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EFFECT OF H2O ON THE INTERCALATION OF KAOLINITE BY AMIDE

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The kinetics of the intercalation of kaolinite by N-methylformamide (NMF) have been recently revisited by real-time near-infrared spectroscopy and X-ray diffractometry [1, 2]. These studies indicated that intercalation is a two-state, fast-switching phenomenon taking place at the level of individual interlayers or crystallites and described by lognormal sigmoidal kinetics. The intercalating capacities of commonly studied kaolinites such as KGa-1b, KGa-2 and Imerys Hywite Alum were measured to be significantly lower than previously estimated and decreasing further with increasing reaction temperature.

The present study introduces H_2O as an additional variable affecting the intercalation kinetics of the aforementioned kaolinites. The minerals were exposed to NMF:H_2O mixtures with up to 30 wt% in H_2O ($x_{H_2O}\leq 0.63$ molar) at 30, 45 and 70°C and the uptake of NMF was monitored for up to 3 days by the intensity of the 2νNH mode of the intercalated species at approx. 6700 cm^{-1}. Remarkably, at any liquid composition and temperature investigated, the position and width of this 2νNH mode was found to be independent of H_2O. This suggested that, even for the largest H_2O contents, H_2O is not entering the interlayer, NMF remains the sole intercalating species, and the interlayers/crystallites display the same binary behavior that was reported for the anhydrous end-members: They are either non-intercalated or fully intercalated, but never partially intercalated. Moderate additions of H_2O (up to 10wt%, $x_{H_2O}=0.34$) were found to shift the lognormal sigmoidal to shorter times with little effect on the shape of the sigmoidal and no effect on the final uptake. In agreement with the older literature [3, 4], this 'catalytic' effect was attributed to the de-structuring effect of H_2O on liquid NMF. Both, higher H_2O contents and increasing temperature caused a progressive decrease of uptake capacity and the broadening of the sigmoidal, presumably due to the antagonism between NMF and H_2O molecules for the edge sites of kaolinite.

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