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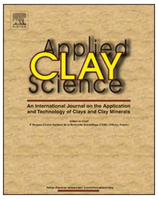

Research paper

Self-supporting thin films of imogolite and imogolite-like nanotubes for infrared spectroscopy

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ABSTRACT

Due to their narrow and well-defined structure, single wall nanotube, aluminosilicate nanotubes (imogolites) are excellent candidates to study how water is modified by either confinement or by the interface nature. A protocol is provided here to produce imogolite films that are ideally suited for infrared studies. Two types of imogolites were selected: a hydrophilic imogolite (IMO-OH) with inner surface fully covered with Si–OH hydrophilic groups and a hybrid imogolite (IMO-CH_3) with inner surface fully covered with hydrophobic Si–CH_3 groups. Films with different thicknesses were characterized by Small Angle X-ray Scattering (SAXS). The initial water content and the porosity of the films were estimated from ThermoGravimetric Analysis (TGA). Infrared spectroscopy was used to deduce the molar absorption coefficient of the bending mode that is significantly modified in confined water as compared to bulk water. Moreover, the interest of these films which allow avoiding extra-absorption features from the salt matrix or the supporting wafer is illustrated by an infrared study of the processes occurring in the IMO-OH film when it is heated from room temperature up to 350 °C. The evolution of the IR bands while heating shows the dehydration/dehydroxylation processes.

1. Introduction

Imogolite is a natural clay mineral discovered by Yoshinaga and Aomine (1962). It has a well-defined tubular shape with an external diameter ranging from 2 to 2.8 nm depending on its formation and composition. In general, the length of imogolite varies from submicron scale to several microns (Yang and Su, 2007; Yang et al., 2008). Due to this very high aspect ratio, imogolite dispersions exhibit birefringence in water which is typical for liquid crystals, even at weight concentrations of a few percent (wt%) (Paineau et al., 2016). At higher concentrations, they can form viscous and transparent dispersions and gels. Interestingly, the structure of dry imogolite samples depends considerably on the drying procedure. When the dispersion is slowly dried at 40 °C, transparent films are usually obtained (Fig. 1a). However, if the dispersions of imogolite are freeze-dried, a very light cotton-like solid is obtained (Fig. 1b).

Infrared (IR) spectroscopy is the technique of choice for the characterization of clay minerals, as it provides information on the chemical bonds present, as well as on their environment. Typical IR technique includes reflectance method such as ATR (Attenuated Total Reflection) and classic transmission methods (*e.g.* KBr-pellet or mull techniques). Compared to transmission methods, ATR experiments require less effort and time for sample preparation, and are hence widespread. Nevertheless, the principle of this measurement (an evanescent wave is created at the interface between a highly refractive medium and the sample) implies that the optical path depends on the wavenumber. Indeed, the penetration depth of the evanescent wave depends on several factors such as the wavenumber, the refractive index of the sample. Therefore, even if ATR provides valuable information on the nature of the bonds present in the sample, corrections to obtain spectra at constant optical paths have to be introduced, and the detailed analysis of the whole spectrum is complex. For transmission methods, clay samples are often pelletized in KBr. However, due to the hydrophilic nature of KBr, it is impossible to accurately quantify the water adsorption properties of the sample. Moreover, it may also modify the structure through exchange of K^+. To successfully study the water interaction with imogolites, experiments are ideally performed in the transmission mode with a thin self-supporting film of well adapted thickness (typically a few microns) (Madejová and Komadel, 2001).

However, obtaining films with an appropriate thickness can be difficult, especially for clay minerals (Madejová and Komadel, 2001). Some recent works reported a solution-based approach to make

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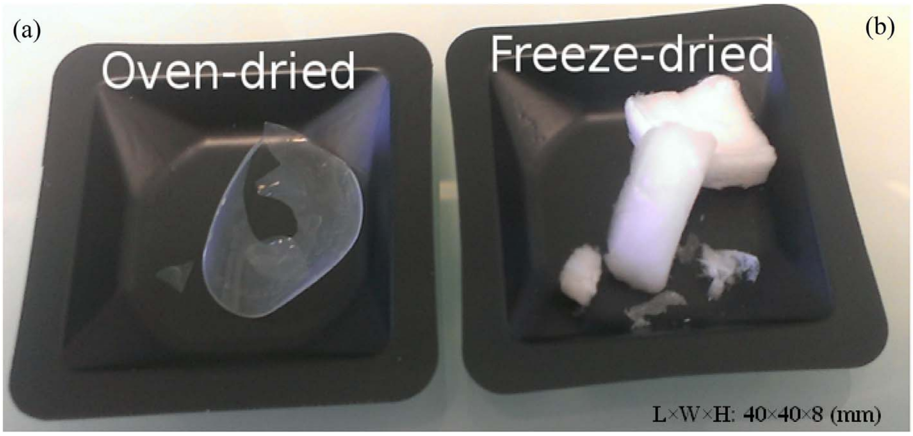

Fig. 1. Influence of the drying method on the aspect of the obtained Al–Ge double-walled imogolite (Thill, 2016). (a) Film obtained by drying in the oven at 40 °C. (b) Cotton-like solid obtained by freeze-drying.

imogolite thin films with the use of poly (vinyl alcohol) (PVA). The obtained films have good mechanical properties (Kang et al., 2012). With an improved method, the PVA content can be decreased to < 10 wt%, but it cannot be completely eliminated (Yang et al., 2016). Therefore there is a need in producing suitable films for IR spectroscopy using aluminosilicate nanotubes only. This will open the door to quantitative characterizations. We describe here an experimental protocol enabling the production of films and the control of their thickness and we compare the obtained spectra with the ones measured with methods commonly used in IR spectroscopy (*i.e.* ATR and KBr pellets). The water content and the porosity of the films are quantified by ThermoGravimetric Analysis (TGA). The relationship between the deposited quantity of imogolite and the absorbance of the water bending mode will be exploited, hence allowing the estimation of the molar absorption coefficient of water. The films are well adapted to directly study the interaction between imogolite and several gases and also to record *in situ* IR water adsorption/desorption processes or temperature changes on imogolite without the interferences from a wafer or a KBr salt. This will be illustrated in the case of the *in-situ* infrared measurement during the heating of the hydrophilic imogolite.

2. Experimental

2.1. Synthesis of standard imogolite and hybrid imogolite

Standard imogolite (IMO-OH) was synthesized following methods inspired by Farmer et al. (1977, 1983). $AlCl_3$ was dissolved in MilliQ water at a concentration of 2 mM together with tetraethoxysilane (TEOS) at a molar ratio Si/Al of 0.55. A slightly higher ratio than the formal Si/Al ratio (0.5) was used here to prevent the formation of undesired hydroxyaluminum (gibbsite). Under continuous stirring, NaOH was slowly introduced in the solution at a rate of 0.5 $mM{\cdot}min^{-1}$ until a molar ratio OH/Al of 2.0 was reached. The dispersion was stirred further for 1 h after NaOH injection until the solution was completely clear. The solution was then placed in an oven for 5 days at a temperature of 90 °C. After heating, the dispersion was concentrated by tangential ultrafiltration using 8 kDa membranes. The concentrated dispersion (about 10 $g{\cdot}L^{-1}$) was then dialyzed against MilliQ water until the conductivity of the external phase was < 2 $\mu S{\cdot}cm^{-1}$.

The hybrid imogolite containing $-CH_3$ groups inside the tubes (IMO-CH_3) instead of –OH was prepared using a protocol inspired by Bottero et al. (2011). Aluminum tri-sec-butoxide was dissolved in water containing hydrochloric acid and trimethoxymethylsilane (TMMS) at the following molar ratios: Si/Al = 0.575 and HCl/Al = 0.5. After mixing, the dispersion was stirred until it was completely clear. After disappearance of the final residual turbidity, the solution was heated at 90 °C for 5 h, 10 h, 24 h, 48 h and 5 days. For each solution, a small portion was dried in an oven to measure its concentration. Finally, the dialysis protocol was the same as the one described above for IMO-OH.

The dispersions were characterized by Small Angle X-ray Scattering (SAXS) (Boyer et al., 2014). The solid content was measured before and after dialysis by drying a known volume at 60 °C.

A rolling-ball viscometer (model Lovis 2000 M/ME, Anton Paar, Graz, Austria) was also used to measure the viscosities (mPa·s) of the obtained imogolite dispersions (20 °C). This set-up is based on a calculation of the viscosity from the rolling time of the ball through a capillary filled with the sample. All the measurements were done within a glass capillary (∅ = 1.59 mm, no. 18957327) using a standard steel ball (∅ = 1.5 mm), with angles varying from 50° to 80°. The equipment was calibrated under the same conditions with Millipore water in a capillary. The average length of imogolite was estimated using the obtained values of the viscosity and the concentration of the solution.

2.2. Film preparation and characterization

The standard imogolite and hybrid imogolite films were obtained by drying a known mass of imogolite per unit surface. To this end, a round polystyrene (PS) plastic substrate with a diameter of 1.8 cm was punctured from pour-boat weighting dishes. The substrate was covered by a 500 μL droplet of the dispersion. The volume of the droplet was selected in order to pin the contact line on the border of the round plastic substrate. The pinning prevented the contact line from shrinking during drying. This enabled obtaining a film which covers the whole surface. The droplet was prepared by mixing the imogolite dispersion and MilliQ water to adjust the concentration. The deposited concentration (C_d^g, with superscript g as global, expressed in $mg{\cdot}cm^{-2}$) was systematically varied in order to obtain a deposited quantity between 0.4 and 1.9 $mg{\cdot}cm^{-2}$. The samples then dried for 1–2 day(s) at room temperature. No oven-dried procedure was used, as this would lead to too brittle films. After drying, the self-supporting films naturally detached from the PS surface. Many tests on other plastics were unsuccessful showing that the nature and the rugosity of the substrate are critical parameters. Assuming that the obtained films have a homogeneous thickness e over the whole deposition surface, and with a careful control of the mass of imogolite that is deposited on the surface, the thickness could be calculated from the density of the film ρ_f ($g{\cdot}cm^{-3}$): $e = C_d^g/\rho_f$. However, in the real situation, the homogeneity of the film may be strongly affected by "coffee-ring" effects for instance, and C_d (deposited concentration in the center of the film, expressed in $mg{\cdot}cm^{-2}$) could be much smaller than the average C_d^g. To measure C_d at the center of the film, X-ray transmission measurements at the copper Kα wavelength were then performed (see Figs. S1 and S2 in the Supporting information, SI).

In order to allow a comparative study, IR experiments were first performed using ATR technique and then in transmission mode using KBr pellets. With the ATR technique, IR spectra were recorded in the