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VIBRATIONAL STUDY OF THE DEINTERCALATION OF KAOLINITE

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Intercalation in kaolinite involves the spontaneous self-assembly of small molecules (e.g. N-methylformamide, NMF) in the interlayer space of the mineral leading to an expansion of its structure from 7 Å to 10-14 Å. Recent kinetic studies by near-infrared spectroscopy (NIR) and X-ray diffractometry (XRD) over a broad temperature range [1, 2] have indicated that intercalation involves switching to the fully intercalated state, which does not distort the layers and does not induce interstratification. The opposite process, i.e. deintercalation, is known to induce stacking faults disorder [3-5] and the appearance of partially hydrated interlayers [6]. This work aims at studying the kinetics of the NMF deintercalation process by vibrational spectroscopy complemented by XRD and TGA.

KGa-1b and KGa-2 kaolinite samples, pre-intercalated with NMF, were subjected to isothermal deintercalation (30-80 ºC) under a flow of wet (~70 RH%) or dry N_2. Synchronous NIR measurements showed that the NMF content (intensity of the 2νNH mode) decreases to almost zero. Layer distortion (proxied by the width of the 2ν inner AlAlOH stretch) appeared independently of the presence of H_2O in the purging gas and had a non-monotonic evolution, first increasing and then decreasing with time. Interestingly, this transient distortion was manifested by a bimodal distribution of 2νOH oscillators, because a part of the original population remained unaffected in position and width.

In all cases, the final material had residual layer distortions depending on the conditions of deintercalation. As a result of these distortions, the as-obtained deintercalated kaolinites re-intercalate much faster than the original material, with decreased or no incubation period, to approximately the same degree of intercalation. Layer recovery was observed during the re-intercalation process. 'Hole' water was detected only in samples deintercalated in the presence of H_2O and did not seem to be a prerequisite for accelerated reintercalation.

[1] Andreou F.T., Barylska B., Ciesielska Z., Szczerba M., Derkowski A., Siranidi E., Gionis V., Chryssikos G.D. (2021). Intercalation of N-methylformamide in kaolinite: In situ monitoring by near-infrared spectroscopy and X-Ray diffraction. Appl. Clay Sci. 212, 106209.
[2] Andreou F.T., Siranidi E., Derkowski A., Chryssikos G.D. (2022). On the Unusual Temperature Dependence of Kaolinite. Intercalation Capacity for N□methylformamide. Clays Clay Miner. 70, No. 5:796–807.
[3] Plastinina M.A, Fedorenko Ju.G., Shpigun A.A. (1993). De-intercalated kaolinites: The nature of created defects and estimation of structural characteristics by the expert system of Plançon and Zacharie. Clay Minerals 28, 101-108.
[4] Heller-Kallai L., Huard E., Prost R. (1991). Disorder induced by de-intercalation of DMSO from kaolinite. Clay Minerals 26, 245-253.
[5] Barrios J., Plançon A, Cruz M.I., Tchoubar C. (1977). Qualitative and quantitative study of stacking faults in a hydrazine treated kaolinite-Relationship with the infrared spectra. Clays Clay Miner. 25, 422-429.
[6] Constanzo P.M., Giese Jr. R.F., Lipsicas M. (1984). Static and dynamic structure of water in hydrated kaolinites. I. The static structure. Clays Clay Miner. 32, 419-428.