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Continuous supercritical hydrothermal synthesis of nanominerals

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1. Introduction

The synthesis of minerals has been pushed in the last decade by their insertion into new and advanced materials as mineral fillers in ceramic, polymer, paper, cosmetic, pharmaceutical, cements ... [1]. Up to now, the main synthesis method was the conventional batch synthesis characterized by long reaction times (few hours). The main objective of this contribution is to show that we have opened a new opportunity for the continuous supercritical hydrothermal synthesis allowing producing minerals in few tens of seconds. This new method presents the advantage to control chemistry and size and to be easily transferable at an industrial scale. This contribution proposes to enlighten the pioneer synthesis of three nanominerals which are: the talc, the xonotlite and the tobermorite.

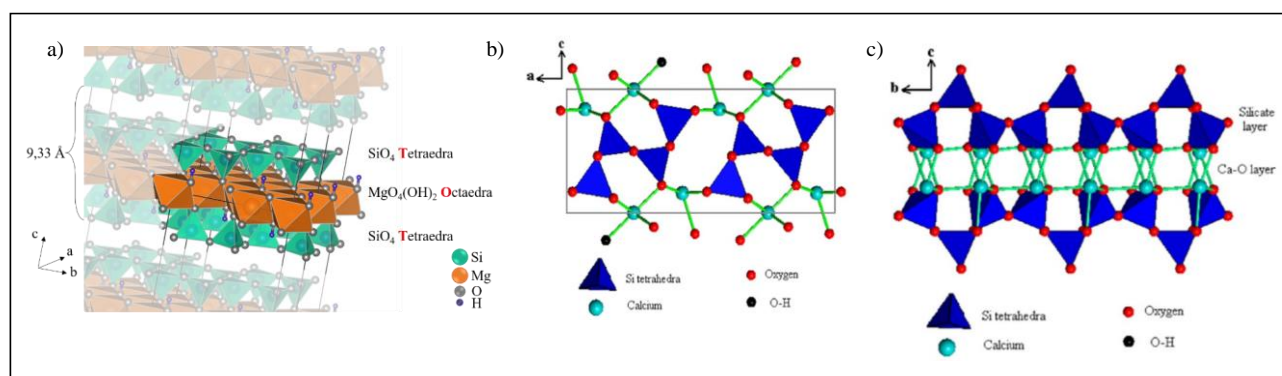


Figure 1. Structures of a) talc, b) xonotlite and c) tobermorite.

2. Results and discussion

A wide range of nanomaterials has already been synthesized with the use of supercritical fluids as described in our recent review paper [2]. In this study, the experimental set-up was composed of two pumps to inject the precursors, two preheaters, a tubular reactor and a back pressure regulator as described elsewhere [3].

The continuous synthesis of talc

Talc is part of our daily life since it is currently used as mineral filler in paper, plastics, cosmetics, due to its lamellarity and chemical inertness. As shown in Figure 1, talc is a clay mineral composed of hydroxylated magnesium silicate with the chemical formula Si₄Mg₃O₁₀(OH)₂. To perform the ultra-fast synthesis of talc in few tens of seconds, a silicon and a magnesium precursors in water, with a Si/Mg ratio equal to the one of talc, are injected into the reactor at 400 °C and 25 MPa. In these conditions synthetic nanotalc is obtained with unique properties. Figure 2 shows a SEM image of this new product. The synthetic nanotalc is a new material defined by a high chemical purity, a nano size and a hydrophilic character, knowing that natural talc is hydrophobic. This study demonstrates

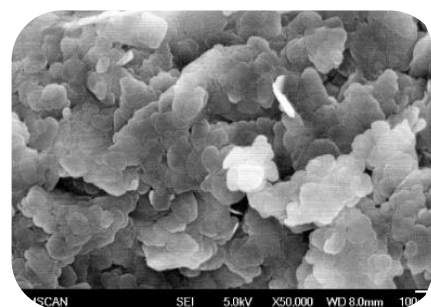


Figure 2. SEM image of synthetic talc

that it is possible to synthesize talc using a continuous flow process in supercritical water. The supercritical domain is a key-parameter for the growth and the structuration of particles in a very short time. This new concept of talc synthesis opens the avenue towards industrialization.

The continuous synthesis of xonotlite

To complete the proof of concept of the ultra-fast synthesis of nanominerals in supercritical water, a calcium silicate, the xonotlite with formula $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$, was considered. In recent years, the interest for this material has increased due to potential applications in additive for friction materials, precursor in the synthesis of aerogels, for orthopedic applications and as addition for cement. Xonotlite has traditionally been synthesized under mild hydrothermal conditions using as a precursor a suspension of silica and calcium oxide; the duration of this process is between 5 hours to 90 days depending on the pressure and temperature conditions [4]. As for talc, we have developed a continuous process in supercritical water for the synthesis of xonotlite. Once again the benefit of using supercritical water is demonstrated for the ultra-fast synthesis of nanominerals. Figure 3 shows a HR-TEM image of a synthetic xonotlite fiber exhibiting a high crystallinity.

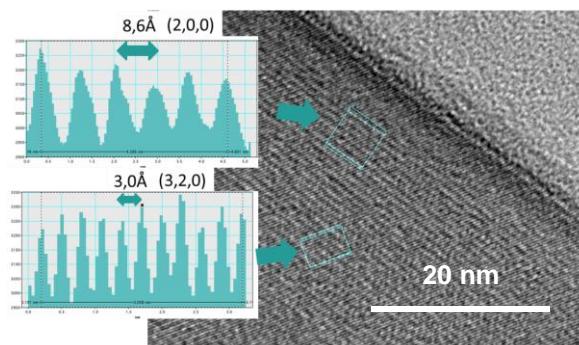


Figure 3. HR-TEM image of synthetic xonotlite

The continuous synthesis of tobermorite

Tobermorite is also a calcium silicate hydrate in form of a fibrillar mineral with the following chemical formula: $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot n\text{H}_2\text{O}$. The importance of this compound resides in the fact that its structure is used as a model to explain the main phase of the cement paste, the C-S-H gel. The most common synthesis method involves a hydrothermal treatment in a batch reactor. Nevertheless, pure crystalline tobermorite is arduous to achieve being usually associated with amorphous or poorly ordered phase. The temperature is a critical parameter since tobermorite is unstable under hydrothermal conditions and xonotlite starts to be formed at 130 °C [5]. In our study, the question was: is it possible to form tobermorite in supercritical water knowing that it is unstable above 130°C? At very short residence times (7s), tobermorite was formed in supercritical water at 400°C (23.5 MPa). These conditions allow being in a kinetic regime avoiding the transformation of tobermorite into xonotlite. The tobermorite synthesized in supercritical water exhibits a morphology and structure similar to those of the natural mineral suggesting that the supercritical process reproduces, in an accelerated basis, the geological genesis.

3. Conclusions

This contribution presents an overview of the possibilities offered today by the continuous supercritical hydrothermal synthesis for the production of continuous nanominerals. By the use of supercritical water, it is now possible to obtain a synthetic phyllosilicate with the synthetic talc and two synthetic inominerals with the synthetic xonotlite and the synthetic tobermorite in only few seconds with a sustainable and scalable technology. A new field of research is now opened with a high relevance industrially and academically.

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