

Preparation of Highly Porous Silica Gel from Poly(tetramethylene oxide)/Silica Hybrids

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Received September 27, 1996. Revised Manuscript Received June 13, 1997[⊗]

Porous silica gels with high surface area were prepared by calcination of silica/poly(tetramethylene oxide) (PTMO) hybrid network materials. The variation of the surface area of these silica gels with PTMO/silica composition and molecular weight of PTMO was investigated. Surface area analysis showed that for all oligomeric molecular weights of PTMO, high values in the range 700–1000 m² g⁻¹ could be obtained. The optimum PTMO/TEOS weight ratio was 30–50. Pore size analysis indicated that samples with high surface areas were mesoporous, while samples with low or medium surface areas were microporous. This unusual result was obtained as a consequence of the particle size of the materials, small for the high surface area materials and large for the low surface area materials. The hysteresis in the adsorption–desorption isotherms indicated that the pores were cylindrical in shape.

Introduction

Inorganic/organic hybrid materials known as “ceramers” or “ormosils”, prepared through the combination of inorganic metal alkoxides and functionalized organics by the sol–gel approach, have been developed and studied since the early 1980s.^{1–6} The incorporation of polymeric or oligomeric materials into inorganic networks by the sol–gel process offers an opportunity to optimize specific properties independently. An important characteristic of inorganic/organic hybrid materials is the homogeneous or near-homogeneous dispersion of the organic species at the molecular level in the inorganic network, which has led to the development of novel hybrid materials that have or will have potential applications in many fields. One such application is the preparation of highly porous metal oxides having microscale pores. This can be readily done by calcination of the hybrid materials at temperatures below the fusion temperature of the metal oxide, normally 500–600 °C.^{7,8} At these temperatures, the organic species will decompose, leaving the inorganic component with nanoscale or microscale pore size.

For porous materials, the control of pore size and structure is very important for their applications such as adsorbents, separation membranes, and catalyst supports.⁹ A number of different types of hybrid materials have been prepared by different synthetic approaches by various researchers and utilized as the

precursors for high surface area porous materials, among them porous silica.^{10–17} Chujo and Saegusa prepared inorganic/organic hybrid materials with silane endcapping poly(*N*-acetyleneimine) (POZO) as the organic component and tetraethoxysilane (TEOS) as the inorganic component, and subsequently produced a porous silica material with surface area as high as ca. 810 m²/g.^{10,11} They indicated in their work that it is possible to control the pore size by using so-called starburst dendrimers as the organic component. Nakanishi et al. also prepared a porous silica gel using poly(acrylic acid) as the organic component.¹⁴ In this work, the structure of the hybrid was controlled by utilizing the competition between polymerization and phase separation in the mixed solution, and the porous silica gel was obtained using solvent extraction of the organic polymer instead of pyrolysis. Other polymers that have been used as organic components include poly(ethylene glycol) (PEG),^{15,16} polymer electrolytes and proteins,¹⁷ and poly(vinyl alcohol) (PVA).¹² Besides porous silica gels, microporous silica/zirconium oxide materials have also been prepared utilizing the calcination approach.

The synthesis and structure of poly(tetramethylene oxide) (PTMO)/silica hybrid network materials have been extensively studied in one of our laboratories over the past 10 years.^{18–24} This paper addresses the preparation of highly porous silica gel from PTMO/silica

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⊗ Abstract published in *Advance ACS Abstracts*, August 15, 1997.

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hybrid network materials through the calcination approach and characterization of these materials by measurements of the surface area, pore size, and pore volume. Adsorption–desorption isotherms are analyzed in terms of the classification scheme discussed in ref²⁵ which distinguishes between materials with different pore diameters (d_p): microporous ($d_p < 2$ nm), mesoporous ($2 < d_p < 50$ nm), and macroporous ($d_p > 50$ nm).²⁵ The surface area and pore size of the microporous materials were obtained by the Dubinin–Radushkevitch (DR) method and Horvath–Kawazoe (HK) method, respectively. While the Brunauer–Emmett–Teller (BET) method was used to obtain surface area and pore size of mesoporous and nonporous materials.

Experimental Section

Materials. (3-Isocyanatopropyl)triethoxysilane was purchased from Huls America, Inc. Hydroxyl-terminated poly-(tetramethylene oxide) (PTMO) with number average molecular weight 650, 1000, 2000, and 2900 g/mol were obtained from Polysciences, Inc. Tetraethoxysilane (TEOS), hydrochloric acid (HCl), and 2-propanol (IPA) were obtained from the Aldrich Chemical Co.

Preparation of PTMO/Silica Hybrids. The hydroxyl-terminated PTMO was first functionalized with (3-isocyanatopropyl)triethoxysilane by our standard route reported earlier.²⁶ Because the triethoxysilane end-capped PTMO oligomers were in crystalline form prior to the reactions, they were heated in a beaker at ca. 70 °C before mixing with the desired amount of TEOS and solvent IPA. The mixture was stirred for about 20 min at room temperature. To this mixture was added water and acid catalyst. The molar ratio of H₂O/ethoxy/HCl was 4/1/0.04 in all cases. The contents of the beaker were stirred for an additional 2 min before being poured into polyethylene sample vials (20 mm (D) × 20 mm (H)) and left at room temperature to cure. The reaction usually proceeded rapidly at ambient temperature and the system turned into a gel within 30 min. However, depending on initial composition, the drying period varied from 1 week to 1 month. A material indicated by TEOS60–PTMO(2000)40 contains 40 wt % of PTMO (MW = 2000) with respect to the total initial weight of TEOS and functionalized PTMO.

Calcination of PTMO/Silica Hybrids. The inorganic/organic composites were calcinated at 540 °C in air for 24 h to dehydrate them thoroughly and remove PTMO. The heating rate from ambient was 1 °C/min, and the cooling rate was 10 °C/min.

Apparatus. Thermogravimetric analysis (TGA) was carried out on a Seiko simultaneous TGA/DTA analyzer (Model TG/DTA200) under air. Surface area, pore size, pore volume, and adsorption–desorption isotherm measurements were done on a Micromeritics ASAP 2010 Chemi system. Prior to nitrogen physisorption experiments the samples were degassed at 473 K for 2 h.

Results and Discussion

Chemistry. The general sol–gel reaction of the PTMO–TEOS system is illustrated in Scheme 1.

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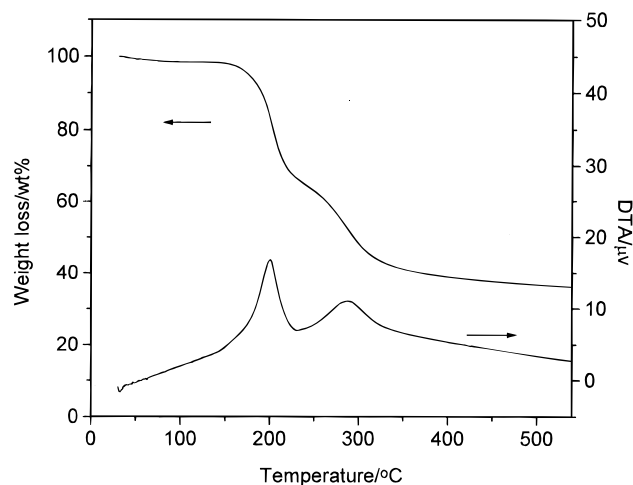
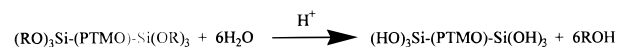
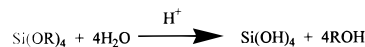


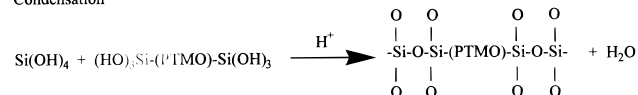
Figure 1. TGA and DTA curves of TEOS 60-PTMO(2000)40 with heating rate 1 °C/min.

Scheme 1

Hydrolysis



Condensation



As shown, the PTMO oligomer is chemically bonded into the SiO₂ network. The high transparency of the final products, along with the large difference in refractive index between the two components demonstrated that no macroscale phase separation occurs. However, these systems do tend to undergo some microphase separation similar to segmented or block polymers. Indeed, structural analysis from previous studies demonstrated that the scale of localized phase separation was also found to be dependent on reaction conditions, composition, and molecular weight (MW) of PTMO. Typically the scale length for this microphase or domain texture is ca. 10 nm.⁴

Evolution of Surface Area and Pore Size. The evolution of the surface area and pore size of silica was studied by following these properties at different stages of the sample pyrolysis in air, as shown by the TGA and DTA results. Figure 1 shows typical results obtained by TGA and DTA. TGA showed that most of the weight loss occurred between 155 and 340 °C when the heating rate was 1 °C/min. There were two distinct weight loss stages within this temperature range, 155–230 and 230–340 °C, each being associated with a thermal degradation process as shown by the two endothermic peaks in the DTA curve. The first weight loss stage is associated with the oxidative degradation of PTMO when heated in contact with air. During this stage, the backbone of the PTMO which contains ether linkages are subject to oxidation and forms hydroperoxides which subsequently undergoes thermal degradation. Under these conditions thermal decomposition starts at ca. 155 °C with the evolution of tetrahydrofuran, and the formation of aldehydes and ketones.²⁷ The second weight loss stage is conjectured to be due to the thermal degradation associated with the (isocyanatopropyl)-

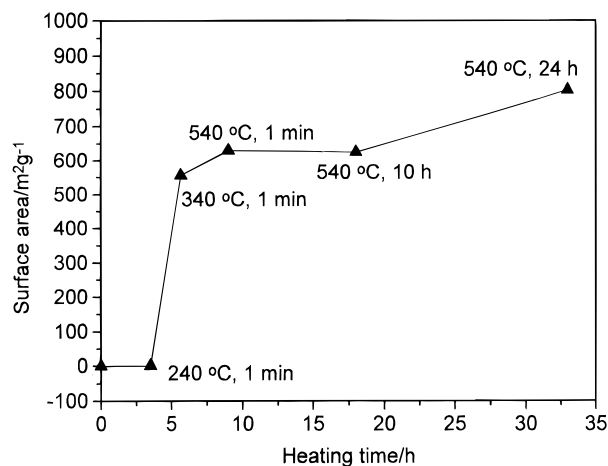


Figure 2. Evolution of surface area of TEOS60-PTMO(2000)-40 during sample preparation.

Table 1. Summary of Surface Area, Pore Size, Pore Volume and Isotherm Type at Different Stages of Thermal Degradation of the Organic PTMO (MW 2000), at a Weight Ratio of 40/60 PTMO/TEOS

temp (°C)	surface area (m ² g ⁻¹)	particle size (nm)	pore volume (cm ³ g ⁻¹)	pore size	isotherm type
240	1.7 ^a	1477	0.002	4.4 ^a	II
340	556 ^b	6.4	0.16	<1.0 ^c	I
540	630 ^b	4.3	0.23	<1.0 ^c	I
540 (10 h)	625 ^a	4.0	0.33	2.2 ^a	IV
540 (24 h)	803 ^a	3.1	0.61	3.1 ^a	IV

^a Obtained by the Brunauer-Emmett-Teller (BET) method.

^b Obtained by the Dubinin-Radushkevitch (DR) method. ^c Obtained by the Horvath-Kawazoe (HK) method.

triethoxysilane species based on the fact that there is no known second weight loss stage for pure PTMO.

Figure 2 and Table 1 show the evolution of surface area and pore size for sample TEOS60-PTMO(2000)-40. The reaction was stopped at the following temperatures: 240 (held for 1 min), 340 (held for 1 min), 540 °C (held for 1 min, 10 h, and 24 h). The surface area, pore volume, pore size were obtained from adsorption-desorption isotherm measurements. The surface area did not start to increase until the temperature reached 240 °C. At this point according to Figure 1, the sample had lost 33% of its original weight although its surface area was only 1.7 m²/g. Following this initial stage, the surface area started to increase and attained 630 m²/g when the temperature reached 540 °C, and the sample had lost 64% of its original weight. It can be noted from Figure 2 that surface area increased as the samples were held at 540 °C for 24 h. There was no weight loss after 10 h under this temperature. This clearly suggests that under these conditions, there is no significant sintering of silica.

From Figure 3 and Table 1 it can be seen that at 240 °C, the isotherm is type II in the classification of ref 25, which is typical of either a nonporous material or a material with pore diameters larger than micropores.²⁵ Pores with diameters less than 2 nm are in the micropore range, pores with diameters between 2 and 50 nm are mesopores, and pores larger than 50 nm are macropores. By comparing the pore size and the pore volume from Table 1 for the 240 °C sample, it can be

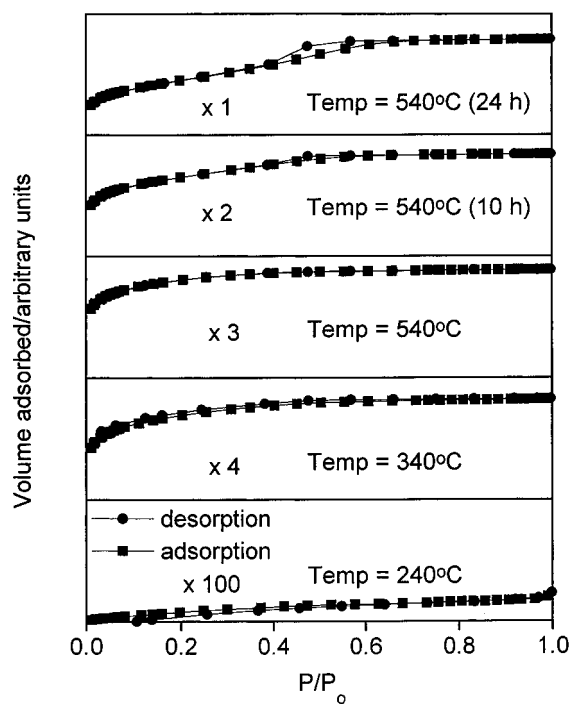


Figure 3. Measured isotherms obtained on PTMO/TEOS samples having a weight ratio of 40/60 having a PTMO molecular weight of 2000. The isotherms were determined following the thermal treatment to the indicated temperature; see text for details.

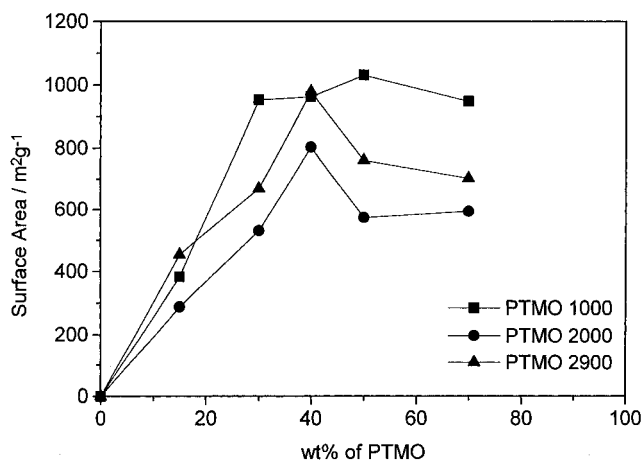


Figure 4. Effects of PTMO molecular weight and composition on the surface area.

inferred that there are probably very few pores whose dimensions are in the mesopore range. Also, based on the pore volume the material is likely nonporous in nature. In the second stage, at 340 °C, the surface area increases considerably and a type I isotherm is observed. In the third stage at 540 °C (held for 1 min), the surface area increases further and a type I isotherm is observed, which matches with the pore size analysis, shown in Table 1. The fifth and sixth stage at 540 °C (held for 10 and 24 h respectively), shows that the surface area increases and a type IV isotherm is observed, indicating pores in the range of mesopores which compares well with the pore size, shown in Table 1. The hysteresis of the type IV isotherm indicates type A which corresponds to cylindrical pores.

Effect of PTMO MW and Content. Figure 4 shows the dependence of the surface area on the MW of PTMO and the composition ratio of PTMO and TEOS. The surface area is a maximum at an intermediate ratio of

Table 2. Summary of BET Surface Area, Pore Size, Pore Volume, and Isotherm Type of the Samples

PTMO MW (g mol ⁻¹)	feed ratio (PTMO/TEOS)	surface area m ² g ⁻¹	pore size (nm)	pore volume (cm ³ g ⁻¹)	isotherm type
1000	15/85	383 ^a	<1.6 ^c	0.13	I
1000	30/70	953 ^a	<0.9 ^c	0.34	I
1000	40/60	963 ^b	2.5 ^b	0.55	IV
1000	50/50	1031 ^b	2.6 ^b	0.66	IV
1000	70/30	948 ^a	<0.9 ^c	0.35	I
2000	15/85	288 ^a	<1.6 ^c	0.10	I
2000	30/70	531 ^a	<1.0 ^c	0.17	I
2000	40/60	803 ^b	3.0 ^b	0.61	IV
2000	50/50	573 ^b	3.5 ^b	0.41	IV
2000	70/30	593 ^a	<0.9 ^c	0.19	I
2900	15/85	454 ^a	<1.0 ^c	0.17	I
2900	30/70	669 ^a	<0.7 ^c	0.20	I
2900	40/60	980 ^b	3.9 ^b	0.95	IV
2900	50/50	760 ^b	2.8 ^b	0.40	IV
2900	70/30	702 ^b	3.3 ^b	0.49	IV

^a Obtained by the Dubinin–Radushkevitch method. ^b Obtained by the Brunauer–Emmett–Teller (BET) method. ^c Obtained by the Horvath–Kawazoe method.

Table 3. Dependence of Surface Area and Pore Size on Different Molecular Weights of PTMO at a PTMO/TEOS Ratio of 40/60

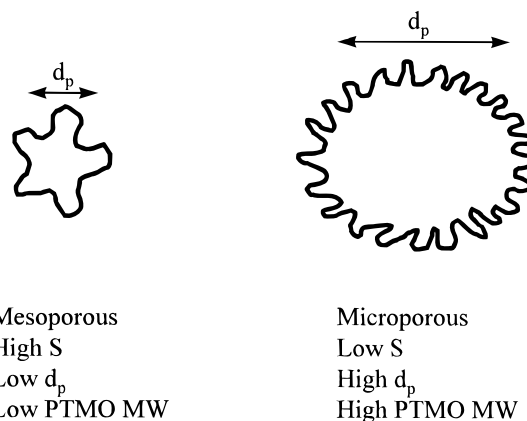
sample	PTMO MW (g mol ⁻¹)	surface area (m ² g ⁻¹)	pore size (nm)	pore volume (cm ³ g ⁻¹)
1	650	1029 ^a	<1 ^b	0.33
2	1000	963 ^c	2.5 ^c	0.55
3	2000	803 ^c	3.0 ^c	0.61
4	2900	980 ^c	3.9 ^c	0.95

^a Obtained by the Dubinin–Radushkevitch method. ^b Obtained by the Horvath–Kawazoe method. ^c Obtained by Brunauer–Emmett–Teller (BET) method.

PTMO/TEOS. For all of the molecular weights of PTMO studied, high surface areas were obtained with an optimum PTMO/TEOS weight ratio of 30–50%. The pore sizes of the samples with high surface areas were in the range of mesopores and the samples with lower surface areas were microporous. This is unusual and can be explained from the particle size of the materials. The particle size of the mesoporous materials is smaller than the microporous materials which results in the higher surface area of the former. This is estimated to be 2.8 nm for sample 4 (Table 3) from the formula $d_p = 6/S\rho$, where S is the surface area and ρ the bulk density of SiO₂ (2.2 g cm⁻³).²⁸ For the microporous material, the relationship between particle size and surface area is

$$d_p = 6\left(1 + \frac{2}{3} \frac{L}{R}\right) / S\rho \quad (1)$$

where L/R is the ratio of the average length to radius of the pores.²⁹ Assuming short pores of $L/R = 4$, this gives for sample 1 (Table 3) a particle size of 9.7 nm. There is a direct relationship between pore size and MW of PTMO with pore size increasing with increasing MW (Table 3). This is consistent with the finding of localized phase separation of scale length 10 nm reported earlier.⁴ The overall relationship between the physical properties of the silica gels is illustrated schematically in Figure 5. The model shows that the silica obtained from low PTMO MW is mesoporous, with high surface area and small particle size, whereas the silica obtained from

**Figure 5.** Schematic representation of the mesoporous and microporous silica gels obtained from low and high PTMO MW.

high PTMO MW is microporous, with low surface area and large particle size.

The types of adsorption–desorption isotherms of the samples studied are summarized in Table 2. The samples with low PTMO/TEOS ratio are type I. With an increase in the ratio of PTMO/TEOS the isotherm changes to type IV, and with further increase in the ratio the isotherm remains type IV in the case of PTMO MW 2900 and changes to type I in the case of PTMO MW 1000 and 2000. This corresponds well with the pore sizes measured as shown in Table 2. The type IV isotherm shows hysteresis for type A which indicates cylindrical pore structures.²⁵

Effect of Molecular Weight of PTMO. Table 3 shows the effect of molecular weight of PTMO for a PTMO/TEOS weight ratio of 40/60. It is evident that silica gels with high surface area can be obtained from the samples with both the lower or the higher PTMO molecular weight systems. As mentioned earlier, the pore size increases with increase in the molecular weight and a microporous material can be obtained with PTMO of the lowest molecular weight. It may be that the templating effect of the PTMO on the silica exerts its influence on surface area at the scale of the lowest PTMO molecular weight. Thus, there is no effect on surface area of further increasing the PTMO chain length.

Conclusions

Porous silica with high surface area were prepared by calcination of silica/poly(tetramethylene oxide) (PTMO) hybrid network materials. The surface area analysis showed that for all oligomeric molecular weights of PTMO utilized, high surface areas in the range 700–1000 m² g⁻¹ can be obtained with an optimum PTMO/TEOS weight ratio of 30–50. The pore size analysis indicated that for samples with high surface areas the pores are mesoporous, and for samples with lower surface areas the pores are microporous. This results from the particle size of the materials which is smaller for the mesoporous materials. The hysteresis of the adsorption–desorption isotherm indicated that the pores are cylindrical in shape.

Acknowledgment. The authors greatly acknowledge the financial support of the Air Force Office of Scientific Research under grant number F49620-94-1-0149DEF, and DOE Basic Energy Science under grant number DE-FG02-96ER14669.

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(29) This is obtained by assuming that cylindrical pores are uniformly spaced at a distance of one diameter from each other.