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Sol–gel preparation of $2CaO{\cdot}SiO_2$

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Abstract

Di-calcium silicate or belite (β-Ca_2SiO_4) is one of the major compounds in Portland cement clinker. Conventionally, belite is produced by long lasting sintering of limestone and quartz at temperatures exceeding 1400 °C. The subject of this paper is the sol–gel synthesis of belite. Both aqueous and non-aqueous sol–gel routes were applied. The preparation of the precursor mixture and the formation of the ceramic product were monitored using TG/DTG, XRD, FT-IR and SEM. The combination of these techniques led to the recording of all the transformations occurring during the processing of the precursors and the formation of the final products. As it was concluded, both routes can be successfully applied for the preparation of di-calcium silicate. The final products consist of very fine spherical crystallites in the range 1–3 μm. Their formation requires a 3-h sintering at 1000 °C. In both cases, β-$2CaO{\cdot}SiO_2$ is obtained without the use of any chemical stabilizers.
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Keywords: Sol–gel processes; Calcium silicate

1. Introduction

Calcium silicates and aluminates are the main constituents of ordinary Portland cement (OPC) which is the main building material of our age. Recently, calcium silicate powders were found to have excellent bioactivity and they are potential candidates of new biomaterials for hard tissue repair. The formation of calcium silicate powders through solid state sintering requires the mixing of very fine powders (usually $CaCO_3$ and SiO_2) and the repeated sintering of the mixtures at temperatures above 1400 °C for several hours with intermediate grinding.[1]

Sol–gel process has been well established for the synthesis of very homogeneous types of glass and ceramics at lower temperatures, than normally used, and there have also been made some efforts to produce pure clinker phases. Roy and Oyefesobi[2] were the first to synthesize clinker phases via a sol–gel process using a commercially available silica sol. Stephan et al. have also prepared calcium silicate and calcium aluminate compounds using silica sol and calcium nitrate,[3] while Hong and Young prepared di-calcium silicate through the Pechini technique.[4] Bioactive calcium silicate glasses have also been prepared using either alkoxides or silica sol as starting materials.[5–10] Finally, Page et al. have explored the application of sol–gel route for the synthesis of white calcium silicate cement.[11]

In this paper, $2CaO{\cdot}SiO_2$ is synthesized via sol–gel process using TEOS and silica sol as Si-sources. A combination of techniques (TG/DTG, XRD, FT-IR, SEM) is applied for the characterization of the intermediate and final products. This work is part of a project aiming to the development of alternative low temperature techniques for the synthesis of hydraulic compounds and materials.

2. Experimental

Pure $Ca(NO_3)_2{\cdot}4H_2O$, silica sol 30% in water and TEOS were used as starting materials. The $CaO{:}SiO_2$ molar ratio in the starting mixture was kept to 2:1 in order to obtain $2CaO{\cdot}SiO_2$. The $CaO–SiO_2$ gel was prepared in two ways, using either TEOS or silica sol as Si-source.

The first way involves the following steps: (i) mixing of TEOS and ethanol (molar ratio $C_2H_5OH{:}TEOS = 1.5$), (ii) dissolution of calcium nitrate in the minimum amount of ethanol, (iii) mixing and stirring of the two solutions, (iv) addition of 10 drops of glacial acetic acid and (v) drop wise addition of water under continuous stirring (molar ratio $H_2O{:}TEOS = 6$). The precursor solution was left to gel overnight at room temperature and a translucent gel was obtained. The second way comprises the

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dissolution of calcium nitrate in water, the addition of the silica sol and the stirring of the mixture at 70 °C. A viscous gel was obtained after approximately 4 h.

Thermogravimetric analysis (TG/DTG) was used in order to record the sintering reactions of the prepared gels. TG and DTG curves were obtained using a Mettler Toledo 851 instrument. The sample was heated from 20 to 1000 °C at a constant rate of 10 °C/min in an atmosphere of air.

XRD and FT-IR were used in order to identify the products and check their crystallinity. X-ray powder diffraction patterns were obtained using a Siemens D5000 diffractometer, with Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å), operating at 40 kV, 30 mA. The IR measurements were carried out using a Fourier transform IR (FT-IR) spectrophotometer (Perkin-Elmer 880). The FT-IR spectra in the wavenumber range from 400 to 4000 cm^{-1}, were obtained using the KBr pellet technique. The pellets were prepared by pressing a mixture of the sample and dried KBr (sample:KBr approximately 1:200) at 8 tonnes/cm^2.

The sintered sample was examined using a JEOL JSM-5600 Scanning Electron Microscope equipped with an OXFORD LINK ISIS 300 Energy Dispersive X-Ray Spectrometer (EDX).

3. Results and discussion

3.1. Thermal decomposition of the gels

Figs. 1 and 2 present the TG/DTG curves of the non-aqueous and aqueous gels, respectively. As it was expected, the total ceramic yield is higher when silica sol was used (32.62% instead of 19.65% in the case of TEOS). The weight loss up to 250 °C is associated with the removal of absorbed water, water of nitrate salts and ethanol (in the case of sample with TEOS). The weight loss in the range 450–700 °C is attributed to the removal of nitrates and residual organics. When TEOS was used, there is an additional weight loss in the range 300–450 °C, which is associated with the completion of the hydrolysis and condensation reactions of TEOS and the consequent removal of by-products (H_2O and C_2H_5OH).

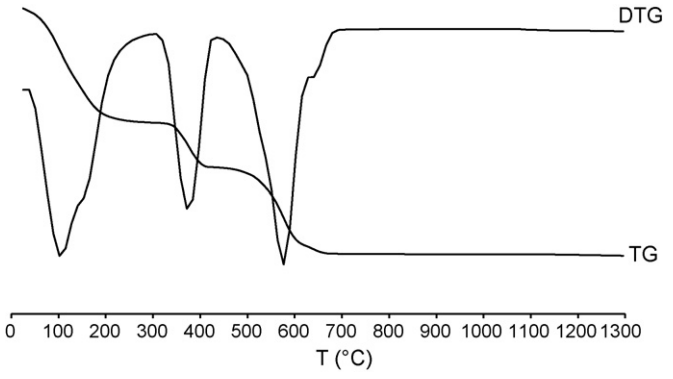

Fig. 1. TG/DTG curves of the gel prepared through non-aqueous route.

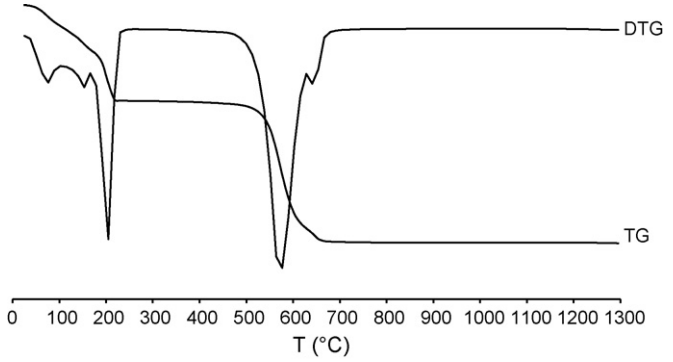

Fig. 2. TG/DTG curves of the gel prepared through aqueous route.

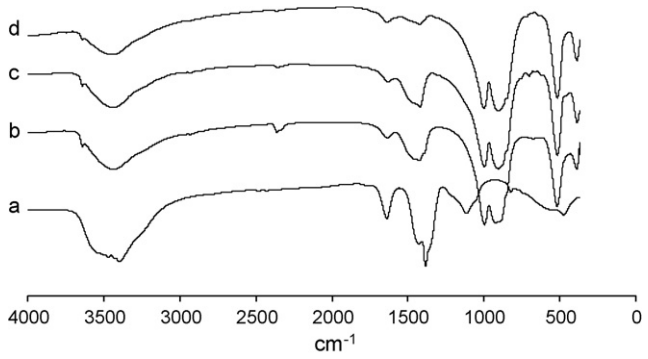

Fig. 3. FT-IR spectra of samples prepared through aqueous route, in relation to the temperature of thermal treatment. (a) 400 °C; (b) 600 °C; (c) 800 °C; (d) 1000 °C.

3.2. Characterization of intermediate and final products

Fig. 3 presents the FT-IR spectra of the samples in relation to the temperature of thermal treatment, when silica sol was used as starting material. The broad peak at 3400 cm^{-1} is typical of the O–H stretching vibration and can be assigned to the water absorbed on the surface of the product. The characteristic NO_3^- bands (about 1380, 1440 and 1630 cm^{-1}) are the main absorbance bands at 400 °C, decrease at 600 °C, indicating that the removal of nitrates is in progress, and disappear at 800 °C. The FT-IR spectrum of the sample treated at 400 °C shows also the characteristic bands of amorphous SiO_2 at 1100 and 780 cm^{-1}. At higher temperatures these bands disappeared and were replaced by the multiple bands at 800–1000 and 400–600 cm^{-1}, which are characteristic of the stretching and bending vibrations of Si–O bonds in SiO_4 tetrahedra, respectively. It must be noted that the stretching band of SiO_4 has shifted to lower wavenumbers and covers a broader range than in the case of pure silica. This has been, also, observed by other researchers and has been attributed to the presence of modifier oxides in the silica network.[12,13]

Fig. 4 presents the FT-IR spectra of the samples in relation to the curing temperature, when TEOS was used as starting material. These spectra are quite similar to those presented in Fig. 3, indicating that the different Si-source (TEOS or silica sol) affect the behavior of the precursor mixture at temperature lower than 400 °C. The absence of absorbance peaks corresponding to alkoxyl or Si–OH groups indicate that the hydrolysis and condensation reactions have come to completion at lower temperature. This fact is also confirmed by TG measurements. In

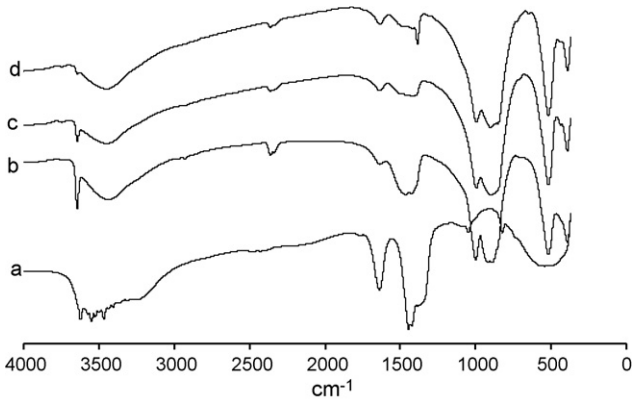

Fig. 4. FT-IR spectra of samples prepared through non-aqueous route, in relation to the temperature of thermal treatment. (a) 400 °C; (b) 600 °C; (c) 800 °C; (d) 1000 °C.

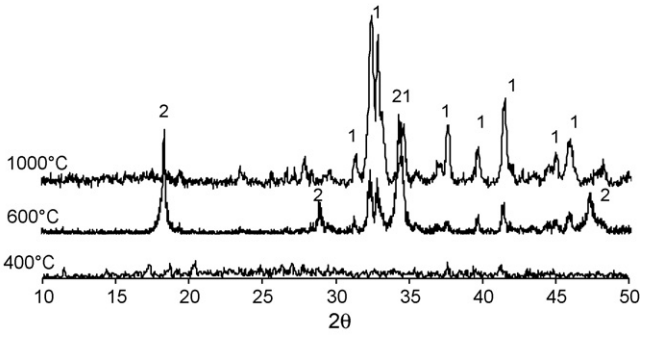

Fig. 5. XRD patterns of samples prepared through non-aqueous route, in relation to the temperature of thermal treatment (1: β-$2CaO{\cdot}SiO_2$; 2: $Ca(OH)_2$).

both cases, the FT-IR spectra show that the formation of ordered Si tetrahedra initiates below 600 °C.

Figs. 5 and 6 present the XRD patterns of the calcined products. In both cases, the samples are completely amorphous at 400 °C. In the case of non-aqueous route, $2CaO{\cdot}SiO_2$ has been already formed at 600 °C, but there is also a significant amount of $Ca(OH)_2$ which comes from the reaction of CaO with the atmospheric moisture. This fact indicates the presence of free CaO in the sample. In the case of aqueous route, the broad peak at 31–32^{o} shows that the formation of calcium silicate has just began at 600 °C. In both cases the final product at 1000 °C is

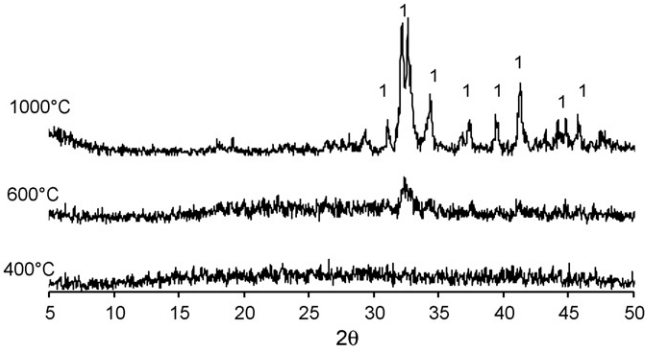

Fig. 6. XRD patterns of samples prepared through aqueous route, in relation to the temperature of thermal treatment (1: β-$2CaO{\cdot}SiO_2$).

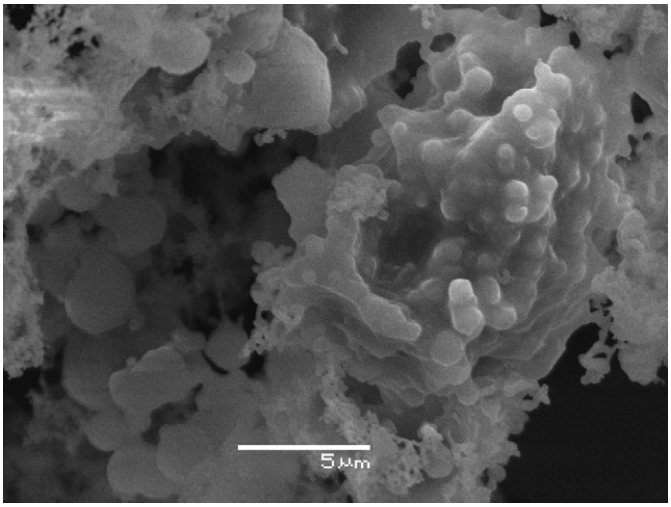

Fig. 7. SEM photo of the sample sintered at 1000 °C for 3 h (aqueous route).

β-calcium silicate without any detectable amount of impurities. It must be noted, that, when conventionally prepared, the β form of calcium silicate is not stable at room temperature without the incorporation of certain foreign ions that act as chemical stabilizers.

Fig. 7 presents the SEM photo of the sample sintered at 1000 °C for 3 h (silica sol was used as Si-source). The photo was selected to be representative as far as the size and texture of grains are concerned. As it is seen, the final product consists of the characteristic spherical-shaped particles of $2CaO{\cdot}SiO_2$. The mean particle size varies in the range 1–3 μm. This small size must be the reason for the stabilization of β-$2CaO{\cdot}SiO_2$ at ambient temperature without the need of any chemical stabilizers. The texture of the sample prepared through non-aqueous route is very similar.

4. Conclusions

This work led to the following conclusions:

- Both aqueous and non-aqueous sol–gel routes can be successfully applied for the preparation of di-calcium silicate.
- The final products consist of very fine spherical crystallites in the range 1–3 μm. Their formation requires a 3-h sintering at 1000 °C.
- β-$2CaO{\cdot}SiO_2$ is obtained, in both cases, without the use of any chemical stabilizers. This is attributed to the very small size of the crystallites.
- The combination of TG/DTG, XRD, FT-IR and SEM leads to the recording of all the transformations occurring during the processing of the precursors and the formation of the final products.

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