Nanostructure of Gel-Derived Calcium Silicate Phosphate and Aluminum Oxide Biomaterials

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The aim of this research work is to develop ceramics in calcium silicate/silicate phosphate and aluminum oxide systems that exhibit suitable properties to be used for biomedical applications. In the calcium silicate systems the effect of various catalysts was investigated on the supramolecular structures [1, 2, and 5]. The acetic acid catalyst yields a very loose structure, the slope of the SAXS curves in log-log plot is close to -2 (Fig. 1). The SAXS investigations prove an open randomly branched structure for wet Ca silicate gel samples produced with acetic acid catalyst. The samples prepared in the presence of ammonia or in water without any catalyst exhibit a more compact structures, the slope of the curves varies from -3 to -3.5. Thus, the SAXS data indicates aggregate systems (Fig. 1). (The aggregate structure defines a random packing of colloidal particles.) In the dried Ca silicate materials, aggregate structures can also be identified even in the samples produced with acetic acid catalyst. The loose open randomly branched structure of samples catalyzed by acetic acid turns into a compact structure during the heat treatment. The Si-O-Si bonds of this loose structure are decomposed by heating (FTIR measurements); and the Ca ions are incorporated into the silicate network. The XRD measurements cannot reveal any well defined homogeneous crystalline phase in the calcium silicate samples. A small amount of crystalline calcium silicate phase (α'-Ca₂SiO₄) can be identified from 400°C in the sample of acetic acid catalyst. The sample prepared by ammonia proved to be amorphous until 800°C. Applying phosphoric acid catalysis, two appreciable calcium phosphate crystalline phases can be detected by XRD in the calcium silicate phosphate samples; γ-Ca₃P₂O₇ and δ-Ca(PO₃)₂ with various rates depending on the amount of catalyst. Considerable changes can be observed in between 500 and 600 ºC regarding the XRD, IR, and SAXS measurements.

Fig. 1. SAXS + USAXS measurements for calcium silicate system prepared with various catalysts.

Fig. 2. HR XRD measurements for calcium silicate/silicate phosphate system prepared with various catalysts.
We have developed a new method to prepare aluminum oxo-hydroxide containing spinnable material and bulk gel systems. Based on the NMR measurements, the main part of the Al is octahedrally bonded in oligomers. The connections between the Al atoms are maintained by shared OH and some carboxylate ions. The coordination of acetate ions plays an important role in the formation of bulk systems. The acetate ions can be coordinated as a monodentate as well as a bidentate bridging ligand connecting two Al atoms. Thus, by occupying coordination sites of the Al atom, they may hinder the formation of (pseudo-) crystalline aluminum-oxo-hydroxide, e.g. boehmite. At the same time, they can also promote the aggregation of small oligomers by forming hydrogen bonds. Following the gelation process by SAXS measurements (Fig. 3) it can be established, there is no well ordered structure directly after the reflux, the samples have very week scattering intensity. Removing the solvent from the hydrolyzed system by vacuum distillation leads to the formation of a characteristic order. The wide peaks do not indicate an uniform crystalline structure, the characteristic lengths associated to these peaks are 23-24 nm and 10-11 nm. By heat treatment at 80 °C, a homogeneous, randomly packing aggregate structure evolves. The surface of aggregates can be featured by 2.5 ±0.05 surface fractal dimension (Fig. 3). The structure keeps the aggregate character during the heat treatment up to 1000°C (Fig. 4). The size of elementary units building up the aggregates increases from 3 nm to 4 nm by heating (180 °C – 800 °C). The size of particles is already 15.5 nm at 1000 °C.

![Fig. 3. SAXS measurements during the gelation process](image1)

![Fig. 4. SAXS measurements versus temperature of heat treatment](image2)

References