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Synthesis of aluminosilicate monolithic system by a novel fast ambient drying process

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Abstract

Aluminosilicate systems with high mechanical strength have been prepared by a rapid ambient pressure drying. A special nanocomposite structure results in the good mechanical properties and strengthens the aluminosilicate system for a rapid ambient pressure drying technique. The nanocomposite consists of an amorphous aluminosilicate network and an Al-containing nanocrystalline, reinforcement phase. The reinforcement phase and the gel network develop simultaneously from the starting solution in the gelation process. The nanocomposite structure can only be achieved at a limited molar ratio of Al/Si. The wet precursor system of drying has been synthesized by sol–gel technique from low cost water glass and environmental saving Al acetate. The bond system, the structure, the morphology, and the mechanical property were investigated in the function of Al/Si molar ratio.

Keywords: Ambient pressure drying; Nanocomposite; Aluminosilicate; Sol–gel method

1. Introduction

The most considerable problem of the sol–gel monolith synthesis is the drying of the wet gels. The evaporation of the pore liquid from inside wet gel during drying results in capillary forces inducing shrinkage and cracking of the gel monoliths. In order to avoid the cracking, the wet gel must generally be dried very slowly at ambient pressure or under supercritical condition or in vacuum by freeze drying techniques.

Many study deal with ambient pressure drying methods of the gel monoliths and offer some possibilities to reduce the cracking of bulk materials over the slow drying [1–10]. The capillary pressure can hence be reduced by decreasing the surface tension of the pore liquid or by preparing a gel with a larger pore size [11]. The shrinkage occurred during the ambient pressure drying can be minimized by enhancing the stiffness of the gel network. The reinforcement of the gel network can be achieved by several routes; one of them is the addition of sodium silicate or tetraethoxysilane (TEOS) Si precursors before drying [12–19] or polymer addition [20]. The strength and stiffness of the wet gel can also be increased by aging of the wet gel either by dissolution and reprecipitation of the silica from the primary particle surfaces onto the point of contact [10,19,21], an attachment of unreacted oligomers from the gelation process [12], or precipitation of silica species added from an aging solution [16]. Some studies reported a successful production of crack-free silica aerogel monoliths by aging a water glass based wet gel in a TEOS/EtOH solution prior to the solvent exchange and surface modification processes [5–7]. Ambient drying is possible through the surface modification of wet gels. Using this modification, the OH species of the surface that lead gel to collapse by condensation reaction are modified into non-reactive groups [22]. Another method is based on a passivation of the pore surface, inside the gel. The passivation can be achieved by silylation with trimethylchlorosilane [3] or hexamethyldisiloxane [2]. A preparation method rests on ion exchange treatments prior to drying [23,24].

The aluminosilicate amorphous monoliths with high mechanical strength may be exploited in applications such as catalysis, separation, chromatography or refractory technique. The roll of

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the Al content in the aluminosilicate systems is to provide the glass or ceramics product with high chemical, electric and heat resistance, and low thermal expansion. Considering the environment protection, Al acetate has been chosen as Al precursor because the organic anions can escape as CO_2 and H_2O molecules during the heating. Water glass provides a low cost Si precursor.

In the present work, a special attention has been paid to produce aluminosilicate systems with high mechanical strength to overcome the usually weak mechanical properties of the sol–gel derived aluminosilicate materials. The good mechanical properties enable the fast ambient pressure drying of the sol–gel derived materials. Since maximum 10% Al content can be achieved by a traditional melting process in aluminosilicate glasses and the sol–gel technique provides the aluminosilicate systems with high Al content, much higher than 10%. Thus, some attention has also been given to keep the high Al content ensured by sol–gel method over the development of a rapid technique for ambient pressure drying.

2. Materials and methods

2.1. Preparation methods

The first step of the sol–gel preparation is the dissolution of initial materials, i.e. $Al(OH)(OOCCH_3)_2$ and Na_2SiO_3. The basic Al acetate is not soluble in water or alcoholic solvent, it can only be dissolved in strongly acidic ($pH \leq 1$) or basic ($pH > 11$) medium. $Al(OH)(OOCCH_3)_2$ was dissolved in aqueous solution of NaOH at ambient temperature and pressure to get a homogeneous solution. The required basic concentration for the dissolution depends on the Al/Si molar ratio; at ≥ 2 ratios 6.0 mol/dm^3 and at 1–2 ratios 2.0 mol/dm^3 NaOH solution is needed, respectively. The NaOH solution provides the starting solution with 10-12 values of pH. In acidic medium a phase separation of (poly)silicic acid occurs. After the addition of the diluted (4 mass %) water glass solution to the basic solution of Al acetate, an aqueous suspension formed. The chemical compositions of the initial solutions were: Al/Si = 1–4 M ratios; NaOH/Al = 4–6; water/Al = 40 M ratio. In order to get hydrogels, the main part of the solvent (water) was evaporated at 60 °C in vacuum. Directly after the distillation, a strongly opaque monolith gel structure evolved. The gel bulks were dried at 80–100 °C in an open vessel in air. 500 °C heating process produced the final xerogel samples. Dried gel monoliths with any kind of size and shape can be prepared by this fast sol–gel technique in limited molar ratios of Al/Si (Fig. 1).

2.2. Characterization methods

Small-angle X-ray scattering (SAXS) measurements were conducted on several instruments. The laboratory equipment was operated with a 12 kW rotating anode X-ray generator and a pinhole X-ray camera with variable distance (20.5–98.5 cm) from the sample to the two-dimensional detector (Bruker, AXS, Karlsruhe). The gels were covered in vacuum tight foil. The two dimensional spectra were corrected for parasitic pinhole scattering, as well as for the foil scattering. Simultaneous small-angle and wide-angle X-ray scattering experiments (SAXS, WAXS) were also recorded on the JUSIFA beamline of HASYLAB at DESY in Hamburg (8 keV photon energy; 925 and 3625 mm sample-to-detector distances). In the

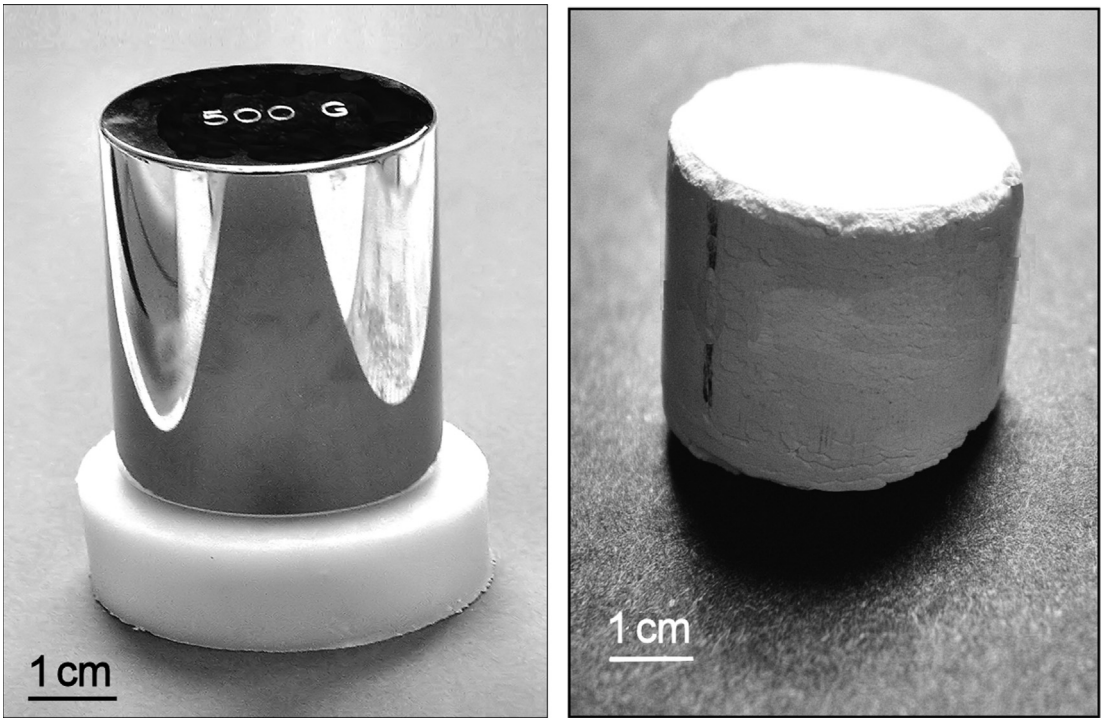

Fig. 1. Samples were synthesized from Na_2SiO_3 and $Al(OH)(OOCCH_3)_2$ with 2.5 Al/Si molar ratio. Left: before drying; right: after drying at 100 °C. (The weight of 500 g on the fresh gel indicates the mechanical resistance of wet gel.).