FTIR Reflectance vs. EPR Studies of Structural Iron in Kaolinites

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Abstract: The substitution of Fe³⁺ in the kaolinite structure is studied by EPR spectrometry and by FTIR spectrometry on a large set of kaolins from different origins (sedimentary and primary ores, soil kaolins). The IR bands at 3598 and 875 cm⁻¹, observed in the literature only in the case of disordered kaolins or in Fe-rich environments (synthetic, lateritic), are revealed by high-resolution IR analysis, whatever the origin and the total Fe content of the samples. The EPR bands corresponding to Fe³⁺ substituted in sites II of the octahedral sheet increase when the IR absorbance near 3600 cm⁻¹ increases. Two IR absorption bands near 4465 cm⁻¹ and 7025 cm⁻¹ are observed for the first time, both in transmission and diffuse reflectance on all samples. These bands are assigned to the combination of the 3598 and 875 cm⁻¹ bands and to the first harmonic of the band at 3598 cm⁻¹, respectively. The area of the band at 4465 cm⁻¹ in diffuse reflectance is quantitatively correlated to the abundance of Fe³⁺ located in centers II as measured by ESR. This directly confirms the assignment of the two IR bands at 3598 and 875 cm⁻¹ to OH stretching and deformation vibration bands in octahedral FE³⁺ environment in the kaolinite structure, respectively. Effects due to the size of particles and to the main kaolins impurities on the near infrared spectra, are also discussed.

Key Words: EPR • Fe • Kaolinite • Mid and near infrared • Substitution

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