Colloids and Surfaces A: Physicochem. Eng. Aspects 436 (2013) 618–632

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

High-pressure cryogelation of nanosilica and surface properties of cryosilicas

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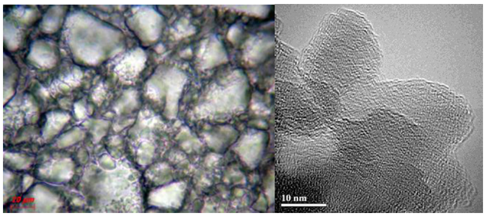
HIGHLIGHTS

- Effects of pressure and concentration on characteristics of silica cryogels.
- Confined space effects on the interfacial behavior of water bound to cryosilicas.
- Effects of cryosilica structure on co-adsorption of water with organics and inorganics.

GRAPHICAL ABSTRACT

Characteristics of cryosilica powders depend strongly on precursor concentration and pressure during cryogelation.



ARTICLE INFO

Article history:
Received 29 May 2013
Received in revised form 26 July 2013
Accepted 27 July 2013
Available online 4 August 2013

Keywords:
Nanosilica powder
High-pressure cryogelation
Interfacial phenomena
Bound water
NMR cryoporometry
Dispersion medium effects

ABSTRACT

Silica cryogels (cryosilicas) in a powder state were synthesized with different concentrations of fumed silica A-300 ($C_{A\text{-}300} = 5\text{–}20$ wt%), sonicated in aqueous suspension, then frozen at −14 °C at different pressures in a high-pressure stainless steel reactor (a freezing bomb), and dried in air at room temperature. To analyze the effects of low temperature and high pressure, samples were also prepared at −14 °C or room temperature and standard pressure. The structural and adsorption properties of the powder materials were studied using nitrogen adsorption, high-resolution transmission electron microscopy, infrared spectroscopy, thermogravimetry, low-temperature ^{1}H NMR spectroscopy and thermally stimulated depolarization current. The structural, textural, adsorption and relaxation characteristics of high-pressure cryogel hydrogels and related dried powders are strongly dependent on the silica content in aqueous suspensions frozen at 1450 or 1000 atm and then dried. The largest changes are found with $C_{A\text{-}300} = 20$ wt% which are analyzed with respect to the interfacial behavior of nonpolar, weakly polar and polar adsorbates using low temperature ^{1}H NMR spectroscopy.

1. Introduction

Cryogelation, used to synthesize soft (polymer) or solid (oxides, carbons) cryogels at temperatures below a bulk solvent's (typically water) freezing point, allows the production of micro/macroporous materials from different organic or inorganic precursors [1–5]. Results of cryogelation of polymeric or solid matters strongly differ from that of freeze-drying. In the case of cryogelation, cryoconcentration of a solution or a suspension occurs in the liquid layers located between ice crystallites (porogens) and chemical (with a cross-linker reacting with a gel precursor) or physical (by intermolecular bonding of polymers or particles) cross-linking of macromolecules or nanoparticles occurs there. Freeze-drying with sublimation of a frozen solvent does not practically result in cross-linking of particles or macromolecules. In other words,

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http://dx.doi.org/10.1016/j.colsurfa.2013.07.036

cryogelation results in strong reorganization of solutes but freeze-drying should remain undamaged texture of the materials. Cryogels can be synthesized with varying textural, structural and adsorption characteristics. Typically, cryogels are macroporous materials with a great porosity and main pore sizes in the micrometer range (1–300 μm) [1–5].

Some examples of reported cryogel syntheses include solid cryogels based on oxide, carbon or hybrid precursors [1–5]. Porous titania cryogel fibers have been synthesized using unidirectional freezing and subsequent freeze-drying of titania hydrogels. The hydrogels were synthesized by sol–gel polymerization of titanium tetraisopropoxide using dialysis [6]. Silica cryogels have been synthesized with properties similar to those of silica aerogels, particularly in terms of particle morphology, density, porosity, and specific surface area [7]. These similarities can be explained by the high pressure produced by ice crystallites onto thin residual liquid films between these crystallites. The resulting conditions are similar to the high-pressure conditions used to synthesize aerogels. The textural characterization of silica cryogels was based on nitrogen adsorption isotherms, scanning electron microscopy (SEM) images, structural analysis using infrared (FTIR) and nuclear magnetic resonance (^{29}Si MAS NMR) spectra [7]. Titania–silica hydrogels were molded into various shapes, microhoneycomb, self-standing bundle, microfibers, and powder, by a unidirectional freezing method [8]. Zeolite was synthesized by ice-templating and steam-assisted crystallization using a structure-directing agent, and silica gel as a precursor was prepared by applying ice-templating to the hydrogels synthesized from colloidal silica [9]. Hybrid SBA-15/carbon cryogel composites have been prepared by sol–gel polycondensation of resorcinol and formaldehyde followed by freeze drying, and subsequent pyrolysis [10]. Characterization of this material was accomplished using nitrogen adsorption, X-ray diffraction (XRD) and SEM methods. A highly conductive carbon cryogel, based on graphene and prepared by the sol–gel polymerization of resorcinol and formaldehyde in an aqueous surfactant, was characterized using nitrogen adsorption, XRD, FTIR, Raman spectroscopy, and SEM [11]. Carbon cryogels have been obtained by freeze-drying and pyrolysis of a family of tannin–formaldehyde organic gels prepared at different pH values [12]. The textural characteristics were analyzed by using nitrogen adsorption isotherms. It is worth mentioning that characterization of structurally more stable (rigid) solid inorganic cryogels is much easier than that of the softer and less rigid hydrated organic cryogels [5].

Inorganic cryogels are often synthesized by freezing sol–gel synthesis products in an aqueous solution, or a mixed organic/aqueous solution, followed by sublimation using a freeze-dryer. Cryogel synthesis can be considered an alternative means to synthesize materials similar to aerogels, as both synthetic methods involve high pressures. As yet there have been no reports dealing with the solid cryogel synthesis utilizing external pressures in special reactors working at very high pressures up to 1000 atm.

The aim of this work was to synthesize silica cryogels ("cryosilicas") at high external pressures using fumed silica A-300 as a precursor. This fumed material is formed by flame pyrolysis of $SiCl_4$. The resulting silica consists of solid nonporous primary nanoparticles of 8.3 nm in mean diameter and $S_{BET} = 330\ m^2/g$. Cryogel powders synthesized at high pressures from this fumed silica were characterized utilizing high-resolution transmission electron microscopy (HRTEM), thermogravimetric analysis (TGA), adsorption of N_2 or Ar to determine the textural characteristics, FTIR to probe surface hydroxyl groups, low-temperature ^{1}H NMR spectroscopy and thermally stimulated depolarization current (TSDC) to analyze the interfacial phenomena.

2. Materials and methods

2.1. Materials

Fumed silica A-300 (pilot plant of the Chuiko Institute of Surface Chemistry, Kalush, Ukraine; $S_{BET} = 330\ m^2/g$) was used as the starting material. Aqueous suspensions of A-300 (5, 10, 15 and 20 wt%) were prepared using doubly distilled water and sonicated (22 kHz) for 5 min. The resulting dispersion was then frozen at $-14\,^{\circ}C$ in thick walled stainless steel reactors at pressures of 450 or 1000 atm, caused by ice formed in the frozen suspension (~10–15 ml) for 24 h. The pressure was estimated according to the literature [13–15], and was controlled using partial (450 atm) or complete (~1000 atm) filling of a freezing bomb with stainless steel. Then cryosilica (CS) samples were placed in a glass dish and dried in air at room temperature for 2–5 days to an air-dry state. The final materials were in the powder state.

2.2. ^{1}H NMR spectroscopy

^{1}H NMR spectra of static samples were recorded using a Varian 400 Mercury spectrometer (magnetic field 9.4 T) utilizing 90° pulses of 3 μs duration. Each spectrum was recorded by coaddition of eight scans with a 2 s delay between each scan. Relative mean errors were less than ±10% for ^{1}H NMR signal intensity for overlapped signals, and ±5% for single signals. Temperature control was accurate and precise to within ±1 K. The accuracy of integral intensities was improved by compensating for phase distortion and zero line nonlinearity with the same intensity scale at different temperatures. Repeated measurements of samples gave identical spectra, within experimental error, at the same temperature. To prevent supercooling, spectra were recorded at $T = 200$ K (for samples precooled to this temperature for 10 min), then heated to 290 K at a rate of 5 K/min with steps $\Delta T = 10$ or 5 K (with a heating rate of 5 K/min for 2 min), and maintained at a fixed temperature for 8 min [16,17] for data acquisition at each temperature.

Cryosilicas CS20 ($C_{A\text{-}300} = 20$ wt% in the aqueous suspension frozen where ice produced a pressure of 450 atm) and CS20m (prepared at ~1000 atm) were studied at different degrees of hydration ($h = 0.08$, 0.75, 1.1 and 5.67 g of water per gram of dry silica). Hydration levels were controlled by addition of a known amount of water to a powder sample placed into an ampoule. Samples were equilibrated at 293 K for 1 h before NMR measurements. Experiments with methane were at a slightly increased pressure because an ampoule was linked to a rubber vessel with methane at 1.1 atm. Liquids (n-decane, chloroform, dimethylsulfoxide (DMSO), acetonitrile, water, or concentrated aqueous solutions of H_2O_2, HCl or CF_3COOH) were added to fill the total volume of a NMR ampoule with hydrated silica (the weight of dry silica was ~100 mg). After addition of hydrophobic decane, the sample was heated to 320 K for 1–2 min to remove air bubbles and to completely fill free pores of hydrated silica powder.

^{1}H NMR signals of static samples were observed only for mobile molecules due to the use of a relatively narrow 20 kHz bandwidth, the short transverse relaxation time of solids (e.g. OH groups at a silica surface), as well as frozen adsorbates. The latter include ice ($T_f \approx 273$ K), solid n-decane ($T_f \approx 243.3$ K), $CDCl_3$ ($T_f \approx 209$ K) and other co-adsorbates. This technique has been applied to a variety of adsorbates and solid and polymeric adsorbents, biomaterials, cryogels, etc.; and methods have been described in detail elsewhere [5,16,17].

To determine the chemical shift of the proton resonance (δ_H), tetramethylsilane (TMS) was used as an internal standard at $\delta_H = 0$ ppm (or methane at $\delta_H = 0$ ppm). The average errors in determination of the δ_H values in the temperature range studied were less than ±0.25 ppm.