



Preparation of monodisperse silica spheres and determination of their densification behaviour

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Abstract

Monodisperse silica spheres in the 50–520 nm size range were prepared by using the Stober process. Diffusive growth has been determined from Nielsen chronomal analysis for the 520 and 310 nm monodisperse silica spheres. The densification behaviour and evolution of the microstructure of the sphere compacts indicated an inverse dependence of shrinkage rate on the sphere size due to viscous sintering. The increase in sphere size from 50 to 500 nm shifted the densification temperature from ~ 1120 °C to 1240 °C. The amorphous nature of the spheres was conserved up to 1200 °C where cristobalite crystal nucleation started and complete transformation to cristobalite phase has been observed upon heat treatment at 1300 °C. The activation energies for viscous sintering according to the Frenkel and Mackenzie/Shuttleworth models were calculated as 125 and 335 kJ/mol, respectively. These substantially low activation energies can be attributed to the presence of a significant level of silanol groups.

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1. Introduction

The use of sol–gel derived monosize silica spheres in the 5–700 nm size range can make the nanodesign of porous materials for specific applications like membranes with interconnected pore structures, catalysts and photonic band gap crystals possible [1–4]. A predefined pore structure can be easily designed by varying the diameter and the packing behaviour of monodisperse silica spheres. There are several approaches for preparing colloidal spheres with narrow particle size distributions [5]. The colloidal sol–gel process, which was originally developed by Stober and coworkers in 1968, is the most commonly used method for the preparation of monodisperse silica sols [6]. In the so called Stober process monodisperse silica spheres with sizes in the 5–2000 nm range can be synthesised by the ammonia-catalysed hydrolysis and

condensation of silicon alkoxides in solvents containing the necessary water for these reactions. The monodisperse silica sphere size depends upon the water and ammonia contents, the solvent type and the synthesis temperature [7–10].

The size of the silica spheres prepared by the Stober process is mainly controlled by the relative rates of nucleation and growth. These two events should occur separately in order to prepare monodispersed uniform particles along with a slow growth rate according to the LaMer model [11]. The growth of spherical particles depends upon the interfacial free energy between a growing nucleus and its chemical environment. The supersaturation necessary for the formation of spheres is provided by the hydrolysis and condensation reactions. As the reactions proceed, the intermediate $[\text{Si}(\text{OC}_2\text{H}_5)_{4-x}(\text{OH})_x]$ concentration increases rapidly generating a supersaturated solution and eventually at a critical level of supersaturation the spheres begin to nucleate. The growth of these nuclei decreases the concentration, after which nucleation terminates. The spheres continue to grow by molecular addition until all intermediates are consumed [11]. The controlled parameters including, type of reactants, reaction temperature,

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$\text{NH}_3/\text{alkoxide}$ and $\text{H}_2\text{O}/\text{alkoxide}$ molar ratios, as well as the solvent type influence the formation of the nuclei and the subsequent growth process.

In the last couple of decades extensive work have been conducted for the development of a better understanding on the formation and growth mechanisms of the monodisperse silica spheres by using different techniques including Si NMR, photon correlation spectroscopy, small angle X-ray scattering, and dynamic light scattering [8,9,12–14]. Monomer addition and controlled addition models have been proposed to explain the monodispersivity of the spherical silica particles. Based on the monomer addition model, the total number of nuclei is fixed (LaMer like burst) initially, and then the resultant sphere size is determined by the growth process which can be controlled by the total concentration of the alkoxide precursor. Nucleation is controlled by the condensation reactions between the reactive monomers. The narrow sphere size distributions are preserved during the growth due to the addition mechanism. The second approach for providing monodispersity is the aggregative growth model where a broad size distribution of primary spheres is assumed to be present in the beginning of the growth process. While nucleation happens continuously, progress of the reaction occurs by the preferential growth of bigger spheres at the expense of smaller spheres providing a narrow sphere size distribution. The rate-determining step is the formation of primary spheres. This model is based on colloidal stability which in turn depends largely to the surface charge of the particles [7]. van Blaaderen et al. [8] claimed that both mechanisms are additive for the formation of spheres in which nucleation is controlled by the aggregation of soluble species while the monomer addition leads to the smoothing of the surface by condensation. The rate-determining step has been found to be the formation of the hydrolysed monomer by ^{13}C NMR [8].

The growth and structural development of spheres occur through either diffusion-limited or reaction-limited processes. The major steps for growth can be stated as the transport of mass to the interface (diffusion) and the incorporation into the particle by surface condensation reactions. The relative rates of these kinetic processes determine the packing characteristics of the final structure, whether it is extended with low fractal dimensions heavily or more compact/dense.

The use of monodisperse silica spheres for the theoretical interpretations of sintering models has been also the subject of considerable body of work [15–17]. Sintering might be accomplished by different mechanisms, including viscous flow, surface/lattice/grain boundary diffusion, and vapour transport depending upon the materials sintered and sintering conditions. Viscous flow is the dominating transport mechanism for amorphous material sintering while the crystalline materials sinter by solid-state diffusion. Analysis of the dominant sintering mechanism is one of the challenges due to the relatively complicated nature of the microstructural evolution in the course of sintering depending on the initial powder properties/microstructure.

In this study, the growth of the silica spheres was investigated by using dynamic particle size data and chronomal analysis was applied in order to understand the growth

mechanism. Dilatometric analysis was used to establish a better understanding of the relationships between the particle size and the densification behaviour of monodisperse silica sphere compacts.

2. Material and methods

Monodisperse silica spheres in the 50–520 nm range were prepared by the Stober process [6]. NH_4OH (28–30 wt% NH_3 , Aldrich)–ethyl alcohol (99.8%, Riedel) solution was added to the Tetraethylorthosilicate (TEOS 98%, Aldrich)–ethyl alcohol solution (0.28 M Si^{4+} equivalent) during the sphere synthesis. TEOS: NH_3 : H_2O :EtOH molar ratio of 1:4.3:12.8:40.7 was used for the precipitation of 310 nm spheres respectively. Synthesis of the monodisperse silica spheres was completed under constant stirring of the precipitation solution overnight at room temperature. The spheres were recovered by centrifugation, washed with ethanol and dried overnight at 40 °C. The molar ratios of the constituents and the sizes of the spheres obtained are further tabulated in Table 1.

Monodisperse silica spheres dispersed in ethanol were centrifuged and dried at 40 °C to prepare the ordered sphere compacts. These binder free dried monodisperse silica sphere powders in the 50–520 nm range were consolidated into cylindrical compacts (5 mm in diameter and 4 mm in thickness) by uniaxial pressing under a pressure of 180 MPa for dilatometric densification behaviour characterizations.

Dynamic light scattering (DLS) was used to determine the particle size distributions and the surface charges of the spheres (ZetaSizer 3000 HS, Malvern). The samples were diluted tenfold with ethanol in order to terminate the reactions before the DLS experiments. The nature of the packing and the monodispersivity/size of the spheres were examined by SEM (Philips XL30 SFEG) analysis of the fracture surfaces of the centrifuged/densified sphere compacts. TGA (LAB SYS Seteram) was used for the thermal behaviour determination of the spheres where the samples were heated at a rate of 3 °C/min up to 1300 °C in air. The densification behaviour of the spheres was investigated by determining the dilatometric shrinkage curves (Linseis, L76/150B) with a heating rate of 5 °C/min up to 1300 °C.

3. Results and discussion

The size and structure of the spheres depend upon the rates of hydrolysis and condensation reactions. The effect of sol–gel process parameters on the final sphere size in a relatively wide range (5–700 nm) was investigated in this work. Spheres with various sizes were prepared by varying the NH_3/TEOS ,

Table 1
Synthesis parameters employed for the preparation of monodisperse spheres.

Size (nm)	TEOS concentration (M)	TEOS	NH_3	H_2O	EtOH
520	0.20	1	2.9	53.6	58.6
310	0.28	1	4.3	12.8	40.7
260	0.28	1	4.3	14	40.7
50	0.20	1	0.43	53.6	58.6

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