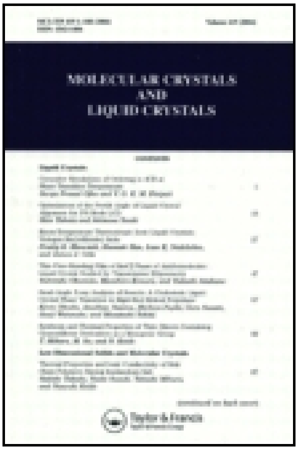

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Sol-Gel Synthesis of Mesoporous Titania using Nonsurfactant Organic Compounds as Templates

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Organic-inorganic composite materials were prepared via HCl-catalyzed sol-gel reactions of tetrabutyl titanate at room temperature in the presence of nonsurfactant compounds, such as 2,2-bis(hydroxymethyl)propionic acid, glycerin and pentaerythritol, as templates or pore-forming agents. Removal of the nonsurfactant molecules from the composites by extraction with water resulted in mesoporous titania materials. Characterized with nitrogen adsorption-desorption isotherms, X-ray diffraction and transmission electron microscopy, these materials were found to have large surface areas (~300 m^2/g) and pore volumes (~0.25 cm^3/g) as well as narrowly distributed pore diameters of around 3.2 nm. Similar results were also obtained when a neutral surfactant poly(ethylene glycol) was used as the templates. In the presence of templates, the titania materials obtained may contain crystalline anatase phase.

Keywords: sol-gel; tetrabutyl titanate; 2; 2-bis(hydroxymethyl)propionic acid; glycerin; pentaerythritol; mesoporous titania

INTRODUCTION

Since 1980s, the synthesis of organic-inorganic hybrid/composite materials through sol-gel reactions has attracted much attention of materials scientists[1]. A variety of new materials have been prepared to contain both inorganic, such as silica and titania, and organic, especially polymers such as poly(methyl

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methacrylate), components[1,2]. The organic components could be removed from the hybrid/composite materials by means of, e.g., thermal degradation to afford porous inorganic materials, though the pore structure and parameters could not be well controlled. In 1992, researchers at Mobil achieved a major breakthrough in the synthesis of mesoporous materials[3,4]. By removing organic surfactant molecules from surfactant-silica sol-gel composites via calcination, they obtained mesoporous silica molecular sieves (MCM-41). Since the surfactant molecules and their assemblies function as templates for the formation of silicate framework in the sol-gel reactions, the structure, size and volume of pores can be designed. Such a surfactant-templated sol-gel process has since been extensively studied and numerous mesoporous silica and other metal oxides have been synthesized using various ionic or neutral surfactants as templates[3-15].

These mesoporous materials might find applications in separation and catalysis, because of their large and uniform pore sizes. Many metal oxides are known for their good catalytic activities and, hence, mesoporous molecular sieves of these metal oxides could be particularly advantageous in catalysis[10-15]. The synthesis of mesoporous titania molecular sieves (Ti-TMS1) was reported in 1995 through the sol-gel reactions of titanium isopropoxide bis-acetylacetonate in the presence of alkylphosphate surfactant templates[12]. Since then there have been a number of works investigating the synthesis of mesoporous titania based on the surfactant-templating routes and the properties of the materials[13-15]. Recently, a nonsurfactant-templating sol-gel route to mesoporous materials has been developed[16-18], in which nonsurfactant organic molecules such as D-glucose, D-maltose, dibenzoyl tartaric acid, etc., were employed as templates or pore-forming agents. Upon removal of the templates by simple extraction, mesoporous silica[16,17] and alumina[18] materials were obtained with large surface areas and pore volumes as well as narrow pore size distributions. In this paper, we report the first synthesis of mesoporous titania materials through the nonsurfactant-templating route. The process consists of HCl-catalyzed sol-gel reactions of tetrabutyl titanate (TBT) in the presence of an organic compound 2,2-bis(hydroxymethyl)propionic acid (BHPA), glycerin, or pentaerythritol as template at various concentrations, followed by removal of the template via solvent extraction.

EXPERIMENTAL SECTION

Tetrabutyl titanate (TBT, from Aldrich Chemical) was pre-treated in absolute alcohol medium (TBT: EtOH = 1: 7 v/v) in the presence of aqueous HCl (0.28 mol/L) catalyst (TBT: HCl=1: 0.01 mol/mol) at 60 °C for 2-3 hours. Upon cooling to room temperature, an appropriate amount of aqueous solution of 2,2-bis(hydroxymethyl)propionic acid, glycerin or pentaerythritol was added into the pre-treated solution under vigorous stirring. The amount of solution added was determined by desired template content (i.e., 0 to 50 % by weight) in the final dry composite gels. The resultant homogeneous solution was cast into several 50-mL beakers, which were then sealed with paraffin films. After standing at room temperature for 24 hours, a number of pinholes were made on the paraffin film covers with syringe needle to allow for slow evaporation of the solvent and by-products of the sol-gel reactions. Upon drying at ambient temperature for 10-15 days, template-containing TiO_2 materials were obtained as yellow solids. The compositions of the template-containing TiO_2 materials, as represented by the template content (wt%), were determined by means of thermogravimetric analysis (TGA) from the weight loss at 800 °C. The solid samples were then ground into fine powders and extracted with methanol or distilled water for 2-3 days using Soxhlet apparatus to remove the template molecules, followed by drying at 70 °C in a vacuum oven to afford the mesoporous TiO_2 materials. The extent of the template removal was also monitored by TGA at 800 °C on the extracted samples.

The TGA measurements were performed on a TA SDT2960 thermogravimetric analyzer with a heating rate of 20 °C/min under an air flow at a rate of 100 mL/min. The Brunauer-Emmett-Teller (BET) surface area and pore parameters were determined by fifty-five points full analysis of nitrogen adsorption-desorption isotherms at 77 K on samples that were degassed at 100 °C for 2 h prior to the isotherm measurement. A Micromeritics ASAP-2010 analyzer was employed for data collection and analysis. The X-ray diffraction pattern (XRD) was recorded on a Rigaku X-Ray Diffractometer DMAX 2000 using Cu Kα radiation (λ=1.5418 Å) at a scan rate of 1°/min. The morphology of the materials was examined on a Hitachi H-9000 NAR HREM transmission electron microscopy (TEM) with an accelerating voltage of 300 kV. The TEM samples were prepared by dipping an alcohol suspension of fine powder of titania on a Cu grid coated with a holey C film and dried at room temperature.

RESULTS AND DISCUSSION

The synthesis of mesoporous titania via the nonsurfactant-templating route generally consists of three major steps: (1) pre-treatment of the inorganic precursor, i.e., tetrabutyl titanate (TBT), with aqueous HCl catalyst, (2) gelation and drying in the presence of nonsurfactant templates and (3) removal of templates by extraction. In the synthesis, we noticed that the concentration of HCl catalyst has a significant effect on the sol-gel reactions. At a low HCl concentration of 0.14 mol/L, the TBT solution in alcohol always becomes translucent or opaque, indicating the occurrence of macroscopic phase-separation. On the other hand, at a higher HCl concentration (0.28 mol/L), the solution remains transparent and homogeneous throughout the entire process.

Before the Soxhlet extraction, the template-containing titania gels exhibit very small BET surface areas and pore volumes. After the extraction, both the surface areas and pore volumes increase drastically. For example, the BET surface area of sample A3 which contained 28.5 wt% 2,2-bis(hydroxymethyl)propionic acid template was about 1.5 m^2/g, which increased to 330 m^2/g after complete removal of the template. The surface area data and pore parameters of the samples after extraction are summarized in Table 1. In general, all the samples prepared with templates have much larger surface areas (~250 to 330 m^2/g), pore volumes (~0.18 to 0.29 cm^3/g) and pore diameters (~2.6 to 3.6 nm) than the control sample (SGT0) prepared without template under otherwise identical conditions (i.e., 1.2 m^2/g, 0.0023 cm^3/g, and 0.5-1.1 nm, respectively). Compare to mesoporous silica materials prepared via both surfactant[3-5] or nonsurfactant[16,17] templating routes, the surface areas of mesoporous titania are relatively smaller. However, the surface area of 300 m^2/g has been considered reasonably, if not remarkably, high for mesoporous titania materials prepared via surfactant-templating route[12-15]. The t-plot analysis of the nitrogen sorption data reveals that the contributions of micropores to the measured BET areas and pore volumes are negligible in all the titania samples prepared with nonsurfactant templates.

TABLE 1. Properties of the TiO_2 sol-gel materials after removal of the templates (A) 2,2-bis(hydroxymethyl)propionic acid, (B) glycerin, (C) pentaerythritol and (D) poly(ethylene glycol) by extraction with water.

Sample code	Template content (wt%)	BET surface area (m^2/g)	Pore volume (cm^3/g)	BJH pore diameter (nm)
SGT0[a]	0	1.2	0.0023	1.11
A1	9.0	268	0.244	3.17
A2	16.5	295	0.266	3.18
A3	28.5	330	0.284	3.23
A4	37.5	338	0.292	3.16
B1	5.0	251	0.235	3.14
B2	16.5	248	0.244	3.25
B3	28.5	272	0.258	3.23
B4	37.5	289	0.259	3.18
B5	44.5	286	0.258	3.14
B6	50.0	267	0.257	3.25
C1	9.0	300	0.274	3.31
C2	28.5	303	0.269	3.38
D1[b]	48.2	292	0.255	3.41
D2[b]	52.5	312	0.247	3.36

[a] Control sample: sol-gel TiO_2 prepared without any templates.

[b] Molecular weights of poly(ethylene glycol) in D1 and D2 are 1000 and 400, respectively.

Fig. 1 shows a representative set of N_2 adsorption-desorption isotherms at various relative pressures (P/P_0= 0 to 1) for the samples of A series prepared with BHPA as template. They all exhibit type IV-like isotherms with type H2 hysteresis loops according to IUPAC[19], which is typical of mesoporosity. The well-defined step in the nitrogen desorption branches at the relative pressure of 0.4 to 0.6 could be attributed to capillary condensation within narrow tubular mesopores of 3-4 nm in effective diameter. In contrast, the control sample prepared without template (SGT0) shows the type I isotherm without hysteresis loop, indicating the lack of mesoporosity[19] (the plot is not shown in Fig. 1 because the scale of the volume adsorbed is too small).

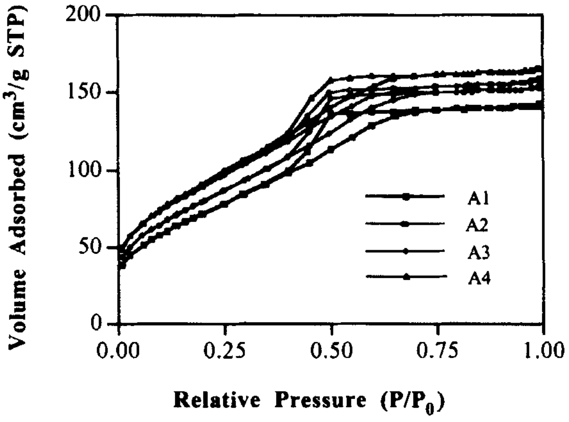

FIGURE 1. N_2 adsorption-desorption isotherms of the A series of mesoporous titania samples.

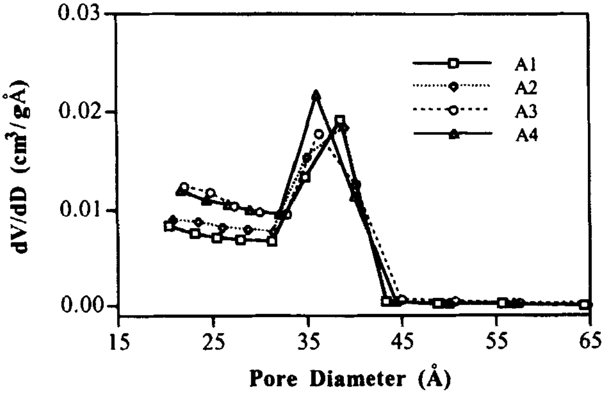

FIGURE 2. BJH pore size distributions of the A series of mesoporous titania samples.

Barrett-Joyner-Halenda (BJH) pore size distributions for samples of A series are given in Figure 2. The distributions are quite narrow as indicated by the small widths (5-8 Å) at half-height of the peaks. Unlike the mesoporous silica prepared via the nonsurfactant-templating route[16], the dominant pore diameter does not change significantly with the template content. As listed in Table 1, the BET surface area and pore volume seem to have some tendency of increase with the template concentration. However, these trends are less profound than those observed for the mesoporous silica materials[16].

The narrow pore size distribution is further confirmed by the powder X-ray diffraction measurements. As shown in Fig. 3, the low angle XRD pattern (2θ: 1°-10°) for sample B6 prepared with 50 wt% glycerin exhibits a broad peak at 2θ of about 2°, which corresponds to a d-spacing of 4.4 nm. Such a XRD pattern is typical for many mesoporous materials including titania prepared by surfactant-templating route[12-15]. Taking into account of the wall thickness, this d-spacing is comparable with the BJH pore diameter (i.e., 3.2 nm) determined from nitrogen sorption experiments. An unambiguous identification of hexagonal ordering of the mesopores cannot be made because of the lack of clear Bragg reflections in the higher angles.

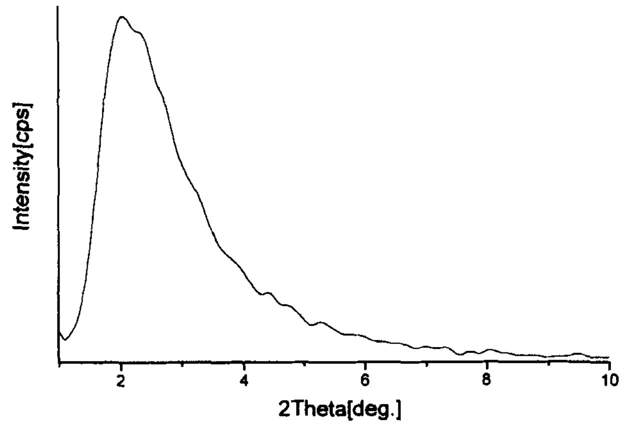

FIGURE 3. Low angle (2θ: 1°-10°) powder X-ray diffraction pattern of sample B6 prepared with 50 wt% glycerin as template.

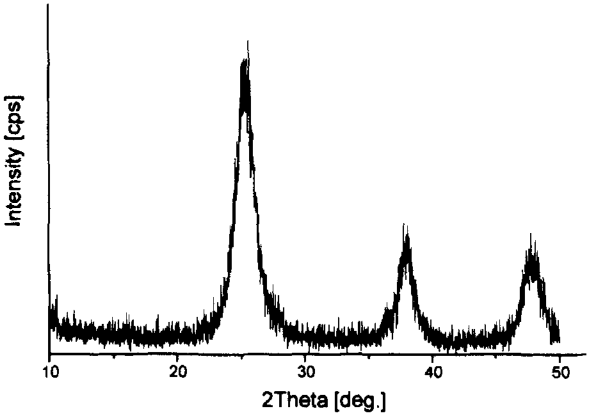

FIGURE 4. High angle (2θ: 10°-50°) powder X-ray diffraction pattern of sample B6 prepared with 50 wt% glycerin as template.

There have been many reports on the synthesis of sol-gel titania with or without surfactant templates[12-15,20-24]. Unless treated at elevated temperatures (e.g., ≥250 °C), the materials are usually amorphous under most synthesis conditions. Our results suggest that partial crystallinity might be induced by certain nonsurfactant templates. Fig. 4 shows the powder XRD pattern for sample B6 in the 2θ range of 10°-50°. At least three peaks are clearly identifiable at about 25°, 38° and 48°. Similar observation was made on the same sample before the extraction. These three peaks correspond well with those (101, 004 and 200 reflections) of the crystalline titania anatase phase[20]. In contrast, these peaks were not found in the XRD of the sol-gel titania prepared in the absence of template under otherwise identical conditions. It is noteworthy that photocatalytic activity of amorphous titania is negligible compared to that crystalline anatase[25]. Further investigation is in progress to understand the crystallization process in our laboratories.

The mesoporosity of the sol-gel titania by the nonsurfactant-templating route is further established by the results from transmission electron microscopy. As a typical example, TEM of the sample B6 is shown in Fig. 5. It is visible that there are numerous cylindrical-shaped interconnected channels with regular diameters. However, the ordering of the channels or pores cannot be identified unambiguously. Using image analyzer, the distribution of the channel diameters as depicted in Fig. 6 is quite narrow and centered at about 3.3 nm, which is comparable with the values from XRD and nitrogen sorption measurements.

Under similar synthetic conditions, we have also prepared mesoporous titania via HCl-catalyzed sol-gel reactions of titanium isopropoxide (TIP) at a molar ratio [TIP]:[H_2O]:[EtOH]:[HCl]=1:3:40:0.01 in the presence of poly(ethylene glycol) (PEG, molecular weights of 400 and 1000), which could be considered as a neutral surfactant. The materials with high surface areas of about 300 m^2/g and pore volumes of about 0.25 cm^3/g were obtained (Table 1). They all exhibit similar type IV isotherms with H2 hysteresis. In all the cases described in this study, the structure of the templates appears to have little effect on the pore parameters. However, when dibenzoyl tartaric acid (DBTA), D-glucose (DG) and D-fructose (DF) were employed as the nonsurfactant templates, either precipitation formed during the sol-gel reactions (DBTA) or the gels became deeply colored from orange to red to nearly black (DG and DF), although these compounds worked well as templates in the preparation of mesoporous silica materials[16,17].

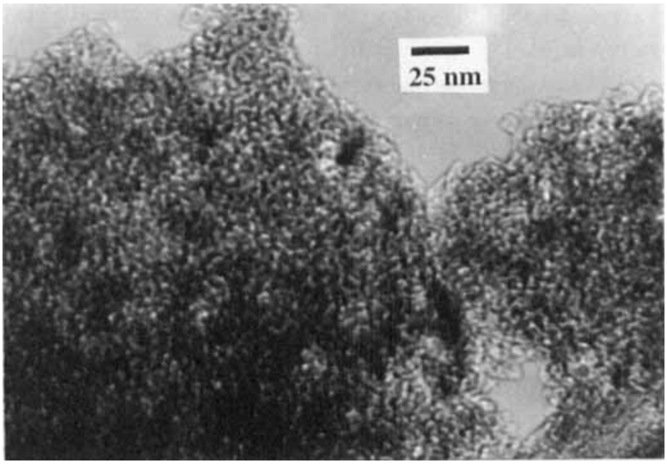

FIGURE 5. Transmission electron micrograph of mesoporous titania (sample B6).

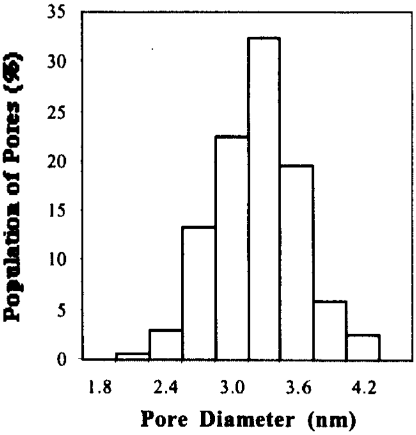

FIGURE 6. Pore diameter distribution of the mesoporous titania (B6) measured by image analysis of the TEM as shown in Fig. 5.

CONCLUDING REMARKS

We have described the first synthesis of mesoporous titania materials via the nonsurfactant-templating sol-gel route. The nonsurfactant organic molecules, i.e., 2,2-bis(hydroxymethyl)propionic acid, glycerin and pentaerythritol, were employed as templates or pore-forming agents in the HCl-catalyzed sol-gel reactions of tetrabutyl titanate at room temperature. These compounds can be removed from the composite gels by simple extraction with water, resulting in mesoporous titania materials with large surface areas of about 300 m^2/g and pore volumes of about 0.25 cm^3/g as well as narrow pore size distributions. The mesoporosity appears to arise from interconnecting channels of uniform diameters of around 3.2 nm. Similar results were also obtained with a neutral surfactant poly(ethylene glycol) as the template. The structure and concentration of these templates were found to have less effect on the pore parameters of the titania in comparison with those of the mesoporous silica. In the presence of templates, the titania materials obtained contain crystalline anatase phase. Though the mechanism of mesophase formation in the nonsurfactant pathway has not yet been understood, the hydrogen bonding between the nonsurfactant molecules or their aggregates and the titanate species during the sol-gel reactions might play an important role. Non-polar compounds such as camphor and naphthalene were found not to yield mesoporosity in both titania and silica sol-gel materials.

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