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INTERCALATION CAPACITY OF HALLOYSITE-(7Å) FOR NMF

Aikaterini A. Kouseri* (1), Lucas Renaudat (2, 1), Eirini Siranidi (1), Georgios D. Chryssikos (1), Stephen Hillier (3, 4)

(1) Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vas. Constantinou Avenue 11635, Athens, Greece, (2) Institute Agro Dijon, 26 Bd Dr Petitjean, 21079 Dijon, France, (3) The James Hutton Institute, Craigiebuckler, Aberdeen, AB15 8QH, UK, (4) Department of Soil and Environment, SLU, SE-75007 Uppsala, Sweden

Halloysite can be detected in the presence of kaolinite by its fast intercalation causing interlayer expansion [1]. Quantification would require prior knowledge of the intercalation capacity of the individual minerals present. Several kaolinites are only partially accessible to e.g. N-methylformamide (NMF) [2]. To the best of our knowledge, the corresponding behavior of halloysite is poorly investigated.

A systematic experimental investigation of the NMF intercalation capacity of halloysite-(7Å) was conducted by high resolution thermogravimetric analysis (HiRes-TGA), mid-infrared, XRD and in situ Near-infrared (NIR) spectroscopy monitoring.

Cylindrical and polygonal halloysites from the Dragon mine (Utah, USA) [3] exhibited different intecalation capacities for NMF: at infinite time of exposure, intercalation was quantitative in the former (2NMF molecules per $Si_2Al_2O_5(OH)_4$) but only about 65% in the latter. In all cases, intercalation was accompanied by the ordering of halloysite layers, as seen by the narrowing of the inner 2νOH band.

A sample of mixed cylindrical-polygonal form from the same locality (85% intercalation capacity) was subjected to step-wise heating from 50°C to 300°C. The unheated sample contained the so-called 'hole' H_2O, $xH_2O \cdot Si_2Al_2O_5(OH)_4$ with infrared bands at 3550 and 1650 cm^{-1}. Heat treatment induced the progressive decrease of x from 0.37 (50°C) to 0.06 (300°C).

Slurries of the heat-treated halloysite with NMF (1:1 wt) were left to intercalate at 30°C with synchronous NIR monitoring. The intercalation kinetics of the original sample were fast and exponential, but turned to a delayed sigmoidal known also from kaolinite after heat treatment above 250°C. The final uptake was gradually decreased from ~85% to less than 40% (300°C).

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