In situ Simultaneous Raman/<High-Resolution X-ray Powder Diffraction> Study of Transformations Occurring in Materials at Non-Ambient Conditions

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Materials containing light atoms, disordered moieties and/or amorphous or liquid-like phases or showing surface- or defect-related phenomena constitute a problem for their characterization using X-ray powder diffraction (XRPD), and in many cases Raman spectroscopy can provide useful complementary information. The novel experimental set-up for simultaneous *in situ* Raman/<High-resolution XRPD> experiments developed at SNBL was employed to study four solid-state transformations: *i)* the kinetics of the fluorene:TCNQ solid-state synthesis, *ii)* the photoinduced 2+2 cyclization of (E)-furylidenoxindole; *iii)* the thermal swelling and degradation of stearate-hydrotalcite nanocomposites; iv) the decarboxilation process of layered zirconium aminophosphonates. The reported experiments demonstrated that, even though the simultaneous Raman/XRPD experiment is more challenging than the separated ones, high resolution XRPD and Raman data can be collected at in situ conditions. The complementarities between Raman and XRPD was fully exploited by an accurate choice of the Green or Red Laser for the Raman experiment.

In the first two experiments the surface-bulk complementarities of the Raman and XRPD probes were exploited. Raman allowed to detect the reaction speed at the surface in the first step of the reactions, when no reaction is detected by XRPD. The mechanism of the reaction for the formation of the Fluorene/TCNQ complex was fully characterized and a kinetic analyses carried out, with the determination of the activation energy and the reaction order for the reaction at the surface and in the bulk. Concerning the photoinduced 2+2 cyclization of (E)-furylidenoxindole, the complex polymorph space of the product phase (one stable and two metastable crystalline phase and one amorphous phase) was fully understood and the structure of one metastable phase was also solved.

In the last two experiments the sensitivity of Raman to the structure and conformation of organic moieties (not easily detectable by XRPD alone, especially when disorder is present) was exploited. Concerning stearate-hydrotalcite experiment, a detailed description of the structural changes occurring at 365 K to both organic and inorganic moieties in the ST-HT sample was obtained. The XRPD data gave clear information on the swelling of the inorganic lamellar component of the hybrid nanocomposite. Raman spectra indicated that, up to 365 K, the all-*trans* conformation is prevalent for the organic chains, whereas above this temperature the occurrence of folded chains due to *gauche* conformations became significant. Finally the decarboxilation of layered zirconium aminophosphonates was studied. When heated this compound shows a phase transformation with a remarkable reduction of its interlayer distance (detected by XRPD), due to the loss of HF and to a change in the zirconium environment (detected by the Raman probe).