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Effects of heat treatment on various properties of organic–inorganic hybrid silica derived from phenyltriethoxysilane

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HIGHLIGHTS

- Residual silanol in hybrid silica from phenyltriethoxysilane is eliminated by heat treatment.
- The elimination is visibly indicated by insolubility in acetone.
- The elimination is also indicated by absence of FT-IR absorbance due to hydroxyl groups.
- Heat treatment at 300 °C for 192 h completely eliminates the residual silanol.
- Å-scale voids are eliminated during the process of the elimination of the residual silanol.

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ABSTRACT

Microparticles of organic–inorganic hybrid silica derived from a tri-functional ethoxysilane (phenyltriethoxysilane (PTES)) still have non-negligible amount of silanol (Si–OH) moiety after it is solidified in its outside appearance. Those residual silanol moiety formed in the Stöber process resumes further polycondensation in a heat treatment at temperatures above 250 °C. The rate of the polycondensation reaction of the residual moiety is dominantly influenced by the temperature at which the heat treatment was carried out. Heating at 300 °C for 192 h completes the polycondensation and entirely eliminates the residual silanol groups. The completion of polycondensation of the residual silanol is detected by visually observable insolubility of the heat-treated powder in acetone. The elimination of the silanol moiety due to the completion of the polycondensation is shown by the complete absence of the infrared absorbance corresponding to hydroxyl groups at approximately 950 cm^{-1}. The completion of the polycondensation leads to densification of the siliceous polymeric network as indicated by the prevention of amphiphilic organic solvent (e. g., *N*,*N*-dimethylformamide) from permeating into the bulk matrix of the organic–inorganic hybrid silica. The thermogravimetric measurement shows that phenyl groups directly bonded to Si remains intact at the temperature region ($\approx$300 °C) wherein the polycondensation reaction of the residual silanol groups is strongly promoted.

1. Introduction

Organic–inorganic hybrid silica is a group of materials with superior chemical durability [1] due to its stable network of siloxane bondings [2]. Moreover, they exhibit various optical, mechanical and thermal properties [3–6] depending on the attached organic functional groups. As well-known, the sol–gel approaches are the preferred routes for preparing those organic–inorganic hybrid silica materials [2]. Coupled with the low processing temperature, those materials can be used to generate a large number of organic–inorganic hybrid silica materials with various properties originating from the attached organic groups [2]. Synthetic glasses prepared by the sol–gel processing [2–7] of organically substituted alkoxysilanes allow preparation of such amorphous materials that can serve as precursors for a number of materials of scientific and technological importance as mesoporous or microporous hybrids, hydrophobic coatings, functional thin films and others [8–12]. Despite their interesting properties and diverse applications, those who handle them face a difficulty in completing the polycondensation of silanol groups. Hybrid materials prepared by the sol–gel method undergo gradual changes in the properties along with time due to the quite gradually continuing polycondensation reaction of the residual silanol groups. From the

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engineering standpoint, eliminating those residual silanol groups is required for terminating or preventing the gradual alteration of the properties of the hybrid silica. Generally, heat treatment [13] is effective for promoting the polycondensation in the sol–gel processes. Although this effect is more prominent in the cases of such tetra-functional alkoxysilanes as tetraorthoethoxysilane (TEOS) [14], the promotive effect on the polycondensation is considered in common with the cases of trifunctional alkoxysilanes. For the formation of stable powders or bulks, completing the polycondensation reaction of the silanol moiety is crucial since the macromolecular network constituted from siloxane bonding works as the backbone to guarantee the firmness of the chemical structure of solidified hybrid silica. Inorganic silica network bonded to phenyl moiety (phenyl-substituted hybrid silica) exhibits fine blending of both organic and inorganic features. In fact, the phenyl group bonded to the central silicon atom causes many interesting properties in the resulting silica materials. A number of works have been reported on the phenyl substituted organic–inorganic hybrid silica prepared by the sol–gel process [15–27]. Kakiuchida et al. found that the increased number density of phenyl groups decreases the number density of the bridging oxygens (–Si–O–Si–) resulting in reduced interactions between siloxane networks [15] whereas the softening behavior of those materials is dominated by the intermolecular entanglements [16]. Yoshinaga et al. ascribed the hindrance in the polycondensation of the hybrid silica to the stereochemical effect due to the covalently bonded phenyl group [17]. Katagiri et al. derived optically transparent glassy film by fusion of microparticles of PTES-derived silica by heating at 200 °C [19]. Tomiyasu et al. concluded that hybrid silica derived from phenyltriethoxysilane becomes completely cured after being annealed at 240 °C [20]. According to Lee and Hsu, the preform of PTES-derived silica needs heating at 350 °C for the completion of the polycondensation [21]. As described above, the temperature region in which the polycondensation reaction is markedly promoted is still unclear. Hence, it is meaningful to seek the proper temperature condition for the completion of the polycondensation reaction.

In the present work, the temperature region where the polycondensation reaction of the residual silanol is promoted will be determined by examining the measurable or observable alteration in the properties of the organic–inorganic hybrid silica derived from phenyltriethoxysilane. The as-prepared hybrid silica by the normal sol–gel scheme still has a considerable amount of unreacted residual silanol moiety. The completion or incompletion of the polycondensation can affect various observable or measurable properties of the hybrid silica. For example, the solubility of the hybrid silica in amphiphilic solvent like acetone indicates the formation of an infinite cluster of silica network as seen in a typical percolation problem. Thus, the insolubility is considered as a signal for the completion of the polycondensation. Our preliminary experiment has shown that the as-prepared hybrid silica by the well-known Stöber method easily dissolves in acetone due to the incompletion of the silica network. Likewise, detecting other properties which show noticeable alteration after the heat treatment gives evidences for the densification of siloxane bondings.

2. Experimental

2.1. Materials

Phenyltriethoxysilane (PTES) was provided from Shinetsu Chemical, Japan and used as provided. Hydrochloric acid (1 M), ammonia aqueous solution (1 M), ethanol, *N*,*N*-dimethylformamide and acetone were purchased from Wako Pure Chemical, Japan and used as provided. Water purified by ion exchange followed by distillation was used for preparing all the samples used in the present study.

2.2. Preparation of organic–inorganic hybrid silica particle

The particles were prepared by the common Stöber method (Scheme 1). 1×10^{-1} mol of PTES, 1 mol of ethanol, 1 mol of water and 1×10^{-3} L of HCl (1 M) were mixed in a sufficiently large plastic bottle. The mixture was vigorously stirred at approximately 1500 rpm using a magnetic stirrer to start the hydrolysis of PTES followed by the subsequent polycondensation. The reaction mixture exhibited detectable exotherm for approximately an hour after starting the stirring. The stirring was continued for three hours, which was sufficiently longer than the duration of the above detectable exotherm.

After the hydrolysis, the particles were prepared by dispersing the above hydrolyzed solution into 1×10^{-1} L of 1 M NH_3 aqueous solution. The primary polycondensation of the silanol moieties occurs due to the catalytic effect of basic ammonia. The onset of the polycondensation of the sol particles could be visually observed as the instantaneously emerging opacity. The colloidal suspension was continuously stirred for a day at 25 °C for aging. The dispersion was moved onto a flat plastic tray for air-drying to obtain the dried as-prepared particle of the hybrid silica. The whole preparation procedure of the organic–inorganic hybrid silica particle is summarized in Scheme 1.

To investigate the effect of the heat treatment, the obtained particle of the organic–inorganic hybrid silica was treated with heating for 192 h at the following temperatures, 260 °C, 280 °C, 300 °C and 320 °C.

2.3. Measurements

2.3.1. Scanning electron microscopy

Platinum sputtering was made on the surface of the sample prior to the observation. The micrographs were taken at 20 kV of the acceleration voltage (JEOL SEM5610V).

2.3.2. Fourier transform infrared spectroscopy

The powdery sample was finely ground in an agate mortar at 1 weight percent in KBr and pressed into a thin tablet for the infrared absorbance spectroscopy (Perkin Elmer Spectrum BX). The infrared transmittance spectrum was recorded in the range of the wavenumber from 400 cm^{-1} to 4000 cm^{-1}.

2.3.3. Dissolution test in acetone

The solubility/insolubility of the sample in acetone was examined using 1 g of the sample powder dispersed in 5 g (6.32 mL) of acetone. The powdered sample was agitated by ultrasonication in acetone for an hour at room temperature. This experimental method is based on our previous result that the hybrid silica turns insoluble in acetone when the polycondensation of residual silanol is completed [23]. Acetone is chosen as the test solvent since the amphiphilicity renders incompletely polycondensed hybrid silica soluble [14,23]. The mass of the powdery sample remaining after the ultrasonic agitation was measured to obtain the dissolved fraction.

2.3.4. Thermogravimetric analysis

The instantaneous mass of the sample was recorded by a thermogravimetric (TG) analyzer (Rigaku, TG-8120) from 30 °C to 800 °C at the heating rate of 10 °C min^{-1} in nitrogen flow of 50 mL min^{-1}. The temperature at which the polycondensation of the residual silanol groups markedly promoted was estimated from the onset of the decrease in the mass of the sample. The TG