

BEHAVIOUR OF DIFFERENT CATIONIC FORMS OF MONTMORILLONITE UPON HEATING: AN FTIR STUDY

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The changes upon heating up to 300 °C in the structure of Jelšovský Potok (JP) montmorillonite (Slovakia) saturated with Li^+ , Cu^{2+} or Cd^{2+} cations have been investigated. The cation exchange capacities (CEC) of the samples heated to 300°C for 24 hours (Li-JP300, Cu-JP300 and Cd-JP300) decreased to 12, 36 and 74%, respectively, of the values determined for unheated samples (Li-JP, Cu-JP and Cd-JP).

The infrared spectra of Li-JP, Cu-JP and Cd-JP show similar positions of the bands in the middle-IR (MIR, 4000–400 cm^{-1}) and near-IR (NIR, 9000–4000 cm^{-1}) regions. The bands related to the OH stretching vibration ($\nu_{\text{OH}} \approx 3628 \text{ cm}^{-1}$) and OH overtone ($2\nu_{\text{OH}} \approx 7070 \text{ cm}^{-1}$) have been selected as diagnostic for indication of a layer charge decrease and/or for creation of the trioctahedral domains. No significant changes are seen in the MIR spectra of Cd-saturated samples heated below 200°C. Cd-JP requires heating at 250 or 300°C to invoke structural changes. The OH overtone of Cd-JP200 shows no modification in comparison with Cd-JP, however, a shift by 20 cm^{-1} for Cd-JP300 is in accord with the CEC value indicating layer charge decrease.

MIR spectra of Li-JP heated up to 300°C indicate a marked structural alteration of the samples. A gradual displacement of the ν_{OH} band to the higher positions and the appearance of a new component near 3670 cm^{-1} (ν_{AlMgLiOH}) reflect layer charge decrease and fixation of Li^+ in the previously vacant octahedral positions. Similar upward shift and splitting of the $2\nu_{\text{OH}}$ overtone into two components at 7170 cm^{-1} and 7100 cm^{-1} is observed in the NIR region. A strong band at 7170 cm^{-1} confirms formation of trioctahedral domains in Li-JP samples heated above 150°C.

The OH stretching region of Cu-JP reveals a shift of the ν_{OH} to 3634 cm^{-1} for Cu-JP200. No further changes occur in spectra of Cu-JP upon heating up to 300°C. The NIR spectrum of Cu-JP300 shows $2\nu_{\text{OH}}$ overtone at 7095 cm^{-1} . Unexpectedly, a new component near 7043 cm^{-1} has appeared in the spectra of the samples heated above 150°C. Presence of Cu(II) in the octahedral sheet is one possible explanation. If Cu^{2+} enters the previously vacant octahedral sites then the most probable grouping would be AlMgCuOH . Based on the IR data published for other clay minerals, the estimated position of $2\nu_{\text{AlMgCuOH}}$ overtone should be near 7110 cm^{-1} . This position, however, is over 60 cm^{-1} higher as the band

observed at 7043 cm^{-1} . It follows that the assignment of the 7043 cm^{-1} band to $2\nu_{\text{AlMgCuOH}}$ is doubtful. Moreover, the EPR spectroscopy revealed that Cu(II) in Cu-JP300 can be partially coordinated by oxygen atoms from the mineral layers and by nitrogen atoms from pyridine molecules, if present in the interlayers (Karakassides et al., 1999). Both IR and EPR spectra suggest that Cu^{2+} cations are fixed deep in the hexagonal cavities close to OH groups. The H^+ –Cu(II) interaction can influence both the length and orientation of OH dipole and thus also the vibrational frequency of the OH group. However, the possibility to attribute the 7043 cm^{-1} band to the existence of isolated clusters formed by Cu^{2+} and water molecules in the interlayers of smectites upon heating cannot be excluded.

Different location of Li(I) and Cu(II) in heated JP montmorillonite has activated the question whether small Li^+ ions can migrate into the vacant octahedral sites after Cu(II) has been trapped in the hexagonal cavities. Therefore, the exchangeable Cu^{2+} ions from Cu-JP200 were exchanged by Li^+ and the obtained sample was heated at 300°C to evoke fixation of Li^+ (Li(Cu)-JP300). No band indicating a presence of Li(I) in the octahedra is visible in the MIR spectrum. However, the NIR spectrum clearly shows three bands in the OH overtone region. In addition to the bands at 7102 and 7048 cm^{-1} , found also in the Cu-JP300 spectrum, a band at 7166 cm^{-1} , present at similar position in Li-JP300, has been identified. This band unambiguously confirms fixation of Li^+ in the octahedral positions of the Li(Cu)-JP300.

Analysis of the IR spectra reveals that both the size and the charge of interlayer cations affect their final position after fixation upon heating. The Li^+ ions migrate into the octahedral vacancies, thus creating local trioctahedral domains. Although ionic radius of Cu^{2+} is comparable to that of Li^+ , Cu(II) is retained in hexagonal cavities of heated Cu-JP. Cd^{2+} ions are too large to enter deep enough into the hexagonal cavities to be fixed close to the OH groups. Some fixation of Cd^{2+} may occur only in the sample heated above 250 °C.

Reference

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