Inelastic neutron scattering analysis of the thermal decomposition of kaolinite to metakaolin

Claire E. White [a,b,c,d,*], Gordon J. Kearley [e], John L. Provis [d,f], Daniel P. Riley [g,h]

[a] Lujan Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, USA
[b] Physics and Chemistry of Materials, Los Alamos National Laboratory, Los Alamos, USA
[c] Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, USA
[d] Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Australia
[e] Bragg Institute, Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia
[f] Department of Materials Science and Engineering, The University of Sheffield, Sheffield, UK
[g] Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia
[h] Department of Mechanical Engineering, The University of Melbourne, Parkville, Australia

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ABSTRACT

Understanding the formation of metakaolin via kaolinite dehydroxylation is extremely important for the optimization of various industrial processes. Recent investigations have reported that the different types of hydrogen atoms in kaolinite are removed concurrently during the dehydroxylation process. Here, inelastic neutron scattering (INS) is used to analyze the location and dynamics of hydrogen atoms in kaolinite, together with the changes induced during dehydroxylation. This is achieved by using prior knowledge of how the *inner* and *inner surface* hydrogen atoms contribute to the kaolinite INS spectrum in the $200-1200 \, cm^{-1}$ range, in combination with a semi-quantitative analysis of the experimental INS spectra. Overall, it is seen that there is a distinct preferential loss of *inner surface* hydrogen-atom types during the dehydroxylation process, as determined from analysis of the Al–O–H vibrational modes (consisting of deformation and torsion) in the INS spectrum.

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1. Introduction

Kaolinite is a 1:1 layered aluminosilicate mineral consisting of alternating silica and alumina sheets. This naturally occurring material is used extensively in the industrial and technological sectors, including as a ceramic precursor and cement filler [1,2]. The atomic structure of kaolinite has been studied extensively over the past years using experimental and theoretical techniques, revealing important details regarding the position and functionality of the hydrogen atoms (H-atoms) [3–14]. Moreover, the structural changes at the atomic level occurring during the thermal decomposition of kaolinite, and subsequent formation of metakaolin (between 550 and 750 °C), have been the subject of recent debate in the community [15–21].

Metakaolin is formed via the dehydroxylation of kaolinite at around 550–750 °C, where the formation of water (via $H^+ + OH^- \rightarrow H_2O$) and its removal from the structure result in an amorphous and metastable aluminosilicate material [22]. Two types of H-atoms exist in the crystalline kaolinite structure, which

are designated as *inner* and *inner surface* H-atoms (Fig. 1) [13]. Previous investigations have reported that the different types of H-atoms in kaolinite are removed concurrently, with increasing temperature [23]. Toussaint et al. [24] concluded, in agreement with other previous studies, that the dehydroxylation process proceeds by successive destruction of the alumina octahedral layers, with the probability of dehydroxylation throughout the process being proportional to the amount of unreacted material (reaction is diffusion limited).

Frost and Vassallo employed Fourier transform in situ infrared emission spectroscopy (IES) to study the changes occurring in the four hydroxyl stretching bands assigned to the four different hydroxyl environments present in the kaolinite structure as dehydroxylation proceeded. Their results showed that the *inner* and *inner surface* H-atoms are lost simultaneously during the formation of metakaolin. In contrast, for dickite and halloysite (which have the same composition as kaolinite) the *outer* H-atoms are removed in preference to the *inner* H-atoms. Furthermore, kaolinite dehydroxylation showed no evidence of proton diffusion or "hopping" (which involved two non-adjacent H-atoms), and therefore the process was classified as homogenous within two temperature regions (420–480 °C and 480–520 °C), which indicated different mechanisms occurring within these two temperature regions. Ortega et al. [25] confirmed that the dehydroxylation process con-

* Corresponding author. Current address: Department of Civil & Environmental Engineering/Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544, USA. Tel.: +1 609 258 6263; fax: +1 609 258 2799.
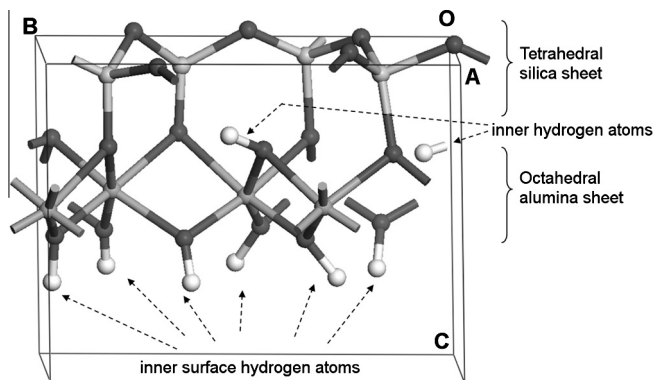*E-mail address:* whitece@princeton.edu (C.E. White).

Fig. 1. Schematic representation of kaolinite (depicted as a unit cell with P1 symmetry). The 1:1 layering of silica and alumina sheets is labeled, as are the two types of H-atoms present (*inner* H-atoms and *inner surface* H-atoms).
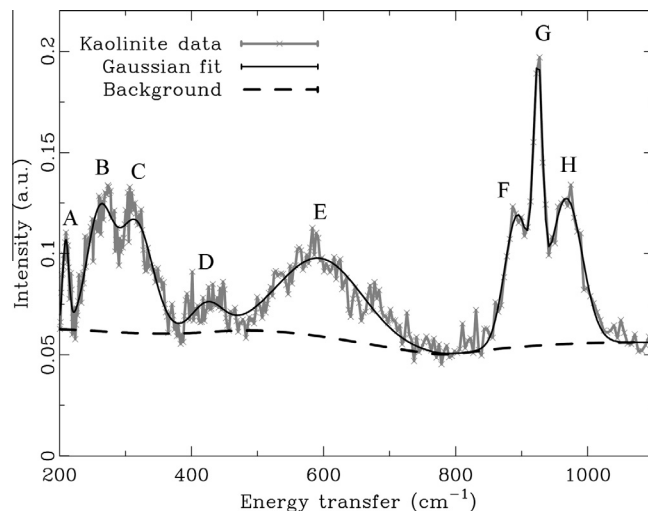

Fig. 2. Experimental INS spectrum of kaolinite (KGa-1b) and the fit obtained using eight Gaussian functions together with a background spline function. The labels *A* through *H* denote the position of the eight Gaussian functions.

tains at least two stages: the first is assigned to nucleation and growth of the nuclei, while the second corresponds to a diffusion process (due to the increased hindrance against water diffusion through the metakaolin regions).

The aim of the current work is to explore the dehydroxylation process of kaolinite using inelastic neutron scattering (INS), which is capable of distinguishing between different types of H-atoms in materials. This experimental technique has recently been used to study the H-atom dynamics and structure of kaolinite [14,26]. Here, we use a semi-quantitative analysis of INS spectra to obtain information that is complementary to that already existing regarding the loss of H-atoms (*inner* and *inner surface*) from the kaolinite structure with temperature.

2. Material and methods

High-purity, well-ordered kaolinite was purchased from the Clay Source Repository, CO, USA (Purdue University). This source of kaolinite is denoted KGa-1b, and has been subjected to detailed analysis elsewhere [27]. The kaolinite sample contains impurities of anatase (1.66%) and cation substitution ($\sim$0.35%) [27]; however, these have a negligible influence on the INS spectrum. For the samples to be analyzed by INS, kaolinite was calcined at temperatures of 450, 500 and 550 °C. Powdered kaolinite was placed in an alumina tray in a small laboratory furnace that had been pre-heated to the desired temperature, calcined for 2 h in air, and then removed directly to cool under ambient atmospheric conditions.

To study the effects of synthesis conditions on the formation of metakaolin, thermogravimetric analysis of KGa-1b kaolinite was conducted using a Perkin–Elmer Diamond TG/DTA with the samples in alumina crucibles. Six runs were made in a nitrogen atmosphere, heating from 50 °C to the target temperature at a rate of 5 °C/min, and then held at the target temperature for 6 h. The six target temperatures studied were: 400, 450, 500, 550, 600 and 700 °C

INS spectra were collected using the TOSCA instrument at ISIS, Rutherford Appleton Laboratory, UK [28]. INS spectra of these materials are severely broadened above $\sim$70 K so spectra for all pre-treated samples were collected at low temperature. The samples were loaded into aluminum sachets and then placed in aluminum sample holders for analysis at a temperature of 30 K. The instrument is an inverted geometry crystal analyzer spectrometer covering a broad energy transfer range (24–4000 cm^{-1}) with high energy resolution ($\Delta E/E \approx 1.5$%). The samples were measured for $\sim$24 h and the data were obtained from the backscattering detector banks. Data were corrected and transformed to the energy scale using standard algorithms. The data were scaled by firstly

normalizing to unity for the total integrated intensity from 200 to 4000 cm^{-1} followed by multiplication by the known hydrogen content, obtained from thermogravimetric analysis data presented in reference [26].

Analysis of the resulting INS spectra has been performed for each sample by fitting a spline background function to account for the non-hydrogen dynamics component of the spectrum, and up to eight Gaussian functions for the hydrogen dynamics in the 200–1200 cm^{-1} frequency range. This does not imply a specific number of vibrational modes, but is principally a convenient means of extracting intensity in diagnostic regions from the overall spectral profile. An example of the fit obtained using this method is displayed in Fig. 2, along with labeling of the location of the eight Gaussian functions.

3. Results and discussion

3.1. Effect of synthesis conditions on kaolinite dehydroxylation

It is well known that the dehydroxylation process of kaolinite is highly dependent on the kinetics of reaction [24,25,29–35]. Ptáček et al. conducted a number of studies on the kinetics of the dehydroxylation process using isothermal and non-isothermal thermogravimetric analysis techniques, revealing that the conversion from kaolinite to metakaolin is dependent on both heating rate, soak temperature and time [33–35]. The effect of soak temperature is displayed in Fig. 3, where the thermally induced weight loss of kaolinite is shown using the same heating rate, but different soak temperatures. Each sample was held at the designated temperature for 6 h. It is evident from this figure that the induced weight loss in the samples used for INS (and therefore residual hydrogen content), is dependent on the synthesis conditions used to produce the samples. Although the method used for scaling the INS spectra in this investigation is approximate, since the water content of the samples used for INS was estimated from thermogravimetric data of KGa-1b kaolinite using a heating rate of 5 °C/min with no soak time, and although this will allow only approximate scaling of the spectra of different samples, our interest is entirely related to how relative intensities over the spectral region change with heat-treatment. This is because our aim is to determine if there is any preferential removal of specific H-atoms (*inner* or *inner surface*) from the kaolinite structure during the dehydroxylation