

A Near edges structures calculations approach for the interpretation of EELS spectra of ill organized materials: application to the study of structural evolution of natural carbonaceous materials during pyrolysis.

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Activated charcoal is mainly obtained by activation of coke or charcoal produced from ligneous precursors. The present study is concerned with the use of by products of agriculture (sugar cane bagasse, stones, seeds shells of fruits...) as activated carbon precursors

Carbonaceous compounds obtained by pyrolysis of such organic materials often present ill organized structure^[1,2] which middle / long range order depends on the pyrolysis temperature.

As it is well known, EEL Spectroscopy can be advantageously used for chemical characterization^[3,4] of such materials. Carbon K edges reveals specific Near Edges Structures (NES) corresponding to mono-electronic dipole allowed transition from inner 1s shell into anti-bonding levels of π^* and σ^* types. The interpretation of the CK NES allows us to follow the chemical evolution of the material as a function of the treatment temperature and more specifically permits the quantitative evaluation of π bonding concentration.

Samples studied are charcoal obtained by pyrolysis, in the range 550 to 900°C, of natural lingo cellulosic materials (fruit stones, seeds...). The samples are crushed and the finest particles are deposited onto a holey carbon support. EELS experiments were carried out on a H 8000 Hitachi microscope, running a 200 kV, fitted with a Gatan Imaging Filter.

The intensities of the 1s $\rightarrow \pi^*$ and 1s $\rightarrow \sigma^*$ features are appropriately measured and reported as a function of pyrolysis temperature.

Such a quantification on the studied materials shows that an optimum of the π bonding concentration is obtained for a temperature of 700°C. At higher temperature the characteristic 1s $\rightarrow \pi^*$ transition does not exhibit significant changes but a weak feature undergoes a clear enhancement which seems related to the organization state of matter.

In order to correlate this feature to local and long range order, band structure calculations have been carried out using a multiple scattering approach (FEFF)^[5] appropriate for ill organized materials.

The more organized material obtained by high temperature pyrolysis is polycrystalline graphite. Pyrolysis of nano / micro-crystalline domains assembly at intermediary temperature leads to less organized materials. Calculations are done on "pseudo graphite" carbon clusters. Densities of empty states diagrams are drawn as a function of clusters sizes from nanoscale up to the bulk and corresponding CK edges are simulated. The numerical results clearly show an increase of the feature attributed to a 1s $\rightarrow \sigma^*$ dipole allowed transition as a function of the increasing cluster size. It strongly supports the correlation between this feature intensity and the ordering of the material.

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