Infrared and Raman study of interlayer anions CO$_3^{2-}$, NO$_3^-$, SO$_4^{2-}$ and ClO$_4^-$ in Mg/Al-hydrotalcite

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**ABSTRACT**

The difference in the local environment of CO$_3^{2-}$, NO$_3^-$, SO$_4^{2-}$, and ClO$_4^-$ in Mg/Al-hydrotalcite compared to the free anions was studied by infrared and Raman spectroscopy. In comparison to free CO$_3^{2-}$ a shift toward lower wavenumbers was observed. A band around 3000–3200 cm$^{-1}$ has been attributed to the bridging mode H$_2$O-CO$_3^{2-}$. The IR spectrum of CO$_3^{2-}$ hydrotalcite clearly shows the split $v_1$ band around 1365 and 1400 cm$^{-1}$ together with weak $v_2$ and $v_4$ modes around 870 and 667 cm$^{-1}$. The $v_1$ mode is activated and observed as a weak band around 1012 cm$^{-1}$. The Raman spectrum shows a strong $v_1$ band at 1053 cm$^{-1}$ plus weak $v_3$ and $v_4$ modes around 1403 and 695 cm$^{-1}$. The symmetry of the carbonate anions is lowered from $D_{4h}$ to $C_2v$, resulting in activation of the IR inactive $v_1$ mode around 1050–1060 cm$^{-1}$. In addition, the $v_1$ shows a splitting of 30–60 cm$^{-1}$. Although NO$_3^-$-hydrotalcite has incorporated some CO$_3^{2-}$ the IR shows a strong $v_1$ mode at 1360 cm$^{-1}$ with a weak band at 827 cm$^{-1}$, and the $v_4$ band is observed at 667 cm$^{-1}$, although it is largely obscured by the hydrotalcite lattice modes. The Raman spectrum shows a strong $v_1$ mode at 1044 cm$^{-1}$ with a weaker $v_4$ band at 712 cm$^{-1}$. The $v_1$ mode at 1355 cm$^{-1}$ is obscured by a broad band due to the presence of CO$_3^{2-}$. The symmetry of CO$_3^{2-}$ did not change when incorporated in hydrotalcite. The IR spectrum of SO$_4$-hydrotalcite shows a strong $v_1$ at 1126, $v_4$ at 614 and a weak $v_1$ mode at 981 cm$^{-1}$. The Raman spectrum is characterized by a strong $v_1$ mode at 982 cm$^{-1}$ plus medium $v_2$ and $v_4$ bands at 453 and 611 cm$^{-1}$; $v_3$ cannot be identified as a separate band, although a broad band can be seen around 1134 cm$^{-1}$. The site symmetry of SO$_4^{2-}$ is lowered from $T_d$ to $C_2v$. The distortion of ClO$_4^-$ in the interlayer of hydrotalcite is reflected in the IR spectrum with both $v_1$ and $v_4$ bands split around 1096 and 1145 cm$^{-1}$ and 626 and 635 cm$^{-1}$, respectively. A weak $v_1$ band is observed at 935 cm$^{-1}$. The Raman spectrum shows a strong $v_1$ mode at 936 cm$^{-1}$ plus $v_2$ and $v_4$ bands at 461 and 626 cm$^{-1}$, respectively. A $v_1$ mode cannot be clearly recognized, but a broad band is visible around 1110 cm$^{-1}$. These data indicate a lowering of symmetry from $T_d$ to $C_2v$.

**INTRODUCTION**

Hydrotalcites or layered double hydroxides (LDHs) are also described as anionic clays, due to their layered structure with a charge opposite to that of cationic clays (like smectites) consisting of negatively charged aluminosilicate layers with cations in the interlayer space to balance the negative charge. The structure of hydrotalcite can be visualized as positively charged octahedral sheets during formation; otherwise a hydrotalcite cannot be formed (Vaccari 1998). Therefore, the variety possible in both the cationic and anionic compositions of hydrotalcite offers the possibility to prepare tailor-made materials for specific applications, such as basic catalysts, as a precursor for the preparation of mixed metal oxidic catalysts, absorbents, and for other specific powder properties such as filler, UV-radiation stabilizer, chloride scavenger and, thermal stabilizer (Titulaer 1993).

The number of counterbalancing anions or anionic complexes in hydrotalcites is essentially unlimited provided that the anion does not form a complex with the cations in the octahedral sheets during formation; otherwise a hydrotalcite cannot be formed (Vaccari 1998). Therefore, the variety possible in both the cationic and anionic compositions of hydrotalcite offers the possibility to prepare tailor-made materials for specific applications, such as basic catalysts, as a precursor for the preparation of mixed metal oxidic catalysts, absorbents, and for other specific powder properties such as filler, UV-radiation stabilizer, chloride scavenger and, thermal stabilizer (Titulaer 1993).