. M.; Baugher, B. M.; Myers, S. A.; Assink, R. A.; Shea, K. J. *Chem. Mater.* **1996**, 8, 656.
- (6) Diré, S.; Campostrini, R.; Ceccato, R. *Chem. Mater.* **1998**, 10, 268.
- (7) Yokogawa, H.; Yokoyama, M. *J. Non-Cryst. Sol.* **1995**, 186, 23.
- (8) Schwerfeger, F.; Glaubitt, W.; Schubert, U. *J. Non-Cryst. Sol.* **1992**, 145, 85.
- (9) Neumann, R.; Levin-Elad, M. *J. Catal.* **1997**, 166, 206.

(10) Lee, K.-H.; Kim, S.-Y.; Yoo, K.-P. *J. Non-Cryst. Sol.* **1995**, 186, 18.

(11) Loy, D. A.; Shea, K. J.; Buss, R. J.; Assink, R. A. *Inorganic and Organometallic Polymers II*, 1995; p 122.

was adapted from a protocol recently described to prepare the corresponding all-inorganic gel,⁹ the key difference being that one-third of the tetraethylortosilicate (TEOS) amount prescribed is replaced by the same amount of moles of silicon in the form of an organic precursor. Specifically, hexamethylcyclotrisiloxane [(Me₂SiO)₃], octamethylcyclotetrasiloxane [(Me₂SiO)₄], and decamethylcyclopentasiloxane [(Me₂SiO)₅] were used as the "organic silicon" precursors. The Ti-containing, organic-silicon-free alcogel (i.e., the alcogel based on TEOS as the sole Si source) of Neumann and Levin-Elad⁹ was also prepared and labeled as Si-Ti. The Si-Ti reference sample gave a BET surface area of 578 m²/g upon drying at 383 K.

As an example, to prepare about 2.5–2.7 g of OSi₄-Ti (organic silicon tetrameric ring, Ti-containing catalyst), 26.66 mmol of TEOS is poured into a solution of 13.33 mmol of (Me₂SiO)₃ in 12 mL of absolute ethanol, and 1.040 g of H₂O in the form of a 0.148 M HCl solution is subsequently added. This mixture was prehydrolyzed for 5 h at 65 °C, and later cooled to room temperature. A freshly prepared solution containing 2 mmol of TiCl₄ in 10 mL of dry 2-propanol was added to the prehydrolyzed mixture, along with more water (0.960 g, deionized). This method results in the in situ formation of the Ti(*i*-PrOH)₂Cl₂ complex. No turbidity or gelation was detected at this point. The "blank" (OSi₄) sample was prepared exactly in the same fashion, except for the Ti-loading step, which was replaced by the addition 10 mL of (Ti-free) 2-propanol instead. The samples (both Ti-free and Ti-loaded) prepared using (Me₂SiO)₃ and (Me₂SiO)₅ as the organic silicon precursors were prepared in the same fashion. Since the oven, set at 65 °C, has no forced air circulation, it was decided to leave the mixtures in open containers, for slow gelation and evaporation. The Ti-containing samples gelled faster (in less than 1 day). All six samples were removed from the oven after 2.5 days. Upon crushing to fine powders and drying at 383 K for 2 h, BET surface area measurements were conducted in a conventional glass adsorption system, equipped with greaseless three-O-ring stopcocks, mechanical and diffusion pumps, and a Baratron pressure transducer. Chemical analysis performed at Galbraith Laboratories (Knoxville, TN) showed that the Ti content of the OSi₄-Ti sample was 2.59 wt %, whereas that of the Si-Ti material was 2.30 wt %.

Solvent extraction of the organic silicon precursors was attempted using three organic solvents, namely, tetrahydrofuran (THF), 2-propanol (2-PrOH), and cyclohexane (cC₆). These have dielectric constants equal to 7.52, 20.18, and 2.02, respectively.¹² Five milliliters of solvent was contacted with 0.150 g of oven-dried (383 K) sample for 12 h in closed vials at 336 K with occasional stirring. Similar tests were conducted by Kohjiya et al.¹³ to determine the amount of removable organic silicon upon copolymerization of hydroxyl-terminated poly(dimethylsiloxane) (PDMS) polymers, and TEOS. The solids were allowed to settle, and the supernatant solutions were carefully drawn out. The samples were oven-dried again at 383 K and the vials and their contents reweighed.

Solid-State ²⁹Si Magic Angle Spinning Nuclear Magnetic Resonance Measurements. The solid-state ²⁹Si FT/MAS and CP/MAS NMR measurements were performed using a ChemMagnetics M-100-Phoenix NMR, operating at 99.56 MHz for ¹H and 19.78 MHz for ²⁹Si observation. The instrument is located at the Instrumentation Center of Department of Chemistry, University of Nebraska.

The CP/MAS experiments were performed with a sample spinning frequency of 3.8 kHz. Variable-contact time experiments were carried out with the Hartmann-Hahn proton decoupling field frequency of 43.1 kHz. Ninety degree proton pulses were calibrated at 6.9 μs, which includes the transmitter dead time of 1.1 μs. Pulse delays of 10.0 s were used for CP/MAS experiments and were determined to be adequate for proton spin-lattice relaxation using progressive saturation

experiments. The CP/MAS spectra were acquired as 128-point datasets with a dwell-time of 83.3 μs. Spectra were the result of signal-averaging between 256 and 1024 transients, resulting in total acquisition times between 0.7 and 2.8 h per spectrum.

Single-pulse (Bloch-decay) ²⁹Si MAS NMR experiments were also performed using a sample spinning frequency of 3.8 kHz. Excitation pulses of 6.9 μs were employed, which represent approximately 90° pulses according to the Hartmann-Hahn match in the CP/MAS experiments. Relaxation delays of 240 s were used, which was determined to be at least 3 times larger than T₁, using progressive saturation experiments. Spectra were the result of signal-averaging 256 transients, acquiring 128 data points at a dwell-time of 83.3 μs. The total acquisition time for each spectrum was approximately 17 h. All NMR experiments were performed at room temperature.

Diffuse Reflectance Infrared Spectroscopy (DRIFTS) Methods. In situ DRIFTS studies were carried out at several different temperatures under flowing nitrogen (UHP grade from Linweld, Lincoln, NE) on a Nicolet 20 SXB Fourier transform infrared spectrometer equipped with a commercial DRIFTS catalytic chamber and associated optical and temperature control systems from Spectratech. The reactor part of the cell consists of a temperature-controlled ceramic cup where the sample is packed and gases are allowed to flow through. The latter are allowed in the cell via a stainless steel reaction system equipped with Brooks 5850D mass-flow controllers. Typically, 0.05 g of sample was placed in the DRIFTS cell and redried in flowing nitrogen at 383 K for 20 min. Temperature was increased stepwise (383, 453, 523, 593, 668, 743, 828, and 928 K), and spectra were collected in the wavenumber interval 4000–400 cm⁻¹ (400 scans, resolution of 4 cm⁻¹). Samples were allowed to equilibrate for about 15–20 min at the chosen temperature prior to data collection. Spectra are presented after the Fourier transformed data in a reflectance scale have been converted to Kubelka-Munk units. As reference samples, mechanical mixtures of the organic silicon precursors and silica Davison grade 823 were prepared, and their DRIFTS spectra were recorded at room temperature.

Temperature-Programmed Pyrolysis and Oxidation Experiments (TPP and TPO). An MKS quadrupole mass spectrometer (MS) was used for the temperature-programmed experiments. Samples were redried at 383 K for 0.5 h prior to TPO and TPP runs. For the TPO runs, the powdered materials were placed in a Pyrex U-tube reactor as a 1:3 mixture with a nonporous silica from Fluka (total mass of 0.34 g), along with a preheating bed of low-surface area α-Al₂O₃. A similar Brooks mass-flow controlled reactor setup to that of the DRIFTS cell was employed. An ultrahigh purity air flow of 40 cm³/min was set. The gas phase was sampled by means of a stainless steel capillary tubing with one end connected to the MS manifold, and the other end located at ca. 5 mm above the small quartz wool plug that prevented sample blowout. The latter was held in place by the 1/16 in. K-type thermocouple used for temperature control. The final temperature (836 K) was achieved by means of a 2.5 K/min ramp. A total of 16 masses were followed simultaneously. These were carefully selected in order to follow total and partial oxidation products, alkenes, and alkanes, as well as potential fragments indicative of siloxane and nonreactive alcohol desorption. The TPP experiments were carried out in a similar fashion, except for the catalyst:solid diluent amount (150 mg of each), the applied ramp (3.33 K/min), and type of flowing gas (UHP He, 26 cm³/min). In the TPO and TPP figures, we typically show those *m/e* ratios that yielded detectable signals.

Results and Discussion

Adsorption and Solvent Extraction Tests. Table 1 shows the BET specific surface areas of all six samples. About an order of magnitude higher surface areas are obtained upon incorporation of Ti, which indicates different nucleation-growth behavior with

(12) *CRC Handbook of Chemical Physics*, 78th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 1997; pp 6–139.

(13) Kohjiya, S.; Ochiai, K.; Yamashita, S. *J. Non-Cryst. Sol.* **1990**, *119*, 132.

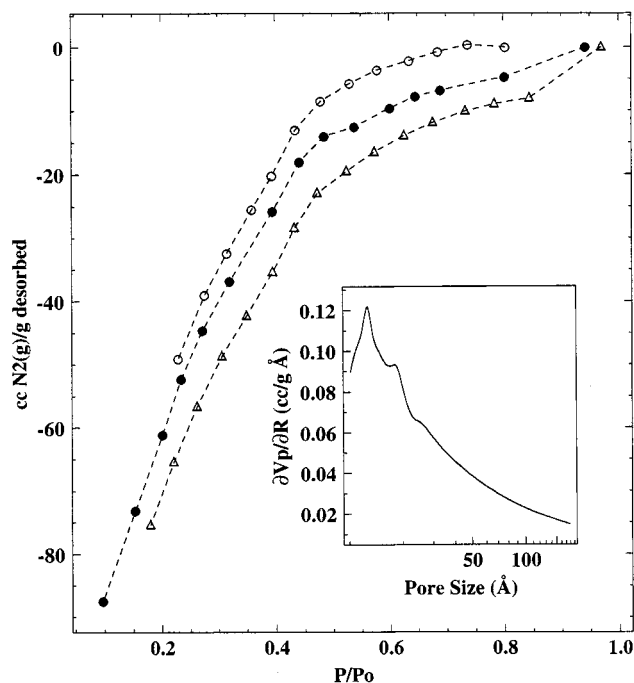


Figure 1. Desorption isotherms for OSi₃-Ti (δ), OSi₄-Ti (\bullet), and OSi₅-Ti (\circ). The inset is the Barret-Joyner-Halenda (BJH) pore size distribution curve of the OSi₄-Ti sample.

Table 1. BET Surface Area Results (m²/g)

sample	BET of organic silicon precursor		
	(Me ₂ SiO) ₃	(Me ₂ SiO) ₄	(Me ₂ SiO) ₅
Ti-free	79	43	43
Ti-loaded	689	776	773

respect to the Ti-free glasses. Figure 1 shows the nitrogen desorption curves for all three Ti-containing samples. The shape of the desorption curves is typical of microporous materials, with a substantial contribution to the total desorption volume at low P/P_0 values. The inset is the pore distribution curve (BJH method) for the OSi₄-Ti sample. One important observation is that all the OSi_{*n*}-Ti samples gave specific surface areas on the order of 100–200 m²/g higher than that of the Si-Ti material, which indicates that the $-\text{Si}(\text{CH}_3)_2-$ moieties (which can only polymerize in one dimension) promote the formation of a less dense structure.

Table 2 shows that only minor amounts of organic silicon may be removed by solvent extraction at 336 K. Our results compare favorably to those of Kohjiya et al.,¹³ who were able to remove 25–15% of the organic silicon by a similar procedure at 323 K, when using PDMS polymers ($M_w \sim 1700$) and TEOS as alcogel precursors. A small weight increase was detected in three samples washed with cyclohexane. While we cannot provide a satisfactory explanation for such weight increase at this point, it is apparent that a very small fraction of the cyclohexane was not removable at 383 K.

Solid-State Nuclear Magnetic Resonance Experiments. Figures 2, 3, and 4 show the stacked ²⁹Si CP/MAS NMR spectra at different contact times for the OSi₃-Ti, OSi₄-Ti, and OSi₅-Ti samples, respectively. For comparison purposes, 1:2 mechanical mixtures of the corresponding permethylated cyclosiloxane precursors and pure SiO₂ (Davison, grade 823) are shown as spectra A in all three figures.

Table 2. Leaching Experiments Using Three Solvents at 336 K for 12 h

sample	solvent	weight loss (%)	organic silicon loss (%)
OSi ₃	THF	3.2	8.4
	2-PrOH	2.1	5.5
	cC ₆	3.9	10.2
OSi ₃ -Ti	THF	1.7	4.4
	2-PrOH	2.0	5.2
	cC ₆	2.8	7.3
OSi ₄	THF	1.7	4.5
	2-PrOH	1.7	4.5
	cC ₆	-0.3	
OSi ₄ -Ti	THF	1.8	4.8
	2-PrOH	3.0 ^a	7.9
	cC ₆	-1.0	
OSi ₅	THF	0.6	1.6
	2-PrOH	2.7 ^a	7.1
	cC ₆	1.0	2.6
OSi ₅ -Ti	THF	0.1	0.3
	2-PrOH	2.4 ^a	6.3
	cC ₆	-0.5	

^a Slight turbidity was detected in the recovered liquid. The small amount of suspended solid in these tests may be responsible for the weight losses observed.

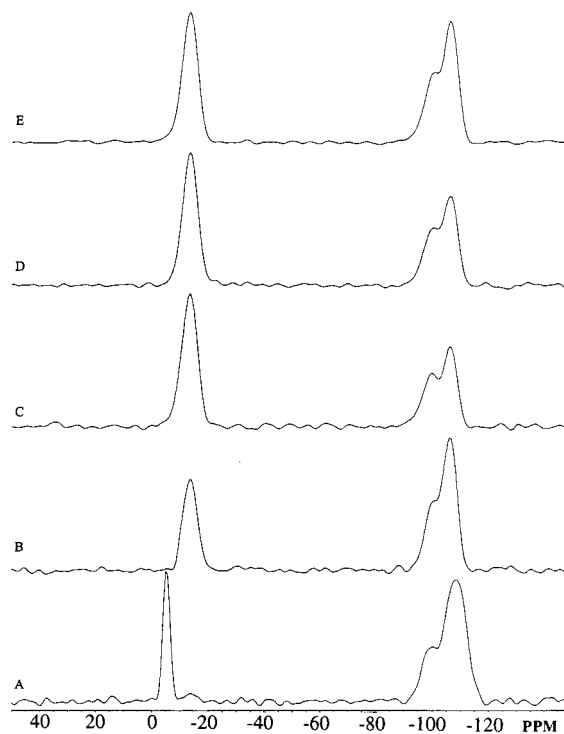


Figure 2. ²⁹Si MAS NMR spectra of the OSi₃-Ti sample: (B) one pulse, 240 s delay, (C) CP/MAS, CT = 1.5 ms, (D) CP/MAS, CT = 3.0 ms, and (E) CP/MAS, CT = 8.0 ms. (A) The corresponding 2:1 SiO₂:cyclosiloxane precursor mechanical mixture, ran as in B.

One spectral feature that is immediately recognized is the broadening of the so-called D² resonance, assigned to (CH₃)₂Si(OX)₂ centers (where "X" is most likely represented by Si, rather than Ti, given the samples' composition).¹⁴ This is taken as indication of incorporation into the amorphous solid structure, given the more liquidlike behavior of the loosely bound permethylated cyclosiloxane molecules in the mechanical mixtures. Note that the latter display sharp D² NMR signals. For

(14) Glaser, R. H.; Wilkes, G. L.; Bronnimann, C. E. *J. Non-Cryst. Sol.* **1989**, *113*, 73.

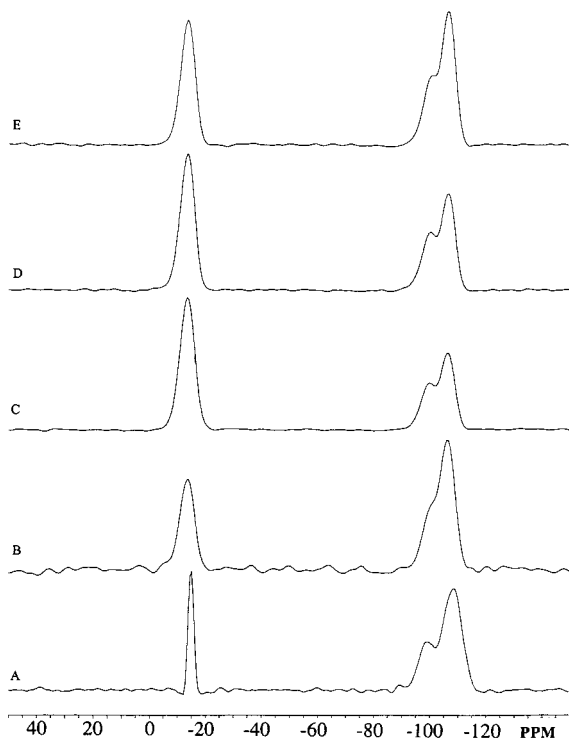


Figure 3. ²⁹Si MAS NMR spectra of the OSi₄-Ti sample: (B) one pulse, 240 s delay, (C) CP/MAS, CT = 1.5 ms, (D) CP/MAS, CT = 3.0 ms, and (E) CP/MAS, CT = 8.0 ms. (A) The corresponding 2:1 SiO₂:cyclosiloxane precursor mechanical mixture, ran as in B.

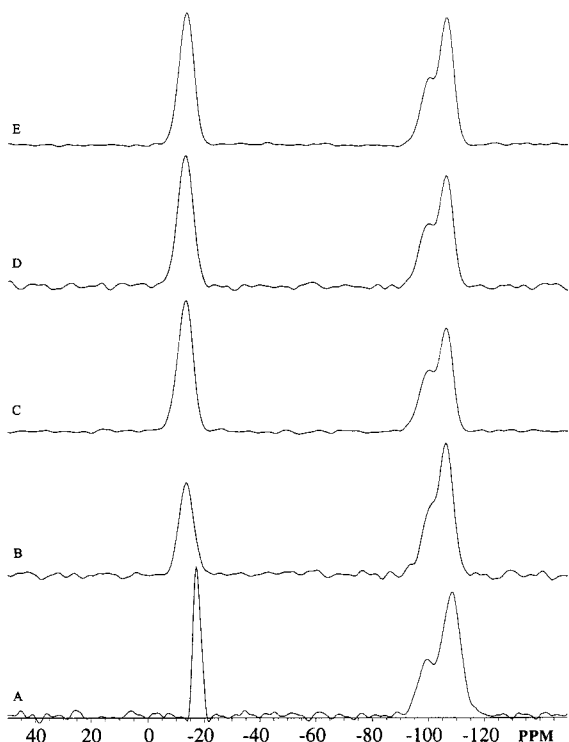


Figure 4. ²⁹Si MAS NMR spectra of the OSi₅-Ti sample: (B) one pulse, 240 s delay, (C) CP/MAS, CT = 1.5 ms, (D) CP/MAS, CT = 3.0 ms, and (E) CP/MAS, CT = 8.0 ms. (A) The corresponding 2:1 SiO₂:cyclosiloxane precursor mechanical mixture, ran as in B.

the standard mixtures, these resonances were found to be at -6, -16, and -18 ppm, for the trimeric, tetrameric, and pentameric permethylated siloxane pre-

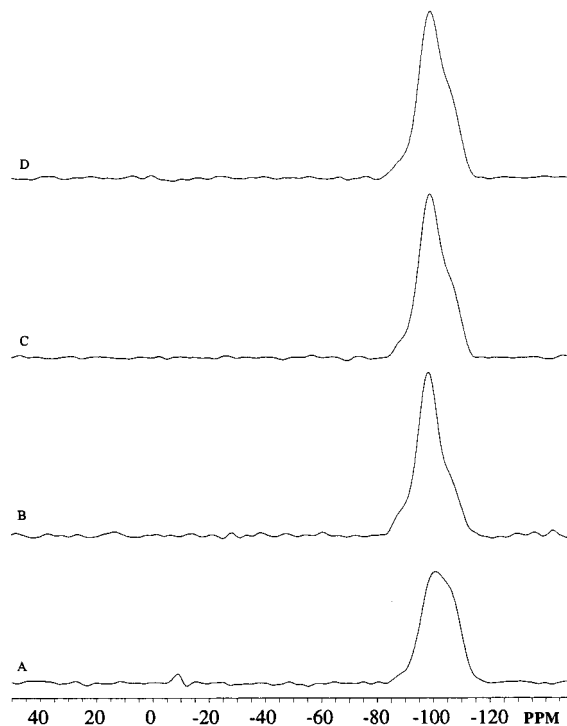


Figure 5. ²⁹Si MAS NMR spectra of the Si-Ti sample: (A) one pulse, 240 s delay, (B) CP/MAS, CT = 1.5 ms, (C) CP/MAS, CT = 3.0 ms, and (D) CP/MAS, CT = 8.0 ms.

cursors, respectively. It is clear that the D² resonances in the cyclic precursors are influenced by bond angle effects, which in turn alter the ²⁹Si-¹H distances. However, our alcogel synthetic scheme led to broad D² signals with a unique frequency shift, regardless of the type of cyclic organic silicon precursor employed in the synthesis. This is an indication of ring opening as a result of the hydrolysis processes, which would lead to similar Si-O-Si angles in all three materials.

The partially resolved signals around -98, and -107 ppm are assigned to Q³ and Q⁴ resonances, respectively.¹⁴ This nomenclature refers to (OR)Si(OX)₃ (R = H, Et, or *i*Pr) and Si(OX)₄, respectively. The CP/MAS NMR spectra for the Si-Ti material is shown in Figure 5. This sample also shows Q³ and Q⁴ bands, even though a relatively larger Q³ contribution is apparent. This would indicate a lower degree of condensation relative to the hybrid materials. The presence of a small Q² resonance ((OR)₂Si(OX)₂) around -84 ppm in the CP/MAS NMR spectra of Si-Ti leads to the same conclusion concerning the extent of condensation of the reference sample relative to the hybrid solids.

Important structural features are also realized from signals that were not observed in our NMR experiments. For example, the absence of a Q⁰ (TEOS) resonance is indicative of a lack of unreactive TEOS entrapment in the gel structure. In addition, Q¹ [(OR)₃Si(OX)] and D¹ [(OR)(CH₃)₂Si(OX)] signals are nonexistent, which shows that singly linked reactive dangling ends do not exist in these hybrid xerogels. The absence of any resonance of the Tⁿ family around -60 ppm, attributed to monomethylated silicon centers, shows the stability of the Si-C bonds upon hydrolysis. As suggested by other authors,^{15,16} the fact that the CP/MAS NMR experiments at different contact times, as well as FT/MAS NMR runs, showed the occurrence of Q⁴ resonances is

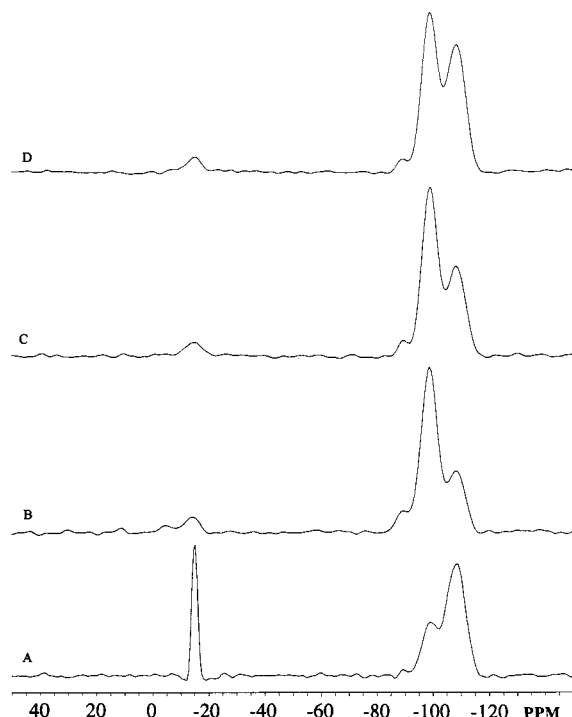


Figure 6. ^{29}Si MAS NMR spectra of the OSi_4 (octamethylcyclotetrasiloxane)/ SiO_2 Davison mechanical mixture: (A) one pulse, 240 s delay, (B) CP/MAS, CT = 1.5 ms, (C) CP/MAS, CT = 3.0 ms, and (D) CP/MAS, CT = 8.0 ms.

indicative of homogeneity in all these samples, since it is required for the Q^4 Si atoms to be no more than 10 Å apart from a proton for polarization transfer to be possible. Indeed, the effect of contact time in the CP/MAS NMR of all three hybrid materials (see Figures 2–4) seems to support this idea, as the different tetrahedral silicate centers in all three samples appear to sense very similar proton environments. Furthermore, contact time experiments show that there is no detectable change in line shape and resonance position of the D^2 signals in all three materials, which leads us to believe that the cyclic chains of different lengths underwent complete hydrolysis of their Si–O–Si bonds. Note that the CP/MAS NMR spectra of the hybrid alcogels are markedly different than those of the mechanical mixtures (Figure 6). The silica Davison grade 823 is a high-surface area solid that had been calcined at high temperature and, as a consequence, displays inhomogeneous proton envelopes around its D^2 , D^3 , and D^4 units.

Pyrolysis Experiments. Since it is of both fundamental and practical interest to understand the thermal behavior of these materials, we proceeded to perform a number of temperature-programmed experiments under different gas environments. We selected one Ti-free sample (OSi_4) with which to conduct a pyrolysis experiment, in an effort to understand the decomposition mechanism of these glasses in the absence of oxygen. The results are shown in Figure 7. There is a slow evolution of alcohols that begins immediately after the temperature ramp is initiated. We ruled out the pos-

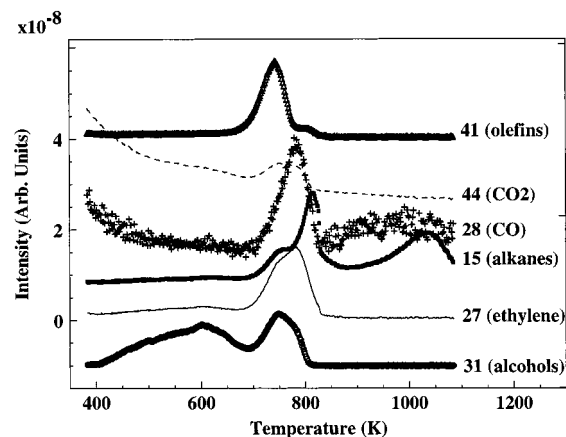
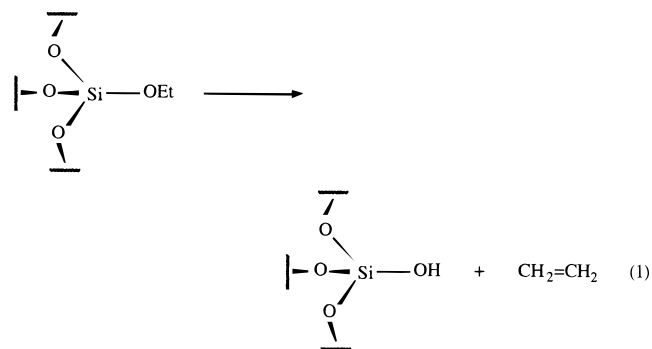


Figure 7. Pyrolysis of the OSi_4 sample.

sibility of low-temperature self-oxidation of the methyl groups from the $(\text{CH}_3)_2\text{Si}$ moieties. First, the lack of gas-phase oxygen makes this reaction improbable. Second, such reaction is difficult, and there is no catalytically active element in the Ti-free glass capable of facilitating such a decomposition pathway. Furthermore, upon drying these materials at 383 K, we observed, by means of DRIFTS, a C–H stretching signature that matches almost perfectly that of adsorbed ethanol.¹⁷ Below, we will discuss this observation in more detail. This implies that the glass contained either trapped alcohol or that heating makes remaining OR groups react with adsorbed H_2O and/or OH groups.

It is interesting to observe that the Si–C bonds in the OSi_4 sample appear to remain stable at least up to about 800 K. Around 700 K, Figure 7 shows that a complex decomposition pattern sets in, involving auto-redox reactions (CO, CO_2 , and olefins), but it must be understood that MS signals due to reactions of $\text{Si}(\text{CH}_3)_2$ groups and to alkoxide (or trapped alcohol) groups need to be deconvoluted. For example, we propose that $m/e = 41$ (allyl cation), a fragment indicative of olefin evolution, is due to propene generated from isopropoxide groups resulting from the use of 2-propanol in the last synthesis step. A similar proposal can be made to explain the occurrence of $m/e = 27$:



One important observation is that the $m/e = 15$ peak around 810 K must reflect the true decomposition of the Si–C bond, because it rises beyond the maxima of all other signals that may be affected by alcohol decomposi-

(15) Babonneau, F.; Maquet, J.; Diré, S. *Polym. Prepr.* **1993**, 34, 242.

(16) Mehring, M. *Principles of High-Resolution NMR in Solids*; Springer: Berlin, 1983.

(17) Larsen, G.; Lotero, L.; Márquez, M.; Silva, H. *J. Catal.* **1995**, 157, 645.

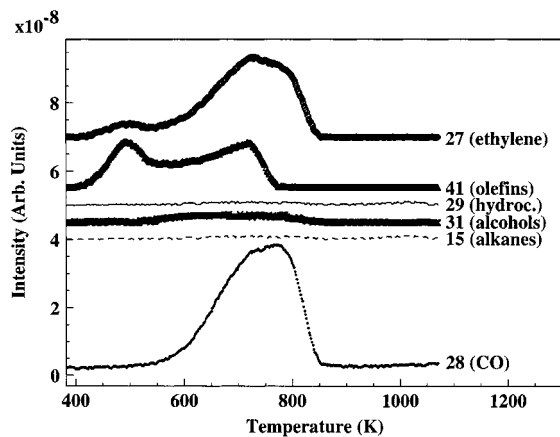


Figure 8. Pyrolysis of the Si-Ti sample.

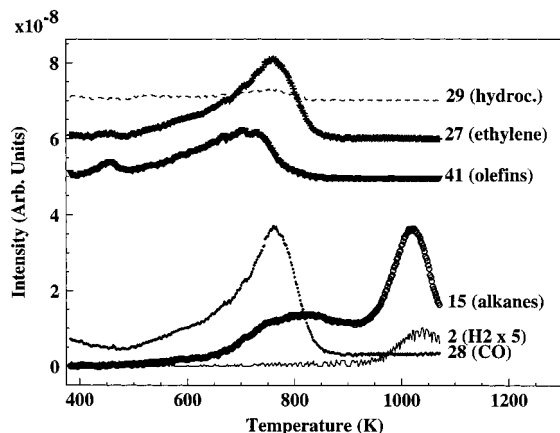


Figure 9. Pyrolysis of the OSi₄-Ti sample.

tion/desorption. By the same token, the $m/e = 15$ peak around 1050 K is also ascribed to Si-C bond rupture.

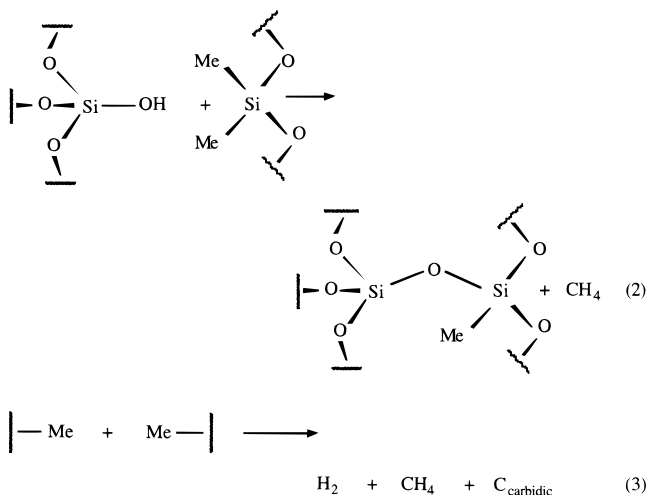
To further study this issue, and to compare the results in Figure 7 with the pyrolytic decomposition pattern of the Ti-containing materials, two more experiments were carried out, namely, the pyrolysis of the OSi₄-Ti sample and of the Si-Ti material (which Si originates from TEOS only). The latter is also a true blank for the Ti/“organic silicon”-containing samples and was also used to sort out DRIFTS spectral features that are solely due to the dimethylsiloxane moieties. Figures 8 and 9 show the pyrolysis of the Si-Ti and the OSi₄-Ti samples, respectively.

In Figure 8, it is immediately noticed that the absence of siloxane units in the Si-Ti sample translates into negligible $m/e = 15$ and 29 signals, which are representative of methane and higher hydrocarbons. However, carbon monoxide and olefins resulting from decomposition of alkoxy groups are still present. This reinforces our idea that such chemical species are generated from partially hydrolyzed species and are not in any way related to the siloxane building units. No carbon dioxide was detected.

Figure 9 completes our picture, as it shows the pyrolysis of the OSi₄-Ti sample. Note the occurrence of $m/e = 27$ and 41 patterns similar to those observed in Figures 7 and 8. Equation 1 seems to apply to all these three materials. On the other hand, $m/e = 15$ shows two peaks, a low-temperature one around 800 K and a high-temperature contribution above 1000 K. At this point, we should mention that the OSi₄-Ti sample

was black after pyrolysis, while the Si-Ti “blank” remained white. This implies that heating in an inert atmosphere does not cause the latter to produce large amounts of carbonaceous residues, either carbidic or coke-type, whereas a significant amount of carbon still remained on the surface of the former. As we will discuss in more detail below, we did not detect any of the typical “coke” DRIFTS bands,¹⁸ a fact that led us to conclude that a highly hydrogen-deficient carbidic form is generated by pyrolysis of OSi₄-Ti.

Using temperature-programmed methods, Diré et al.³ have shown that nanocomposites prepared from Zr *n*-propoxide and poly(dimethylsiloxane) (PDMS) also produce a pyrolysis decomposition pattern having important contributions from $m/e = 41$ and 15. These authors indicated that methane from PDMS chains is also formed in more than one step. From Figure 9, it is apparent that the last methane peak is accompanied by hydrogen production, whereas the 800 K release is not. The loss of hydrogen, coupled with the absence of coke bands in the DRIFTS spectra, suggests carburization around 1100 K. The low- and high-temperature CH₄ peaks are assigned to the following reactions, respectively:



In the past, it has been proposed that heteroatoms such as Al cause the Si-C bond to become unstable,¹⁹ and such instability was used to explain early methane evolution during pyrolysis of PDMS-zirconia nanocomposites.³ Such a reaction would essentially be the same as pathway 2, except for the involvement of a M-OH heteroatom instead of the Si-OH group shown in eq 2. Inspection of Figures 7 and 9 reveals that Ti does not appear to lower the temperature for the pyrolytic decomposition of the Si-C bond, as opposed to Al- and Zr-containing materials.^{3,19} This indicates that, in the absence of oxygen, Ti does not destabilize the Si-CH₃ function in these materials.

In Situ Diffuse Reflectance Infrared Studies. Figure 10 shows the variable temperature DRIFTS spectra of the Si-Ti sample in the C-H stretching region. The features are characteristic of chemisorbed alcohols,^{17,20,21} where methyl and methylene groups are

(18) Larsen, G.; Lotero, E.; Nabity, M.; Petkovic, L.; Querini, C. A. *Stud. Surf. Sci. Catal.* **1997**, *111*, 147.

(19) Peeters, M. P.; Kentgens, A. P. M.; Snijkers-Hendrickx, I. J. M. *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 415.

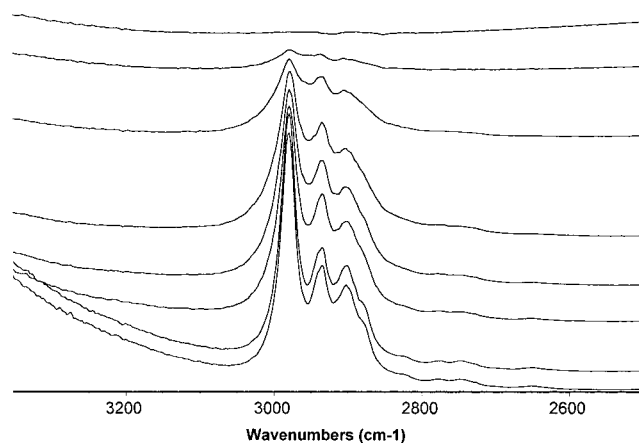


Figure 10. Variable-temperature DRIFTS spectra of the Si-Ti sample. Spectra are stacked in order by increasing temperatures (383, 453, 523, 593, 668, 743, 828, and 928 K).

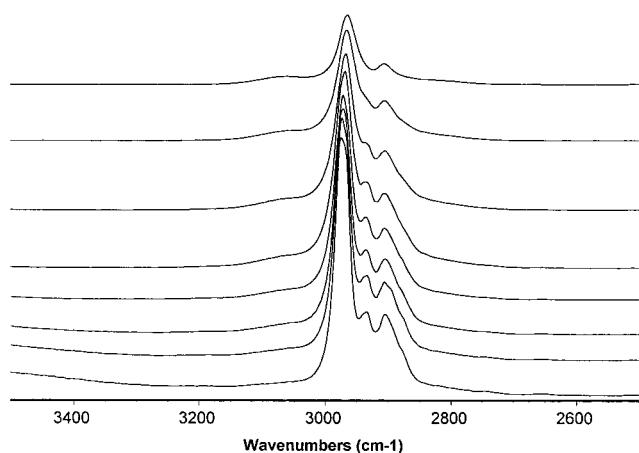


Figure 11. Variable-temperature DRIFTS spectra of the OSi₃-Ti sample. Spectra are stacked in order by increasing temperatures (383, 453, 523, 593, 668, 743, 828, and 928 K).

present. Note the complete disappearance of the signal at the highest temperature shown. This is consistent with our picture of complete alcohol reactive desorption in Si-Ti.

Figure 11 shows the same spectral region for the OSi₃-Ti sample. The DRIFTS experiments on the OSi₄-Ti and the OSi₄-Ti samples resulted in temperature-programmed spectra essentially identical to that of OSi₃-Ti. The spectra are largely dominated by alcohol features at low temperatures, but as the temperature is raised, they become dominated by characteristic methyl C-H stretching from the siloxane moieties. Note, however, that at low temperatures the most intense band around 2975–2980 cm⁻¹, which is due to asymmetric methyl stretching, is actually a convolution of two signals in all three OSi_n-Ti samples. This must be the case, as there are two contributions to this band, namely, that from the Si-CH₃ groups and that from the methyl groups in the alkoxides. Note that a single asymmetric methyl stretching peak is apparent in the Si-Ti sample (Figure 10). Upon heating, the high-

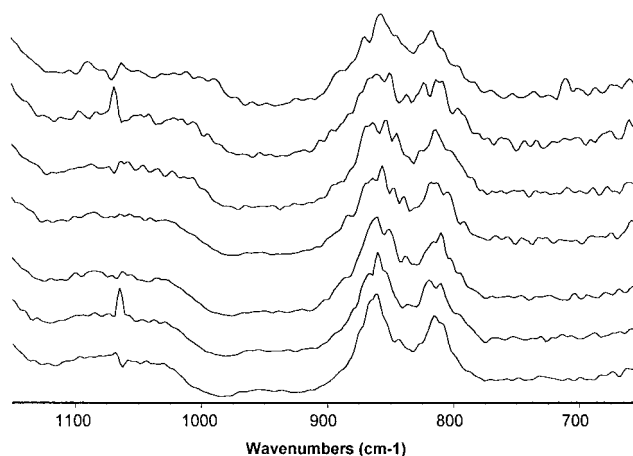


Figure 12. Variable temperature DRIFTS spectra of the OSi₃-Ti sample in the Si-C region. Spectra are stacked in order by increasing temperatures (383, 453, 523, 593, 668, 743, and 828 K).

frequency component of the asymmetric methyl stretching vanishes due to alkoxide reactive desorption. We have confirmed these observations by comparing these spectra with those of mechanical mixtures made of a high surface area silica and the methylated cyclosiloxane precursors.

At present, we do not have a satisfactory explanation for the small band around 3070 cm⁻¹ that appears immediately upon heating of the OSi_n-Ti samples, since this signal was not present in the standard silica-cyclosiloxane mechanical mixtures. Initially, we were inclined to believe that adsorbed olefins formed from the reactive alkoxide groups were responsible for it, because it falls in the expected methylene C-H stretching region. However, this band does not show in the Si-Ti sample, which also undergoes reactive desorption of isopropoxide and ethoxide groups in the form of olefins. Therefore, we infer that it must be due to partial decomposition of the methyl groups in the siloxane moieties. This band is also unlikely to be due to C-H stretching from coke-type carbonaceous residues, since we found no evidence in the 1450–1650 cm⁻¹ region for formation of the latter. Diré et al.³ observed a shift to higher frequencies in the asymmetric methyl stretching during pyrolysis of PDMS-zirconia composites. These authors ascribed such a shift to a more constrained environment around the methyl groups upon heating and concomitant structure densification. However, we suspect that a 100 cm⁻¹ blue shift in the stiff C-H bond is unlikely to be caused by such second-order effects.

Similar variable temperature DRIFTS analysis could have been made by inspection of the 700–1000 cm⁻¹ region, which shows two bands assigned to Si-C stretching (800–820 cm⁻¹) and Si-CH₃ deformation (865 cm⁻¹).³ Figure 12 shows the variable-temperature DRIFTS spectra of OSi₃-Ti in the Si-C region. Again, it is seen that these signals persist upon heating. This is consistent with the high temperatures required for pyrolytic destruction of the Si-C bond (see Figures 7 and 9). Some overlap of the 800–820 cm⁻¹ Si-C component with weak CH₂ rocking signals from the alkoxide function is expected. Nevertheless, the two bands assigned to the Si-CH₃ moieties still remain upon high-temperature treatment under nitrogen.

(20) Moser, W. R.; Chiang, C.; Thompson, R. W. *J. Catal.* **1989**, *115*, 532.

(21) Glisenti, A.; Favero, G.; Granozzi, G. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 173.

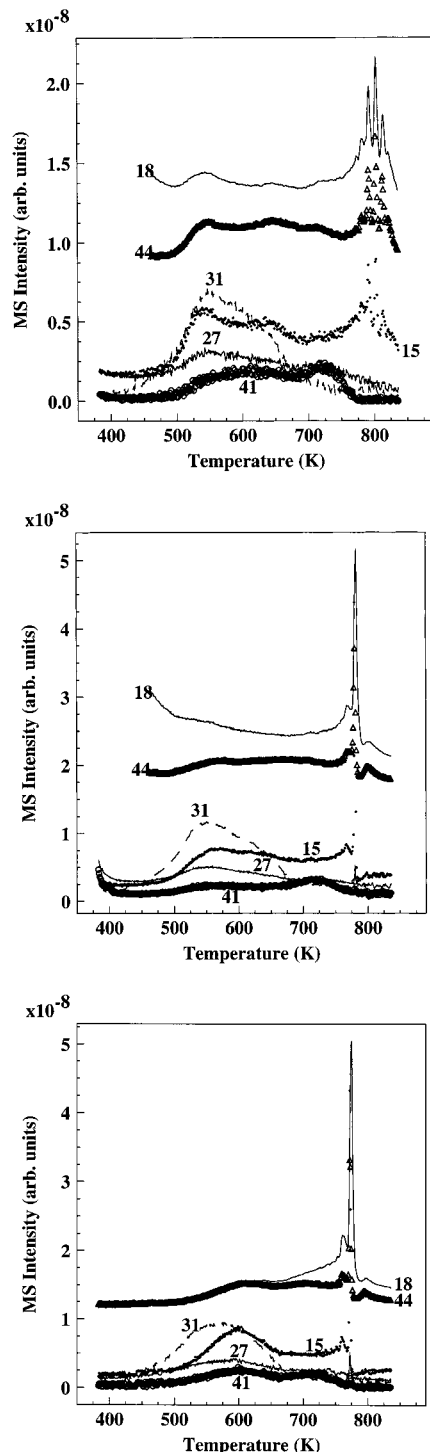


Figure 13. (a) Temperature-programmed oxidation of the OSi_3 sample. The water and carbon dioxide signals have been multiplied by 0.1 for display. (b) Temperature-programmed oxidation of the OSi_4 sample. The water and carbon dioxide signals have been multiplied by 0.1 for display. (c) Temperature-programmed oxidation of the OSi_5 sample. The water and carbon dioxide signals have been multiplied by 0.1 for display purposes.

Temperature-Programmed Oxidation. Since our ultimate goal is to design hybrid inorganic/organic catalysts and catalyst supports for low-temperature applications in which an oxidizing environment may be present, we proceeded to study the TPO of all six hybrid gels. These are shown in Figures 13a–c and 14a–c, for the Ti-free and the Ti-loaded materials, respectively.

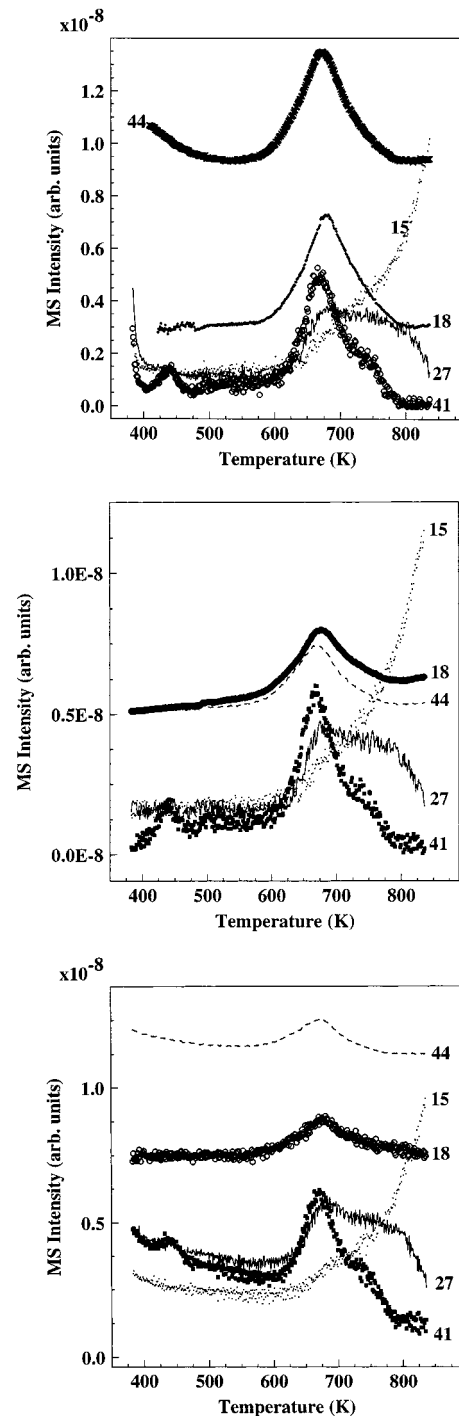


Figure 14. (a) Temperature-programmed oxidation of the OSi_3 -Ti sample. The water and carbon dioxide signals have been multiplied by 0.1 for display. (b) Temperature-programmed oxidation of the OSi_4 -Ti sample. The water and carbon dioxide signals have been multiplied by 0.05 for display. (c) Temperature-programmed oxidation of the OSi_5 -Ti sample. The water and carbon dioxide signals have been multiplied by 0.05 for display.

For the set of conditions used in our TPO studies, the Ti-free glasses appear to become highly unstable in the presence of air around 750–800 K. Around that temperature, the materials apparently ignite, as evidenced by oscillations and a sudden release of CO_2 typical of the generation of “hot spots” in a packed bed due to highly exothermic reactions (see Figure 13a–c). In all three Ti-free samples, alcohol and olefins are still

released in the presence of air. As in the pyrolysis experiments, ethylene and propylene are produced via dehydration of alkoxide groups. This is a process in which the gaseous atmosphere appears to play little role.

The TPO pattern of all three Ti-containing samples is also very similar. However, deep oxidation of carbon-containing moieties appears to be catalyzed by the presence of Ti, in the light of the lower temperatures observed for CO₂ and H₂O evolution, relative to the Ti-free glasses. Nonoxidative alcohol reactions are also apparent, judging from the $m/e = 41$ and 27 signals. However, no $m/e = 31$ (alcohols) was observed. Since, for the more limited temperature range employed for the TPO experiments, a high-temperature pyrolysis process that is not affected by the presence of oxygen seems to have triggered above 650 K (see $m/e = 15$), it is apparent that an important fraction of the Si(CH₃)₂ groups are relatively stable in the Ti-loaded materials, even in the presence of oxygen. This observation coupled with the lack of $m/e = 31$ suggests that it is the alkoxide groups, rather than the siloxane moieties, that undergo low-temperature oxidation facilitated by the presence of Ti.

Conclusions

The alcogel state of organic/inorganic hybrid TiO₂/SiO₂ materials prepared using permethylated cyclooligosiloxanes was characterized by nitrogen adsorption and ²⁹Si NMR. The CP/MAS NMR experiments suggest that deep hydrolysis of the cyclooligosiloxane rings occur and that the resulting hybrid matrix structure is the same, regardless of cyclic permethylated siloxane ring

size. Conventional drying results in microporous solids, with a substantial contribution to pore diameter in the 15–20 Å range.

The thermal stability of hybrid SiO₂, and SiO₂-TiO₂ alcogels and their stability in the presence of oxygen at high temperatures were studied by means of DRIFTS, TPP, and TPO techniques. In the absence of oxygen, siloxane groups decompose in two steps upon heating. The first step (~800 K) involves the formation of methane, but no hydrogen is detected. On the other hand, the second step (~1100 K) is accompanied by hydrogen generation, which suggests that methyl groups produce both methane and surface carbon at the same time. The decomposition of alkoxide groups, regardless of gaseous environment, appears to be independent of the fate of the methyl groups from the siloxane moieties. Alkoxide decomposition occurs at lower temperatures than that of methyl groups from siloxanes, primarily resulting in olefin formation. The C–H stretching region in the DRIFTS spectra confirms this observation, as it gradually uncovers the presence of a siloxane pattern at increasing temperatures. The presence of titania catalyzes the oxidation of alkoxide moieties, whereas the Ti-free glasses undergo ignition around 780 K.

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