

In situ EELS study of dehydration of Al(OH)₃ by electron beam irradiation

Nan Jiang*, John C.H. Spence

Department of Physics, Arizona State University, Tempe 85287-1504, AZ, USA

ARTICLE INFO

Available online 19 November 2010

Keywords:

EELS
Dehydration
Al(OH)₃

ABSTRACT

The dehydration of Al(OH)₃ by an electron beam has been investigated using the time-dependent electron energy-loss spectroscopy (EELS) technique. Based on an analysis of low-loss EELS, Al L₂₃ and O K-edge, it is found that the processes are initially induced by the loss of H, followed by sputtering of O, which induce local structural changes. Some of the octahedrally coordinated Al transfer to tetrahedrally coordinated Al. The time-dependent O K-edge shows that the pre-edge peak in the O K-edge of Al(OH)₃ is induced by the formation of unpaired O, rather than an intrinsic feature of the OH bond.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Dehydration of hydroxides on heating is a fascinating phase transition phenomenon, and has been extensively studied [1]. The products usually consist of nanoparticles and nanopores, and thus are widely used in industries as adsorbents, catalysts or catalyst carriers. These remarkable properties have attracted a great deal of scientific research on their structure, and on the kinetics of their chemical reactions. Among the hydroxides, dehydration of Al(OH)₃ is probably one of the most complicated. Although α -Al₂O₃ (corundum) is the most stable phase of alumina at room temperature, several transition forms occur during the dehydration of Al(OH)₃ (gibbsite) at different temperatures [2,3]. These transition forms are reproducible and stable at room temperature. Interestingly, a similar dehydration sequence of Al(OH)₃ has also been observed using electron irradiation in a transmission electron microscope (TEM) [4,5].

In situ monitoring of chemical reactions can provide valuable insights into the kinetics and mechanisms of the processes that occur. Recently, we carried out a series of studies on the dehydration of Mg(OH)₂ by an electron beam using *in situ* electron energy-loss spectroscopy (EELS) [6,7]. It was demonstrated that the EELS technique could provide a complimentary tool to electron diffraction for the analysis of structural change during the transition [8]. The latter is more sensitive to the long-range order, while the former is determined by the local structure and chemistry [9]. In this work, we carried out an *in situ* study in which the dehydration of Al(OH)₃ was induced by a beam of electrons, while the local structure and chemistry was monitored by changes in near-edge fine structures of EELS in real time.

2. Experimental

Al(OH)₃ crystals (Alfa Aesar) were used in this study. The TEM samples were prepared by blowing dry Al(OH)₃ powders into air and picked up using a Cu grid covered with lacy carbon films. The experiments were carried out using a 200 kV JEOL 2010 TEM, equipped with a field emission gun and a Gatan Enfina electron spectrometer. The energy resolution of EELS was about 0.9 eV. The dispersion of the spectrometer was 0.2 eV per channel, thus both the zero-loss peak and the Al L₂₃ edge at 80 eV can be simultaneously recorded in a 1024-channel CCD. The O K-edge at 530 eV was recorded separately. For the low-energy loss and Al L₂₃ edge, the spectra were acquired in the image mode, while for the O K-edge, the diffraction mode was used. To exclude the contribution from large angle scattering, an objective aperture was used in the image mode. The acquisition times were 5 s for the low-energy-loss spectra and the Al L₂₃ edge and 10 s for the O K-edge. Throughout this work, electron beam intensity I_0 on the sample was monitored using a combination of the current readout on the small observation screen and the magnification.

All calculations of electronic DOS and simulations of O K-edge EELS were performed using the computer code FEFF8, which is based on the real-space full multiple scattering theory within the self-consistent muffin-tin potential approximation [10]. The core-hole effect was included in the simulations using the final state approximation, in which one core electron was placed in the valence band. The clusters, including 180–200 atoms, were generated from the crystal structure of gibbsite, Al(OH)₃.

3. Results

The depletion of H in hydroxide specimens is unavoidable under high-energy electron irradiation in TEM. Fig. 1 shows a typical example of time-dependent low-energy-loss EELS of Al(OH)₃ under

* Corresponding author. Tel.: +1 480 7277169.
E-mail address: nan.jiang@asu.edu (N. Jiang).

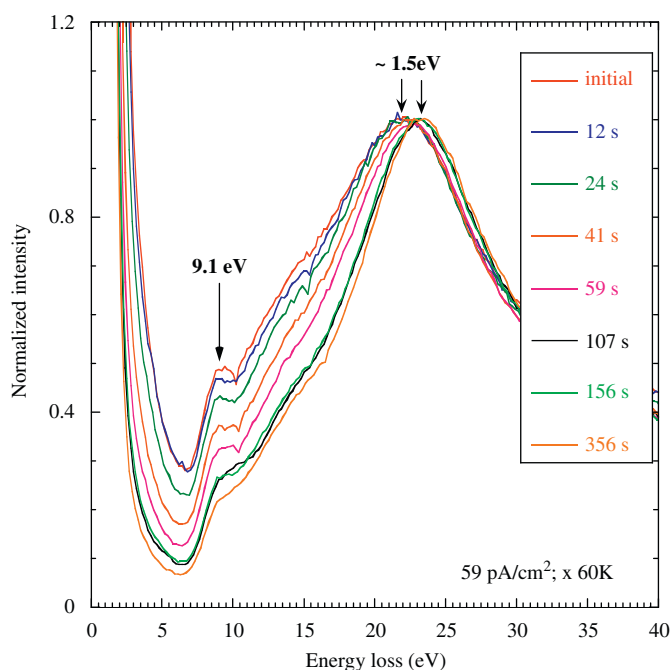


Fig. 1. Time-dependent series of EELS of Al(OH)₃ at low energy loss region. “Initial” refers to the first recorded spectrum immediately after sample was exposed to electron illumination.

normal illumination conditions, of which the beam intensity and magnification were 59 pA/cm² and 60k, respectively. The thickness of the data-collection area was quite small, about one-third of the effective mean-free-path for inelastic scattering of Al(OH)₃ [9], and thus no de-convolution process was applied to the data. All the spectra were normalized to the height of the plasmon peak, which is located at about 23 eV [11]. The following two significant changes can be identified in this time series EELS: the intensities before the plasmon peak gradually decrease with increase in irradiation and the plasmon peak position shifts towards higher energy.

It should be pointed out that all the changes in low-energy-loss EELS during irradiation are rather smooth. There is no abrupt occurrence of signatures of an O–O π* peak around 5 eV [12], H–H peak around 13 eV [13] or H₂O [14]. In other words, there is no evidence for the formation of H₂ and O₂ bubbles and H₂O during the irradiation in this study. Therefore, it is reasonable to assume that the depletion of H occurred mainly by the removal of H atoms, either knocked out by high-energy electrons or expelled due to radiolysis, or a combination of both. The depletion of H may result in the formation of unpaired O. This phenomenon can be observed in time-dependent O K-edge EELS.

Fig. 2 shows an example of the time-dependence of the O K-edge of Al(OH)₃, acquired from the same area, under the conditions 59 pA/cm² and × 50k. For comparison, the O K-edge spectrum was also acquired separately from a different area under slightly weaker illumination conditions (22 pA/cm² and × 50k). Evidently the pre-edge peak in the O K-edge (marked as the shaded area in Fig. 2) is not an intrinsic feature of the original Al(OH)₃, but is induced by electron irradiation. The relative intensity of this pre-edge peak (to the major peak) slightly increases initially, and then decreases with increase in irradiation.

A typical time-dependent EELS of the Al L₂₃ edge is shown in Fig. 3, in which the beam intensity and magnification were 228 pA/cm² and 80k, respectively. For convenience, we divide the time series into the following three approximate stages: “initial”, before 40 s; “intermediate”, between 52 and 493 s and “final”, after 513 s.

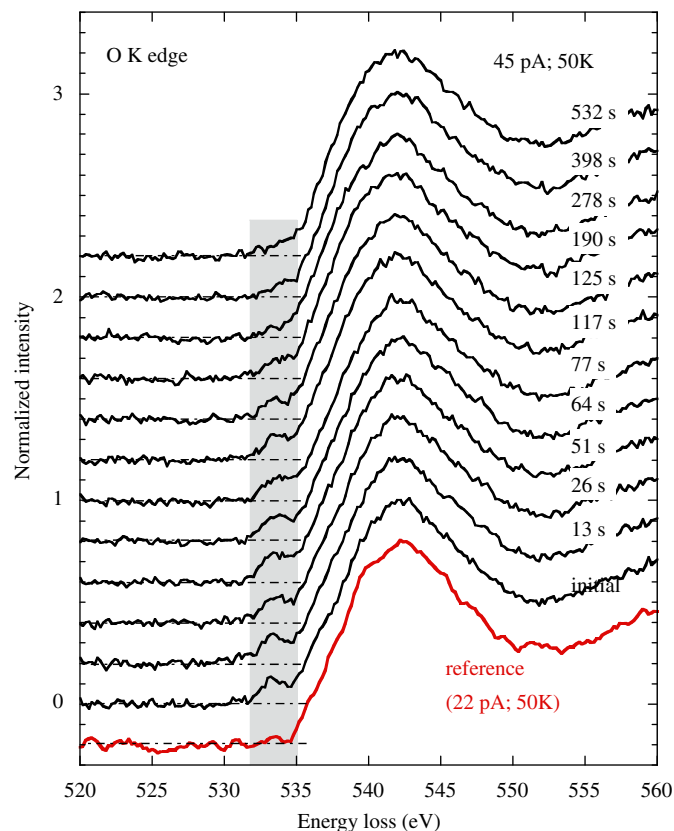


Fig. 2. Time-dependent series of O K-edge EELS of Al(OH)₃ under same beam intensity. The shaded area indicates the pre-edge peak region.

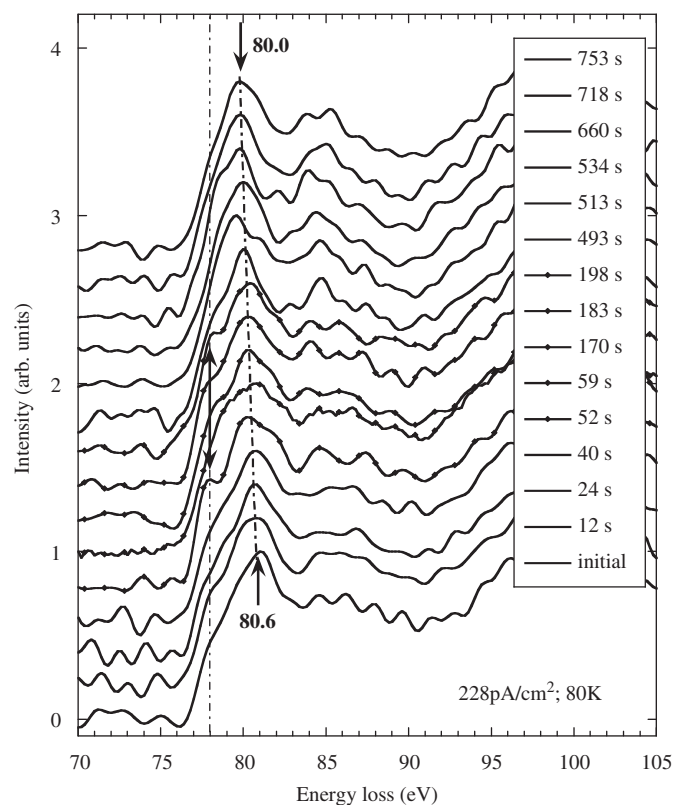


Fig. 3. Time-dependent series of Al L₂₃ edge EELS of Al(OH)₃. The vertical lines are a guide for the eye.

Download English Version:

<https://daneshyari.com/en/article/1677882>

Download Persian Version:

<https://daneshyari.com/article/1677882>

[Daneshyari.com](https://daneshyari.com)