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SYNTHESIS OF CALCIUM ALUMINATES THROUGH THE POLYMERIC PRECURSOR ROUTE

The Pechini method is a polymeric precursor route for the synthesis of polycrystalline ceramics of high purity. The conventional solid state synthesis of calcium aluminate compounds requires long-term lasting sintering at high temperatures. In this study, the Pechini method was applied for the preparation of pure $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Solid state synthesis was also used in order to compare the final products obtained by the two methods. The intermediate and final products obtained were characterized by XRD and FTIR spectroscopy. It was concluded that the Pechini method can be successfully applied for the preparation of high purity $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. The formation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ requires three-hour sintering at 1000°C and 900°C , respectively. The main intermediate product was $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ in the case of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, while in the case of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ there were no other crystalline intermediate products. The samples prepared through solid state synthesis, contain a considerable amount of secondary phases, even after sintering at $1350\text{--}1400^\circ\text{C}$ for more than 15 hours.

Key words: Pechini method, Calcium aluminates, XRD, FTIR.

Calcium aluminates have been long involved in practical applications in the cement and concrete industry, as well as in refractories and ceramic materials. Recently new advanced applications of calcium aluminates have appeared in optical and structural ceramics. Tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is one of the main constituents of ordinary Portland cements (OPC), and monocalcium aluminate, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, is the main constituent of calcium aluminate cements (CAC) [1,2]. Cement systems are quite complex, due to the appearance of a mixture of multiple binary and ternary compounds and, therefore, the use of pure clinker phases can be of great interest in fundamental research on cement chemistry (sintering and hydration reactions, effect of minor elements, etc.).

Conventionally, pure phases are prepared by solid-state synthesis, requiring repeated intermediate grinding and long-term sintering at elevated temperatures. According to the literature, pure $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is prepared by the repeated sintering of a CaCO_3 and Al_2O_3 mixture at 1450°C , while the formation of pure $\text{CaO} \cdot \text{Al}_2\text{O}_3$ requires repeated sintering at temperatures often exceeding 1400°C . 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 [2–4].

Wet chemical synthesis methods can be applied for the preparation of ceramic powders with enhanced properties, such as high purity, high surface area and

well-defined and controllable chemical composition. According to the literature, techniques such as sol-gel [1,2,5,6], polymeric precursor processes [7–9] and combustion synthesis [3,4] have been applied for the synthesis of calcium aluminate compounds. The sol-gel synthesis involves the use of alkoxides which are expensive and cannot be used on a large scale. They are, also, moisture sensitive and must be processed under dry and inert atmosphere. Besides, the sol-gel synthesis is a multi-stage procedure which requires careful control of each stage. The combustion synthesis needs large amounts of organic reactants and produces a large volume of gases such as NO_x and CO_2 . The Pechini method is an alternative, low temperature polymeric precursor route for the synthesis of high purity ceramics, which is also known to be quite simple, cost effective and versatile. It is based on the ability of certain alpha-hydroxycarboxyl acids, such as citric acid, to act as a polydentate ligand, forming chelates with most metallic ions. These chelates when heated with a polyhydroxylic alcohol, undergo a polyesterification reaction. The calcination of the obtained resins yields oxides of high purity at much lower temperatures than these required in conventional solid synthesis methods [10,11].

In the present study, the Pechini method was applied for the preparation of pure $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, using nitrate salts as metal-ion sources, citric acid for the chelation of the ions and ethylene glycol for the esterification reaction. The preparation of the gels was monitored through constant conductivity measurements, while the intermediate and final products were characterized by means of XRD and FTIR spectroscopy. Finally, solid state synthesis was also applied for the preparation of these phases, in order to compare the final products obtained by the two methods.

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EXPERIMENTAL

Synthesis

Nitrate salts were used as the cation sources; aluminium nitrate nonohydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ > 95%, Merck Germany, calcium nitrate tetrahydrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ \geq 99%, Fluka. Citric acid monohydrate $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ 99.5–100.5%, Merck, Germany, was used as the complexing agent, and ethylene glycol GR, $\text{C}_2\text{H}_6\text{O}_2$, min. 99.5%, Merck, Germany for the completion of the polyesterification reaction.

The preparation procedure was the same in both cases. Appropriate amounts of the nitrate salts were dissolved in 50 ml of de-ionised water on a hot-stirring plate. The nitrate salt ratio used was $\text{Ca}(\text{NO}_3)_2 : \text{Al}(\text{NO}_3)_3 = 1:2$ for $\text{CaO} \cdot \text{Al}_2\text{O}_3$, while the ratio $\text{Ca}(\text{NO}_3)_2 : \text{Al}(\text{NO}_3)_3 = 3:2$ for $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Once the nitrate salts were dissolved, citric acid (CA) was added to the solution in the molar ratio $\text{CA}:\text{total cations}=1$. Ethylene glycol (EG) was then added to the solution in the molar ratio $\text{EG} : \text{CA} = 2$. The solutions were continuously stirred at 80°C , to achieve the evaporation of excess water and accelerate the polyesterification reaction, which was monitored through continuous conductivity measurements, until the conductivity was diminished and viscous gels were obtained. The gels were then dried at 150°C in an oven for 24 h. The dried gels were ground to powder and calcined at 400°C for 2 h to form the powder precursors. Finally, the powder precursors were sintered at 800, 900 and 1000°C for 3 hours. Solid state synthesis was also applied for comparison reasons. Stoichiometric amounts of CaCO_3 and Al_2O_3 powders were mixed and calcined at 1400°C for 15 hours and at 1350°C for 20 h, for $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, respectively.

Characterization techniques

X-Ray powder diffraction data were collected using a Siemens D-5000 Diffractometer with $\text{CuK}\alpha_1$ radiation ($\lambda=1.5405 \text{ \AA}$), operating at 40 kV and 30 mA. FTIR measurements were carried out using a Fourier Transform IR spectrophotometer (Perkin Elmer 880). FTIR spectra in the range from 400 cm^{-1} 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 tons/cm^2 . Finally, the free CaO content of the sintered products was determined by the ethylene glycol extraction method [12].

RESULTS AND DISCUSSION

Gel Preparation

The conductivity measurements during the preparation of the gels are presented in Figure 1. The measurements began after ethylene glycol was added and the temperature reached approximately 80°C .

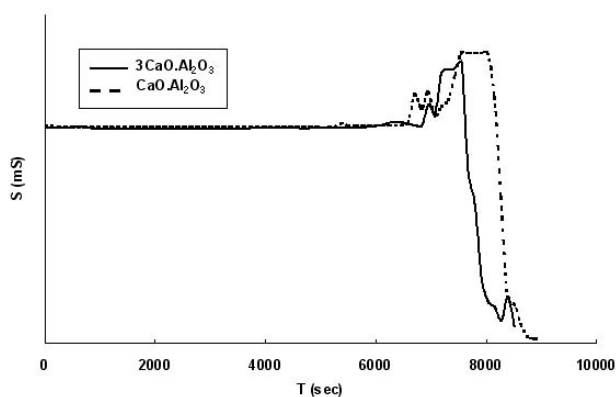


Figure 1. Conductivity of the starting solutions as a function of time

About 1.5 hours later a sudden and unexpected increase of the solution temperature, reaching 100°C , followed by a significant increase of the conductivity, was observed along with the evolution of red-brown vapors. The heating was lowered and the solution was left on the stirring plate until the temperature dropped to 80°C . This unexpected temperature increase 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 vapors. The fact that the same event took place during the preparation of both $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ indicates that these redox events are part of the gelling procedure. The conductivity was diminished after approximately three hours at 80°C , confirming that all the cations are captured in the polymer network and viscous gels were obtained. In both cases, the gelling procedure lasted for 3 hours. Heating at 150°C for 24 h was required to complete the polyesterification reaction, as well as the evaporation of most of the volatile compounds. The resulting xerogels were swollen out, aerated and very easily disintegrated.

CHARACTERIZATION OF INTERMEDIATE AND FINAL PRODUCTS

Figure 2 presents the XRD patterns of the xerogel, the powder precursor after sintering at 800°C and 1000°C for 3 hours and the product of solid state synthesis after sintering at 1350°C for 19 h, in the case of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. As seen, the dried gel is completely amorphous. Crystalline $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and free lime are formed at 800°C . At 1000°C , the sample consists of pure $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. It seems that binary oxides rich in Al_2O_3 , are the first to be formed. The product of the solid state synthesis at 1350°C for 19 hours contains $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and CaO .

Figure 3 presents the XRD patterns of the xerogel, the powder precursor after sintering at 800°C and 900°C for 3 hours and the product of solid state synthesis after sintering at 1400°C for 15 h, in the case of $\text{CaO} \cdot \text{Al}_2\text{O}_3$. The dried gel is completely amorphous, while at 800°C the sample continues to be mainly amorphous with

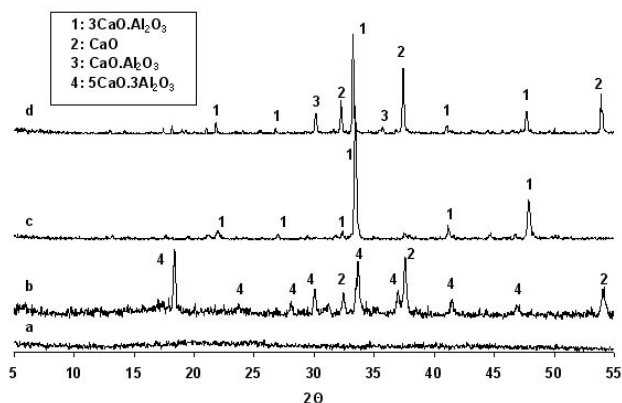


Figure 2. X-Ray diffraction patterns of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ samples prepared by the Pechini technique (a: xerogel, b: $800^\circ\text{C}/3\text{h}$, c: $1000^\circ\text{C}/3\text{h}$) and by solid state synthesis (d: $1350^\circ\text{C}/19\text{h}$)

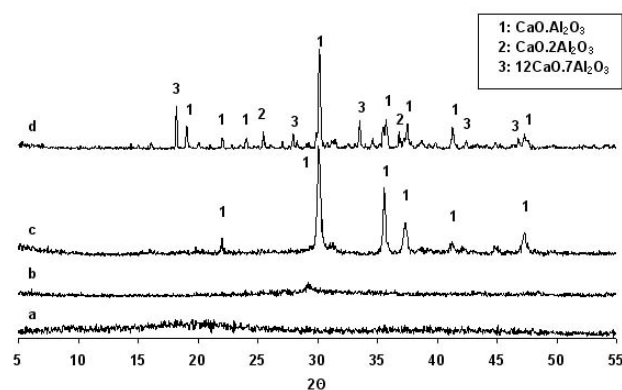


Figure 3. X-Ray diffraction patterns of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ samples prepared by the Pechini technique (a: xerogel, b: $800^\circ\text{C}/3\text{h}$, c: $900^\circ\text{C}/3\text{h}$) and by solid state synthesis (d: $1400^\circ\text{C}/15\text{h}$)

minor amounts of calcium carbonate. At 900°C , the sample consists of pure $\text{CaO} \cdot \text{Al}_2\text{O}_3$. The product of solid state sintering at 1400°C for 15 hours consists of $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$.

The free lime (CaO) content of the samples is presented in Table 1. The results indicate the very good combinability of the reactants in the Pechini synthesis. The products obtained through solid state synthesis contain substantial amounts of free CaO and secondary phases making the method inappropriate for the synthesis of pure phases.

Table 1. Free CaO content (% w/w) of the intermediate and final products

	Pechini synthesis			Solid state synthesis
	800°C	900°C	1000°C	
$\text{CaO} \cdot \text{Al}_2\text{O}_3$	0.08	0.32	–	1.34
$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	1.50	–	0.30	16.23

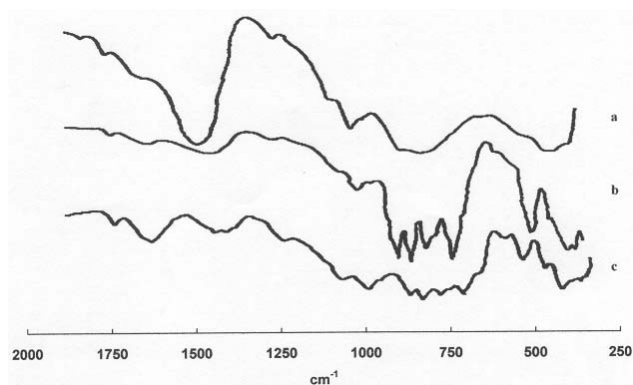


Figure 4. FTIR spectra of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ samples prepared by the Pechini technique (a: $800^\circ\text{C}/3\text{h}$, b: $1000^\circ\text{C}/3\text{h}$) and by solid state synthesis (c: $1350^\circ\text{C}/19\text{h}$)

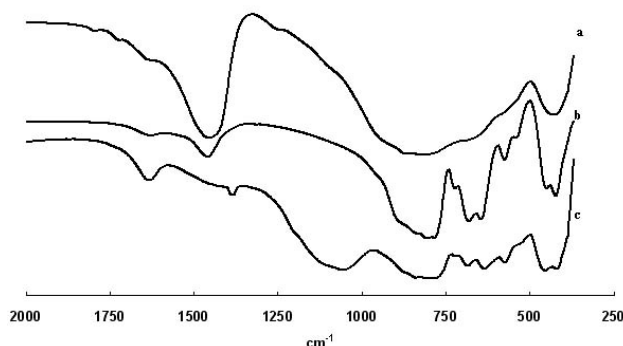


Figure 5. FTIR spectra of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ samples prepared by the Pechini technique (a: $800^\circ\text{C}/3\text{h}$, b: $900^\circ\text{C}/3\text{h}$) and by solid state synthesis (c: $1400^\circ\text{C}/15\text{h}$)

Figure 4 presents the FTIR spectra of the samples sintered at 800°C and 1000°C , as well as the sample prepared through solid state synthesis, in the case of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. The strong bands between 500 and 900 cm^{-1} are assigned to the vibrations of Al–O bonds, while the strong band at 1450 cm^{-1} indicates the presence of carbonate ions. The Al tetrahedra bands are very clear in the sample sintered at 1000°C . At 800°C there is a broad band which indicates that the formation of Al tetrahedra is just beginning. The characteristic bands of Al tetrahedra are also present in the sample prepared through solid state synthesis, but the difference in intensities indicate that the solid state sample is not as well formed as the Pechini sample.

Figure 5 presents the FTIR spectra of the samples sintered at 800°C and 900°C , as well as the sample prepared through solid state synthesis, in the case of $\text{CaO} \cdot \text{Al}_2\text{O}_3$. The spectrum at 800°C indicates the presence of carbonate groups and the beginning of the formation of the Al–O bonds of the oxides. The spectrum at 900°C shows well-formed sharp peaks in the area of interest, below 1000 cm^{-1} , where the characteristic frequencies of the Al–O bonds are found [13]. In the spectrum of the sample prepared through solid state

synthesis, the peaks in that area are less sharp and not as well formed, indicating poor crystallization of the oxides obtained through this method.

CONCLUSIONS

This study led to the following conclusions:

- The Pechini method can be successfully applied for the preparation of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Their formation requires three-hour sintering at 900°C and 1000°C , respectively.
- The final products prepared through the Pechini method are of high purity, without any impurities of reactants or secondary phases.
- There are no intermediate crystalline products at lower sintering temperatures for $\text{CaO} \cdot \text{Al}_2\text{O}_3$, while for $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ the main intermediate crystalline product is $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$.
- The samples prepared through solid state synthesis, contain secondary phases and show pure crystallinity, even after long-lasting sintering at high temperature.

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IZVOD

SINTEZA KALCIJUM ALUMINATA KORIŠĆENJEM POLIMERNOG PREKURSORA

(Naučni rad)

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Pečinijeva metoda (Pechini) sinteze polikristalne keramike visokog stepena čistoće se zasniva na primeni polimernog prekursora. Uobičajene konvencionalne sinteze kalcijum aluminata se zasnivaju na reakcijama u čvrstoj fazi koje zahtevaju dug proces sinterovanja na visokim temperaturama. U ovom radu je primenjen Pečinijev metod za sintezu čistih $\text{CaO} \cdot \text{Al}_2\text{O}_3$ i $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Sintaza ovih jedinjenja u čvrstoj fazi je takođe korišćena sa ciljem da se uporedno analiziraju proizvodi nastali primenom različitih metoda. Međuproizvod i finalni proizvod su analizirani primenom XRD i FTIR. Zaključeno je da se Pečinijeva metoda može uspešno primeniti u cilju dobijanja $\text{CaO} \cdot \text{Al}_2\text{O}_3$ i $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ visoke čistoće. Navedeni alumosilikati su dobijeni procesom sinterovanja na 1000°C ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) i 900°C ($\text{CaO} \cdot \text{Al}_2\text{O}_3$). Glavni identifikovani međuproizvod pri nastajanju $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ je $5\text{CaO} \cdot \text{Al}_2\text{O}_3$, dok kod dobijanja $\text{CaO} \cdot \text{Al}_2\text{O}_3$ nisu identifikovani druge kristalne strukture nekog međuproizvoda. Uzorci pripremljeni sintezama u čvrstoj fazi sadrže značajne količine drugih faza čak i posle sinterovanja na $1350-1400^\circ\text{C}$ tokom više od 15 sati.

Ključne reči: Pečinijeva metoda, Kalcijum aluminati, XRD, FTIR.