
Hydroxyl Deformation in Kaolins

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Abstract: The hydroxyl deformation modes of kaolins have been studied by Fourier transform (FT) Raman spectroscopy. Kaolinites showed well-resolved bands at 959, 938 and 915 cm^{-1} and an additional band at 923 cm^{-1} . For dickites, well-resolved bands were observed at 955, 936.5, 915 and 903 cm^{-1} . Halloysites showed less-resolved Raman bands at 950, 938, 923, 913 and 895 cm^{-1} . The first 3 bands were assigned to the librational modes of the 3 inner-surface hydroxyl groups, and the 915- cm^{-1} band was assigned to the libration of the inner hydroxyl group. The band in the 905 to 895 cm^{-1} range was attributed to " free" or non-hydrogen-bonded inner-surface hydroxyl groups. The 915- cm^{-1} band contributed $\sim 65\%$ of the total spectral profile and was a sharp band with a bandwidth of 11.8 cm^{-1} for dickite, 14.0 cm^{-1} for kaolinites and 17.6 cm^{-1} for halloysites. Such small bandwidths suggest that the rotation of the inner hydroxyl group is severely restricted. For the inner-surface hydroxyl groups, it is proposed that the hydroxyl deformation modes are not coupled and that the 3 inner-surface deformation modes are attributable to the three OH₂-4 hydroxyls of the kaolinite structure. For intercalates of kaolinite and halloysite with urea, a new intense band at $\sim 903 \text{ cm}^{-1}$ was observed with concomitant loss in intensity of the bands at 959, 938 and 923 cm^{-1} bands. This band was assigned to the non-hydrogen-bonded hydroxyl libration of the kaolinite-urea intercalate. Infrared reflectance (IR) spectroscopy confirms these band assignments.

Key Words: Deformation Mode • Dickite • FT Raman • Halloysite • Hydroxyl • Infrared • Intercalation • Kaolinite • Libration • Reflectance

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