Nanostructure of gel-derived calcium silicate, calcium silicate phosphate biomaterials

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The main aim of this study is to synthesize calcium silicate ceramics that exhibit suitable properties in order to be used for biomedical applications. In the present work, attention was paid to the understanding of processing - structure relationships [1, 2, 7, 8]. The calcium silicate systems were prepared via sol-gel route, varying the chemical compositions; the catalysts concentration; the temperature and time of aging and heat treatment. The processes and the phases evolved during the sol-gel procedure were determined. The aggregate structures were investigated by SEM, SAXS, WAXS, and XRD measurements [1, 2, 7, 8].

The scattering data present in the samples synthesized under basic conditions are built up from aggregates. The aggregate structure is defined here as a random packing of colloidal particles. The SAXS curves follow the Porod’s law: the slope of the curves in a log-log plot is close to -4, which indicates large aggregated structures. The surface of the aggregates obtained by drying at 80 °C is possibly slightly rougher with an increasing amount of NH₃ catalyst considering the slightly lower value for the slope in the log-log plot. However, in the size range above 50 nm, only aggregates with smooth surfaces can be confirmed by SAXS. If the systems are heat treated at 700 °C, the elementary units are 3-D compact particles of 20-23 nm size, independent from the catalyst. The heating leads to a slightly rougher surface visible by the slope differing from -4 in the log-log curve. At lower molar ratios of NH₃, this seems to be more efficient. The SEM images give information on the size of these calcium silicate aggregates and the density of bulk systems. The size of aggregates varies from 100 to 300 nm at 1.0 molar ratio of NH₃/Ca; from 140 to 160 nm at 5.0 molar ratio, and from 100 to 130 nm at 10.0 molar ratio of NH₃/Ca, respectively. The size of particles is reducing in the function of increasing NH₃ molar ratio and the materials seem to become denser (Figure 1).

![SEM images of calcium silicate samples prepared with different NH₃ ratios (1, 5, 10) and heated at 700˚C (10000x top, 50000x bottom).](image)

Figure 1: SEM images of calcium silicate samples prepared with different NH₃ ratios (1, 5, 10) and heated at 700˚C (10000x top, 50000x bottom).

The structural evolution of the systems during the preparation process were investigated with in-situ small-angle and wide-angle X-ray scattering and XRD (Figure 2). The first two new crystalline phases appear simultaneously at 160 °C; silicon dioxide (α-quartz) and calcium carbonate (calcite). These phases disappear together at around 500 °C indicating a reaction between crystalline silica and
calcite above 400 °C. The FTIR spectroscopy detects carbonate groups in the range of 300 – 500 °C. The system is amorphous between 500 and 700 °C. The broad diffraction lines between 500 °C and 700 °C denote a temporary amorphous calcium silicate phase, which turns into crystalline β-dicalcium silicate at 700 °C. Above 800 °C, β-dicalcium silicate transforms into a new crystalline phase, mono-calcium silicate, which can be characterized by a well or poorly defined crystalline wollastonite lattice (Figure 2).

Figure 2: WAXS curves for calcium silicate samples (1.0 mol NH₃ / Ca) heat treated at various temperatures.

XRD data depict a much higher crystallinity in the sample prepared by acetic acid catalyst comparing to the structures obtained by base catalysis. The XRD patterns verify therefore the reduction of crystallinity degree with rising volume of NH₃ catalyst. No crystalline phase of calcium silicate was revealed in the samples of 5 – 10 mole NH₃ / Si until 800 °C (Figure 9). The higher Ca content promotes the presence of carbonate ions, but the higher NH₃ content inhibits that. The full amount of SiO₂ does not react during the heat treatment in the acid-catalyzed samples (Tab. 4), a part of that remains up to 1000 °C.

References