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New aspects of kaolinite intercalation by NIR spectroscopy

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It is well known that only a few molecules such as hydrazine, DMSO, NMF, etc., spontaneously intercalate the interlayer space of kaolinite by disrupting the dense H-bonding network that holds the asymmetric neighboring layers together. The present work reviews the first systematic N-methylformamide (NMF) intercalation study of three kaolinites (KGa-1b, KGa-2 and Hywite) by vibrational spectroscopic monitoring as a function of temperature. Sealed slurries of kaolinite with 5x excess NMF were measured *in situ* by FT-NIR while intercalating over long time periods (up to 1 week) and in the 5-150 °C temperature range.

Kinetics studied in the 25-80°C range were symmetric sigmoidals in the logtime scale with steepness unique for each kaolinite. Interlayers/crystallites switched from the pristine to the fully intercalated state, as in XRD. The sigmoidals were attributed to the temporal distribution of intercalation events. The amount of non-reactive kaolinite was considerably larger than previously estimated (Andreou et al., 2021).

Increasing temperature accelerated the reaction but decreased the final NMF uptake, which almost vanished at temperatures above 100°C. Complementary thermogravimetric analysis (TGA) confirmed this unexpected trend. All kaolinites exhibited the same behavior, but the amount of inert material at any temperature was in the order: KGa-2>Hywite>KGa-1b. Subjecting the samples to stepwise temperature changes showed that once intercalated, NMF could not deintercalate and was removed from the equilibrium with the surrounding fluid.

References

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: Insitu monitoring by near-infrared spectroscopy and X-Ray diffraction. Appl. Clay Sci. 212, 106209.