

# Controlling Fe speciation, sitting and nuclearity in Fe/Hydroxyapatite: effects on the catalytic performances in NH<sub>3</sub>-SCR reaction

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Hydroxyapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH), HAP) is a natural and versatile inorganic material, which, analogously to zeolites, is susceptible to undergoing ion exchange reaction (involving Ca<sup>2+</sup> ions) and thus to being easily functionalized with several active metal species. In fact, metal-loaded hydroxyapatites (Me/HAP) are recently emerging as eco-friendly materials in heterogenous catalysis [1-4]. The control of metal sitting, speciation, and nuclearity represents a key step in the identification of active catalytic sites. Actually at least two different Ca-sites with different coordination environment, Ca(I) (high coordination number, 9) and Ca(II) (low coordination number, 7), are available to allocate isolated metal species in HAP framework. In addition, the added metal centers can undergo agglomeration with formation of aggregates of different size, ranging from small oligomers up to clusters and small metal oxide nanoparticles [4]. In many cases, the final metal sitting and speciation is a delicate process driven by the experimental conditions during the deposition of metal phases [4].

Herein, iron has been deposited in different amount (ca. 2-7 wt.%) onto a synthetic hydroxyapatite from iron(III) nitrate, as precursor, according to three preparative methods (ionic exchange, deposition-precipitation and wetness impregnation). A suite of techniques of characterization (UV-Vis and Mössbauer spectroscopies, NH<sub>3</sub> adsorption) was used to determine iron speciation and sitting and to deduce relevant structure-activity relationships. Ion exchange procedure gave rise to the co-presence of isolated Fe<sup>3+</sup> centers in the Ca(I) sites, together with small Fe-O-Fe oligomers. Isolated Fe<sup>3+</sup> centers in Ca(II) sites and Fe<sub>x</sub>O<sub>y</sub> nanoparticles coexisted in the catalysts prepared by deposition-precipitation method. Finally, the cooccurrence of Fe<sub>x</sub>O<sub>y</sub> nanoparticles and isolated Fe<sup>3+</sup> centers in Ca(I) sites characterizes Fe/HAP catalysts prepared by wetness impregnation. H<sub>2</sub>-TPR analysis evidenced the different reducibility of these systems, as shown in figure 1. These dissimilar redox properties unavoidably have an impact on the catalytic behavior. Fe/HAP samples have been tested as catalysts in the NO<sub>x</sub> reduction by ammonia (NH<sub>3</sub>-SCR) in the 120-500°C interval with different NH<sub>3</sub>/NO ratios at fixed GHSV (30,000 h<sup>-1</sup>). All Fe/HAP samples were active and selective in the NH<sub>3</sub>-SCR reaction in the temperature interval studied and best performances were observed for the catalysts prepared by deposition-precipitation (about 60% of NO<sub>x</sub> conversion and selectivity to N<sub>2</sub> higher than 95% at 350°C). These results suggest that the speciation and coordination environment of iron species are determining features to be finely tuned in the optimization of Fe/HAP catalysts.

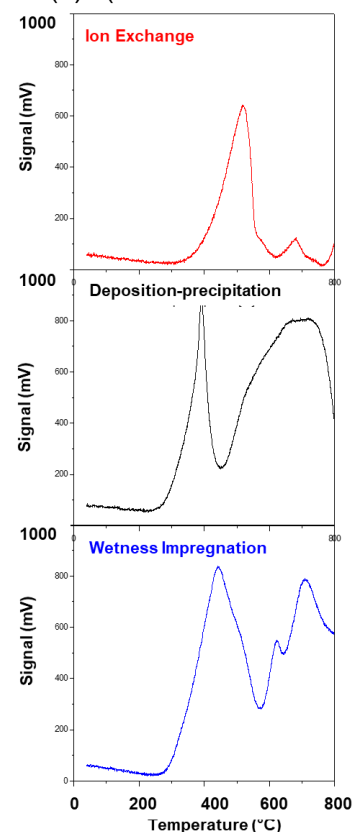


Figure 1 : H<sub>2</sub>-TPR profiles for Fe7/HAP catalysts

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