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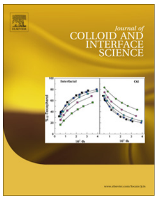

Evolution of microstructure in mixed niobia-hybrid silica thin films from sol–gel precursors

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ABSTRACT

The evolution of structure in sol–gel derived mixed bridged silsesquioxane-niobium alkoxide sols and drying thin films was monitored in situ by small-angle X-ray scattering. Since sol–gel condensation of metal alkoxides proceeds much faster than that of silicon alkoxides, the incorporation of *d*-block metal dopants into silica typically leads to formation of densely packed nano-sized metal oxide clusters that we refer as metal oxide building blocks in a silica-based matrix. SAXS was used to study the process of niobia building block formation while drying the sol as a thin film at 40–80 °C. The SAXS curves of mixed niobia-hybrid silica sols were dominated by the electron density contrast between sol particles and surrounding solvent. As the solvent evaporated and the sol particles approached each other, a correlation peak emerged. Since TEM microscopy revealed the absence of mesopores, the correlation peak was caused by a heterogeneous system of electron-rich regions and electron poor regions. The regions were assigned to small clusters that are rich in niobium and which are dispersed in a matrix that mainly consisted of hybrid silica. The correlation peak was associated with the typical distances between the electron dense clusters and corresponded with distances in real space of 1–3 nm. A relationship between the prehydrolysis time of the silica precursor and the size of the niobia building blocks was observed. When 1,2-bis(triethoxysilyl)ethane was first hydrolyzed for 30 min before adding niobium penta-ethoxide, the niobia building blocks reached a radius of 0.4 nm. Simultaneous hydrolysis of the two precursors resulted in somewhat larger average building block radii of 0.5–0.6 nm. This study shows that acid-catalyzed sol–gel polymerization of mixed hybrid silica niobium alkoxides can be rationalized and optimized by monitoring the structural evolution using time-resolved SAXS.

1. Introduction

Molecular separation with membranes is an attractive alternative for distillation since it can lead to substantial energy savings in the dehydration of biomass fuels [1] and organic solvents [2,3]. Hybrid organosilica membranes are very suitable for such tasks, since these materials combine the advantages of both organic and inorganic membranes, i.e., the high fracture resistance and hydrothermal stability of organic membranes and the high flux and thermal stability of inorganic membranes [4,5]. Exposure of silica to moisture at 70 °C already leads to hydrolysis of Si–O–Si bonds. The presence of organic bridges in the network made the network less susceptible for hydrolysis. However, further improvement is desirable for industrial application.

A possible approach to improve the hydrothermal and chemical stability of siloxanes and silsesquioxanes is by doping transition metals into the silicon oxide network, such as titanium [6], zirconium [7,8], niobium [9], nickel [10], or cobalt [11] However, sol–gel synthesis of transition metal-doped siloxanes usually leads to the formation of dense nano-sized transition metal oxide building blocks embedded inside an amorphous silica matrix, [12] as was observed by transmission electron microscopy (TEM) or small-angle X-ray scattering (SAXS) [13,14]. Transition metal centers easily form cationic complexes that are surrounded by a large number of ligands (coordination number 6–8), in contrast to silicon which commonly forms neutral tetragonal complexes [15]. Moreover, the metal alkoxide bonds are more labile and susceptible toward hydrolysis and condensation compared to the more covalently bonded tetragonal silicon alkoxide bonds [16]. Several strategies have been applied to improve the homogeneity of mixed transition metal/silicon oxide materials, but the intermixing on atomic scale, which is crucial for sufficient membrane permeability, is still a challenge.

Our interest is particularly focused on the atomic mixing of niobium in a hybrid silica matrix. ^{17}O MAS NMR experiments revealed that acid-catalyzed sol–gel synthesis leads to a high degree of atomic mixing at low niobium concentrations, i.e., Nb/Si = 14/86

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and 6/94 [17]. Even if amorphous niobia building blocks were formed, their crystallization would only occur at temperatures above 400 °C [18], which is higher than the annealing temperature of 300 °C of hybrid organosilica membranes [19]. No limitations are thus expected with regard to matrix integrity. Hydrated Nb_2O_5 forms strong Lewis and Bronsted acid sites upon annealing at 100 °C at pH < 5.6 (indicator method) [20]. Substitution in a silica matrix was found to enhance the Lewis acidity of the Nb centers as compared to that in Nb_2O_5 [21]. Contrary to vanadium (V) oxides, which are frequently used as acid catalysts, niobium oxides are more difficult to reduce and chemically more stable [22]. It is therefore a promising catalyst for application at moderate temperatures, in e.g., preferential CO oxidation in hydrogen-rich environments [23], esterification [24,25], dehydrogenation [26], aldol condensation [27], and conversion of the biomass derivative γ-valerolacetone into pentanoic acid [28]. The presence of acid sites was found to enhance chemisorption of CO_2 on mixed SiO_2–Nb_2O_5 and hybrid silica Nb_2O_5 microporous membranes and therefore strongly reduced the CO_2 permeability in comparison with nonpolar gases like H_2, CH_4, and SF_6 [29,30]

The final microstructure is established after a sol has been coated and dried on a support. The details of the drying processes of sol–gel films are often not well understood. In situ small X-ray scattering has been found to be a valuable method for monitoring the reorganization of meso/microstructure in drying systems, for instance in the self-assembly of mesostructured sol–gel films [31] and the formation of different electron dense/lean phases in barium titanate films from alkoxide–carboxylate systems [32] We used time-resolved SAXS to investigate the reorganization of the microstructure and the formation of different electron dense/lean phases during the drying process of thin sol–gel films of niobium penta-ethoxide and 1,2-bis(triethoxysilyl)ethane.

2. Experimental section

2.1. Synthesis of mixed niobia/BTESE sols

All precursor solutions were prepared inside a glove box under nitrogen atmosphere. The reflux synthesis was performed under atmospheric conditions. A 0.45 mol/L 1,2-bis-triethoxysilyl-ethane (BTESE) sol was prepared by adding dropwise an acidic ethanol solution [33] to a 0.9 mol/L solution of BTESE (ABCR chemicals, 97%) in dry ethanol with a hydrolysis ratio $[H_2O]/[(Si){-}OEt] = 1$ and an acid ratio $[HNO_3]/[(Si){-}OEt] = 1/30$. In a separate bottle, niobium penta-ethoxide (NPE, ABCR chemicals, 99.99%) was diluted in ethanol yielding a molar concentration [NPE] = 0.54 mol/L. The BTESE sols were all refluxed at $T = 60$ °C for 60 min. The NPE solution was added after either 0, 30, or 60 min of refluxing, and these samples are designated as p00, p30, and p60, respectively. Hence, the NPE solution was refluxed at $T = 60$ °C for 60, 30, or 0 min, respectively. The molar ratio [Nb]/[Si] was kept constant at 1/4 in this series, and the overall initial ethoxide concentration was kept constant at [OEt] = 2.7 mol/L. The samples were dried as thin films using a drying setup with a rotating aluminum rotor-hear that was covered with Kapton foil as described in more detail elsewhere [32]. All samples were heated using a 150 W infrared lamp. Samples p00 and p60 were dried at $T = 60$ °C and samples p30 were dried at $T = 40$, 60, or 80 °C, respectively.

2.2. SAXS Experiments

The colloidal samples were placed in capillary glass tubes (Hilgenberg, Germany) of 80 mm length, 1.5 mm diameter, and ~10 μm wall thickness. Small-angle X-ray scattering was carried out using synchrotron radiation on the Dutch–Belgian beamline, DUBBLE BM-26B of the ESRF in Grenoble [34]. The X-ray beam with an energy of 16 keV was focused on a corner of the 2D Pilatus 1 M CCD-detector to maximize the covered range of scattering angles. A beam stop was applied to shield the detector from the direct beam and avoid saturation of the outgoing signal. The detector was placed at a distance of 1.5 m from the sample, which allowed us to obtain data in the range $0.20 < q < 9.00$ nm^{-1}. All scattering data were found to be independent of the scattering angle in the plane of the detector. As this indicates that the samples were isotropically dispersed, the measured intensities from all channels with the same q value were averaged. Silver behenate was used as calibration standard for the determination of the absolute scale of the scattering vector q in our experiments [35].

The scattering intensity of the capillary containing a given colloidal sample was collected as a function of the scattering vector q. All curves were normalized by dividing the scattering intensity by both the time of data acquisition and the total intensity of the scattered signal. A background subtraction procedure was carried out. For sols, the scattering signal of a capillary filled with ethanol was subtracted, while for the drying sols, only the scattering signal of the clean Kapton foil was subtracted. The static SAXS data of sols were obtained in 5 min data collection periods and the in situ-measurements in 1 min periods.

2.3. TEM measurements

From sample p60, 30 μL sol was spin-cast (Laurell WS-400B-6NPP-Lite spin coater) onto holey carbon TEM copper grids (CF200-Cu, Electron Microscopy Sciences) at 4000 rpm for 40 s. Then, the as-prepared films were dried at 60 °C for 24 h in a furnace and used for transmission electron microscopy characterization (Philips CM300STFEG at 300 kV). Samples were investigated at low magnification to find typical areas, and features of interest were examined at high magnification (GATAN 2048 2048 Ultrascan1000 CCD camera). The microscope software packages GATAN Microscopy Suite 1.8.

3. Scattering intensity of mixed sol and condensed solid phase

Positive interference of scattered waves originates either from electrons within the same particle (intraparticle interference) or from electrons located in different particles (interparticle correlations). The scattering intensity can therefore be divided into a form factor, $P(q)$ and a structure factor $S(q)$, scaled with the number density of particles, N, and the contrast in electron density between particles and their surrounding medium, $\Delta\rho$ (the following equation):

$$I(q) = N \cdot (\Delta\rho)^2 \cdot S(q) \cdot P(q) \tag{1}$$

In the model that is described below to model the scattering of X-rays by drying sol–gel films, the sol particles are described in terms of self-assembled small primary building blocks. A building block contains a small number of niobium and/or hybrid silicon monomers and is considered as the smallest cluster of atoms that can be discriminated from the surrounding solvent in a SAXS pattern by a difference in electron density. For the sake of simplicity, we assume that these building blocks (primary scatterers) are spherical with radius r_0. This assumption was in agreement with the majority of scattering curves that indicated a $I \sim q^{-4}$ dependence in the high q-region. Only the initial stages of the drying process revealed a deviating behavior. These building blocks can be described by a spherical form factor $P(q)$, the following equation [36–38].

$$P(q, r_0) = \left[3 \cdot \frac{\sin(q \cdot r_0) - q \cdot r_0 \cdot \cos(q \cdot r_0)}{q^3 \cdot r_0^3}\right]^2 \tag{2}$$