
Hydrothermal Synthesis (250° C) of Copper-Substituted Kaolinites

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Abstract: To obtain Cu-kaolinites with a controlled range of chemical compositions, syntheses were performed by hydrothermally ageing gels with kaolinite stoichiometric compositions. Gels were prepared with sodium metasilicate and nitrates of octahedral cations. Temperature of synthesis was 250° C with a corresponding equilibrium water pressure of 38 bars.

Three samples with copper contents ranging from 0.1 to 7% and another one with the chemical composition of the Cu end-member were synthesized. While this fourth sample led to tenorite after the hydrothermal treatment, the three others crystallized well into kaolinite.

Up to almost 1% CuO was measured by TEM in some isolated ' clean' and hexagonal kaolinite particles. EPR and XPS spectroscopies were consistent with an octahedral position of Cu²⁺. In IR spectra, ν Al-OH-Cu absorption bands were not observed, but ν Al₂OH bands appeared more and more blurred when Cu content of samples increased. Weak bands situated at 868 cm⁻¹ and 840 cm⁻¹ are tentatively attributed to δ AlCuOH. By differential thermal analysis, a downward shift of 20° C in temperature of the endothermic peak from the less Cu-rich sample to the most Cu-rich one, argued for the existence of some Al-OH-Cu bonds, whose binding energies are presumed to be less than the Al-OH-Al ones.

In view of these results, Cu²⁺ appears incorporated in the octahedral sheet of kaolinite. Moreover, this incorporation is made without major perturbation of the kaolinite structure.

Key Words: Cu²⁺ • Kaolinite • Octahedral substitution • Synthesis

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