European Mineralogical Conference
Vol. 1, EMC2012-669, 2012
European Mineralogical Conference 2012

Evolution of Host/Guest Interactions with Heating in a Palygorskite/Methyl Red (Maya Red) Nano-Composite Material

R. Giustetto (1), J.G. Vitillo (2), I. Corazzari (3), and F. Turci (3)

(1) Department of Earth Sciences and NIS Centre of Excellence, University of Turin, via Valperga Caluso 35, 10125 Torino (Italy) (roberto.giustetto@unito.it), (2) Department of Chemistry and NIS Centre of Excellence, INSTM Research Unit, University of Turin, via Giuria 7, Torino 10125 (Italy), (3) Department of Chemistry, "G. Scansetti" Interdepartmental Centre for Studies on Asbestos and other Toxic particulates, and NIS Centre of Excellence, University of Turin, via Pietro Giuria 7, 10125 Torino (Italy)

An exceptionally stable hybrid material, fit for possible use as an innovative, cheap and ecologic nano-composite pigment in the Cultural Heritage and Materials Science fields, can be obtained by grinding and heating palygorskite clay with the methyl red dye (2 wt%). Due to its multiple analogies with the famed Maya Blue pigment (an ancestor of modern hybrid materials formed by indigo incorporation in palygorskite/sepiolite clay minerals), such a red/purple adduct can be considered an analogous Maya Red composite.
As per its renowned blue predecessor, the chemical and photo-thermal stability observed for this red equivalent is guaranteed by peculiar nano-structural features which imply methyl red diffusion and bonding within the palygorskite tunnels, triggered by heating or evacuation of a properly ground clay/dye mixture. Specific interactions form inside the host nano-pores between the clay framework and dye reactive groups, contributing to this composite stabilization at different temperatures.
An innovative analytical approach, consisting of in-line coupled TGA-FTIR-GC-MS, synchrotron XRPD and molecular mechanics, was performed on both pristine palygorskite and the related composite with methyl red with the aim to monitor the development of the interactions formed at the nano-scale between the host and the guest while progressively heating. Such a study evidenced that several kinds of bonds exist, each characterized by specific binding energies and subjected to a dynamic but reversible evolution as a function of the magnitude of the heating treatment. Weak to moderate temperatures (120-300°C) trigger zeolitic H_2O loss and methyl red diffusion but do not imply release of Mg-coordinated OH2, which acts as H-bond donor to the dye carboxyl group. More severe heating (300-490°C) causes a two-step structural OH2 loss and triggers a ligand-displacement mechanism which favors straight interactions between octahedral Mg and the dye COOH acceptor atoms (i.e. oxygen).
Reversibility and shift between different host/guest interactions severely affect the dehydration/rehydration process of the host framework, compared to the pristine clay. Several interrelated phenomena mutually interact in a sort of positive feedback: guest incorporation inside the tunnels prevents structural folding typical of pure palygorskite and modifies the release of both zeolitic H_2O and structural OH2, consequently influencing both the nature and the strength of the established host/guest interactions. Such a situation is further complicated by the different palygorskite polymorphs (monoclinic and orthorhombic) showing peculiar and distinct behaviors, which concern both their affinity to form specific bonds with the encapsulated dye and the release of structural OH2 while heating.
Sheltering granted by incorporation in the host nano-tunnels dramatically enhances methyl red thermal stability, whose degradation occurs at temperatures sensibly higher than those causing decay of the isolated dye.