Time resolved SAXS investigation of the formation and structure of extremely hard aluminosilicates prepared by a sol-gel route

K. Sinkó, V. Torma, G. Goerigk, C. Baehtz and R. Gehrke

Institute of Chemistry, Loránd Eötvös University, Pázmány P. sétány 1/a, 1117 Budapest, Hungary

1Institute for Physical Chemistry, Budapest University of Technology and Economics, Budafoki u. 8., 111, Budapest, Hungary

2Insitut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich

3Hasylab at DESY, Nothestrasse, 85, D-22603 Hamburg

Aluminosilicate amorphous materials as porous ceramics with high surface areas and small pore sizes may be exploited in applications such as filtration, separation, catalysis, and chromatography. The roll of 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. The purpose of the present work was to prepare very hard aluminosilicate systems with as high as possible, i.e. higher aluminum content as that can be achieved by traditional high-temperature melting methods. A new preparation method has been developed for procedure of aluminosilicate systems with high aluminum content. The disadvantage of this aluminosilicate system is the fragility in wet as well as aerogel states. The other problem of the use of Al nitrate is the release of nitrous gases noxious to the environment. Another newly developed sol-gel procedure got rid of these disadvantages. It starts from in the respect of environmental advantageous Al acetate and from cheap water glass solution. Gel samples can be obtained only in basic condition (pH = ≥ 12). In acidic medium a phase separation of (poly)silicic acid occurred. Directly after mixing the aqueous solutions, an opaque monolith gel structure formed. At 2.5 mole ratio of Al/Si, monolith gel structure with extremely large stiffness was obtained comparing with the other wet aluminosilicate gel samples. Thus, this preparation method suits the requirements of the environmental protection and the hardness of gel systems. According to the 27Al MAS NMR measurements, the large hardness may be induced by a separated crystalline alumina phase inserted in the aluminosilicate network.

The mechanism of the structure formation can be followed over the gelation process with time resolved recording of the scattering curves. Regarding the composite structure of aluminosilicate system, the gelation starts with the formation of elementary units of a 3-D, amorphous network parallel with the development of crystalline nucleation centrum. The elementary units aggregate to higher building blocks. The average size of the network elements increases up to the gelling point, here it becomes equal to the size of the vessel. The SAXS experiments during gelation process were performed with the JUSIFA (SAXS) and BW4 (USAXS) beamlines at HASYLAB, DESY Hamburg. For SAXS and USAXS measurements during the gelation process, the scans were recorded for of 900 and 60 s in every 30 minutes, respectively. The structure and concentration of the crystalline nucleation centers were followed by XRD measurements on the B2 beamline in quartz capillaries of 1 mm in diameter, and with a measurement time of 10-60 seconds.

The scattering curves have proved a nanocomposite structure of aluminosilicate systems prepared from waterglass solution and Al acetate in basic medium (Fig. 1). The structure is a combination of an 3-D, randomly branched, amorphous aluminosilicate network and crystalline Al-containing aggregates. The Al content of crystalline phase has been verified by Al MAS NMR spectroscopy. The size of crystalline aggregates determined by SAXS was varied around 10-12 nm. Comparing the systems prepared with different mole ratios of Al acetate and water glass solution, the samples of higher mole ratios (2.5 and 4) show the best arrangement at small q-range (Fig. 2 and 4). In this range, the slope of the curves is between 2.5-2.8 indicating a branched, fractal-like structure.

Both SAXS and high resolution powder X-ray diffraction methods could follow very well the kinetic of gelling process (Fig. 1 and 3). First a sodium aluminum silicate phase (NaAlSiO₄) formed in the drying process (Fig. 4). At higher temperature, further crystalline phases (mainly Al₂Si₂O₇(OH)₄ 2 H₂O) developed in the material providing it with very large stiffness.
Figure 1: SAXS curves for gelation process of aluminosilicate systems prepared from waterglass solution and Al acetate in basic medium. *Chemical composition:* 1 mole Na$_2$SiO$_3$, 2.5 mole Al(OH)(OOCCH$_3$)$_2$

Figure 2: USAXS curves for aluminosilicate systems prepared from waterglass and Al acetate with various mole ratios of Al(OH)(OOCCH$_3$)$_2$ and Na$_2$SiO$_3$.

Figure 3: High resolution XRD pattern for aluminosilicate system versus temperature. *Chemical composition:* 1 mole Na$_2$SiO$_3$, 2.5 mole Al(OH)(OOCCH$_3$)$_2$ in basic aqueous medium.

Figure 4: XRD pattern for aluminosilicate systems prepared with various mole ratios of Al(OH)(OOCCH$_3$)$_2$ and Na$_2$SiO$_3$.

References