

## Synthesis of Imogolite Fibers from Decimolar Concentration at Low Temperature and Ambient Pressure: A Promising Route for Inexpensive Nanotubes

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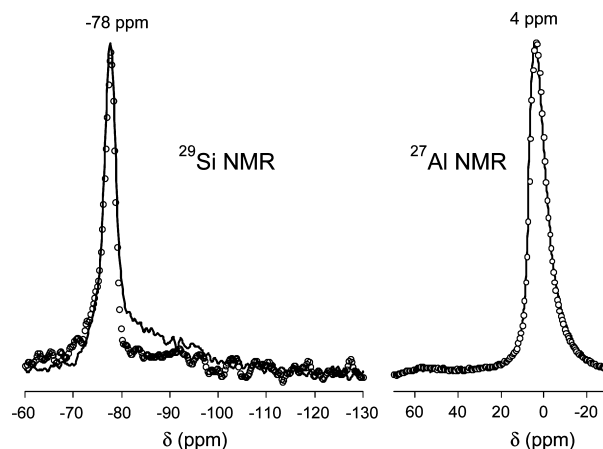
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Nanotubes are likely to be used in an increasing number of fields due to their known or expected specific properties (surface structure, reactivity, mechanical strength, etc.). The successful application of such materials in a given process depends of course not only on the nature of the nanotubes but also on how these nanophases are obtained. Points to be taken into consideration include reliability and reproducibility of the synthesis, simplicity of the protocol, environmental aspects (e.g., use of solvents), cost/yield, etc. In this context, imogolite, a naturally occurring aluminosilicate nanotube, is of special interest since it meets most of the above mentioned requirements: This single-walled nanotube ( $\varnothing = 2$  nm,  $L =$  few tens to several hundred of nanometers) has been first synthesized in small quantities in 1977<sup>1</sup> using a very simple one-step synthesis in aqueous solution followed by aging under mild conditions, i.e. 5 days at 95 °C and ambient pressure. Using the same synthesis protocol, structural analogues of imogolite, where Si is substituted by Ge, were recently obtained<sup>2</sup> with an excellent yield (defined here as the mass of nanotubes/mL of reaction volume). The shorter tube length and the higher cost due to the Ge reagent may limit the attractiveness of these structures, as compared to Si-imogolite. However, reports of the successful synthesis of imogolite all describe the use of initial concentrations in the milimolar range and atmospheric pressure. As opposed to the syntheses using Ge, the use of decimolar concentrations of Al and Si results in the formation of a different phase: allophane, i.e. an aluminosilicate with the same stoichiometry as imogolite but whose structure is described as spheroids with a diameter of ca. 4 nm.<sup>3,4</sup> The mechanisms governing tubular vs spheroidal growth as a function of initial reagent concentration remain unclear, especially since the syntheses of Ge analogues always lead to the formation of tubes regardless of the concentration.<sup>2</sup>

However, these observations were made while strictly adhering to the synthesis protocol. In particular, the structure of the solids formed from decimolar solutions has not been investigated for systems aged beyond 1 week.<sup>3–5</sup>

In this study we report that imogolite nanotubes can be obtained with decimolar concentrations by simply allowing for slower growth kinetics.

Aluminosilicate compounds were synthesized by coprecipitation of aluminum and silicon monomers in aqueous solution, from initial decimolar concentrations (see Supporting Information (SI)). Prod-



**Figure 1.** <sup>29</sup>Si and <sup>27</sup>Al NMR spectra after  $t = 5$  (full line) and  $t = 60$  days (circles) of aging.

ucts obtained at different aging times ( $t = 5, 14, 30,$  and  $60$  days) were characterized using NMR, XRD, and TEM (see SI).

The <sup>29</sup>Si NMR spectra of the products at  $t = 5$  and 60 days exhibit a main resonance at  $-78$  ppm (Figure 1). This chemical shift is characteristic of Si bound to 3 Al atoms and a OH.<sup>6</sup> Such Si coordination has been widely described for both imogolites and allophanes compounds.<sup>6,7</sup> The wide contribution observed in the  $-80$  to  $-110$  ppm range at  $t = 5$  days (ca. 20% of the Si) is attributed to polymerized Si species, presumably silica-type particles. This contribution, observed previously for allophane compounds,<sup>8</sup> was not detected in our samples at  $t = 60$  days of aging.

The two <sup>27</sup>Al NMR spectra ( $t = 5$  and 60 days) are superimposable. The main resonance has a chemical shift of  $4 \pm 0.1$  ppm and is characteristic of the octahedral environment of Al polymerized in a gibbsite-like layer.<sup>9</sup> This chemical shift corresponds to the Al arrangement in imogolite and allophanes.<sup>7,10</sup> The amount of 4-fold coordinated Al, giving rise to a peak at  $\sim 55$  ppm as in the case for allophane compounds, was very low ( $<2\%$ ). The local environment of Si and Al shows very little changes during aging and is characteristic of an imogolite-type configuration at the molecular scale.

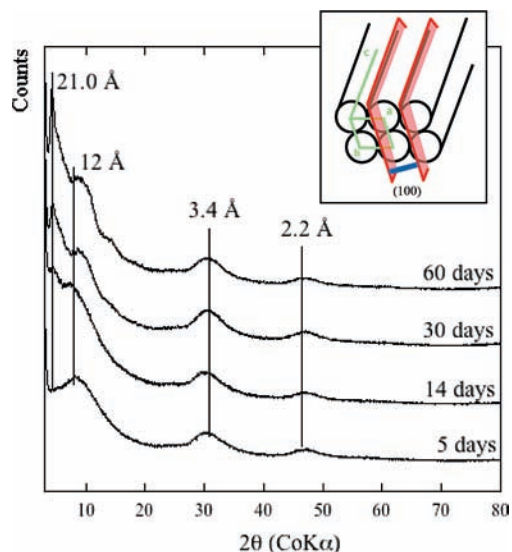
At a larger scale, the structure of the synthesized products is modified with aging. At  $t = 5$  days, the X-ray diffraction pattern exhibits three diffuse bands at 2.2, 3.4, and 12 Å (Figure 2). These bands have been reported in literature as being characteristic of the allophane structure.<sup>11,12</sup> With increasing growth time, more defined diffraction bands appear. A remarkable diffraction peak

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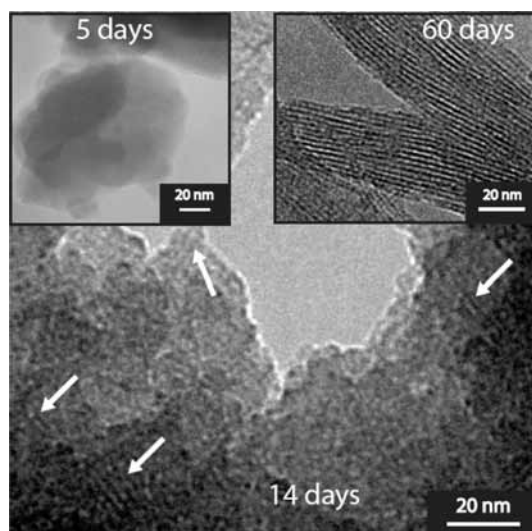
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**Figure 2.** X-ray diffraction pattern after  $t = 5, 14, 30,$  and  $60$  days of aging and illustration of the characteristic diffraction planes of imogolite (inset).



**Figure 3.** TEM pictures after  $t = 14$  days,  $5$  and  $60$  days (insets) of aging. White arrows indicate the presence of short imogolite fibers.

appears at  $21 \text{ \AA}$  for  $t = 14$  days and increases in intensity with aging. This well-defined reflection has been previously attributed to the overall packed structure and is linked to the outside diameter of the imogolite nanotubes (100) (Figure 2, inset).<sup>13</sup>

TEM observations confirmed the XRD findings and provided unequivocal evidence for the formation of imogolite nanotubes from decimolar solutions at short aging times (Figure 3). Indeed, as expected, no organized structure was observed at  $t = 5$  days. However, at  $t = 14$  days, the first short imogolite fibers were detected within a predominantly amorphous phase (Figure 3); this

coincides with the emergence of the XRD peak at  $21 \text{ \AA}$ . Finally the imogolite nanotubes aggregated into a fibrous network. Image analysis revealed an average tube diameter of  $26 \text{ \AA} \pm 1 \text{ \AA}$  indicating a very homogeneous diameter size distribution (see SI) consistent with previous reports.<sup>14,15</sup>

The mechanism(s) leading to delayed imogolite growth in a concentrated solution could not be determined from our present data. However, since in the case of the synthesis of the Ge analogues there is no visible concentration dependence of the growth kinetics at the scale of a week, it is reasonable to assume that the differences observed for imogolite are due to Si chemistry and presumably Si polymerization/depolymerization rates, since Ge does not polymerize in similar conditions.

The initial concentration of the reagents is not a limiting factor for the synthesis of imogolite under mild conditions: with decimolar solutions, the first tubular structures are formed as little as 14 days of aging and evolve into long fibers, which, to date, were only reported for 100 times less concentrated solutions under similar conditions. This improved yield in the synthesis of long nanotubes from inexpensive starting materials may stimulate a renewed interest in these structures, despite the slow reaction kinetics, and open the road for large scale applications. It is important to note that the nanosized allophane and allophane-like spheroids obtained previously under similar conditions could not be detected in our systems.<sup>3–5</sup> Consequently, considering their evolution into well-formed nanotubes, the solids obtained at a “standard” aging time of 5 days could be designated as imogolite precursors or proto-imogolite. Thus the question of the formation mechanisms of spheroidal allophane-like phases by simple coprecipitation remains unresolved.

**Supporting Information Available:** Detailed synthesis protocol, TEM data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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