Chemical Synthesis of Microporous Nonoxide Ceramics from Polysilazanes

John P. Dismukes,*,† Jack W. Johnson, John S. Bradley,‡ and John M. Millar

Exxon Research and Engineering Company, Route 22 East, Annandale, New Jersey 08801

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In a search for a generic synthesis methodology to produce microporous, nonoxide ceramics, pyrolysis of silicon-based preceramic polymers has been studied in inert (He or Ar) and reactive (NH_3) atmospheres over the temperature range 25−1300 °C. Pyrolysis of polysilazanes in an inert atmosphere in the absence of additives produced only low-density, nonmicroporous solids. However, four successful approaches to induce microporosity were developed, involving controlled reaction of selected low molecular weight polysilazane preceramic polymers. The first method employs the formation of colloidal polysilazane mixtures with micron-size particles of ceramics such as Si_3N_4, SiC, and AlN, followed by their pyrolysis in He or NH_3 to form a ceramic−ceramic composite. The second method involves the synthesis of a nanoscale, polysilazane-stabilized metal colloid of a noble or transition metal and its conversion to a metal− or cermet−ceramic composite by pyrolysis in He or NH_3. In the third method, a polysilazane is pyrolyzed in NH_3 at low heating rates, to form an amorphous, covalent ceramic. The fourth method involves the pyrolysis of polysilazane/metal−organic mixtures in He or NH_3. The microporous solids formed by these techniques have surface areas up to >500 m^2/g and micropore volumes up to >0.20 cm^3/g as determined by nitrogen adsorption measurements. Hexane adsorption measurements indicate that the micropore space is accessible to hydrocarbons.

Introduction

In the three decades since the proposal of the concept[1] of converting ceramic precursors in the form of preceramic polymers to covalently bonded ceramics, an ever-growing body of research has been conducted to explore the development of processes for the synthesis of preceramic polymers and their controlled decomposition into nonoxide ceramics[2−9] such as Si_3N_4, SiC, AlN, and BN. Target applications of extensive interest include ceramic fibers,[10−14] ceramic fiber composites,[15] monolithic ceramics,[16−17] powders,[18] and coatings.[19−21]

Our interest in ceramics from preceramic polymers stemmed from the report by Lipowitz[22] that Si−C−N fibers are about 20% less dense than the ideal value for a covalently bonded network and that they contain closed pores of approximately 15 Å diameter. Hence we reasoned that it should be possible to convert preceramic polymers, for example, silicon-based materials including polysilazanes, polycarbosilanes, and polysilanes, into microporous, amorphous Si−C, Si−C−N, and Si−N materials that might be expected to exhibit superior thermal shock resistance and stability in reducing

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† Current address: The University of Toledo, College of Engineering, 1016 Nitschke Hall, Toledo, OH 43606-3390.

‡ Current address: Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm Platz 1, D45470 Mülheim an der Ruhr, Germany.

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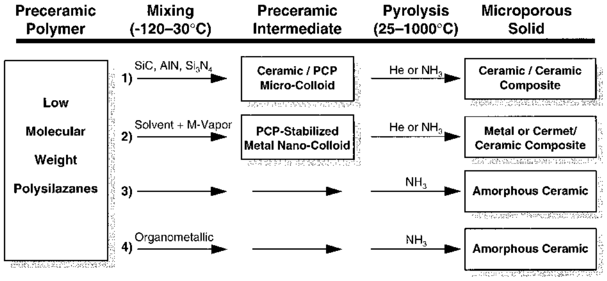

Figure 1. Chemical synthesis routes from preceramic polymers (PCP) to microporous nonoxide ceramics.

environments compared to microporous oxide materials. Although the generic use of preceramic polymers for this purpose has been proposed,[23] investigation of the pyrolysis of typical silicon-based preceramic polymers yielded either a low surface area material[24] with some closed porosity[25] or a high surface area nanoparticulate material.[26] Reports of microporous materials by reactions of preceramic polymers are relatively limited. These include the decomposition of a specially synthesized B−N precursor[27] at temperatures up to 800 °C, the decomposition of polycarbosilanes[28] at temperatures above 1300 °C, and the decomposition of photolytically cross-linked polysilastyrene[29] and oxidatively cross-linked polycarbosilane[30] at temperatures below 700 °C.

In an investigation of the pyrolysis behavior of preceramic polymers upon heating in inert (He or Ar) and reactive (NH_3) gas atmospheres from room temperature to a maximum temperature in the range 400−1300 °C, we have discovered general methods,[31−34] namely, routes 1−4 summarized schematically in Figure 1, for converting these materials to nonoxide ceramics with substantial surface area and micropore volume. In the present work, we summarize results of detailed investigation of each of the four routes for pyrolysis of low molecular weight (1300−6500 Da) polysilazanes to maximum temperatures of 650−700 °C. The first route[31] involves mixing the polysilazane with micron-size ceramic particles to form a microcolloid, followed by controlled heating in helium or ammonia to form a microporous, ceramic−ceramic composite. The second route[32] involves vaporization of a metal into an organic solution of the polysilazane and evaporation of the solvent to form a polysilazane-stabilized metal nanocolloid, followed by heating to form a microporous metal− or cermet−ceramic composite. The third route[33] involves heating of the polysilazane in ammonia at a gradual heating rate to form a microporous, amorphous ceramic. The fourth route[34] involves heating a polysilazane/metal−organic mixture in ammonia or helium at a gradual heating rate to form a microporous, amorphous ceramic.

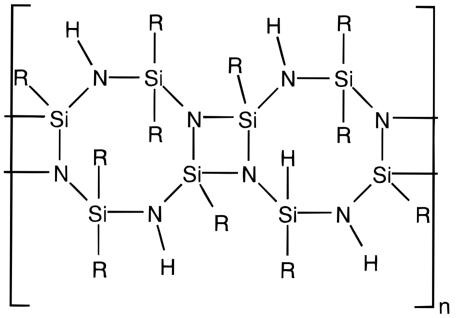

Figure 2. Schematic structural formulas for polysilazanes used in this research. The symbol R denotes methyl, and *n* denotes the degree of oligomerization. For $n = 2.5$, MW $\approx$ 1300, the structure approximates the Chisso NCP-200. For $n = 12.5$, MW $\approx$ 6500, the structure approximates the Chisso NCP-100.

To provide insight into the thermal stability of the products, we also include representative data (route 3) for pyrolysis at 850 and 1000 °C.

Experimental Methods

Reagents. The inert gases employed in this study were supplied by Air Products and used as supplied: He (99.995%) and Ar (99.998%). The NH_3 (99.999%) was supplied by Matheson and was either used as supplied, for heating schedule B, or as further purified by passing it through a Matheson ppB filter for removal of trace O_2 and H_2O, for heating schedule C and linear heating rates of 0.5−10 °C/min.

The following chemicals were used without further purification. Polysilazane preceramic polymers[35,36] of molecular weight $\approx$1300 (NCP-200) and $\approx$6500 (NCP-100) were obtained as powders from Nichimen Corp., Los Angeles, CA, manufactured by Chisso Corp., Japan. These precursors were synthesized by reaction of NH_3 with mixtures of methyldichlorosilane and dimethyldichlorosilane, followed by condensation reactions,[37] involving KH, to increase the molecular weight and form oligomers based on a repeat unit represented in the approximate formula, $T{-}[Si_8N_8R_{12}H_5]_n{-}T$, where $R = CH_3$, and T = a terminating group such as H or OH. The structure of these oligomers is based on alternate linking of 8-member and 4-member silicon−nitrogen rings, illustrated in Figure 2,

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Table 1. Synthesis of Microporous Ceramic−Ceramic Composites by Pyrolysis of a Colloidal Polysilazane−Ceramic Mixture

sample	PSZ (MW)	ceramic mixture (wt %, ceramic)	pyrolysis condition	heating schedule	total surface area (m^2/g)	meso surface area (m^2/g)	micropore vol (cm^3/g)
D35-3	1300	0	700 °C, He	B	<1		
D35-2	6500	0	700 °C, He	B	<1		
D27-5	6500	0	700 °C, He	A	<1		
D17-2	1300	40, Si_3N_4	700 °C, He	A	300	21	0.1164
D34-2	6500	40, Si_3N_4	700 °C, He	A	288	6	0.1169
D17-1	1300	40, SiC	700 °C, He	A	260	19	0.1000
D17-4	6500	40, SiC	700 °C, He	A	242	18	0.1089
D34-1	1300	40, AlN	700 °C, He	A	192	3	0.0769
D39-2	1300	40, Si_3N_4	700 °C, NH_3	B	308	16	0.1289
D39-5	6500	40, Si_3N_4	700 °C, NH_3	B	262	14	0.1079
D28-2		D17−1	1300 °C, He	A-to-1300 °C	5	5	

Table 2. Synthesis of Microporous Metal− or Cermet−Ceramic Composites by Pyrolysis of a Polysilazane-Stabilized Metal Nanocolloid

sample	PSZ (MW)	metal in stabilized colloid (wt %)	pyrolysis condition	heating schedule	total surface area (m^2/g)	meso surface area (m^2/g)	micropore vol (cm^3/g)
HB-3	6500	4.6, Ni	650 °C, Ar	D	329	18	0.1260
HB-4	1300	4.2, Ni	650 °C, Ar	D	391	22	0.1461
EX-19	1300	≈4,[a] Pd	700 °C, Ar	D	227	88	0.0531
JB10-2	1300	≈4,[a] Pd	700 °C,NH_3	C	343	23	0.1339
JB11-2	1300	≈4,[a] Pd	700 °C,He	C	295	24	0.1120
HB-6	6500	1.8, Fe	650 °C, Ar	D	419	19	0.1621
EX-10	6500	1.8, Fe	700 °C, NH_3	C	278	29	0.1034

[a] Estimated based on evaporated Pd.

where the degree of polymerization, n, is about 2.5 for NCP-200 and 12.5 for NCP-100. The ratio of $-Si-R_2$ and $-HSi-R$ type silicon atoms in the 8-member rings is dictated by the ratio of methyldichlorosilane and dimethyldichlorosilane used by Chisso in precursor synthesis. The Fe (99.99+%) and Ni (99.99%) were supplied by Johnson Matthey, Ward Hill, MA. The Pd (99.99+%) was supplied by Aldrich. Aluminum trisacetylacetonate, $Al(acac)_3$, and gallium trisacetylacetonate, $Ga(acac)_3$, were recrystallized superconductor grade from Strem Chemicals, Inc., Newburyport, MA. The silicon nitride, Si_3N_4 designation SN-9S, of particle size ≤1 μm was obtained from Denki KKK of Japan; the silicon carbide, SiC, of average particle size ≈1 μm was obtained from Johnson Mathey; the AlN, grade D50 of average particle size ≈1.6 μm, was obtained from Advanced Refractory Technologies, Inc., Buffalo, NY.

Preparation of Mixtures for Pyrolysis. Polysilazane−ceramic mixtures (Table 1) for pyrolysis studies were prepared by mixing the polysilazane and ceramic powders in a mortar and pestle, followed by further homogenization of the initial mixture in a 40 cm^3 polystyrene jar containing 0.6-cm alumina balls, typically for 2−6 h. The polysilazane−ceramic mixtures were then placed in an alumina boat, and inserted into a steel retort in a pyrolysis furnace. For long-term stability and durability of the steel retort, heating for extensive periods was limited to temperatures <1050 °C. Polysilazane-stabilized metal nanocolloids (Table 2) for pyrolysis studies were prepared using procedures previously described for the condensation of transition-metal vapors into hydrocarbon solutions of oligomeric aluminoxanes,[38−39] which results in the formation of highly dispersed metal organosols stabilized by the organoaluminum oligomer. For the relatively volatile metals described in this work, namely, iron, nickel, and palladium, a Torrovap Industries rotary reactor cooled to −120 °C was used to generate the metal vapor by thermal evaporation from a resistively heated alumina-clad tungsten wire crucible. A solution of the stabilizing polysilazane polymer (typically 10−15 mg/mL) in methylcyclohexane (≈250 mL) was degassed through three freeze−pump−thaw cycles and added to the evacuated flask of the rotary reactor. The flask was cooled to −120 °C and rotated at ≈120 rpm. When the vapor pressure had equilibrated at 10^{-3} Torr the system was diffusion pumped to 5×10^{-5} Torr, and the metal (Fe, Ni, or Pd) was evaporated into the polymer solution from the resistively heated crucible. Just above the melting point of the metal a brown color became noticeable in the liquid film. After 1−2 h the furnace was cooled, the flask was allowed to warm to room temperature, and the deep brown liquid was transferred to a Schlenk tube. Any bulk metal suspended in the liquid product was filtered out by passage through a 0.2-μm Teflon filter, and the filtrate was evaporated to yield a dark brown solid, which was used in subsequent pyrolysis. Polysilazanes (Table 3) for pyrolysis studies were used as in powder form as supplied, or ground in a mortar and pestle. Polysilazane/metal−organic mixtures (Table 4) for pyrolysis were prepared by mixing the powders in a mortar and pestle.

Pyrolysis Conditions. The polysilazane−ceramic mixtures, the polysilazane-stabilized metal nanocolloids, the polysilazanes, and the polysilazane/metal−organic mixtures described above and indicated in Tables 1−4, respectively, were heated in flowing He, Ar, or NH_3 at flow rates of about 300−500 cm^3/min using temperature profiles A, B, C, D, or linear heating rates of 0.5−10 °C/min, shown schematically in Figure 3, from room temperature to a maximum temperature of either 650 or 700 °C. After holding for about 2 h at the maximum temperature, the furnace power was turned off and the samples allowed to return to room temperature under flowing gas over a period of about 12 h. *Profile A*: 30 min at 25−30 °C, 60 min to 200 °C, 60 min at 200 °C, 120 min to 300 °C, 120 min at 300 °C, 120 min to 500 °C, 120 min at 500 °C, 120 min to 700 °C. *Profile B*: 30 min at 25−30 °C, 60 min to 200 °C, 240 min at 200 °C, 120 min to 300 °C, 300 min at 300 °C, 120 min to 400 °C, 300 min at 400 °C, 120 min to 600 °C, 120 min at 600 °C, 120 min to 700 °C. *Profile C*: 30 min at 25−30 °C, 60 min to 200 °C, 240 min at 200 °C, 120 min to 300 °C, 300 min at 300 °C, 120 min to 400 °C, 300 min at 400 °C, 120 min to 500 °C, 120 min at 500 °C, 120 min to 700 °C. *Profile D*: 10 min at 25−30 °C, 60 min to 200 °C, 60 min at 200 °C, 60 min to 400 °C, 60 min at 400 °C, 60 min to 650 °C (or 90 min to 700 °C). In representative experiments (route 3) assessing the thermal stability of microporosity in products pyrolyzed to maximum temperatures in the range 700−1000 °C, heating was continued for about 2 h from 700 to 850 °C (D49−1 and D49−2, Table 3), or for about 4 h from 700 to 1000 °C (D42−1 and D42−2, Table 3), respectively, and held at the maximum temperature for an additional 2 h before cooling. Typical yield of solid pyrolysis product heated to 700−1000 °C was about 70−80%. In one experiment (D28−2, Table

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Table 3. Synthesis of Microporous Ceramics by Reactive Pyrolysis of a Polysilazane in Ammonia at Low Heating Rates

sample	PSZ (MW)	pyrolysis condition	heating schedule	total surface area (m^2/g)	meso surface area (m^2/g)	micropore vol (cm^3/g)
D35-3	1300	700 °C, He	B	<1		
D39-1	1300	700 °C, NH_3	B	318	9	0.1316
D64-7	6500	700 °C, NH_3	B	312	9	0.1170
D49-1[a]	1300	850 °C, NH_3	B to 850 °C	312	9	0.1334
D49-2[a]	6500	850 °C, NH_3	B to 850 °C	303	15	0.1238
D42-1[a]	1300	1000 °C, NH_3	B to 1000 °C	111	73	0.0066
D42-2[a]	6500	1000 °C, NH_3	B to 1000 °C	202	55	0.0590
JB3-1	1300	700 °C, NH_3	C	337	28	0.1294
JA6-1[b]	1300	700 °C, NH_3	C	341	22	0.1350
JA9-1	1300	700 °C, NH_3	C	300	24	0.1157
JA19-1	1300	700 °C, NH_3	C	302	19	0.1107
JB16-1	1300	700 °C, NH_3	C	314	4	0.1318
D61-1	1300	700 °C, NH_3	1.67 °C/min	341	10	0.1293
D61-2	6500	700 °C, NH_3	1.67 °C/min	269	21	0.1059
D63-1	1300	700 °C, NH_3	6.64 °C/min	74	35	0.0200
D63-2	6500	700 °C, NH_3	6.64 °C/min	47	37	0.0049

[a] Representative samples with 2-h heat from 700 to 850 °C, or 4-h heat from 700 to 1000 °C, followed by 2-h hold at the highest temperature, prior to cooling to room temperature.[33] [b] Analysis: Si: 61.62%; N: 32.78%; C: 0.57%; H: 1.83%; total 96.8%.

Table 4. Synthesis of Microporous Ceramics by Pyrolysis of a Polysilazane/Metal−Organic Mixture

sample	PSZ (MW)	metal−organic mixture (wt % OM)	pyrolysis condition and heating schedule	metal analysis in product (wt %)	total surface area (m^2/gm)	meso surface area (m^2/gm)	micropore vol (cm^3/gm)
JA20-2	1300	≈14, $Al(acac)_3$	700 °C, He (C)	1.06, Al	215	12	0.0912
JB3-3	1300	14, $Al(acac)_3$	700 °C, NH_3 (C)	0.67, Al	504	46	0.1875
D50-1	1300	14 $Al(acac)_3$	700 °C, NH_3 (B)	1.13, Al	637	23	0.2421
JB3-4	1300	20, $Al(acac)_3$	700 °C, NH_3 (C)	1.21, Al	522	46	0.1944
JB15-1	1300	20, $Ga(acac)_3$	700 °C, He (C)	4.5, Ga	260	17	0.1063
JA7-2	1300	20, $Ga(acac)_3$	700 °C, NH_3 (C)	4.5, Ga	423	34	0.1611

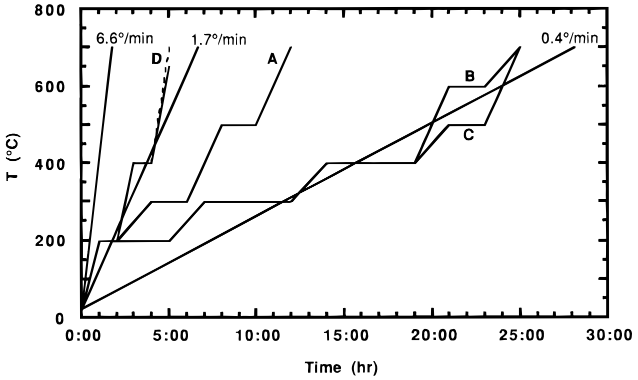

Figure 3. Heating schedules for pyrolysis and reactive pyrolysis of polysilazanes. Schedule A has a mean heating rate of 0.9 °C/min; schedules B and C, 0.45 °C/min; and schedule D, 2.1 °C/min.

1), a sample previously pyrolyzed to 700 °C was reheated at a rate of ≈200 °C/h from room temperature to 1300 °C in a special high-temperature ceramic tube furnace under flowing He, followed by cooling under flowing He to room temperature.

Characterization Techniques. NMR analyses were obtained for ^{29}Si and ^{27}Al on a commercial system (Chemagnetics CMX-500) using magic-angle spinning. Solid samples of approximately 0.1 g were contained in zirconia rotors, typically 4 mm in diameter, and the spectra were obtained using a rotation speed of approximately 10 kHz. All ^{29}Si chemical shift values were referenced to tetramethylsilane, and all ^{27}Al chemical shift values were referenced to aluminum sulfate hexahydrate. Silicon NMR spectra were obtained using either a single 90° pulse (Bloch decay) or using Si−H cross polarization. All Si and Al spectra were obtained using proton decoupling.

The pyrolyzed ceramics were examined by X-ray diffraction (XRD) for the presence of crystalline phases. The XRD patterns were collected using a Siemens D-500 powder diffractometer at a scan rate of 2°/min from 2θ values of 2° to 80° for Cu Kα radiation.

Thermogravimetric analysis of the pyrolysis of NCP-100 at 10 °C/min in flowing He and infrared analysis of the gaseous pyrolysis products were conducted using a TA Instruments TGA-51 interfaced with a Nicolet 550 FTIR spectrophotometer. Chemical analyses for Si, N, C, H, Ni, Pd and Fe were performed by Galbraith Laboratories, Knoxville, TN. Chemical analysis for Al and Ga was conducted on solid samples by a nondestructive X-ray fluorescence technique.

Nitrogen adsorption measurements were performed at 77 K using an Omnisorp 360 instrument operating in the continuous adsorption mode. Surface areas were determined from BET analysis of the low-pressure segment of the isotherm. Micropore volumes and meso- and macropore surface areas were determined from *t*-plot analysis using the Omnisorp routines. Hexane adsorption measurements were conducted gravimetrically at ambient temperature using an evacuated Cahn Instruments microbalance equipped with an automated vapor dosing system.

Results

The literature on preceramic polymer pyrolysis[3−8,14] shows that the decomposition reactions are complex, depend on the atmosphere (e.g., inert gas or ammonia) employed, and proceed in several stages with successive weight loss of typically 20−40% in branched preceramic polymers as heating proceeds from room temperature up to >1000 °C. In our work the particle size of the ceramic product powders obtained using synthesis routes 1−4 of Figure 1 at heating rates of Figure 3 was typically of the order of 100 μm, which is consistent with the observed formation of bubbles and subsequent cracking[40,41] of pyrolyzed material on this length scale. TGA/FTIR analyses under helium gas at 10 °C/min for the polysilazanes used in this work indicated a weight loss of about 20% upon heating from room temperature to 700 °C. The gaseous products of pyrolysis of the NCP-100 oligomer, determined in the effluent gas by means of FT-IR spectroscopy, are indicated in Figure

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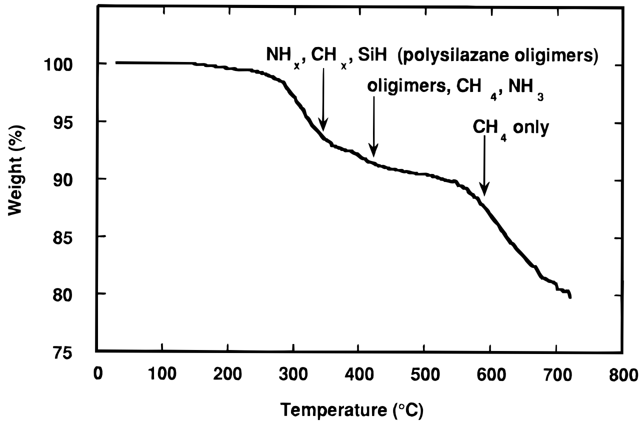

Figure 4. TGA-FTIR analysis of polysilazane in flowing helium at a heating rate of 10 °C/min. Polysilzane molecular weight ≈6500 Da.

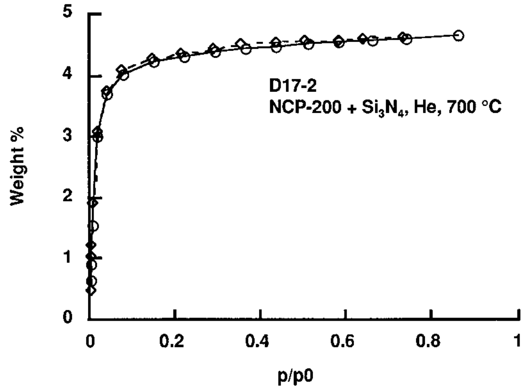

Figure 5. Typical hexane adsorption isotherm of microporous ceramic–ceramic composite by pyrolysis in helium: sample D17–2, Table 1.

4. The data showed that this polysilazane precursor decomposes in an inert atmosphere in three stages: (1) volatilization of polysilazane oligomers from 250 to 350 °C, (2) evolution primarily of ammonia and methane from 350 to 500 °C, and (3) evolution of methane alone above 500 °C. This result is similar to that previously reported in the literature for decomposition of polysilazanes.[5,25]

Route 1: Synthesis of Microporous Ceramic–Ceramic Composites by Pyrolysis of a Colloidal Polysilazane–Ceramic Mixture. The first three samples listed in Table 1 show that pyrolysis of polysilazane NCP-200 (1300 Da) and polysilazane NCP-100 (6500 Da) in helium, using heating profiles A and B of Figure 3 to a maximum temperature of 700 °C, produces powdered ceramics of very low surface area. The next five samples, prepared according to the same pyrolysis schedules, but from colloidal mixtures containing 40 wt % of micron-size particles of either Si_3N_4, SiC, or AlN, exhibited type 1 nitrogen-adsorption isotherms and had total surface areas in the range 190–300 m^2/g and micropore volumes in the range 0.08–0.12 cm^3/g. Heating rate showed no effect over the range investigated, ≈0.4 and ≈0.9 °C/min for schedules B and C, respectively. Since the original ceramic particles do not contribute to the microporosity, the actual micropore volume of the decomposed preceramic polymer phase appears to be about double that reported in Table 1. The hexane adsorption isotherm in Figure 5, of a typical sample D17–2 in Table 1, exhibits a reversible 4.5 wt % adsorption, indicating that about 70% of the micropore volume measured by nitrogen adsorption is accessible to hexane.

Microporous ceramic–ceramic composites[31,32] with surface areas greater than about 150 m^2/g were also obtained (1) for 40 wt % ceramic mixtures with NCP-200 and NCP-100 heated to temperatures in the range 500–1000 °C and (2) for a maximum pyrolysis temperature of 700 °C using micron-sized particles of other nonoxide or oxide ceramics and for a range of ceramic particle concentrations from about 30 to 75 wt %. The surface area and micropore volume of the sixth and seventh samples in the table, heated to 700 °C in ammonia, show little difference compared to those heated in helium, but chemical analysis indicates that use of ammonia significantly reduces the carbon content of the amorphous phase[24,25] in the composite. The last sample in the table illustrates that upon heating to a temperature of 1300 °C, the amorphous phase has densified with elimination of the microporosity.

Route 2: Synthesis of Microporous Metal– or Cermet–Ceramic Composites by Pyrolysis of a Polysilazane-Stabilized Metal Nanocolloid. Table 2 shows typical results for pyrolysis of polysilazane-stabilized metal colloids of Ni, Pd, and Fe in inert atmosphere (He or Ar) and NH_3 to maximum temperatures of 650 or 700 °C, following heating schedules D or C, averaging 1.7 or 0.4 °C/min, respectively. The metal content of the pyrolyzed product was approximately 30% higher than in the stablized colloid reactant, reflecting the weight loss due to volatiles from the polysilazane pyrolysis. The samples exhibited type 1 nitrogen adsorption isotherms and had total surface areas in the range of about 280–420 m^2/g and micropore volumes in the range of about 0.10–0.15 cm^3/g. The measured micropore volume closely approximates the micropore volume of the amorphous, microporous phase since the volume percent of the metal phase is of the order of 1%.

Heating rate showed no effect over the range investigated. However, it is significant that the presence of the metal reduces the temperature for the onset of weight loss[33] from about 250 °C (Figure 4) to about 100 °C and results in the formation of highly microporous materials for maximum pyrolysis temperatures as low as 400 °C. In contrast, the final weight loss at >500 °C (Figure 4) appears unchanged by the presence of the colloidal metal. This suggests that the metal has a catalytic effect on the formation and elimination of oligomers, CH_4 and NH_3, in the range of about 100–300 °C where the polymer chains retain sufficient mobility to bring them in contact with the metal particles, but that this effect ceases once the amorphous network has become rigid due to three-dimensional cross-linking. For pyrolysis in ammonia rather than in argon or helium, the principal effects are (1) reduction in the carbon content of the amorphous, microporous phase,[24–25] and (2) for the case of iron, formation of iron nitride.

Route 3: Synthesis of Microporous Ceramics by Reactive Pyrolysis of a Polysilazane in Ammonia at Low Heating Rates. Table 3 summarizes the results of a systematic study of the reaction of polysilazanes with ammonia as a function of heating schedule (Figure 3) and average heating rates from 0.4 to 10 °C/min, to a maximum pyrolysis temperature of 700 °C. Data for sample D35–3, pyrolyzed in helium following

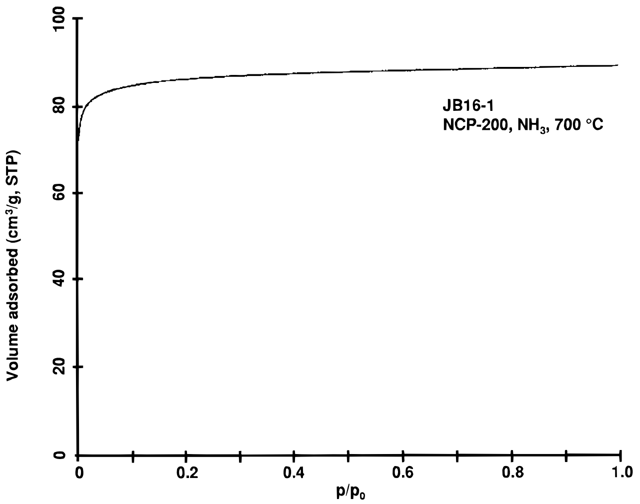

Figure 6. Typical type 1 nitrogen-adsorption isotherm of microporous ceramic by pyrolysis of polysilazane in ammonia: sample JB16−1, Table 3.

heating schedule B, are repeated from Table 1 to illustrate the key role of ammonia in achieving microporosity. All the samples pyrolyzed in ammonia at 700 °C, with the exception of samples D63−1 and D63−2, exhibited type 1 nitrogen-adsorption isotherms and had total surface areas in the range of about 270−340 m^2/g and micropore volumes in the range of about 0.11−0.14 cm^3/g. Figure 6 shows a reversible nitrogen adsorption plot, over the range of reduced pressure $p/p_0 = 0-1$, for a typical sample, JB16−1 in Table 3. Polysilazane molecular weight showed no effect on the adsorption characteristics of the pyrolized ceramic products for the molecular weight range 1300−6500 evaluated in the present work. No effect of heating rate was observed over the range 0.4−1.7 °C/min. However, there is a dramatic reduction in the level of surface area and micropore volume when average heating rate is increased above 1.7 °C/min, as illustrated by the last four samples in the table. Essentially no microporosity was observed for heating rates ≥ 10 °C/min. These findings appear consistent with studies[25] of the pyrolysis of polysilazanes in ammonia at very high heating rates, which yielded ceramic pyrolysis products with low surface area (i.e., <10 m^2/g).

Typical data for polysilazanes pyrolyzed[33] to temperatures of 850−1000 °C (Table 3) provide an indication of the upper temperature limit for stability of microporosity. Materials heated to 850 °C (D49−1 and D42−1) had comparable properties to materials heated to 700 °C. Materials heated to 1000 °C (D49−2 and D42−2) showed reduced (MW 6500) or substantially eliminated (MW 1300) microporosity.

X-ray diffraction analysis of the powdered products from reaction of ammonia with polysilazanes in this study indicated the absence of crystalline phases. Figure 7 shows typical diffractometer traces for samples from Table 3 heated to 700 °C (JA9−1) and to 850 °C (D49−1), respectively. The data show a broad peak in the 2θ range 25−35° corresponding in interatomic dimensions to silicon−nearest neighbor bonding, primarily to nitrogen, as well as a low-angle maximum at ∼4° corresponding to a *d* spacing of 20−25 Å due to scattering from the micopores. Typical chemical analysis of these microporous ceramics synthesized by route 3 at 700 °C (e.g., sample JA6−1, Table 3) indicates a composition which can be written as $Si_{3.00}N_{3.20}C_{0.06}H_{1.80}$.

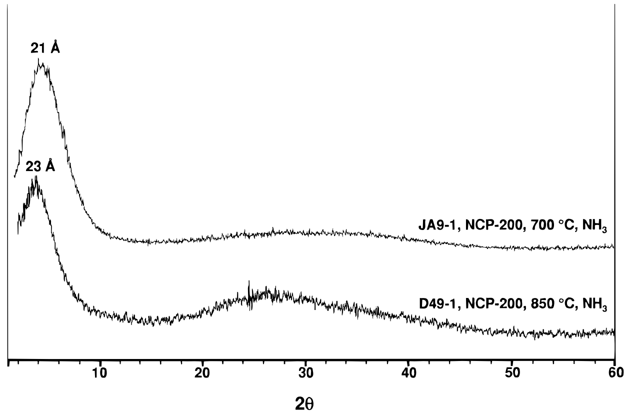

Figure 7. X-ray diffractometer traces of samples from Table 3 pyrolyzed in ammonia at 700 °C (JA9−1) and 850 °C (D49−1), respectively.

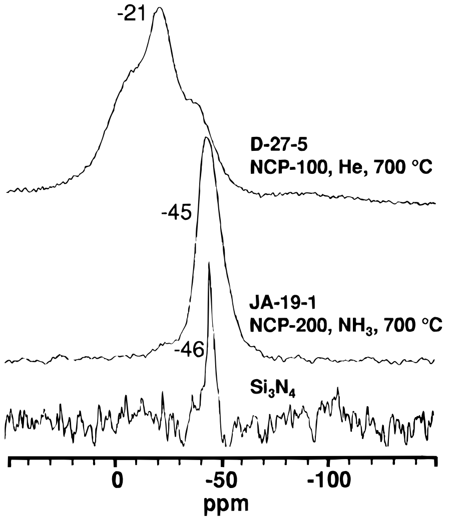

Figure 8. MAS ^{29}Si NMR spectra of (a) polysilazane pyrolized in helium (top), (b) polysilazane pyrolized in ammonia (middle), and (c) crystalline Si_3N_4 (bottom).

The data indicate that for low heating rates carbon is almost totally eliminated but that an atomic concentration of hydrogen equivalent to slightly more than one-half that of Si or N is retained.

Further investigation of the local, nearest-neighbor bonding of silicon in the ceramic pyrolysis products of Table 3 was conducted by MAS NMR spectroscopy (Figure 8). The top MAS ^{29}Si NMR spectral trace of sample D27−5, the product of polysilazane NCP-100 heated in helium to 700 °C, exhibits a strong, broad peak centered at about −21 ppm relative to tetramethylsilane, with shoulders at about −7 and −40 ppm. These peaks are within the range of chemical shifts expected for silicon atoms in a carbon[42] or mixed carbon−nitrogen environment.[43] The middle MAS ^{29}Si NMR spectral trace in Figure 8, of sample JA-19 pyrolyzed in ammonia to 700 °C, exhibits a broad peak[44] at about −45 ppm, corresponding closely to the chemical

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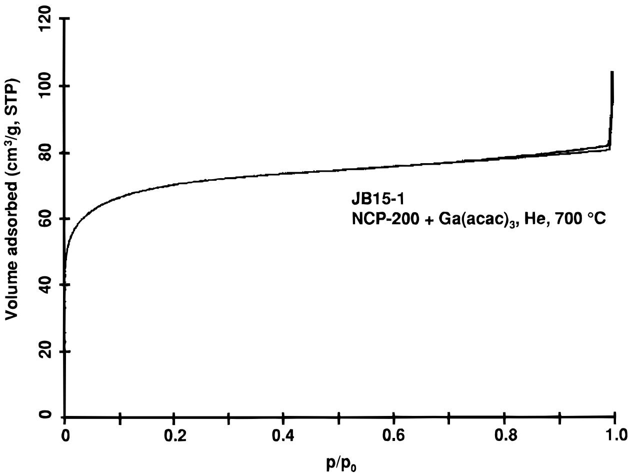

Figure 9. Type 1 nitrogen-adsorption isotherm of microporous ceramic by pyrolysis of a polysilazane/metal–organic mixture in helium: sample JAB15–1, Table 4.

shift of the sharp peak measured for crystalline Si_3N_4 at −46 ppm, the bottom trace in Figure 8. This result indicates the formation of an amorphous phase with a tetrahedral nearest neighbor configuration of the silicon, SiN_4. However, since typical chemical analysis indicates a H/N ratio of approximately ≈0.5, the amorphous, microporous silicon nitride phase probably contains some hydrogen bonded to nitrogen, similar to the result observed for nanoscale silicon nitride powders.[45]

Synthesis of Microporous Ceramics by Pyrolysis of a Polysilazane/Metal–Organic Mixture. From a systematic study of the pyrolysis of preceramic polymer/metal–organic mixtures,[34] Table 4 summarizes the results of heating polysilazane–acetylacetonate mixtures of $Al(acac)_3$ or $Ga(acac)_3$ in ammonia or helium to a maximum temperature of 700 °C, following heating schedule C of Figure 3. The samples pyrolyzed in ammonia exhibited higher surface area (420–640 m^2/g) and micropore volume (0.16–0.24 cm^3/g) than those pyrolized in helium, 200–260m^2/g and 0.09–0.11 cm^3/g. All the samples exhibited type 1 nitrogen-adsorption isotherms, as illustrated by the reversible nitrogen adsorption plot shown in Figure 9 for sample JB15–1 in Table 4.

The local coordination number and nearest-neighbor bonding of aluminum and silicon in a microporous ceramic prepared by reacting a mixture of NCP-200 and $Al(acac)_3$ in ammonia were investigated by MAS NMR spectroscopy. The middle trace of Figure 10 compares the ^{27}Al MAS NMR spectrum of sample JB3–4 (Table 3) with that of crystalline AlN, top trace, and with that of crystalline $Al(acac)_3$, bottom trace. The AlN peak at −113 ppm has been identified[46] with tetrahedral AlN_4 local bonding, and the $Al(acac)_3$ peak at −4 ppm has been identified[47] with octahedral AlO_6 local bonding. The peak for JB3–4 at −51 ppm appears to indicate a tetrahedral, nearest-neighbor bonding to aluminum, AlO_4 , since it is close to that observed[48] for Al in zeolites, for example, at −60 ppm in zeolite A. The ^{29}Si MAS NMR spectrum of sample JB3–4 exhibits a strong peak at −47 ppm, indicative of tetrahedral nearest-neighbor bonding to silicon, SiN_4, with a weaker peak at about −61 ppm which is close to the peak observed[49] in crystalline Si_2N_2O at −63 ppm attributed to tetrahedral nearest-neighbor bonding to silicon, SiN_3O. These data are consistent with the interpretation that in sample JB3–4, local AlO_4 tetrahedra are widely dispersed in an amorphous silicon nitride matrix, since the atomic ratio of Si/Al in this sample is ≈50/1.

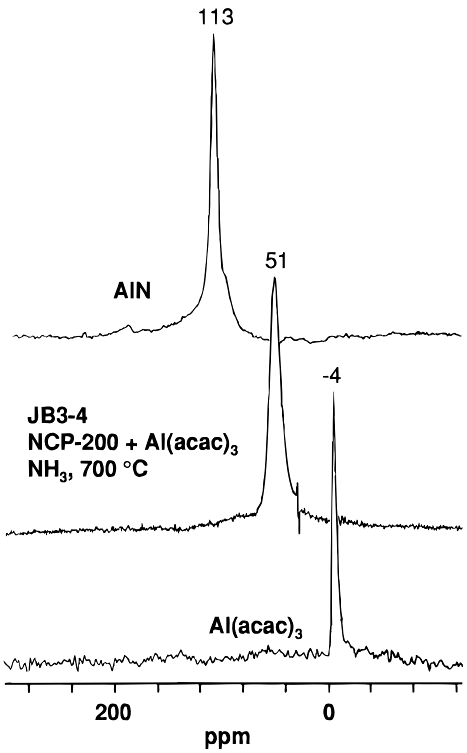

Figure 10. MAS ^{27}Al NMR spectra of (a) crystalline AlN (top), (b) pyrolized polysilazane–$Al(acac)_3$ (middle), and (c) crystalline $Al(acac)_3$ (bottom).

Discussion

Summary of Previous Literature. The formation of pores at length scales from the nanoscale to the micron scale in ceramics synthesized by pyrolysis of preceramic polymers has been discussed by a number of workers[2,3,8,16,17,22,40–41,50] over the past 15 years. It has been well recognized that as the preceramic polymer with a density typically ≈1 g/cm^{-3} decomposes upon heating from room temperature to high temperatures to form a ceramic with a density ≈3 g/cm^{-3}, considerable bulk shrinkage must occur if pores are to be totally avoided, which for pores of micron dimensions limits the bulk dimension[40,41,49] of the ceramic phase to $\cong$100 μm. Total avoidance of pores in bulk parts is also made more difficult because volatiles having a volume several hundred times that of the ceramic product are evolved. Although investigation of the volatile species evolved during preceramic polymer pyrolysis process and characterization of the ceramic products formed are prominent research directions[8] in preceramic polymer chem-

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istry and engineering, the generic factors governing the formation of micropores (i.e., <20 Å) in ceramics synthesized by preceramic polymer decomposition are not well understood. Despite the generic proposal[23] for synthesis of microporous materials by this method, only a few reports of their formation have appeared, for relatively specialized synthesis and processing conditions.[27–30]

Criteria for Formation of Microporous Products. The studies of the pyrolysis of low molecular weight polysilazanes reported in the current work provide some insight into the factors that are important for the synthesis of microporous ceramics from preceramic polymers. It is to be noted that a type 1 nitrogen-absorption isotherm, not the surface area of the pyrolysis product, is the valid criterion for microporosity. Prior results on pyrolysis of vinyl-based preceramic polymers[26] up to 1000 °C have shown the formation of high surface area materials (>200 m^2/g) as a result of formation of very fine powdered materials, which decreased substantially in surface area at higher temperatures due to sintering to large particles with low surface area.

In the present work, use of low average heating rates, typically ≤2 °C/min, appears the most useful in achieving the microporosity in each of the four routes discussed above. However, the absence of microporosity in ceramic products pyrolyzed at 700 °C and above in inert gas from a pure polysilazane even at low heating rates indicates this is not the sole factor. In routes 1 and 2 for synthesis of microporous ceramics from mixtures of polysilazanes with (1) micron-size ceramic particles and (2) nanoscale metal particles, respectively, catalysis and surface reaction of the particles appear effective in forming at relatively low temperature a rigid, three-dimensional amorphous network, which can maintain its rigidity upon subsequent decomposition to evolve volatile species, leaving behind open micropores. For route 3, reaction of ammonia gas appears effective in achieving a three-dimensional amorphous network, which undergoes decomposition at higher temperatures to form a microporous ceramic when low heating rates are employed. For route 4, the acetylacetonates of aluminum and gallium also appear effective in achieving a rigid network which develops microporosity upon further heating. It is also apparent, however, that ammonia aids in the process, since a factor of 2 higher surface area and micropore volume result from the combined use of ammonia and the acetylacetonate.

Scientific Questions for Further Study. The discovery of four synthesis routes reported here for pyrolysis of polysilazanes to microporous ceramics provides a stimulus for further research in this area. Despite numerous studies of pyrolysis products of preceramic polymers by FTIR and mass spectroscopic methods, almost no direct evidence is available upon which to base conclusions or hypotheses regarding the mechanism of condensation of the solid pyrolysis products and the formation of microporosity. By inference, the relatively small oligomer molecules (e.g., ≈ 25 Å × 10 Å × 10 Å for NCP-200) appear to undergo a rapid and extensive cross-linking reaction with either ammonia or the surfaces of the ceramic or metal particles. Otherwise, unzipping of the relatively low molecular weight polysilazane would lead to almost complete volatilization. In fact, just such complete volatilization behavior was observed[51] when heating a linear polysilane preceramic oligomer, permethylpolysilane, to a temperature of 700 °C.

The limit of stability of microporosity was 850 °C < T < 1000 °C for materials pyrolyzed from polysilazanes. However, pyrolysis[33] of polycarbosilane and polysilastyrene to 1000 °C yielded highly microporous materials with surface areas of 300–400 m^2/g. These results confirm that molecular structure and molecular weight of the polymeric ceramic precursor[27] are also important variables that must be investigated.

Complete understanding and control of the factors involved will require much additional investigation, including (1) study of the kinetics and mechanisms of reactions of particles, ammonia, and metal–organic compounds with preceramic polymers of controlled molecular weight and molecular structure, (2) precise characterization of the rate and nature of gas evolution, and (3) investigation of the possible mechanisms by combining systematic experimental investigations with detailed molecular modeling studies of bond breaking, gas evolution, and topological relaxation of the three-dimensional amorphous networks formed during the pyrolysis process. A particularly critical issue is the determination of criteria which differentiate between the formation of open microporosity (i.e., measurable by nitrogen absorption) and closed microporosity (i.e., detectable by density measurements or scattering techniques). A final issue is the question of thermal stability of the microporous ceramics. The results reported here for polysilazanes show that there is little difference in the stability of the materials pyrolyzed over long times to maximum temperatures in the range 850–1000 °C. However, all open microporosity is lost at some temperature in the range 1000–1300 °C, which depends upon the molecular weight and the molecular structure of the precursor. This may involve closure of pore openings with retention of closed porosity, since temperatures above 1300 °C are typically required[24] for long-range lattice rearrangement of amorphous ceramics, such as silicon carbide or silicon nitride, leading to recrystallization.

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