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Wet chemical synthesis of monocalcium aluminate

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Abstract

Monocalcium aluminate, $CaAl_2O_4$, is the main constituent of calcium aluminate cements (CACs), which are used in a wide range of applications. Conventionally, monocalcium aluminate is prepared by long lasting sintering of the solid oxide mixture in temperatures exceeding 1400 °C. The Pechini process is an alternative, low temperature polymeric precursor route for the synthesis of high purity oxides. In the present work, $CaAl_2O_4$ is prepared through the Pechini technique. Conventional solid-state synthesis is used in order to compare the final products with those obtained through the Pechini technique. As it is concluded, the Pechini technique can be successfully applied for the synthesis of $CaAl_2O_4$. Its formation requires a 3-h sintering at 900 °C. The final product is crystalline $CaAl_2O_4$ of high purity, without any impurities of reactants or secondary phases.

Keywords: Powders-chemical preparation; Calcium aluminate

1. Introduction

Monocalcium aluminate, $CaAl_2O_4$ (CA),[b] is the main constituent of calcium aluminate cements (CACs), which are used in a wide range of applications in the construction and mining industries, and in recent applications in optical and structural ceramics, and high performance polymer-modified cement-based materials.[1]

Cement systems are quite complex, due to the appearance of a mixture of multiple binary and ternary compounds, and therefore the use of pure doped or undoped clinker phases can be of great interest in fundamental research on cement materials, as the investigation of the hydration process or the influence of minor elements on the reactivity of cement.[2] Conventionally pure phases are prepared through solid-state synthesis, requiring repeated intermediate grinding and many-hour calcination at elevated temperatures; in the case of CA long lasting calcination of the solid oxide mixture at temperatures often exceeding 1400 °C is required. However, powders prepared by this method are usually agglomerated, have irregular size and shape and poor sinterability, while the final product may still contain secondary phases.[3,4]

Wet chemical synthesis methods can be applied for the preparation of ceramic powders with special characteristics, such as high sinterability, high surface area, well-defined and controlled chemical compositions and homogeneous distribution of the elements.[4] Alternative low temperature techniques such as sol–gel,[2,5–7] polymeric precursor processes[8,9] and combustion synthesis[3,4,9] have been applied for the synthesis of calcium aluminate compounds, instead of the solid-state synthesis.

The Pechini technique is an alternative, low temperature polymeric precursor route for the synthesis of high purity ceramics, which is based on the ability of certain alpha-hydroxycarboxyl acids, such as citric acid, to form polybasic acid chelates with certain metallic ions.[10] The citric solution, when heated with a polyhydroxilic alcohol, undergoes a polyesterification reaction. The sintering of the resulting polymer produces oxides of high purity at much lower temperature than the conventional solid synthesis.

In the present work, the Pechini technique is applied for the preparation of CA, using nitrate salts as metal-ion sources, citric acid for the chelation of the ions, and ethylene glycol for the polyesterification reaction. The sintering of the polymeric precursor yields the desired oxide. The preparation of the gel is monitored through constant conductivity measurements, and the intermediate and final products are fully characterized by XRD, TG-DTG, FTIR and SEM experiments in order to further understand the mechanism of the oxide formation during sintering at various temperatures. Finally, the product obtained

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[b] Cement chemistry notation: C, CaO; S, SiO_2; A, Al_2O_3; F, Fe_2O_3.

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from the Pechini technique is compared to the product obtained through solid-state synthesis.

2. Experimental procedure

2.1. Synthesis of the CA powders

Nitrate salts were used as cation sources; aluminium nitrate nonhydrate $Al(NO_3)_3 \cdot 9H_2O$ >95%, Merck Germany, calcium nitrate tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O \geq 99\%$, Fluka. Citric acid monohydrate $C_6H_8O_7 \cdot H_2O$ 99.5–100.5%, Merck, Germany, was used as complexing agent, and ethylene glycol GR for analysis $C_2H_6O_2$ min. 99.5%, Merck, Germany for the completion of the polyesterification reaction.

The gel preparation was monitored through continuous conductivity measurements. First suitable amounts of the nitrate salts were dissolved in 50 ml deionised water, on a hot-stirring plate, followed by the addition of citric acid (CA) in a molar ratio CA:total cations = 1. Ethylene glycol (EG) was added to the solution in a molar ratio EG:CA = 2. The solution was continuously stirred at 80 °C, to achieve the evaporation of the excess water and accelerate the polyesterification reaction, until the conductivity was diminished and a viscous gel was obtained. The gel was then heated at 150 °C in an oven for 24 h. The dried gel obtained was ground to powder and calcined at 400 °C for 2 h to form the powder precursor, which was heat-treated at temperatures 600–1000 °C for 3 h.

Solid-state synthesis was also applied for comparison. Appropriate amounts of $CaCO_3$ and Al_2O_3 powders were mixed and calcined at 900 °C for 3 h (for comparison with the Pechini method), and at 1400 °C for 15 h.

2.2. Characterization methods

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

XRD and FTIR were used in order to identify the products and check their crystallinity. The phase distribution of the powders as a function of calcination temperature was investigated by X-ray diffraction. The X-ray patterns were obtained using a Siemens D-5000 diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å), operating at 40 kV, 30 mA. FTIR measurements were carried out using a Fourier Transform IR spectrophotometer (Perkin Elmer 880). The FTIR spectra in the wave number 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 t/cm^2.

The dried gel and the sample sintered at 900 °C were examined using a JEOL JSM-5600 Scanning Electron Microscope equipped with an OXFORD LINK ISIS 300 Energy Dispersive X-Ray Spectrometer (EDX).

Finally, the ethylene glycol method was used to measure the free CaO content in the sintered products.

3. Results and discussion

3.1. Gel preparation

The conductivity measurements during the gel preparation are presented in Fig. 1. The conductivity indicates an abrupt increase, due to the dissolution of the nitrate salts. A sudden and unexpected raise in the solution's temperature, reaching 100 °C, followed by a significant increase of the conductivity, is observed after approximately 1 h of stirring at 80 °C, along with the evolution of visible red-brown vapours. The heating is lowered and the solution is left on the stirring plate until the temperature and conductivity falls back to normal. The same incident occurs again during the gel preparation, but to a lower extent. This unexpected temperature raise probably indicates that certain exothermic events take place in the solutions. Such an event could be ascribed to the reduction of the nitric anion to NO_2, as indicated by the red-brown vapours. The conductivity is diminished after approximately 3 h at 80 °C, and a viscous gel occurs. Heating at 150 °C for 24 h is required to complete the polyesterification reaction, while dehydration and evaporation of most of the volatile compounds take place. This result to the swelling of the material and the formation of a yellowish, brittle, aerated xerogel.

3.2. Thermogravimetry measurements

The TG and DTG curves, presented in Fig. 2, indicate a weak weight loss around 100 °C, and a strong loss within 200 and 550 °C. The first weight loss is attributed to the moisture loss, absorbed after the thermal treatment of the gel at 150 °C. The major weight loss of the sample (62%) takes place between 200 and 550 °C in two stages. The first around 300 °C can be ascribed to the decomposition of the polymer network, while the second around 420 °C can be ascribed to the further decomposition of organic compounds and the burning of the residual carbon. The total weight loss of the sample is 72.4%, according to the TG curve, while the ceramic yield is 27.6%.

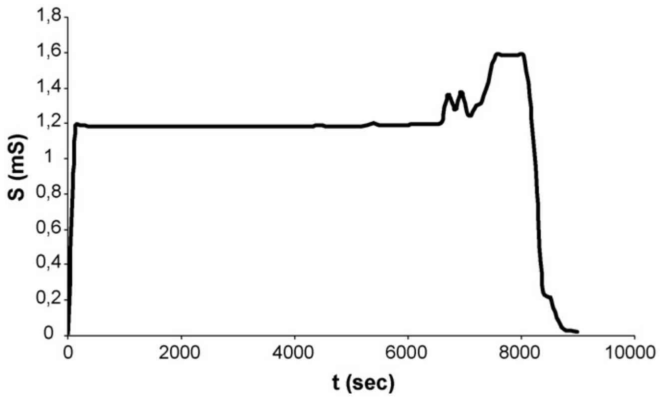

Fig. 1. Conductivity of the starting solution vs. time.

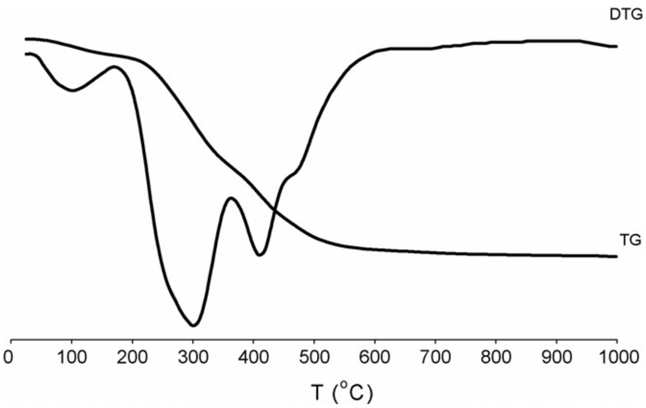

Fig. 2. TG and DTG curves of dried gel.

3.3. X-ray diffraction

X-ray diffraction experiments indicate that the xerogel is amorphous. All samples calcined up to 800 °C are amorphous, while at 900 °C a crystal phase identified as CA is observed. The phase evolution of the samples calcined at various temperatures is presented in Fig. 3. Calcination of the sample at 1000 °C does not vary the phase distribution, indicating that crystalline CA can be prepared at 900 °C. Free CaO is not detectable at any temperature. The solid-state synthesis product sintered at 900 °C for 3 h consists mainly of uncombined CaO and Al_2O_3 and small amounts of $C_{12}A_7$. The product of the sintering at 1400 °C for 15 h consists of CA and secondary phases CA_2 and $C_{12}A_7$.

The crystal structure of CA, prepared through the Pechini technique, was refined by Rietveld profile analysis. The structural data resulting from the refinement are presented in Table 1. All data are very close to those reported in literature for CA, indicating the satisfactory formation of this compound.

3.4. Uncombined CaO measurements

The free CaO content of the sintered products measured by the ethylene glycol technique is presented in Table 2. The results indicate the very good combinability of the reactants.

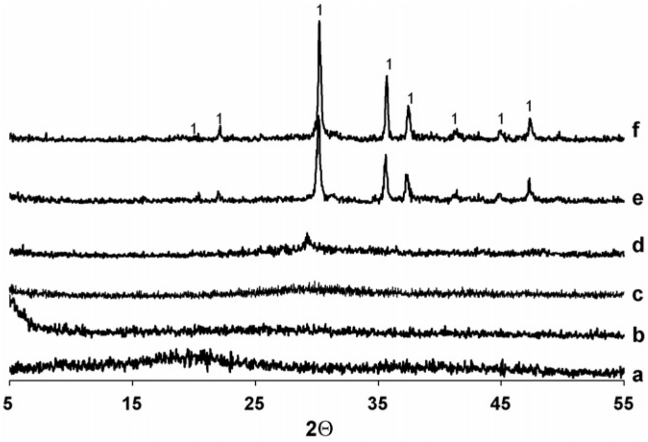

Fig. 3. X-ray diffraction patterns of dried gel and calcination products: (a) xerogel, (b) 400 °C/2 h, (c) 600 °C/4 h, (d) 800 °C/3 h, (e) 900 °C/3 h and (f) 1000 °C/3 h. (1) $CaAl_2O_4$.

Table 1
Structural data resulting from Rietveld refinement of the final product

Rietveld—crystal structure	
Space group	$P12_1$
Lattice parameters	$a = 15.1299932$ Å $b = 8.0795993$ Å $c = 17.4655963$ Å $\beta = 149.9964°$
Cell volume (Å^3)	1067.65123

Table 2
Uncombined CaO measurements

Temperature of thermal treatment (°C)	fCaO (%)
400	0.00
600	0.06
800	0.08
900	0.32

3.5. FTIR spectroscopy

The FTIR spectra of the samples as a function of calcination temperature are given in Fig. 4. The broad peak at 3400 cm^{-1} is typical of the O–H stretching vibration and can be assigned either to the hydroxyl ions of the organic compounds (at lower temperatures) or at the water absorbed on the surface of the highly reactive calcium aluminates at higher temperatures. The dried gel spectra indicates the presence of citrate ions (2950, 1630 and 1440 cm^{-1}) and ester bonds (1730 and 1070 cm^{-1}). The citrate ion bands are still present after calcination at 400 °C, while the ester bands are eliminated, indicating that the decomposition of the polymer starts from the carboxyl sites. Only after calcination at 800 °C do the bands of the organic compounds disappear, and only a strong band at 1450 cm^{-1} remains, due to carbonate ions. The FTIR spectra of samples calcined at higher temperatures (900 and 1000 °C) indicate the decrease of carbonates and the further formation and development of crystalline CA, as seen in the X-ray patterns.

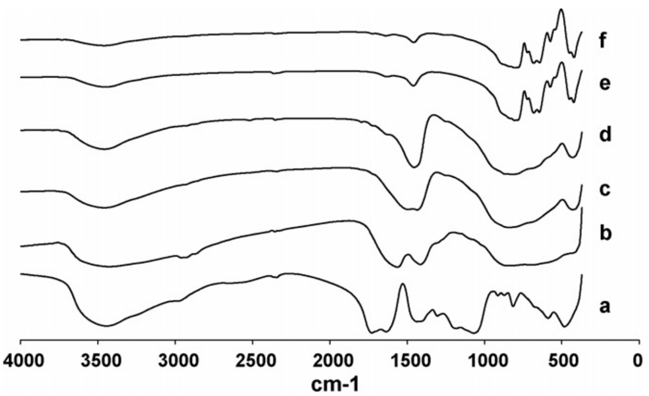

Fig. 4. FTIR spectra of dried gel and sintered products: (a) xerogel, (b) 400 °C/2 h, (c) 600 °C/3 h, (d) 800 °C/3 h, (e) 900 °C/3 h and (f) 1000 °C/3 h.

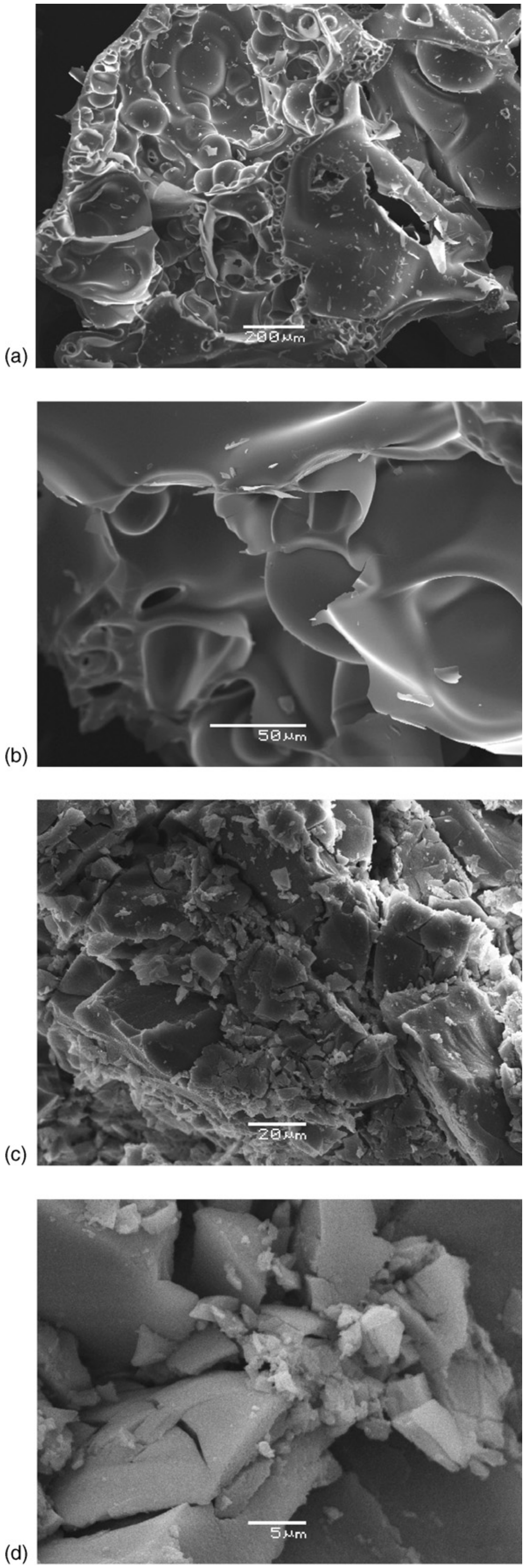

Fig. 5. SEM photos of samples: (a and b) dried gel and (c and d) final product (900 °C/3 h).

3.6. Scanning electron microscopy—SEM

Fig. 5 presents the SEM photos of the dried gel and the sample sintered at 900 °C for 3 h. The photos were selected to be representative of the size and texture of the grains. The dried gel consists of small fragments, as seen in Fig. 5a and b. The shape of these particles indicates an abrupt rupture of the material due, probably, to gas evolution. The microanalysis on the surface of selected particles (Fig. 5b) shows a molar ratio of Al:Ca approximately 1.9, which indicates a uniform distribution of the cations in the gel. The sintered product consists of polygonal-shaped grains, with a wide size distribution of 5–50 μm (Fig. 5c). The microanalysis on the surface of selected grains (Fig. 5d) shows a Al_2O_3 to CaO molar ratio 1.07, which is very close to the value of 1, as expected in the case of CA.

4. Conclusions

This work led to the following conclusions:

- The Pechini technique can be successfully applied for the preparation of CA. Its formation requires a 3-h sintering at 900 °C. There are no intermediate crystalline products at lower sintering temperatures.
- The final product is crystalline CA of high purity, without any impurities of reactants or secondary phases.
- The combination of TG, XRD and FTIR leads to the recording of all the transformations that occur during the processing of the precursors and the formation of the final products.

Acknowledgements

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References

1. Mohamed, B. M. and Sharp, J. H., Kinetics and mechanism of formation of monocalcium aluminate, $CaAl_2O_4$. *J. Mater. Chem.*, 1997, **7**(8), 1595–1599.
2. Stephan, D. and Wilhelm, P., Synthesis of pure cementitious phases by sol–gel process as precursor. *Z. Anorg. Allg. Chem.*, 2004, **630**, 1477–1483.
3. Tas, A. C., Chemical preparation of the binary compounds in the calcia–alumina system by self-propagating combustion synthesis. *J. Am. Ceram. Soc.*, 1998, **81/11**, 2853–2863.
4. Fumo, D. A., Morelli, M. R. and Segadaes, A. M., Combustion synthesis of calcium aluminates. *Mater. Res. Bull.*, 1996, **31/10**, 1243–1255.
5. Goktas, A. A. and Weinberg, M. C., Preparation and crystallization of sol–gel calcia–alumina compositions. *J. Am. Ceram. Soc.*, 1991, **5**, 1066–1070.
6. Narayanan, R. and Laine, R., Synthesis and characterization of precursors for Group II metal aluminates. *Appl. Organomet. Chem.*, 1997, **11**, 919–927.

7. Pati, R. K., Panda, A. B. and Pramanik, P., Preparation of nanocrystalline calcium aluminate powders. *J. Mater. Synth. Process.*, 2002, **10/4**, 157–161.
8. Gulgun, M., Popoola, O. and Kriven, W., Chemical synthesis and characterization of calcium aluminate powders. *J. Am. Ceram. Soc.*, 1994, **77**, 531–539.
9. Aitasalo, T., Holsa, J., Jungner, H., Lastusaari, M., Niittykoski, J., Parkkinen, M. and Valtonen, R., Eu^{2+} doped calcium aluminates prepared by alternative low temperature routes. *Opt. Mater.*, 2004, **26**, 113–116.
10. Hernández, M. T. and González, M., Synthesis of resins as alpha-alumina precursors by the Pechini method using microwave and infrared heating. *J. Eur. Ceram. Soc.*, 2002, **22**, 2861–2868.