The effect of pressure on the intercalation of an ordered kaolinite

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ABSTRACT

Intercalation of an ordered kaolinite with potassium acetate (KCH₃COO) under a pressure of 20 bars and 220 °C, induced new Raman bands at 3590, 3603, and 3609 cm⁻¹ in addition to the normal kaolinite bands. These bands are attributed to the inner surface hydroxyls hydrogen bonded to the acetate. It is proposed that the intercalation under 20 bars pressure at 220 °C caused the differentiation of the inner surface hydroxyl groups, resulting in the appearance of these additional bands. Diffuse reflectance infrared spectra of the potassium acetate intercalated kaolinite that was formed at 20 bars and at 220 °C showed new bands at 3595 and 3605 cm⁻¹. Upon formation of the intercalate at 2 bars and at 120 °C additional infrared (IR) bands were found at 3592, 3600, and 3606 cm⁻¹. These IR bands correspond well with the observed Raman spectra. It is proposed that the effect of intercalation of the highly ordered kaolinite under pressure caused the kaolinite to become disordered and this disordering was dependent on the temperature of intercalation. It is suggested that when pressure is applied to the kaolinite crystal in the presence of an intercalating agent, the hydrogen bonds between adjacent layers are broken to create space for the intercalating agent between the layers. A direct result is that the order of the kaolinite crystals shows a decrease resulting in more defect structures. This is evidenced by the additional spectroscopic bands in both the Raman and IR spectra.

INTRODUCTION

Structural disorder or degree of crystallinity is produced by either geological conditions of formation, transport, or deposition or by mechanical treatment, such as grinding (Brindley et al. 1986). Structural disorders in layer silicates, particularly in clay minerals are of many kinds including: thermal disorder, disorder in the distribution of cations, long-range and short-range order, disorder in layer stacking, order-disorder in mixed-layer systems, finite crystal size as a lattice disorder, structures with non-planar layers, and mechanically disordered structures (Brindley 1984). The most widely accepted and used method for the comparison of different kaolinites with regards to order and disorder is the Hinckley index (Hinckley 1963). Disorder due to layer stacking is common in clay mineral structures. For any particular type of layer structure and interlayer bonding mechanism, a great variety of theoretical polytype structures can be developed, for example, one- and two-layer kaolinite-type structures (Newnham 1961; Dornberger-Schiff and Durovic 1975). Clay minerals characteristically exhibit considerable variations in layer stacking order-disorder. Disorders arise commonly from the presence of variable amounts of intercalated material between the layers, such as variable hydration from layer to layer and from the presence of layers of other kinds irregularly distributed as in the many forms of interstratified structures.

Raman microscopy has proven most useful for the study of the kaolin structures (Frost and van der Gaast 1997) and for the determination of order-disorder relationships. In their work, kaolinites were classified according to the ratio of the intensities of the two types of inner surface hydroxyls at 3685 and 3695 cm⁻¹. The intensity of the 3650 and 3670 cm⁻¹ bands were found to vary concomitantly with the 3685 and 3695 cm⁻¹ bands. A relationship between the degree of defect structures and the intensity of the 3685 cm⁻¹ band was found. In their work, correlation between the Raman spectrum of the hydroxyl stretching vibrations and the degree of disorder using the Hinckley Index was attempted and a linear relationship between this index and the ratio of the 3685 and 3695 cm⁻¹ bands was found. Thus Raman spectroscopy provided a method for studying the defect structures of kaolinites. The application of Raman microscopy to the study of intercalated kaolinites also has proved most useful (Frost et al. 1997a; Frost and Kristof 1997; Frost et al. 1997b). An additional Raman band, attributed to the inner surface hydroxyl groups hydrogen bonded to the acetate, was observed at 3605 cm⁻¹ for the potassium acetate intercalate with the concomitant loss of intensity in the bands at 3652, 3670, 3684, and 3693 cm⁻¹. In this paper, we report the changes in the defect structures of a...