Analysis of ZrO_2-intercalated montmorillonite clays

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Montmorillonite clay is a layered 2d structure, where each layer consists of two tetrahedral, aluminium substituted, silicate sheets sandwiching an octahedral, magnesium substituted, alumina sheet, resulting in a negatively charged surface towards which positive ions are drawn [1]. These 2d sheets are stacked on top of each other, resulting in a layered structure with a 11.3 Å interlayer spacing with some variation depending on local conditions. The large surface area and the ability to intercalate metal ions in between the layers, opens up the possibility of using MMT-clay as a template and stabilizer for nanoscale structures. Here we investigate ZrO_2-intercalated MMT clays with potential applications in water treatment.

From this, a few questions arise,

1) How does the ZrO_2 intercalation affect the interlayer distance?
2) Is ZrO_2 intercalated in between every clay layer?
3) How large are the ZrO_2 crystallite domains that forms in the intercalation?

(1) High resolution TEM imaging reveals a layer expansion from 11.3 Å to 13.7 Å indicating that there was an average expansion of the interlayer distance due to the ZrO_2 intercalation.

Images were acquired parallel to the viewing direction with a 0.98 Å/px sampling. In these images, the distinct layers were clearly visible. In order to extract statistics about the interlayer spacings from the multitude of curved layers with different orientations, a rotational averaging technique was be used.

The averaging technique used herein makes use of a background corrected radial profile of the Fast Fourier Transform (FFT) of the image. To reduce the impact of Fresnel effects, both from defocus and from the presence sharp edges arising from the morphology of the sample, the FFT was filtered by applying a sequential median filter: any values below the median at the given radius were set to zero.

Applying the rotational averaging technique to a set of images from a ZrO_2 intercalated MMT clay shows that there is a wide distribution (σ = 1.9 Å, μ = 13.7 Å) of different interlayer spacings.. Applying the same technique to a set of non-intercalated MMT clay images shows a narrower distribution (σ = 0.7 Å, μ = 11.3 Å) of interlayer spacings. Because of the overlap of these ranges, there is an indication that the intercalation does not happen on all layers, and that some parts of the of the clay remain in the un-intercalated form.

(2) Because Zr is by far the heaviest element present in the clay samples, it should be possible to elucidate its distribution on the sample using STEM-HAADF. The STEM-HAADF images for the intercalated clays contained thin, bright regions separated by darker regions. These bright lines, corresponding to Zr-rich areas, were found to be approximately 2 ± 1 nm thick, and separated peak-to-peak by approximately 3.5 ± 1 nm. From this we interpret that the ZrO_2 platelets tend to intercalate a few layers, then leave a few layers without intercalation, before

once again intercalating a few layers. This offers an explanation as to why the analysis of the HR-TEM images gave an overlap: there is a combination of intercalated and un-intercalated layers. Note that XRD was not able to identify the two domains.

To confirm the ZrO_2 distribution found in STEM-HAADF, these images were compared with STEM-EDX maps of the same area. The EDX maps were analysed with principal component analysis (PCA) using the HyperSpy [2] library for Python. Comparing the PCA component corresponding to areas rich in Zr with the STEM-HAADF images, it was seen that there was good correspondence between the two.

(3) The in-plane extent of the ZrO_2 platelets was determined to be between 5-15 nm from HR-TEM images acquired perpendicular to the clay basal-planes. Plane spacings unique to ZrO_2 were found by comparing the FFT of HR-TEM images of intercalated clay samples with those of untreated MMT-clay. The additional lattice spacings in the intercalated clay were found to correspond well to either tetragonal or monoclinic ZrO_2. However, the HR-TEM images were acquired at the edge of the agglomerates, where the clay is only a few layers thick which may not be representative of the bulk material.

In conclusion, we found that ZrO_2 platelets can be templated between MMT-clay basal planes. We found that this intercalation does not occur on every layer, rather it seems to occur between some layers but not others.

[1]: M.F. Brigatti, et al. *Developments in Clay Science*. Ch. 2 - *Structure and Mineralogy of Clay Minerals*. Elsevier. 2013. DOI: 10.1016/B978-0-08-098258-8.00002-X

[2]: F. de la Peña, et al. hyperspy/hyperspy: Release v1.6.1. 2020, Nov 28. Zenodo. DOI: 10.5281/zenodo.4294676