Temperature dependence of intercalation capacity of kaolinite

Fevronia T. Andreou[1,*], Eirini Siranidi[1], Arkadiusz Derkowski[2], Georgios D. Chryssikos[1]

[1]Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vas. Constantinou Avenue 11635, Athens, Greece

[2]Institute of Geological Sciences, Polish Academy of Sciences, Research Centre in Cracow, Senacka 1, 31-002 Kraków, Poland

*fandreou@eie.gr

The self-assembly of small molecules (such as urea, formamide, DMSO) in the interlayer of kaolinite, known as intercalation, is a process of fundamental and technological importance. The properties of kaolinite determine the rate and extent of intercalation in a manner that is not fully understood, despite efforts (Fashina and Deng, 2021 and references therein). Recent studies have shown that the amount of non-reactive kaolinite in otherwise pure samples is larger than previously estimated (Andreou et al., 2021). Elevated temperatures (60-80 °C) are commonly employed to accelerate the reaction but the effect of temperature on the intercalation capacity of kaolinite is controversial and rarely addressed.

This is the first systematic investigation of the intercalation capacity of three kaolinites (CMS reference KGa-1b, KGa-2 and Hywite from Imerys) by vibrational spectroscopic monitoring as a function of temperature. Sealed slurries of kaolinite with 5x excess N-methylformamide (NMF) were measured *in situ* by FT-near infrared spectroscopy (NIR) while intercalating over long time periods (up to 1 week) and at different temperatures in the 5-100 °C range. A temperature-independent indicator of the degree of reaction was based on the amplitude of the 2nd derivative 2vNH mode of the intercalating NMF molecules normalised by the corresponding intensity of the 2v inner OH mode of kaolinite. In all kaolinites investigated, increasing temperature was found to accelerate the reaction, as expected, but also to decrease very significantly the final NMF uptake. The latter unexpected finding was confirmed by independent thermogravimetric analysis (TGA) of the final intercalation products.

Additional experiments showed that stepwise changes from higher to lower temperatures caused the stepwise increase of intercalation capacity to the levels reached by the corresponding single-temperature experiment. However, increasing the temperature of pre-intercalated systems did not cause deintercalation, indicating that once intercalated the NMF molecules were no longer in equilibrium with the surrounding fluid. The hindering of intercalation at higher temperatures is discussed in light of the interlayer energetics and the partition of NMF between the liquid and the edges of the mineral particles.

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