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Understanding the behaviour of a CoB catalyst for sodium borohydride hydrolysis: An electron microscopy study

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Sodium borohydride ($NaBH_4$, SBH) is a stable, non-flammable and non toxic hydride that permits a safe and versatile generation of hydrogen. SBH solutions at high pH (fuel) are stable and only produce hydrogen when in contact with suitable catalysts (on demand H_2 generation). The release of hydrogen can be carried out in a controlled way in ambient conditions, which makes it suitable to feed a PEMFC (Polymer Exchange Membrane Fuel Cell) for small scale and portable applications [1]:

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2$$

Among metal based catalysts, the Co-B materials are the most investigated owing to its reactivity and low cost. In this work the Co-B based catalyst was prepared by chemical methods (reduction of cobalt salts by SBH) in powder form and also supported on pre-treated stainless steel homemade monoliths. The monoliths were prepared for its use in a continuous working reactor designed and built to allow a constant and adaptable generation of hydrogen (in the range of 0.3-1.7 L/min) over a long period of time.

The exact microstructure of these catalysts was not well known and was usually considered as an amorphous material. Herein we present an exhaustive study which shows a new and complete microstructural view of a Co·B-based material together with the chemistry of the cobalt and boron involved. By using nanoscale-resolution microscopy and spectroscopy techniques (i.e. scanning TEM (STEM), high angle annular dark field detector (HAADF) and electron energy loss spectroscopy (EELS)), we have elucidated the role of boron compounds as stabilizers in a complex microstructure, which also explains its high catalytic performance and long-term stability. The catalyst is proposed to be made up of 1–3 nm hcp Co nanoparticles embedded in amorphous Co_xB (x=1, 2, 3), Co_xO_y, $Co(BO_2)_2$, and B_2O_3 phases alternatively or all together [2]. Figure 1 shows some selected results as the HAADF image in STEM mode, accompanied of the localized EELS spectra as obtained from the spectrum imaging data.

Special interest was also laid on deactivation, reactivation and durability of the supported catalyst working under high conversion conditions in our continuous reactor [3]. A deactivation of the catalyst was observed after long time of use, depending largely of the mode of experiment (start/stop cycles, continuous run). The deactivation and the intents of reactivation of the Co-B catalysts were studied and will be discussed in terms of borate formation and elimination (see Figure2). For this study the use of a SEM-FEG microscope with EDX mapping facilities will be presented showing the capabilities for working with pieces of monoliths coming directly from the reactor.

We can conclude that catalysts for practical applications and reactors in hydrogen generation reactions are systems with a complex microstructure were electron microscopy, together with other techniques, are very efficient tools to determine their behaviour and to draw-up the best operation conditions. Nevertheless the borohydride in this system acts both, as a fuel for the hydrogen generation, and as a reduction agent that can modify the catalysts "in operando" conditions what is also giving an example of how the microstructural analysis should be always considered in the context of the operation behaviour.

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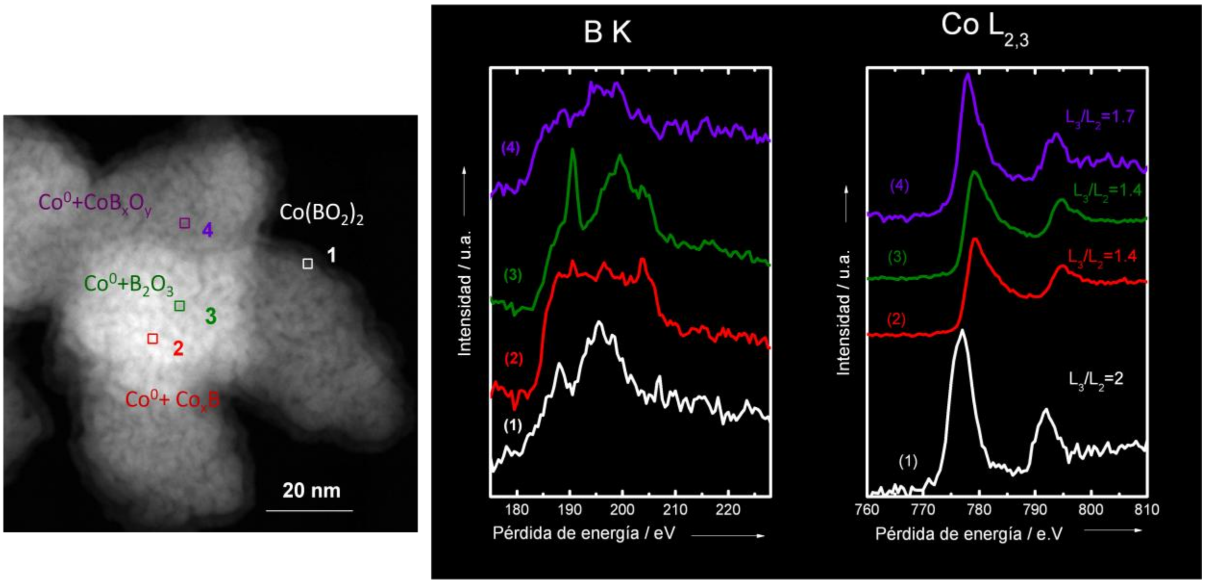

Figure 1.STEM/SI study on the prepared Co·B catalyst. Left) HAADF image, centre) EELS B K-edge spectra, and right) EELS Co $L_{2,3}$ spectra for the zones as defined in the left figure

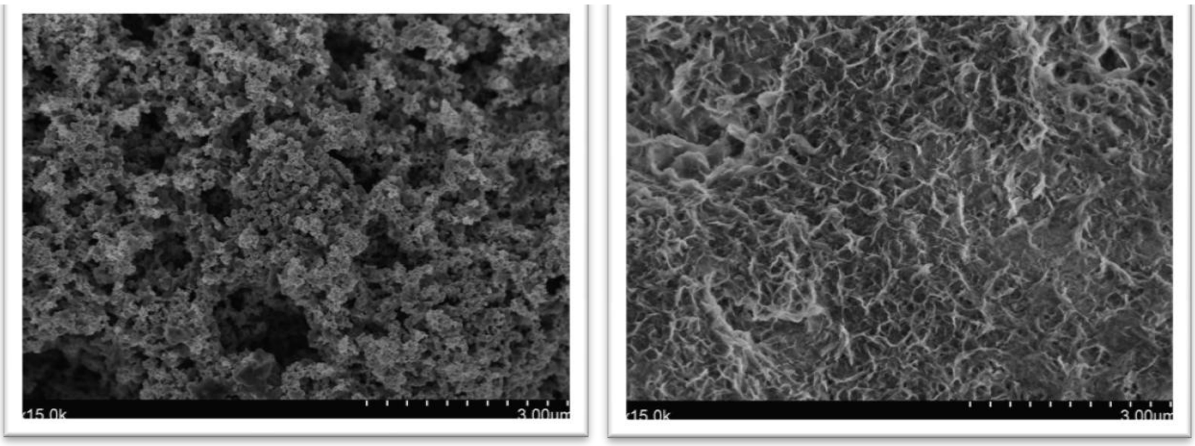

Figure 2.SEM micrographs from the catalysts supported in a steel monolith: As prepared (left) and after total deactivation showing a borate layer (right).