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Characterization of Cu-complexes in smectite with different layer charge location: Chemical, thermal and EXAFS studies

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Abstract—The retention of Cu and Cu-amino acid complexes by montmorillonite and beidellite, before and after repeated acidified aqueous solution treatments, was studied using X-ray diffraction, chemical and thermal analyses, mass spectrometry and synchrotron-based X-ray absorption spectroscopy (XAS).

The results indicate that the extraction of metal complexes from smectites depends on the nature of the layer charge and on the kind of organic species. Cu-cysteine complexes are strongly retained in the interlayer position, whereas Cu-glycine complexes are mostly adsorbed in cationic form which can be easily removed from the silicate layer. The layer periodicity for Cu-smectites treated with glycine shows little or no layer expansion, whereas significant swelling of the layer periodicity is observed in smectites treated with cysteine.

Thermal decomposition of both smectites with sorbed Cu-amino acid species shows the evolution of H_2O , NO, CH_3CH_3 , and CO_2 . In Cu-cysteine treated smectites, the release of H_2S , NO_2 , SO_2 , and N_2O_3 also occurs.

X-ray absorption spectroscopy (XAS) was used to assess the relationships between the structure of the Cu complexes and their desorption from smectites. In Cu-exchanged smectites, the first coordination shell agrees with the hypothesis that the Cu coordinates to oxygen atoms to form monomer and/or dimer complexes. The first coordination shell of Cu in smectites treated with glycine shows four atoms at distances of -2 Å. Two of these bonds are with nitrogen and two with oxygen atoms. For copper-cysteine complexes XAS data are compatible with the existence of Cu-N clusters, thus suggesting that Cu links to the amino acid by the aminic group. Copyright © 2004 Elsevier Ltd