Inelastic neutron scattering spectroscopy applied to supported metal nanoparticles in catalysis

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Inelastic Neutron Scattering (INS) spectroscopy is a powerful technique for measuring the vibrational spectra of materials and molecules. It is characterized by the absence of selection rules and by a strong sensitivity toward the vibrational modes involving hydrogen atoms, providing information not accessible to the most commonly employed FT-IR and Raman spectroscopies. In the frame of this talk, we will provide examples of its potentials in chemical research, by showing two examples related to the study of supported Pt and Pd industrial catalysts for hydrogenation reactions.

Applied to the characterization of Pt and Pd catalysts on different activated carbons [1], INS spectroscopy provides details about the interaction between the metal nanoparticles and the support. Figure 1A shows the INS spectra of three Pd and Pt-based catalysts and of the corresponding bare carbon support measured on the LAGRANGE spectrometer at the ILL. The deposition of the metal nanoparticles results in a decrease of the spectral intensity, which indicates a reduction in the number of the C-H terminations of the support. The central band is the most affected, meaning that not all the terminations are perturbed by the nanoparticles at the same extent. The experimental spectra were compared with the results of DFT simulations on a very large number of aromatic models, that provided the INS fingerprints of regular and defective C-H terminations in activated carbons. By fitting the experimental spectra with a linear combination of the simulated ones (Figure 1B) we found that the species most affected by the metal nanoparticles deposition are benzene rings exposing a single C-H group, indicating that the metal nanoparticles preferentially interact with these sites. Moreover, we also found that a large concentration of these terminations in the support favors higher metal dispersion values (i.e. the formation of smaller nanoparticles).

INS spectroscopy has enormous potentials also in the investigation of Pd- and Pt-hydrides, which are important players in the hydrogenation catalytic processes. As an example, Figure 1C shows the INS spectrum of a Pt/γ-Al$_2$O$_3$ catalyst in the presence of hydrogen, after subtraction of the spectrum collected prior exposure to H$_2$. The experimental spectrum, collected on the LAGRANGE spectrometer at the ILL [2], is compared to the result of DFT simulation performed on the γ-Al$_2$O$_3$-supported Pt$_{13}$H$_{32}$ model shown in the inset [3]. The comparison allows assigning the experimental spectral features to the vibrational modes of multi-folded Pt-H species and to the bending modes of top ones. These data are in very good agreement with the hypothesis of a reconstruction of the Pt-H nanoparticles to high symmetry cuboctahedric structures in which H inserts between the nanoparticle and the support [3].

The selected examples demonstrate that the combination of INS spectroscopy and DFT simulations is a powerful strategy to obtain new insights on the interaction between nanoparticles and supports, as well as about the reconstruction underwent by the nanoparticles under reaction conditions.
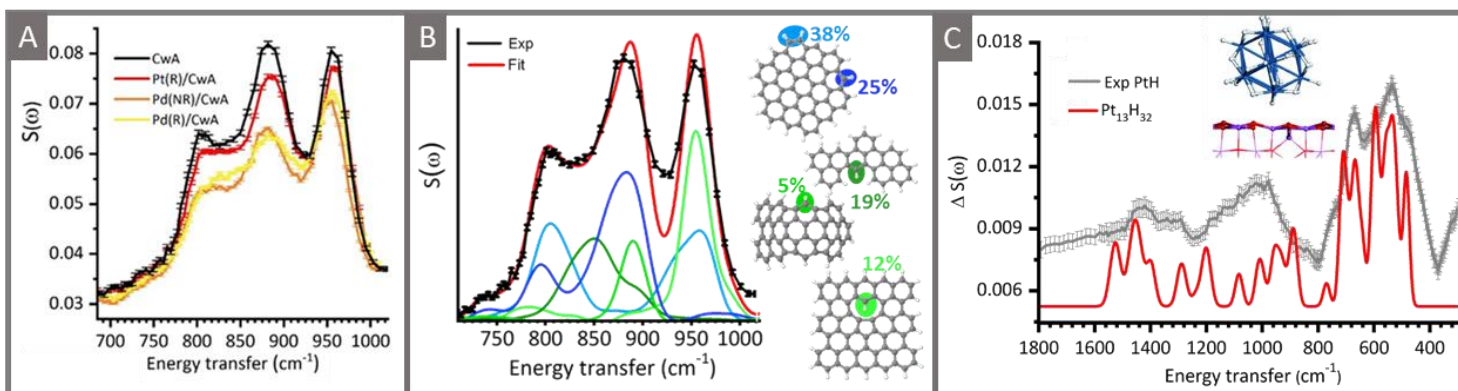

Figure 1A) Experimental spectrum of a steam-activated carbon CwA (black) and of three catalysts obtained after deposition of Pd or Pt nanoparticles on it (red, orange and yellow). B) Results of the linear combination fit for CwA. Regular, disordered and defective terminations are needed to describe the spectrum. C) Comparison between the experimental difference spectrum containing the fingerprint of the Pt-H species and the simulated spectrum for the supported Pt$_{13}$H$_{32}$/γ-Al$_2$O$_3$ nanoparticle.

[1] E. Vottero *et al*, Carbon 2020, 169, 357-369. [2] M. Carosso *et al*, *ACS Catal.* **2019**, *9*, 7124-7136. [3] C. Mager-Maury *et al*, *ChemCatChem* **2011**, *3*, 200-207