

Insight into the structure of polymer–silica nano-composites prepared by vapor-phase



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ABSTRACT

Using a new synthesis technique, in which mesoporous Amberlite XAD7HP resin beads swollen with TEOS were exposed to vapors of either (H₂O + HCl) or (H₂O + NH₃), we obtained smooth, porous, mechanically stable silica gel spheres after burning out the sacrificial organic template. Combined N₂ sorption, SEM, TEM, ²⁹Si NMR, and Raman measurements were used to characterize the physical properties and molecular structures of the intermediate and final gels. Our atomically resolved TEM pictures provide the first visual demonstration of the presence of 3 to 6 member siloxane rings predicted by our Raman studies and other indirect methods. It is demonstrated that the physical appearance, morphology and porosity of the acid and base set gels are different from each other and also from those silica gels that were earlier polymerized from TEOS or Na-silicate saturated Amberlite XAD7HP with aqueous NH₄OH or HCl solutions in liquid phase. We show that the different physical properties of the vapor-phase set gels are associated with different gelling rates at acidic and basic conditions, which generates molecular differences both in the intermediate and the final products.

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1. Introduction

Silica gel fabrication using the sol–gel method has many interesting scientific and technological aspects due to a wide array of applications in the fields of sorption, encapsulation, sensing, catalysis, and separation sciences. This versatile method makes it possible to easily obtain nanoparticles with different morphologies and porosities which are among the most important parameters in the utilization of silica gels. These parameters can be optimized by appropriately choosing the gelling conditions as well as by using post-treatment techniques.

We have recently demonstrated [1,2] that also the molecular constitution of bulk silica gels might depend on the synthesis conditions employed, including for example the temperature, pH, aging time, and composition of mother solution. Most frequent precursors for gel fabrication are aqueous alkaline silicate solutions and non-aqueous alkoxy silanes. Their selection depends mostly on the purity and cost requirements associated with the product. Starting from the former ingredient, the whole gelling procedure is conducted in the presence of a large excess of water and some residual alkaline ions and salt byproducts might contaminate the

final gel even after thorough washing. Moreover, in the aqueous solution the amount of excess water strongly affects the kinetics of hydrolysis and the diffusion of molecules. The hydrolyzed cations and anions of acids and bases also affect the surface charge of colloidal silica particles, which in turn influences their morphology upon further growth [1,2]. From the more expensive alkoxy silanes cation-free, pure silica gel can be obtained by using only a small amount of water for hydrolysis. Both procedures involve pH adjustment to slightly acidic or slightly basic conditions (gelling is fastest in the vicinity of pH ~ 7) which induces formation of sol-like nanoparticles and their subsequent polymerization into the final solid silica gel network. The acids and bases are usually added in liquid form to the liquid phase gel-precursors. However, some acids and bases, e.g., HCl and NH₃, also exist in vapor form. It has been reported that using such vapor phase acids and bases for making silica thin films is advantageous because it provides increased structural stability and water resistance to the material and provides better control over the film thickness [3].

Since virtually nothing has been published about using such gaseous reactants for making bulk silica gels, we decided to test the effect of this unusual synthesis method on the properties of bulk silica gels made from TetraEthyl-OrthoSilicate, TEOS. However, for our bulk material we could not use TEOS in vapor phase, which is a favorite ingredient for many authors to deposit thin silica films onto various substrates [3–8]. Instead we made an organic–inorganic

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nano-composite first by saturating and physically swelling a commercial porous polymer resin, Amberlite XAD7HP, with TEOS, which is a proven starting material for making silica gel beads with aqueous HCl or NH_4OH solutions [1,2]. At this juncture we use vapor mixtures of ($\text{H}_2\text{O} + \text{HCl}$) and ($\text{H}_2\text{O} + \text{NH}_3$) to initiate silica polymerization. In this paper we report the first results pertaining to the morphology, porosity, and molecular constitution of gels obtained in this way.

2. Experimental

2.1. Synthesis procedure

Commercially available Amberlite XAD7HP (from Dow Chemical Co.) was used as a porous organic support for sample preparation. Prior to experiment the polymer beads were rinsed carefully with deionized water and dried at 80°C for 12 h. Next they were saturated with the silica precursor TEOS using the swelling method [1,2]. This composite material was placed into a closable vessel that contained aqueous solutions of either 6.7 M NH_4OH or 6.15 M HCl in the bottom. Thus, after closing this vessel, the TEOS-saturated polymer beads were exposed to vapors of acid or base along with steam at autogenous pressure. The closed system was kept at room temperature for 24 h. The Amberlite beads, which contained thereafter solid silica gels, were dried at 80°C under vacuum for 12 h. The acid and base set polymer–silica composites were designated to PV-A and PV-B, respectively. These composites were calcined at 550°C for 12 h in air to obtain our final silica gel products, PV-AC and PV-BC, in the form of spherical beads, free of the organic component.

2.2. Instrumentation

N_2 adsorption–desorption measurements were conducted at 77 K using a Micromeritics ASAP 2420 sorption analyzer. Before

measurements, composite samples and silica gels were degassed under vacuum for 8 h at 60°C and 200°C , respectively. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method [9]. The pore size analysis was based on the Barrett–Joyner–Halenda (BJH) procedure from the desorption branch of the nitrogen isotherm [10].

The surface morphology of the investigated samples was imaged using a scanning electron microscope (FEI Phenom microscope) working at 5 kV. The high resolution transmission electron microscope (TEM) studies were conducted on a Titan3™ G2 60–300 microscope (FEI Company USA).

The silica frameworks were assessed by solid state ^{29}Si NMR spectroscopy using magic angle spinning on a Bruker Avance-300 spectrometer. The chemical shifts, expressed in ppm, were referred to a tetramethyl silane standard ($\text{dTMS} = 0$).

Dispersive Raman spectra were measured on a Kaiser RXN spectrometer using a 200 mW, 532 nm wavelength laser source connected to a Mark II probe head via fiber optics.

Thermogravimetric measurements on a NETZSCH STA 449 F1 Jupiter® instrument indicated that the SiO_2 contents of PV-A and PV-B were 38 wt.%. For these measurements ~ 10 mg of sample was placed into a platinum crucible and heated under air flow at a rate of 10 K min^{-1} from room temperature to 800 K.

We also used a Perkin–Elmer CHN Analyzer 2400 to determine the residual organic contents in our calcined PV-AC and PV-BC samples and found $0.15 \pm 0.05\%$ carbon, $0.20 \pm 0.02\%$ nitrogen and $1.2 \pm 0.2\%$ hydrogen content in both materials. The high hydrogen content is presumably due to H_2O adsorbed during sample transfer from the calcining furnace to the CHN analyzer.

3. Results and discussion

Similar to our earlier experiments, in which the TEOS-swelled Amberlite was treated with aqueous solutions of HCl and NH_4OH

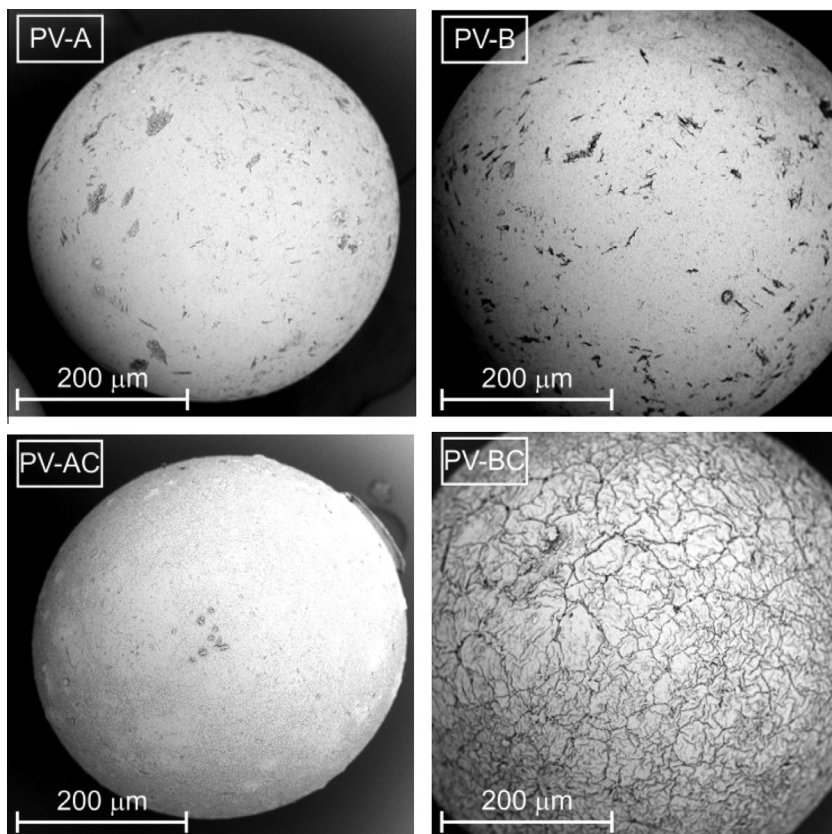


Fig. 1. SEM micrographs of PV-A and PV-B composites and PV-AC and PV-BC silica gels (see other magnifications in [Supporting Information](#)).

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