

Copper and Iron functionalized hydroxyapatites as efficient catalysts for several environmental reactions

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Abstract: In this study, we present the catalytic performances of hydroxyapatite materials functionalized with different amount of Cu or Fe ($1.5 < \text{wt.}\% < 12$), from different precursors and preparation methods. Good catalytic performances have been measured in NH_3 -SCR and NH_3 -SCO reactions, at lower or higher temperature intervals depending on the presence of Cu or Fe. Metal sitting has been studied by XRPD, Uv-vis-DRS, EPR, and Mössbauer analyses, besides others. Ionic exchange procedures of metal addition provided well dispersed and tuneable Cu^{2+} or Fe^{3+} species sited in the [Ca(I)] and [Ca(II)] exchange positions of HAP lattice, irrespective of the amount of Cu(Fe) addition.

Keywords: Cu(Fe)-Hydroxyapatite, NO_x Reduction, NH_3 Oxidation.

1. Introduction

The development and improvement of technologies of environment protection is today the object of intensive worldwide research efforts devoted to comply with ever more stringent legislation for minimizing air pollution. The perspective to attain zero-emission of NO_x from polluted gaseous streams vented from mobile and fixed sources still remains an open challenge. Copper- and iron-containing zeolites catalysts are currently among the best choice for efficient NO_x reduction in the NH_3 -SCR (*selective catalytic reduction of NO_x*) process [1]. NH_3 -SCR can be associated with NH_3 -SCO (*selective catalytic oxidation of NH_3*) in *cascade* with the aim of pursuing zero NO_x emissions without *ammonia-slip* [2]. For this goal, the design of active and selective catalysts constitutes a real challenge. To look for a new generation of efficient catalysts for these reactions, low-cost, ecofriendly, and robust materials should be found.

Hydroxyapatites (HAPs, $\text{Ca}_{10-x}(\text{PO}_4)_{6-x}(\text{HPO}_4)_x(\text{OH})_{2-x}$, with $0 < x \leq 1$) are a class of natural minerals, which to date has only had a limited success in catalysis. Hydroxyapatite structures are flexible to both cationic and anionic substitutions, with the possibility of modulating the number of acid–base sites in the crystal. HAPs present various advantages including bioavailability, biocompatibility, high mechanical and thermal resistance, they are of facile synthesis from cheap precursors. In addition, the intrinsic capability to exchange the Ca^{2+} cations in the [Ca(I)] and [Ca(II)] positions and to allocate some other metal ions in the hydroxyapatite lattice allows obtaining interesting functionalized materials. In this perspective, the use of Cu- or Fe-functionalized hydroxyapatites can offer a valid alternative to the current catalytic systems used in several reactions of environmental protection. Herein, we present our recent results aimed to show the potentiality of HAP as innovative material to prepare Cu or Fe containing catalysts for the NH_3 -SCR and NH_3 -SCO reactions, with the final goal to realize the above mentioned *cascade* SCR and SCO process.

2. Experimental

A synthetic hydroxyapatite (HAP, from Solvay, Belgium) with addition of Cu^{2+} or Fe^{3+} metal ions (1.5-12 wt.%) deposited from Cu-acetate, Cu-nitrate, and Cu-chloride or from Fe-nitrate precursors with ionic-exchange and impregnation procedures, was used in this study. The Cu-samples prepared by ionic exchange maintained light blue color after calcination (400°C for 4 h), while the samples prepared by impregnation turned towards green-grey color; the Fe-samples were all orange-brown colored. Powder diffraction (Philips powder XRD with a PW 1830 generator in graphite, copper pipe, Cu $\text{K}\alpha$, $\lambda=1.5418\text{\AA}$ radiation) analyses was used to study structural properties of the samples. Cu- and Fe-sitting and aggregation state was controlled with UV-vis-DRS (Shimadzu UV-3600 plus, Japan, with a BIS-603 integrating sphere from), EPR (Bruker Elexys

with ER4102ST rectangular cavity working at of 9.4 GHz frequency) and Mössbauer spectroscopy (spectrometer of constant acceleration with ^{57}Co source). Catalytic activities of Cu(Fe)/HAP samples were evaluated in both the NH_3 -SCR and NH_3 -SCO reactions in the 120-500°C interval, feeding variable NO to NH_3 ratios (from 0.5 to 2, with $150 < [\text{NH}_3]/\text{ppm} < 1000$) for the SCR reaction, and variable NH_3 concentrations (from 50 to 500 ppm) for SCO reaction, with 10,000 ppm of O_2 in any case, and working typically at GHSV of ca. 30,000 h^{-1} . The reaction line comprised a tubular flow reactor coupled with an on-line FT-IR spectrophotometer (Biorad) with a gas-cell able to monitor continuously NH_3 and NO_x (i.e., NO, N_2O , NO_2) species as a function of time/temperature.

3. Results and discussion

Crystalline structure typical of HAP (JCPDS 00-009-0432) was preserved in all the samples after the introduction of the metal phase. Additional peaks typical of Cu-oxide (JCPDS 00-048-1548) were present in the patterns of the Cu/HAP samples prepared with impregnation, while HAP was the unique crystal phase detectable in all the Cu/HAP and Fe/HAP samples prepared with ionic exchange, irrespective of the Cu(Fe)-loading. The catalysts prepared with impregnation method presented more aggregated metallic phase. UV-vis-DRS and Mössbauer (only for the Fe/HAP samples) measurements confirmed, for the catalysts prepared with ionic exchange, the high dispersion of Cu^{2+} and Fe^{3+} species sited in the [Ca(I)] and [Ca(II)] exchange sites of HAP lattice.

All the Cu(Fe)/HAP samples were active in the NH_3 -SCR reaction in lower (Cu/HAP) or higher (Fe/HAP) temperature intervals (Fig.1,left). Typically, Cu/HAP catalysts provided higher NO_x conversions than Fe/HAP samples. NO_x conversion was higher on Cu/HAP catalyst prepared from Cu-chloride precursor than on those prepared from Cu-nitrate and Cu-acetate precursors [3]. Concerning the NH_3 -SCO reaction, the catalysts worked in the reaction of ammonia oxidation at higher temperatures than those observed for the NO_x reduction (NH_3 -SCR) (Fig.1,right). In general, in the NH_3 -SCO reaction, Fe/HAP samples gave high selectivity to N_2 over a small temperature interval, while for higher temperatures, NH_3 was oxidized to NO_x with decrease of N_2 selectivity.

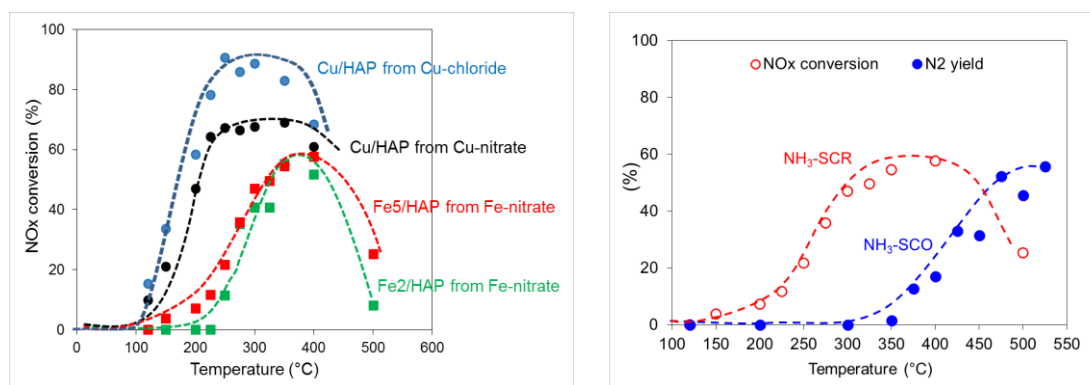


Figure 1. NH_3 -SCR activity on selected Cu(Fe)/HAP (left) and NH_3 -SCR plus NH_3 -SCO activity on Fe/HAP (5 wt.%) (right).

4. Conclusions

The potentiality of hydroxyapatite materials properly functionalized with metal species (Cu or Fe) has been enlightened in two reactions of environmental protection (NH_3 -SCR and NH_3 -SCO). The nature of the metal species (Cu or Fe), the precursors used for the metal deposition, and the metal loading were all parameters that influenced the activity, the selectivity, and the temperature interval of activity of the catalysts. The possibility to couple the two reactions in cascade to improve NO_x removal without NH_3 -slip will be discussed.

References

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