

Understanding B inclusion in Fe nanoparticles through EXAFS measurements

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An important research activity is dedicated to finding new means of hydrogen storage. One route envisages chemicals such as NH_3BH_3 as a convenient source of H_2 due to their high weight content of H and low temperature of H_2 release in the presence of metal catalysts. Recently, some low cost nanomaterials (Fe nanoparticles) have been demonstrated to afford H_2 from NH_3BH_3 in high yield.¹ Still, the exact nature of the catalytically active nanoparticle is not clearly established, as such a study on nanoscale catalysts is far from trivial. Formation of iron borides was suggested as well as their possible implication in the poisoning or activation of the catalysts. Our previous studies on core/shell FeBi nanoparticles (NPs) synthesized using the amine borane reducing agent, especially EXAFS measurements also carried out at HASYLAB (projects II-20060202 EC and II-20090183 EC) at both Fe and Bi edges, indeed evidenced the presence of a light element inside the first formed iron seeds, likely boron [1-2]. The goal of this new study was to synthesize oxide-free Fe NPs of well controlled size, shape and surface state and, in order to evaluate their interest for the production of H_2 from amine borane complexes, follow the inclusion of boron and especially determine boron location (inserted or substituted).

Several samples including 2-4 nm large Fe nanoparticles were prepared from the $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$ precursor in different synthesis condition and measured on beamline C at Fe K absorption edge. Because of the highly disordered atomic packing in these objects and the closely related structure adopted by some iron-boron materials, the classical FT analysis of the EXAFS signal confirmed the polytetrahedral packing already observed by other techniques but was ambiguous regarding the possible inclusion of boron. So we used a wavelet transform (WT) of experimental data. Indeed, due to the different k-dependence of backscattering amplitude of Fe and B, the WT offers the possibility to visualize the chemical environment of absorbing atoms directly without any structural assumptions and further data treatment.

Figure 1 displays the result obtained for one sample as a typical result obtained by this method. To better visualize the boron content in the samples, the Fe + O contribution (middle) to the total WT (left) was subtracted: the boron contribution is thus well observed on the right part of Figure 1. In all samples but one, boron was found in close vicinity to iron.

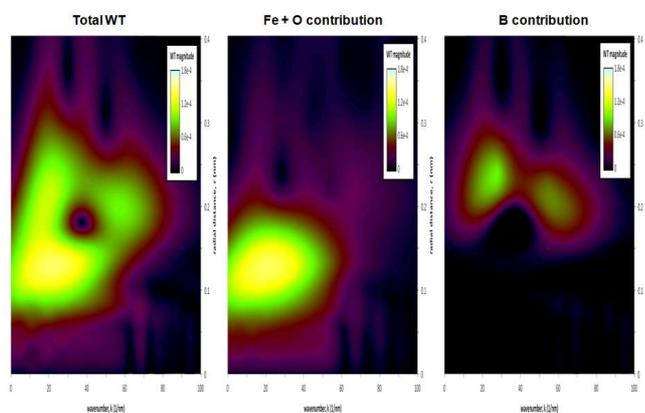


Figure 1: Wavelet transform of the EXAFS data for sample 1 (Due to the EXAFS phase shift, the radial distance obtained after WT is not the geometric distance between atoms).

Finally, a variable amount of boron could be observed for the different nanoparticles, resulting most probably from the reaction of the amino-borane by-product at the surface of the first formed nanoparticles, in agreement with the proposed scheme (Figure 2):

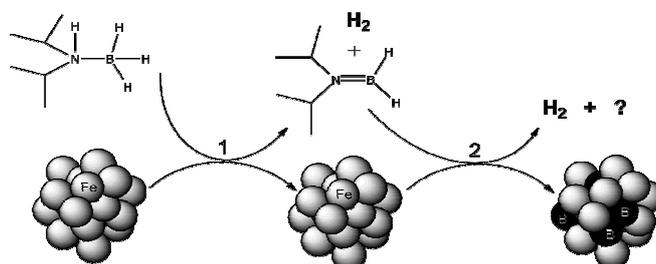


Figure 2. Proposed steps for boron incorporation in reference iron nanoparticles

Transmission EXAFS at Fe K edge combined to other tools (e.g. SQUID and Mossbauer spectroscopy) contributed to elucidate the mechanism leading to boron inclusion in Fe Nps [3]. This study opens a route to the use of amine-borane complexes as a source of boron for the preparation of iron boride nanoparticles and evidences the catalytic activity of iron nanoparticles for dehydrogenation of both diisopropylamine borane and diisopropylamino borane derivatives.

References

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